TESIS DE LA UNIVERSIDAD DE ZARAGOZA

2024 178

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Hybrid quantum-classical systems: Statistical mechanics, thermodynamics and field theory

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ISSN 2254-7606

Prensas de la Universidad Universidad Zaragoza

Universidad de Zaragoza
Servicio de Publicaciones

ISSN 2254-7606

Universidad Zaragoza
1542

Tesis Doctoral

HYBRID QUANTUM-CLASSICAL SYSTEMS: STATISTICAL MECHANICS, THERMODYNAMICS AND FIELD THEORY

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UNIVERSIDAD DE ZARAGOZA
Escuela de Doctorado

Programa de Doctorado en Física

2024

Hybrid quantum-classical systems: Statistical mechanics, thermodynamics and field theory.

Carlos Bouthelier Madre

5th November 2023

Acknowledgements

Me gustaría agradecer el apoyo recibido en el desarrollo de esta tesis doctoral a todos los que me han acompañado en estos años.

A mis directores, Jesús y Alberto, por su paciencia, su consejo, su guía y su experiencia, determinantes en todo mi trabajo, en mi formación y en mi desarrollo como científico y como persona. Para ellos, todo agradecimiento se queda corto.

A José Luis, compañero en este viaje desde el principio, amigo e inagotable fuente de ánimo, ímpetu científico y referencias bibliográficas que motivaron gran parte de los estudios de esta tesis.

A Federica e Francesco, per ospedare me e aver reso il mio soggiorno di dottorato a Parigi un'esperienza memorabile.

A David, ahumador y licuador de reses que sustentaron la carcasa mortal del autor, a quien también agradezco innumerables discusiones científicas *a cara de perro* que, finalmente, se resolvieron con consenso (o capitulación), pero que siempre resultaron enriquecedoras.

A Javier y Laura, ha sido un placer llegar a conocerlos personalmente y colaborar científicamente con ellos. Les auguro una brillante carrera científica, a pesar de las dudas que nos asaltan a todos en el camino.

Al muy fuerte y sombrío Sergio, por horas y horas de escritura de tesis compartida, por su alentadora compañía a lo largo de todos estos años, por la amistad que perdurará, por ser la vanguardia en los tortuosos caminos de la burocracia y lograr regresar siempre con valiosa información.

A Nacho, siempre un apoyo en el día a día. A Pablo, a quien le agradezco, sobre otras muchas cosas, cómo es. Sé que seguiré compartiendo vivencias con ellos por muchos años.

A Laura, por haber tenido paciencia, por su incondicional apoyo y comprensión, por su espera.

Finalmente, a Sergio, a Pilar, a Cris, a Yolanda, a mi familia, por estar siempre ahí.

Compendium of articles

This thesis is presented as the compilation of the following previously published research articles, of which the PhD candidate is the main author:

- J. L. Alonso, C. Bouthelier-Madre, A. Castro, J. Clemente-Gallardo, and J. A. Jover-Galtier. Entropy and canonical ensemble of hybrid quantum classical systems. *Physical Review E*, **102**(4):042118, 2020. [1]

- J. L. Alonso, C. Bouthelier-Madre, A. Castro, J. Clemente-Gallardo, and J. A. Jover-Galtier. About the computation of finite temperature ensemble averages of hy-brid quantum-classical systems with molecular dynamics. *New Journal of Physics,* **23** (6):063011, 2021. [2]

- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, D. Martínez-Crespo, and J. Pomar. Effective nonlinear Ehrenfest hybrid quantum-classical dynamics. *The European Physical Journal Plus*, **138** (7):649, 2023. [3]

- C. Bouthelier-Madre, J. Clemente-Gallardo, L. González-Bravo, and D. Martínez-Crespo. Hybrid Koopman $C^\star$-formalism and the hybrid quantum-classical master equation. *Journal of Physics A*, **56** (37):374001, 2023. [4]

Additionally, given its scientific relevance and the work devoted to it, this memoir includes a fifth article which has been submitted for publication, but is still under editorial review:

- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, and D. Martínez-Crespo. Hybrid geometrodynamics: A Hamiltonian description of classical gravity coupled to quantum matter. Submitted for publication. [5]

Finally, in order to provide the reader with a comprehensive picture of the academic background of the PhD candidate, the following list encompasses additional research work developed during this thesis, although only the former five are included in this thesis.

- F. Arias-Aragón, C. Bouthelier-Madre, J. M. Cano, and L. Merlo. Data driven flavour model. *The European Physical Journal C*, **80**:1-23, 2020. [6].

- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, and D. Martínez-Crespo. Geometric flavours of quantum field theory on a Cauchy hypersurface. Part I: Geometric quantization and star products. *arXiv*:2306.148442. [7].
- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, and D. Martínez-Crespo. Geometric flavours of quantum field theory on a Cauchy hypersurface. Part II: canonical and geometrical QFT. *Unpublished*. [8]
- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, and D. Martínez-Crespo. A sufficient condition for confinement in QCD. *arXiv*:2211.01047. [9].

Resumen

Esta tesis aborda la mecánica estadística y la teoría de campos de los sistemas híbridos. Los sistemas híbridos son aquellos que permiten caracterizar los fenómenos físicos que, para una determinada precisión, requieren una descripción conjunta formada por un subsistema clásico y un subsistema cuántico. En la mayoría de los casos, como en dinámica molecular, los sistemas híbridos son una descripción efectiva obtenida a partir de una descripción cuántica completa más fundamental. En algunos otros casos, como en el de la gravitación acoplada a la materia cuántica, los sistemas híbridos podrían considerarse la descripción fundamental.

Las principales contribuciones originales de este trabajo a la mecánica estadística de los sistemas híbridos son las siguientes. En primer lugar, se introduce la definición de entropía y conjunto canónico para este tipo de sistemas, en términos de una matriz de densidad híbrida. De esta forma, se corrige una noción de entropía errónea que puede encontrarse en la literatura, basada en la entropía de Gibbs para una distribución de densidad de probabilidad sobre un espacio de fases híbrido.

En segundo lugar, se proporciona una corrección de los promedios temporales ergódicos para trayectorias acopladas a termostatos clásicos, con el fin de que reproduzcan *ensembles* termodinámicos híbridos apropiados. Esta forma de calcular promedios contrasta con los *ensembles* mal definidos alcanzados en la literatura preexistente. Estos estaban asociados a magnitudes termodinámicas no aditivas, a un límite termodinámico trivial y a *ensembles* condicionales y marginales incorrectos para ambos subsistemas, clásico y cuántico.

En tercer lugar, derivamos la dinámica estadística Liouvilliana para *ensembles* híbridos a partir de la microdinámica Hamiltoniana. Además, se caracteriza en un nuevo formalismo una inconsistencia históricamente bien conocida de la dinámica estadística híbrida. La inconsistencia residía en el hecho de que la representación de *ensembles* híbridos en términos de matrices de densidad híbridas (primer momento cuántico) constituye una clase de equivalencia para distribuciones de probabilidad sobre el espacio de fases que comparten el primer momento (pero difieren en el resto de momentos). La dinámica dada por el teorema de Liouville rompe esta clase de equivalencia. Nuestra solución reside en la descripción de la dinámica estadística en términos de un sistema de ecuaciones diferenciales acopladas

para todos los momentos estadísticos cuánticos, que pueden considerarse matrices de densidad generalizadas. También se proporciona una expresión truncada de este sistema de ecuaciones diferenciales para la implementación de la dinámica Liouvilliana en aplicaciones prácticas. En el aspecto teórico, el formalismo tiene todavía un fuerte potencial para caracterizar la interacción entre las magnitudes termodinámicas y la dinámica estadística para estos sistemas híbridos.

La última contribución a la mecánica estadística presenta *ensembles* híbridos en un nuevo marco teórico, en el que el subsistema clásico se representa mediante el formalismo de Koopman para la mecánica estadística clásica y el subsistema cuántico en términos de matrices de densidad de von Neumann. A continuación, se propone un nuevo tipo de matriz de densidad para caracterizar los estados estadísticos híbridos, que, aunque parece totalmente cuántica, es parcialmente Koopmaniana. Este formalismo es capaz de caracterizar un amplio conjunto de dinámicas híbridas de una manera formalmente análoga a la mecánica estadística cuántica. Además, se demuestra que la entropía híbrida previamente caracterizada corresponde a la entropía de von Neumann para estas matrices de densidad Koopman-von Neumann. Poder caracterizar tanto la dinámica como la termodinámica en términos de matrices de densidad es una novedad que ayudará a estudiar algunos de los aspectos más delicados de los sistemas híbridos.

El último trabajo presentado en esta tesis aborda sistemas híbridos de teoría de campos. En particular, se combina una formulación Hamiltoniana de la relatividad general de Einstein conocida como *geometrodinámica* con una formulación Hamiltoniana de la teoría cuántica de campos (QFT). Esta última se basa a su vez en la versión geométrica de la imagen de funcional de onda de Schrödinger en espacio-tiempo curvo. En este trabajo se utilizan nuevos ingredientes geométricos (respecto a los anteriores sistemas híbridos) que demuestran ser necesarios para la consistencia en la descripción de este tipo de sistemas híbridos. La fenomenología resultante de la teoría muestra algunas propiedades que suponen una mejora con respecto a trabajos previos de QFT en espacio-tiempo curvo, como la conservación de la norma para el estado cuántico y la conservación de las magnitudes híbridas necesarias. Algunas de las aplicaciones potenciales de la teoría incluyen el estudio de la evaporación de agujeros negros y la radiación de Hawking, el efecto de los campos cuánticos en cosmología de universo temprano, la formación de singularidades o censura de las mismas bajo colapso de polvo cuántico, el estudio de la creación de partículas bajo espacio-tiempo dinámico y, en general, la caracterización precisa de la *backreaction* de los campos cuánticos sobre la gravitación clásica y *viceversa*.

Abstract

This thesis tackles the statistical mechanics and field theory of hybrid systems. Hybrid systems are used for those physical phenomena whose characterization, for a given accuracy, requires the joint description of a classical and a quantum subsystem. In most cases, such as in molecular dynamics, hybrid models are effective descriptions, obtained from a more fundamental full quantum one. In some other cases, such as in gravitation coupled to quantum matter, hybrid systems could be regarded as the fundamental description.

The main original contributions of this thesis to the statistical mechanics of hybrid systems are the following. Firstly, the definition of entropy and canonical ensemble for this kind of systems is introduced in terms of a hybrid density matrix. This corrects a mistaken notion found in the literature, based on a Gibbs entropy for a probability density distribution over a hybrid phase space.

Secondly, a correction to the ergodic time averages for the trajectories of hybrid systems coupled to classical thermostats is provided. In this way, those averages yield the appropriate hybrid thermodynamical ensembles, in contrast to the ill-defined ensembles reached in some previous works. Those errors were associated with the consideration of non-additive thermodynamical magnitudes, wrong trivial thermodynamical limits, and incorrect conditional and marginal ensembles for the classical and quantum subsystems.

Thirdly, a derivation of Liouvillian statistical dynamics for hybrid ensembles from Hamiltonian microdynamics is obtained. Furthermore, a historically well known inconsistency of the hybrid statistical dynamics is characterized in a new formalism. The inconsistency lied in the fact that the representation of hybrid ensembles in terms of hybrid density matrices (first quantum moments) constitutes a class of equivalence for all those probability distributions over phase space that share the first moment, but may differ in higher order ones. The dynamics given by Liouville's theorem breaks this equivalence class. Our solution lies in the description of statistical dynamics in terms of a system of coupled differential equations for all the quantum statistical moments. These can be regarded as generalized density matrices. A truncated expression of this system of differential equations is also provided, for the implementation of Liouvillian dynamics in practical applications. On the theoretical side, the formalism has strong potential to characterize the interplay

between thermodynamical magnitudes and statistical dynamics for hybrid systems.

The last contribution to statistical mechanics casts hybrid ensembles in a new framework, where the classical subsystem is represented by Koopman's formalism for classical statistical mechanics and the quantum subsystem in terms of von Neumann's density matrices. A new kind of density matrix is then proposed to characterize hybrid statistical states, which, while looking fully quantum, is partially Koopmanian. This formalism is able to characterize a wide set of hybrid dynamics in a way that is formally analogous to quantum statistical mechanics. Furthermore, it is shown that the hybrid entropy previously characterized corresponds to von Neumann's entropy for this Koopman-von Neumann density matrices. Being able to characterize both dynamics and thermodynamics in terms of density matrices is a novelty that will help to study some of the most puzzling aspects of hybrid systems.

The last work presented in this thesis tackles hybrid field theoretical systems. In particular, a Hamiltonian formulation of Einstein's general relativity known as *geometrodynamics* is combined with a Hamiltonian formulation of quantum field theory (QFT), based on the geometric version of the Schrödinger wave function picture. New geometric features are shown to be necessary to obtain a consistent description of this kind of hybrid systems. The resulting phenomenology of the theory already shows some improved properties with respect to previous works of QFT in curved spacetime, such as norm conservation for the quantum state, and conservation of the necessary hybrid magnitudes. Some of the potential applications of the theory comprise (but are not limited to) the study of black-hole evaporation and Hawking radiation, the effect of quantum fields in early cosmology, the formation or avoidance of singularities under quantum dust collapse, the study of particle creation under dynamical spacetimes and, in general, the precise characterization of the *backreaction* of quantum fields on classical gravitation and *viceversa*.

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Chapter 1

Introduction

Science may be described as the art of systematic over-simplification – the art of discerning what we may with advantage omit.

Karl Popper.

The objective of this thesis is to characterize physical systems where, by mercy of some hierarchy on key physical magnitudes, some degrees of freedom can be accurately described by classical mechanics, while others require quantum mechanics. These systems are referred to as *hybrid* systems. Specifically, two primary avenues of investigation have been pursued, employing similar mathematical methodologies.

As it will be comprehensively explained later, the first one delves into the statistical mechanics of hybrid systems. This investigation encompasses several pivotal contributions, including the development of an entropy function for hybrid statistical ensembles, the identification of the root cause of some inconsistencies between microdynamics and statistical mechanics in hybrid systems previously described in the literature (and two distinct proposals for their conciliation), and the formulation of a master equation derived from hybrid Hamiltonian microdynamics. To accomplish these objectives, the essential mathematical tools that we have employed are symplectic geometry (leveraging Liouville's theorem), probability theory (for the precise characterization of hybrid entropy and ensembles), and $C^\star$-algebras (for establishing a robust connection between hybrid physical observables and collective states).

The second field of study extends the scope of traditional hybrid systems, with classical mechanics and *ordinary* quantum mechanics as their constituents, to hybrid field theories. This generalization is performed in the context of the Hamiltonian description of classical gravity interacting with matter described by quantum field theory. The main results are the implementation of Dirac's symmetry group of hypersurface deformations with con-

straints (equivalent to general covariance in a Hamiltonian framework of the Universe) for the hybrid system, the norm conservation for the states of quantum field theory in curved spacetime, and the depiction of the *backreaction* of quantum matter on the geometry of spacetime. In order to do so, we extend the framework known as *geometrodynamics*, which describes in a Hamiltonian way Einstein's general relativity (or, for that matter, any geometric description of gravity, not necessarily based on a metric tensor field) to contain a geometric description of quantum field theory as matter sources. The mathematical prerequisites in this case involve the development of infinite dimensional calculus for classical tensors and quantum states, and the generalization of the geometric formulation of quantum mechanics to the Schrödinger functional picture of QFT.

To fully appreciate the significance of these results, we must firstly delve into a brief review of the field and its state of the art at the inception of this thesis. This will help the analysis of the articles that follow. Next section will thus examine the historical and logical development of hybrid systems, with special focus on Ehrenfest dynamics. Section 1.2 reviews the geometric formulation of classical, quantum and hybrid Hamiltonian systems. The key result from that section is Liouville's theorem, based on the symplectic geometry of the phase spaces. Naturally, this is followed up by the introduction of the statistical mechanics of hybrid systems in section 1.3, where the first four articles of this compendium are contextualized. The last section in this introduction presents the Hamiltonian formulation of general relativity and quantum field theory, providing the necessary ingredients for the understanding of the hybrid field theory presented in the fifth and last article of this thesis.

1.1 Introduction to hybrid systems

The objective of physics is the description of the natural world, from the tiniest elementary particles to the vast expanse of cosmological objects. Despite the allure of a unified description encapsulating the entirety of this broad spectrum of phenomena, its realization, even the computation of the most standard everyday problem with it, proves to be impracticable. Therefore, when studying a particular physical event, to avoid obfuscating the relevant phenomenology with unnecessarily high resolution, the adoption of effective descriptions becomes imperative. In this sense, it is commonplace (although many times it is done implicitly) to analyze the dynamics of the physical observables of interest in relation with the needed accuracy (given by the direct resolution of a measurement aparatus or by indirect means, such as time averages, convolutions accounting for coarse grained observations, interest on collective behaviour such as intensive magnitudes, etc.), and dispense with certain degrees of freedom of the system that remain beyond observational reach. We

will call this approach, that goes from higher detail and complexity to the simplified description (i.e. from fundamental to effective theories) a *top-down* approach. Nevertheless, despite this logical structure, from a historical point of view, the theories have developed in the opposite way, since the simplified descriptions (e.g. classical mechanics) were developed earlier than the precise ones (e.g. quantum mechanics) from which they can be obtained as simplifications. The steadily increasing falsifiability power of experiments constantly leads to the identification of an established theory as an effective simplification of a more fundamental one that then dethrones the former one, given the disagreement of the experimental results with its predictions. A canonical example of this historical procedure is Newtonian gravity, which can be obtained as a limit of General Relativity and is still valid in a certain range of applications, but failed to describe with sufficient accuracy relevant observations, such as the advance of Mercury's perihelion [10]. Nevertheless, the original theory may have a range of validity on certain physical scales and, therefore, to be a suitable generalization, the new and more fundamental theory must share compatible predictions with the old effective one on that range. Usually, such compatibility is mathematically understood with a limit on a certain ratio of physical scales characterizing the common range of application which simplifies the fundamental theory, and yields the effective one.

In the context of hybrid systems, the role of such fundamental theory is quantum mechanics (including quantum field theory), which is widely accepted as our best description of the physical world at small scales. Historically, the effective theory (which, naturally, arose first) considered for most of broad-scope phenomena is classical mechanics, providing a simplified, macroscopic description that effectively captures the relevant behavior with the desired accuracy. Nevertheless, such phenomena can, theoretically, also be described by quantum mechanics, albeit baroquely detailed. Therefore, one may ask, how does a description at one scale emerge from a deeper and more detailed description? This question about scales is identified with the mathematical notion of limit introduced above. Even though a plethora of methods are employed to zoom out and capture *solely* the relevant aspects of a system, if the original theory is quantum mechanics and the resulting one is classical mechanics, such procedure is usually dubbed *classical limit* (or semi-classical, if some features of the quantum mechanical description are partially preserved).

This clarifies the relation between both theories in reference to their respective scales of application, allowing us to choose *either* quantum *or* classical mechanics depending on the studied phenomena. Nevertheless, the previous discussion does not include yet the possibility of hybrid systems, i.e those that contain a subsystem that still requires quantum mechanics to capture its behavior with the desired accuracy, but the rest of the system can be simplified through a *semiclassical limit*.

The most notable examples of theories tailored for this kind of systems are the various types of molecular dynamics. Born and Oppenheimer's work [11] on the approximations

to the factorization of the molecular wave function is the precursor work on the subject: an expansion dominated by the quotient of electron-nuclear masses is employed for the different terms in the kinetic energy of the nuclei (rotational, translational and related to quantum dispersion of momenta). Later, in the 50's, these bounds are applied to perform calculations under the name of Born-Oppenheimer molecular dynamics (see [12, 13] for recent reviews), where the electrons are described under the frame of quantum mechanics, but the nuclei follow the simpler classical description. Therefore, despite their fundamentally quantum nature, it is shown that the nuclear mean position is usually enough to characterize the chemical properties of the molecule, together with the electronic molecular orbitals, allowing for an accurate hybrid description of the studied phenomena while simplifying the computational complexity.

Other situations for which hybrid descriptions are mandatory include: problems in solid state physics (for example, quantum electrons in a lattice subject to classical perturbations, or the dynamics of molecules on metallic surfaces as in [14]) and classical electromagnetic fields (following Maxwell's equations) interacting with quantum electrons (e.g., for dissociation or ionization of dimmers under intense laser pulses as in [15, 16] and effective descriptions of absorption, emission and scattering of light by quantum matter). They also have crucial applications in biological processes (a paradigmatic example is the dynamical description of photosynthesis, where the electronic system in charge of photon absorption must be quantum mechanical, although the description of chlorophyll itself, being a huge molecule, is only viable classically) and even diagnostic applications (in [17], hybrid systems are used to characterize nuclear spin and position in order to characterize spin dynamics in solids in the context of nuclear magnetic resonance).

Hybrid theories, despite being regarded as effective, have also been applied to tackle the arguably most fundamentally puzzling principle of quantum mechanics, which is the measurement postulate on the collapse of the wave function [18–20]. There, the measurement aparatus is described classically (as, such a large system would be unfathomable as a quantum object), while the measured system is of course quantum mechanical. The former induces decoherence on the latter, through a very intense interaction governing the coupled dynamics for a short time. In this way, there is no need for considering the collapse of the wave function as a postulate, but rather as an incomplete description.

One last example of hybrid theory of particular interest for this thesis, presented in the fifth article included here, is the interaction of matter described with quantum field theory with the geometry of spacetime, depicted by classical tensor fields. In an epistemic sense, this hybrid theory is profoundly different from the former ones, as, with our current knowledge, it could be a fundamental theory, instead of an effective one. In the first place, gravity itself could be fundamentally classical, as there is no single fundamental theory for quantum gravity with falsifiable particular phenomenology (as the accuracy of

experiments will not reach Planck scales in any foreseeable future), nor there exists any consistency criteria that strictly requires quantum gravity [21]. On the other hand, the most fundamental accepted description of particles is quantum field theory, and we have no experimental hint that pushes us to go beyond it. Therefore, a joint description of both of them as argued in [22], under some consistency criteria that will be summarized later, could very well be the fundamental theory that described current observable phenomenology. Nevertheless, the top-down approach still exists for hybrid theories (such as [23] and [24]) that arise from a semiclassical procedure on the gravitational degrees of freedom applied to canonical quantum gravity, which describes both matter and gravity quantum mechanically (see, for example, [25] for a careful summary).

1.1.1 Brief summary of different hybrid theoretical models

Even though hybrid systems are widely used for computational purposes, they have attracted less attention from the theoretical point of view. Perhaps, they have been eclipsed by the dazzling attraction towards more fundamental theories, and hindered by the difficulty that supposes reconciling the different mathematical frameworks of quantum and classical mechanics. In particular, some very relevant aspects of statistical mechanics, thermodynamics, and even analytic mechanics (in the case of field theories) that have been deeply studied in both classical and quantum mechanics separately, have been neglected in the case of hybrid systems, and it is the objective of this thesis to help to alleviate such scarcity.

In order to do so, we will concentrate on one of the most historically relevant models: Ehrenfest dynamics. Nevertheless, alternative models are widely considered in the literature to describe a variety of phenomena, such as (but not limited to) the following:

- Born-Oppenheimer molecular dynamics (based on the namesake approximations developed originally in [11]), which usually assume adiabaticity of the quantum system.

  These models were tailored for molecular dynamics and are based on the assumption that the electrons are limited to be in an eigenstate of the associated Hamiltonian operator. The effective potential producing the forces for the classical nuclei exerted by the electrons is given by the associated eigenvalue to the frozen eigenstate of the electrons (which is dependent on the nuclear positions as so was the electronic Hamiltonian accounting for electron-nuclear interaction). A canonical example of its application can be found in reference [26], later generalized to consider multiple energy levels in [27]. An important feature of the Born-Oppenheimer approximation from the theoretical point of view is that it must be endowed with a geometric connection. In turn, such connection produces geometric phases for the quantum states. This is a result of the restriction to a single eigenstate of a Hamiltonian which, in turn, is dependent on the positions of the nuclei, as can be seen in [28].

Even though this feature will be absent in Ehrenfest's molecular dynamics, a similar structure will appear in the hybrid theory of quantum fields and gravitation developed in this thesis [5].

- Those based on the semiclassical limit of the Exact Factorization, summarized in [29]. The key feature of this approach is that the entanglement between nuclei and electrons is not neglected in the partial semiclassical limit. In order to better preserve the enetanglement, one may choose to arrive to a semiclassical-quantum system, instead of a proper hybrid classical-quantum one, once the limit is performed. The computational consequence of preserving semiclassical features is that one needs a bundle of classical trajectories. One must therefore start the simulations from a distribution of initial conditions for the nuclei that evolve almost-classically in time, accounting for the width of the nuclear wave function. These trajectories are however coupled to each other and to the electronic quantum system, as can be seen for example in [30, 31].

- In the line of multi-trajectory approaches, in [32] an algorithm is proposed to effectively reproduce at the semiclassical level the phenomenology of molecular dynamics. It is based on sampling a set of initial conditions for the nuclear system from a thermal Wigner distribution, and propagating a sheaf of classical trajectories coupled to the electronic states. The novelty arises in the linearization of the dynamics, which allows to treat the electrons in an apparently classical way. This results in a computationally efficient simulation method to approximate the fundamentally quantum molecular dynamics.

- The "surface hopping" method [33] also departs from the Born-Oppenheimer approximation, and somehow generalizes the BOMD scheme attempting to lift the adiabaticity requirement. It was later optimized through the *fewest switches* algorithm, introduced in [34]. The model permits stochastic transitions between the energy levels, but is equivalent to an adiabatic Born-Oppenheimer approach within said transitions. Phenomenologically, one can consider that the model acounts for absorption and emission of energy quanta by the quantum subsystem.

- Other models attempted to generalize Liouville's equation to be applicable to hybrid statistical systems, either in the spirit of von Neumann's equation for quantum systems or through a modification of the classical Poisson bracket. The paradigmatic example in the literature of this approach is proposed by Kapral and Ciccotti in [35], and further explored in many subsequent works [36–38]. We note that a previous work by Aleksandrov can be considered a pioneer in this field [39], although it was based on a different mathematical formalism. Star products, Wigner functions, the Moyal's bracket and, in general, deformation quantization play a significant role in these constructions.

- However, the brackets proposed in both approaches (Kapral and Ciccotti [35] and Aleksandrov [39]) did not fulfil Jacobi's identity and other desirable properties. A corrected version was introduced by Diosi *et al.* in [40], with more robust mathematical properties.

- These discussions paved an avenue for follow-up proposals of more "consistent" hybrid brackets. For example, Kisil's quantum-classical bracket [41] built on the concept of p-dynamics. It constitutes a highly technical generalized geometric framework for several quantization procedures summarized in [42], whose applications in the context of hybrid systems had been previously delineated in collaboration with Prezhdo (see [43]), ultimately proposing dynamics based on the representations of the Heisenberg group over different hypercomplex numbers. The bracket, and in general the p-mechanics formalism, was shown to be mathematically consistent regarding several mathematical requirements. Nevertheless, Agostini *et al.* [44] argued that the dynamics was ultimately classical, and provided by an artificial coupling between the subsystems. The criticism was answered in a comment by Kisil, [45], which did not silence the critics. In fact, they were restated in a reply to such comment in [46]. On the other hand, the method was constructed in terms of two abstract Planck constants, $\hbar_1$ and $\hbar_2$, to define the respective generalized star bracket (analogous to the commutator of operators) for two respective subsystems. Then, the formal limit $\hbar_2 \to 0$ is taken over the total Moyal bracket summed to its derivative with respect to $\hbar_2$, while the other constant is identified with the actual Plank constant $\hbar_1 = \hbar$. This method allows to avoid the classical limit, but the price to pay is the assumption of two "quantum constants" with different values, which is fundamentally non-physical given the well known universality of $\hbar$. In the end, without consensus on the physicality of the theory, the method did not find its way into the mainstream literature, and further applications of this hybrid formalism are difficult to find. A recent summary on this field is provided in [47], although hybrid systems are not explicitly treated, both quantum and classical mechanics are successfully reproduced with a non-commutative structure and non-null $\hbar$-constant.

- Also searching for a consistent hybrid bracket, Prezhdo proposed a different solution to Diosi's for the inconsistencies of Kapral-Ciccoti's bracket in [48] . The new proposal was shown to fulfil Jacobi's identity for three particular observables of interest. Nevertheless, in [49], Salcedo *et al* showed that it did not fulfil Jacobi's identity for generic observables to arbitrary orders in $\hbar$, failing therefore to constitute a proper Lie bracket. This comment was replied in [50], where the author clarified that the procedure intended to be valid after taking the limit $\hbar \to 0$ for the subsystem for which a classical description is desired, in which case Jacobi's identity is recovered. Nevertheless, the author concedes that the procedure is not entirely satisfactory in providing with a quantum-classical theory, as the droped-off $\hbar$ terms must be retained

for the quantum subsystem.

- In the line of the attempts to generalize Liouville's equation, Buric's work [51] analyzes the statistical dynamics induced by Hamiltonian hybrid systems, such as Ehrenfest's equations. He concludes that a conventional density matrix formalism requiring a modified bracket to define von Neumann-esque dynamics is not possible. Instead, one needs to work with a probability density distribution over a hybrid phase space to characterize the statistical ensembles. This work is followed up by [52], where Liouville's equation for hybrid statistical ensembles is further explored and its relation with hybrid density matrices (a concept that will be explored later in this introduction) is stablished, showing that the kind of Hamiltonian dynamics considered cannot be defined without reference to a probability density distribution. In turn, it is shown that the differential equation of the marginal quantum density matrix only refers to the hybrid density matrix. The third article of this compendium, [3] will further expand on this analysis.

- Following these contributions on the phase space formulation of hybrid Hamiltonian systems, Buric *et al.* proposed a hybrid theory based on stochastic differential equations for constrained dynamical systems in [53]. The theory shows the ability to describe the measurement process with a classical apparatus, avoiding the necessity of imposing the collapse of the wave function as a postulate.

- In an analogous fashion, Oppenheim *et al.* proposed in [54] a consistent coupling of quantum and classical systems under the scope of stochastic hybrid dynamics. The theory is demonstrated with several toy models. In relation with this thesis, an interesting feature is that the authors suggest that the theory would be most suitable for the description of the *backreaction* of quantum field theoretical matter over curved spacetime, as it does not require the pathological semiclassical Einstein field equations, attributed to Moller and Rosenfeld. This is further commented at the end of this introduction.

- In another fashion, Zhang and Wu followed in [55] a formulation of Hamiltonian hybrid theory that is analogous to the one of Buric *et al.*, also in terms of a hybrid Poisson bracket. They partially recovered the geometric features of some Born-Oppenheimer approaches, namely, the presence of a Berry phase on the quantum system and of a geometric force (Lorentz like) on the classical dynamics. This dynamics presents analogous features to the semiclassical limit of the Exact Factorization [29]. The authors also proved the equivalence of several hybrid bracket approaches with the mean field dynamics (another name for Ehrenfest's) in [56], in the sense that the brackets were defined for the statistical dynamics of hybrid ensembles, while Ehrenfest's reproduces the microdynamics of the pure states.

- In a different framework, Hall and Reginato characterized in [57–59] hybrid systems in the formalism of ensembles on configuration space. They succeeded in achieving all consistency requirements posed by Salcedo in [60], and were able to recover good thermodynamical ensembles for the classical subsector, which was considered a sign for the theory to be physically complete. Nevertheless, the consistency of the construction relies on the assumption that the quantum subsector is not directly accessible to measurement, but only the classical one.

- Peres and Terno explored the Wigner function - Liouville density quantum-classical theory [61]. However it did not fulfil a natural benchmark for consistency defined by the authors, which will be summarized in the following section. The failure of some hybrid dynamics to fulfil this benchmark will be further explored by the authors in [62], and is also taken into account by Salcedo as one of his consistency criteria for hybrid dynamics.

- In [63], Elze introduced what he called "linear hybrid dynamics", which satisfied all of Salcedo's requirements, including the benchmark of Peres and Terno mentioned above. The theory was based on the representation of quantum mechanics in the geometric framework developed by Heslot [64]. In essence, he used the notions of phase space, observables, and Poisson brackets for both the classical and quantum subsystems. The hybrid system inherits these structures and the resulting theory is precisely Ehrenfest's dynamics, in its geometric formulation. Nevertheless, for generality, the interaction Hamiltonian between the classical and quantum subsystems is allowed to depend on both classical momenta and positions. The sense of linearity arises from the consideration of Liouville's equation over distributions on phase space, characterizing hybrid ensembles. This is very much in line with Buric's approach in [51].

- It is relevant to note that in a previous work, Anderson [65] used a variational principle to derive the dynamics from a hybrid action. This turns out to be formally equivalent to Elze's approach, also based on Heslot's picture of quantum mechanics presented as classical analytical mechanics [64].

- One of the foundational works on the formulation of hybrid dynamical theories was written by Boucher and Traschen [66], based on operator valued functions over classical phase space. This is one of the first attempts to build a theory based on a hybrid density matrix with a closed dynamical equation under the assumption of some physically sensible constrains for the dynamics. Nevertheless, the theory failed to preserve the positivity of the density matrix, necessary for a consistent probabilistic interpretation.

Note that this list of hybrid dynamics is far from complete. Instead, it consists of a

selection of the works that are deemed most relevant to set the context of this thesis. In view of this pandemonium of possible hybrid dynamical systems, we choose to focus on Ehrenfest dynamics, for reasons that are justified in the following section. However, we anticipate that, to avoid compromising the thermodynamics of hybrid systems with the choice of a particular microdynamics, when treating *solely* thermodynamical matters (such as the definition of entropy and equilibrium ensembles) we assume a probabilistic approach, which is indeed independent of the underlying single-particle dynamics. The alternative would be to build the statistical mechanics departing from the dynamics of a single particles and generalize it for ensembles, as it is done for example by Balescu [67], but this procedure would be tied to the choice of microdynamics and the associated concepts of ergodicity and detailed balance. Consequently, thermodynamical ensembles appear as an abstract representation as distributions of the averages of visitation times over subregions of the phase space under appropriately thermostatted trajectories. Given the lack of consensus on the "more physical" hybrid microdynamics, the visitational approach for any given microdynamics would compromise the consistent definitions of hybrid thermodynamics. Thus, when introducing the hybrid entropy and canonical ensemble in the first article of this compendium, the discussion is independent of Ehrenfest dynamics or any other, even if later in this thesis we analyze the relation of such dynamics with thermodynamical properties in two different contexts. The first one is treated in [2], and corresponds to molecular dynamics simulations coupled to a thermostat, where, in order to yield appropriate hybrid thermodynamical ensembles under time averages, we correct the computational application of the hybrid version of the ergodic hypothesis. The second one is in relation with a fundamental long-stanging issue regarding the statistical mechanics of some Hamiltonian hybrid dynamics and, in particular, of Ehrenfest dynamics. The issue was originally raised in [51, 52]. In this thesis, it is treated in [3] and, to a lesser extent, in [4].

1.1.2 Ehrenfest dynamics

Even though Ehrenfest dynamics is chosen for illustrative purposes in this introduction, its prominent role in this thesis is justified due to its historical significance and proven viability as an effective theory [68]. Furthermore, Ehrenfest dynamics has some physical and mathematical properties which make it an outstanding candidate beyond other approaches:

- It can be naturally derived through a partial semiclassical procedure from the full quantum description, and allows for a rigorous control of the order of magnitude of the errors introduced by the partial classical limit [68].
- It defines microdynamics for hybrid pure states (a given pure quantum state and a given point in classical phase space), not only for statistical mixtures.
- The dynamics for the quantum subsystem is not bound to a single eigenstate of

the Hamiltonian operator (either at all times as in Born-Oppenheimer MD, or for finite periods of time, as in surface-hopping). Instead, it constitute an unrestricted *non-adiabatic* evolution through the Hilbert space, allowing for the natural linear combinations appearing in quantum mechanics. This makes it a more accurate than Born-Oppenheimer MD with a viable computational cost, even for large systems.

- The nature of this dynamics is neither algorithmic nor stochastic, as it is in surface hopping and in other algorithmic approaches. It is continuous and, within a certain accuracy, *physical*. Furthermore, it does not require time or multiple trajectory averages, but instead a single trajectory contains the physical information, as in ordinary quantum or classical mechanics.

- It is *Hamiltonian*, and it can be written in terms of a hybrid Poisson bracket (see [69], based on [70], which will be summarized later). This ensures the conservation of energy at all times.

- Being a symplectomorphism, one can naturally make use of Liouville's theorem and define statistical mechanics for distributions over a hybrid phase space. However, the thermodynamical implications are quite intricate, as is explained in the third paper of this compendium.

- Ehrenfest dynamics incorporates a concrete backreaction effect of the quantum subsystem on the classical one and *vice versa*, contrarily to other hybrid approaches (this issue is also considered in the fourth paper of this compendium).

- Most importantly, as proven by Elze [63], Ehrenfest dynamics satisfies the following compatibility axioms of hybrid theories summarized by Reginatto and Salcedo in [60, 71] (resulting from previous some no-go theorems introduced in [61, 72, 73]).

    1. Conservation of energy and probability, despite the fact that the non-linear character of the quantum evolution makes it non-unitary.
    2. Concrete description of the *backreaction* of the quantum subsystem on the classical degrees of freedom.
    3. Provides the correct classical and quantum independent dynamics in the limit of no interaction.
    4. Presents a proper definition of hybrid states and observables. There is a well defined Lie bracket structure on the algebra of observables that suitably generalizes Poisson and commutator brackets for classical and quantum subsystems respectively.
    5. The observables can be regarded as the generating functions of canonical transformations corresponding to their Hamiltonian vector fields, and, for those ob-

servables only dependent on quantum d.o.f., the classical sector remains invariant under the correspondent canonical transformations, and *vice versa*.

6. Fulfilment of a generalized Ehrenfest theorem for the expectation values of observables which may also depend on the classical variables. Historically, Ehrenfest dynamics is regarded as insatisfactory in this aspect, due to a naive generalization of the theorem. As it will be later explained, the theorem can be rigorously fulfiled with a proper extension of the hybrid algebra of observables.
7. Fulfilment of the Peres-Terno benchmark test [61]. In relation to the previous point, this implies that the expectation value of momenta and positions fulfil classical equations of motion if the potential is quadratic in both classical and quantum positions (bilinear in their coupling).

Despite these boons at the micro-dynamical level, Ehrenfest dynamics presents unsettling features in relation with the statistical mechanics that its Liouvillian induces, if one wants to relate it with the density matrix formalism, as explained in [51]. This will be explored later and partially solved in this compendium.

Let us now formally present Ehrenfest dynamics. A hybrid system is composed of two subsystems: a quantum one, whose states are represented by vectors in a certain Hilbert space, $|\Psi\rangle \in \mathcal{H}$, and a classical one, characterized by its generalized positions and momenta, which we will collectively denote as $\xi = (Q, P) \in \mathcal{M}_C$, being $\mathcal{M}_C$ the classical phase space. The phase space of both subsystems are considered independent of each other, but the dynamics is coupled. To illustrate this coupling and the nature of this kind of hybrid systems, we will invert the narrative, saving for later the formal derivation of Ehrenfest dynamics from a full quantum description and directly presenting the equations:

$$\frac{d}{dt}Q_i = -\frac{\partial}{\partial P_i}\langle\Psi|\hat{H}(Q,P)|\Psi\rangle\,, \tag{1.1}$$

$$\frac{d}{dt}P_i = -\frac{\partial}{\partial Q_i}\langle\Psi|\hat{H}(Q,P)|\Psi\rangle\,, \tag{1.2}$$

$$\frac{d}{dt}|\Psi\rangle = \frac{-i}{\hbar}\hat{H}(Q,P)|\Psi\rangle\,. \tag{1.3}$$

Here, $\hat{H}(Q,P)$ is called the hybrid Hamiltonian operator, which, for each value of the classical variables (Q,P), is a self-adjoint operator over $\mathcal{H}$, the Hilbert space of quantum states. The notion of hybrid operators is further characterized later. For most applications, such as molecular dynamics, the interaction between classical and quantum subsystems does not depend on their momenta, and therefore this Hamiltonian operator is usually decomposed as:

$$\hat{H}(Q,P) = \sum_i \frac{P_i^2}{M_i}\hat{\mathbb{I}} + V_C(Q)\hat{\mathbb{I}} + \hat{V}_q + \hat{V}_{qc}(Q) + \hat{K}_q\,, \tag{1.4}$$

where the first two terms only affect the classical subsystem, with the first one being the kinetic energy (M_i denote the masses of the classical particles) and the second one, its

potential energy without the interaction with the quantum subsystem. Analogously, the term $\hat{V}_q$ represents the potential energy operator for the quantum subsystem without interaction with the classical one. The potential energy of such interaction is thus captured in $\hat{V}_{qc}(Q)$, which is a non-derivative self-adjoint operator over $\mathcal{H}$ which depends on the classical positions. Lastly, $\hat{K}_q$ represents the kinetic energy terms for the quantum subsystem. Therefore, for this kind of systems the former Ehrenfest dynamics are particularized to be:

$$\frac{d}{dt}Q_i = \frac{P_i}{M_i} \tag{1.5}$$

$$\frac{d}{dt}P_i = -\langle\Psi|\frac{\partial}{\partial Q_i}\hat{V}_{qc}(Q)|\Psi\rangle \tag{1.6}$$

$$\frac{d}{dt}|\Psi\rangle = \frac{-i}{\hbar}\hat{H}_q(Q)|\Psi\rangle\ , \tag{1.7}$$

where $\hat{H}_q(Q) := \hat{V}_q + \hat{V}_{qc}(Q) + \hat{K}_q$ includes a kinetic and two potential terms affecting the quantum subsystem, and is a Hamiltonian that defines a Schrödinger-like equation for the quantum state. The terms in $\hat{H}(Q,P)$ that are proportional to the identity can be removed from the Schrödinger equation, as they would only produce a global phase change. Note that the system is non-linear because the quantum state *back-reacts* on $d_t P_i$ through the expectation value of the forces, and, in turn, it modifies Q_i, which ultimately determines the Hamiltonian operator governing the quantum equation of motion. Given this non-linearity, this dynamics cannot be unitary (as linearity is a prerequisite, as discussed in [69]). However, one can prove that this dynamics does preserve the norm of the quantum state.

To exemplify this construction with a physical system we will focus in the following on the case of molecular dynamics, where nuclei will be considered classical and electrons quantum mechanical (although the description is general and can be used in any other example). Consider a molecule described in three spatial dimensions, with n electrons and N nuclei. We can therefore identify $\mathcal{H} \equiv L^2(\mathbb{R}^{3n}, dx^3)$, where dx^3 will represent Lebesgue measure over $\mathbb{R}^{3n}$, for which we may use dx to simplify the notation. This yields the usual wave function $\Psi(\vec{\mathbf{x}}) \in L^2(\mathbb{R}^{3n}, dx^3)$ interpretation of the Hilbert space, where the scalar product is given by the Lebesgue measure and $\mathbf{x}_i = (x_i, y_i, z_i) \forall i \in [1, n]$ accounts for the three spatial coordinates of the positions of the i-th electron. On the other hand, the classical phase space is constructed as the cotangent bundle of the positions of the nuclei, $\mathcal{M}_C \equiv T^\star(\mathbb{R}^{3N}) \sim \mathbb{R}^{3N} \times \mathbb{R}^{3N}$ which in turn (given the triviality of the bundle) is isomorphic to twice $3N$ real coordinates (the first time for the positions, and the second one for the momenta).

In this context, the common prescription is to describe all interactions through Coulomb potentials. Thus, we model the interaction between nuclei with the potential as:

$$\hat{V}_c(Q) := \alpha \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{Z_i Z_j}{|\mathbf{Q}_i - \mathbf{Q}_j|}\,, \tag{1.8}$$

being Z_i the atomic number of the i-th nuclei and α, Coulomb's constant. For the electrons we define

$$\hat{V}_q := \alpha \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}\,, \tag{1.9}$$

and, lastly, for the electron nuclei-interaction, we have:

$$\hat{V}_{cq} := -\alpha \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_i}{|\mathbf{Q}_i - \mathbf{x}_j|}\,. \tag{1.10}$$

On the other hand, the kinetic terms are given by

$$\hat{K}_c := \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2M_i}\,, \tag{1.11}$$

and

$$\hat{K}_q := \sum_{i=1}^{n} \frac{-\hbar^2}{2m_e} \nabla_{\mathbf{x}_i}^2\,. \tag{1.12}$$

In this last equation, we have explicitly used the representation of the momentum operator over the given L^2 space for the electronic variables, as $\hat{p}_i = -i\hbar\nabla_{\mathbf{x}_i}$.

Therefore, the total potential energy operator is represented as:

$$\hat{V}(Q,x) = \hat{V}_c(Q) + \hat{V}_{cq}(Q,x) + \hat{V}_q(x)\,, \tag{1.13}$$

while the quantum Hamiltonian governing its dynamics is functionally represented by the sum of a derivative operator and a multiplicative one:

$$\hat{H}_q(Q) = \hat{K}_q + \hat{V}_{cq}(Q,x) + \hat{V}_q(x). \tag{1.14}$$

Naturally, we may identify the total Hamiltonian operator introduced above with:

$$\hat{H}(Q) = \hat{H}_q(Q) + \hat{K}_c(P) + \hat{V}_c(Q)\,. \tag{1.15}$$

Substituting these expressions in equations (1.5,1.6,1.7) yields the usual prescription of Ehrenfest's molecular dynamics. Note that, for simplicity, we have been ignoring the spin degrees of freedom in this presentation. Nevertheless, their inclusion is possible within the same mechanical formalism, just through the addition of the appropriate interaction terms to the Hamiltonian.

These equations are not a postulate or a heuristic proposal, but instead, they can be rigorously derived as an effective theory from a more fundamental theory, with appropriate bounds for the neglected terms. Indeed, following for example Bornemann [68], Ehrenfest's dynamics can be derived from a well defined semiclassical limit from a full quantum description . In such a full quantum description, the molecular Hilbert space $\mathcal{H}_M$ is described

by the tensor product of two Hilbert spaces, the nuclear one $\mathcal{H}_n \sim L^2(\mathbb{R}^{3N}, dQ^{3N})$ and the electronic one, $\mathcal{H}_e \sim L^2(\mathbb{R}^{3n}, dx^{3n})$:

$$\mathcal{H}_M := \mathcal{H}_n \otimes \mathcal{H}_e \, . \tag{1.16}$$

A generic state of such Hilbert space presents electron-nuclear entanglement[1], such that $\Psi_M(Q, x) \in \mathcal{H}_M$ cannot be decomposed by an ordinary product of $\Psi_n(Q) \in \mathcal{H}_n$ and $\Psi_e(x) \in \mathcal{H}_e$. From this departure point, the following steps yield Ehrenfest dynamics.

- The first approximation at the core of most hybrid dynamics (except for those based on the Exact Factorization) is the so called *Self Consistent Field approximation* (SCF), which consists in neglecting entanglement, and therefore:

$$\begin{array}{rcl} \mathcal{H}_n \otimes \mathcal{H}_e & \rightarrow & \mathcal{H}_n \times \mathcal{H}_e \\ \Psi_M(Q, x) & \rightarrow & \Psi_n(Q)\Psi_e(x) \end{array} \tag{1.17}$$

  Its justification is mostly based on the negligible magnitude of such entanglement for most phenomena, given by the small spatial variance of the nuclear positions relative to the width of the electronic wave packet. It is also sometimes justified by an environment-induced decoherence between the subsystems. In any case, this separability is considered to be preserved not only at an instant in time, but also during the evolution, which is an approximation of the real behavior. After this step, the state of the molecular system is given by two states for each subsystems that are now unentangled and therefore, any further approximation can be taken over any of the subsystems independently of the other one. Thus, in the following approximation steps, given that it must remain as truthfully quantum mechanical as possible, the electronic subsystem is left untouched.

- The second approximation is thus applied solely to the nuclear subsystem, and makes use of any semiclassical limit which yields a statistical classical system from quantum mechanics. The justification of applying the semiclassical limit solely to the nuclear subsystem is given by the mass ratio $M_i/m_e \gg 1$, allowing us to consider nuclear dynamics much slower than electronic ones. In order to perform the semiclassical limit one can choose between Hagerdorn's semiclassical Gaussian ansatz that approximately follows classical paths (see [74] for such semiclassical limit and [75] for its application to reach a hybrid system), a quantum coarse graining procedure (for example, [76–78]), Maslov's WKB procedure [79] (favoured in Bornemann *et al.* analysis [68] due to the tighter mathematical control of the approximation) or any other suitable limit.

[1] In the density matrix formalism, the state is represented by $\hat{\rho}$, a dual to the representation of physical observables as self-adjoint operators $\mathcal{O}(\mathcal{H}_M)$ over the molecular Hilbert space. In such formalism, the entanglement of the pure state $\hat{\rho} \in \mathcal{O}^\star(\mathcal{H}_M)$ implies that the partial trace over one of the subsystems, for example over the nuclear one $\hat{\rho}_e := \mathrm{Tr}_n(\hat{\rho})$, is not a pure state, meaning $\mathrm{Tr}(\hat{\rho}_e^2) < 1$.

After this step, the nuclear wave packet is effectively described as a classical density of probability $\rho_C \sim |\Psi_n|^2$ that follows, in one way or another, classical paths. Following Bohm's approach, even before the semiclassical limit we can identify such paths as bundles of classical trajectories which are solution to a Hamilton-Jacobi (HJ) equation, where the role of the action S is played by $\hbar$ times the phase of the nuclear wave function, $\Psi_n \simeq |\rho_C| e^{i\hbar^{-1}S}$, so that:

$$\partial \rho_C(Q;t) = \nabla_Q \left(\rho_C \frac{1}{M} \nabla_Q S \right) \quad \text{and} \tag{1.18}$$

$$\frac{\partial}{\partial t} S + \frac{1}{2M} \left((\nabla_Q S)^2 - \hbar^2 \nabla_Q^2 \rho_C \right) + V_C + \langle \Psi | \hat{H}_{qc} | \Psi \rangle = 0 \, . \tag{1.19}$$

If one identifies $P := \nabla_Q S$, the first equation is just a continuity equation, and the second one a HJ equation for the action S with the natural quadratic momenta term. As it can be seen, this classical system is coupled to the quantum system through the electronic expectation value of the electron-nuclear Hamiltonian. Furthermore, theres is a term quadratic in $\hbar$ that is dubbed *quantum potential*, and accounts, as a force, for the dispersive nature of the quantum evolution of localized wave packets. In the *short-wave-asymptotics* approximation, at the core of Maslov's semiclassical limit, the quantum potential does not appear in the HJ equation, neither does the kinetic term for the electrons. Therefore, we end with a set of trajectories $(Q(t), P(t))$ that are solutions to this approximation to the original HJ equation. We may the define a density for these trajectories in the full phase space $\rho_C(Q, P)$ – as opposed to the previously ρ_C, a function of the coordinates only. This is the key conceptual result of Maslov's semiclassical procedure.

In the end, the system is described by a classical probability density for the nuclei. These nuclei follow classical paths, and each of those paths is coupled to a quantum mechanical state, which in turn evolves under the influence of the classical subsystem. If one performs a multiple-trajectory semiclassical simulation of nuclei coupled to quantum electrons, making up for a statistical description of the nuclei, this would be the end of the hybrid limit procedure. Nevertheless, this statistical system does not define hybrid microdynamics, as one does not have a single hybrid trajectory, but an effective approximation to quantum mechanics in terms of a statistical description following a sheaf of hybrid paths. In this approach, each classical trajectory is coupled to the same electronic wave function, on which they react with a weighted average. Therefore, the classical trajectories are indirectly coupled between them, through their interaction with the quantum subsystem, which is described by a single quantum state.

- The last step to obtain hybrid *microdynamics* is the *infinite localization* approximation. This means onsidering that the width of the nuclear wave packet, defined as $\epsilon^2 := \langle \Psi_n | Q^2 | \Psi_n \rangle - \langle \Psi_n | Q | \Psi_n \rangle^2$, is negligible in relation with the relevant spatial

scales for the studied phenomenology (such as Bohr's radius, a_0, characterizing the order of magnitude of the electronic dispersion). If this ratio is such that the approximation $\frac{\epsilon^2(t)}{a_0^2} \simeq 0$ is reasonable for the finite time in which the studied process occurs, we can consider that a single classical trajectory survives with probability 1. In other words, the distribution $\lim_{\epsilon \to 0} \rho_c(Q,P;t) = \delta\left((Q,P) - (Q_C(t), P_C(t))\right)$ yields expectation values for all the relevant observables that are compatible with the full quantum ones under a given tolerance.

A subtlety arises in this context: the term known as quantum potential appearing in the original HJ equation governing the nuclear path dynamics is inversely proportional to the width σ_n of the nuclear wave function. Therefore, it becomes huge when the formal limit $\sigma_n \to 0$, and could be seen as the dominant term governing the dynamics. This is natural from the point of view of Bohmian dynamics, as explained in [80]: the quantum potential is negligible when the classical trajectories do not clump together, but, at the focal points (when all the trajectories converge to a value, or when the distribution tends to Dirac's delta), the quantum potential becomes dominant in the dynamics and avoids such focalization.

Nevertheless, it can be shown that classical trajectories (without the quantum potential) reproduce accurately enough the expectation values for the full quantum scheme when the width of the wave function is negligible compared with the relevant physical scales (shown under the criterium of convergence in probability as detailed in [81]). From another point of view, neglecting the quantum potential for sufficiently small times is justified by de Gosson and Hiley in [82].

With these approximations (and in the absence of focal points in the evolution of the classical trajectories characterizing the evolution of the nuclear wave function), provided that the initial width of the nuclear wave packet is small enough and nuclei masses, heavy enough (in relation with its electronic equivalents), the nuclear subsystem is effectively described by a single point in the phase space of classical positions and momenta (its wave-packet's width neglected). On the other hand, the electronic wave function remains full quantum mechanical, their evolution coupled precisely as in equations (1.5,1.6,1.7). Such an effective description may accurately approximate sometimes the full quantum behavior for finite times, as shown in [68, 83].

Another important feature of Ehrenfest dynamics is that it can also be naturally derived from a *bottom-up* approach, based on the Lagrangian formalism and the definition of a hybrid action.

We will firstly consider the action for the classical variables, in the absence of the

quantum subsystem:

$$S_C := \int_{t_0}^{t_1} \left(\sum_i^N P_i \partial_t Q_i(t) - \left(\sum_i^N \frac{P_i^2(t)}{2M} + V_c(Q) \right) \right) . \tag{1.20}$$

One may the formulate an extreme action principle, $\frac{\delta S_C}{\delta P_i(t)} = \frac{\delta S_C}{\delta P_i(t)} = 0 \quad \forall i \in [1, N]$. This yields Hamilton's equations of motion for classical mechanics with potential V_c. Anagously, one can consider the Schr$^{\acute{}}$odinger-Hilbert action for the quantum subsystem:

$$S_Q := \int_{t_0}^{t_1} \int_{\Sigma} dx \bar{\Psi}(x,t) \left(i\hbar\partial_t - \hat{H}_q(Q) \right) \Psi(x,t) , \tag{1.21}$$

which yields the Schrödinger equation and its conjugate for the self-adjoint Hamiltonian operator $\hat{H}_q(Q)$ under its extreme action principle[2], $\frac{\delta S_Q}{\delta \Psi(x,t)} = \frac{\delta S_Q}{\delta \bar{\Psi}(x,t)} = 0$.

Note that such Hamiltonian operator is considered to be dependent on Q, treated as some external parameter (which may have its own dynamics), giving rise to Schrödinger equation for a time-dependent Hamiltonian operator. Besides, in the context of molecular dynamics, such Hamiltonian operator can be decomposed as above in terms of a kinetic term, a potential term for the electrons, and an interaction term of the electrons with the Q-external variables, $\hat{H}_q(Q) = \hat{K}_q + V_q(x) + V_{qc}(Q, x)$.

Now, if we consider the sum of both actions:

$$S_H := S_Q + S_C \tag{1.22}$$

and identify Q with the classical positions (which are kinematical variables, and therefore we must take the extreme of the action over their associated paths $Q(t)$), once we perform the extreme action principle, $\frac{\delta S_H}{\delta Q_i(t)} = \frac{\delta S_Q}{\delta P_i(t)} = 0 \quad \forall i \in [1, 3N]$ and $\frac{\delta S_H}{\delta \Psi(x,t)} = \frac{\delta S_H}{\delta \bar{\Psi}(x,t)} = 0$, we arrive precisely to Ehrenfest dynamics as defined above.

Given the Lagrangian formulation, the interest on the hybrid conserved quantities (in particular, the total energy and other symmetry generators), the need of a hybrid Lie bracket structure to generalize Poisson brackets and, most importantly, the relevance of the construction for the later definition of statistical mechanics by means of Liouville's

[2]The extreme action principle in this context requires the derivative with respect to $\Psi(x)$ and $\bar{\Psi}(x)$. Given their functional nature they are infinite dimensional, and consequently we cannot identify such derivatives with variations over a finite number of variables at each fixed time t (as are usually defined the derivatives along paths in textbooks). Nevertheless, such functional derivatives can still be defined either over a discretization of the Hilbert space, truncating a certain basis and derivating over the coordinates on such truncated basis, or exactly, over the infinite dimensional Hilbert space, at the cost of considering the dense definition of Fréchet derivatives over a nuclear Fréchet dense subset of the L^2-space[84]. For a deeper review on these mathematical subtleties, check the supplementary material of [5], at the end of section 3 of this thesis.

theorem, a natural historical step was the development of the Hamiltonian formalism of hybrid systems. In the following section we summarize such construction, introduced in [69] as a generalization of Kibble's geometric formulation of quantum mechanics [70] and particularized for Ehrenfest dynamics.

1.2 The geometric formulation of mechanical systems

Classical analytical mechanics

We will start by reviewing the geometry of classical mechanics, that will be part of the hybrid construction, and as we shall show later, is analogous to the one of the quantum subsystem. In order to do so, we will roughly follow the theory presented in Ref. [85].

In most cases, the classical phase space of positions and momenta is constructed as a cotangent bundle to the configuration manifold (space of all generalized positions). Given the duality of momenta and position velocities, it is an even dimensional manifold and is naturally endowed with a canonical symplectic form

$$\omega_C := dP^i \wedge dQ_i \ , \tag{1.23}$$

where repeated upper and lower indices imply Einstein's summation convention. The classical phase space is therefore a symplectic manifold $(\mathcal{M}_C, \omega_c)$, and the space of classical observables, defined as $C^\infty(\mathcal{M}_C)$, is in turn provided with a Poisson bracket, a bilinear differential operator given by:

$$\{f,g\}_C := \partial_{[Q_i} f \partial_{P^i]} g \equiv \partial_{Q_i} f \partial_{P^i} g - \partial_{P^i} f \partial_{Q_i} g \quad \forall f,g \in C^\infty(\mathcal{M}_C) \tag{1.24}$$

where we have introduced the subindex commutation notation for derivatives, together with Einstein's summation convention. The Poisson bracket fulfils, besides bilinearity, skew-symmetry, $\{f,g\} = -\{g,f\}$; the Leibniz identity for the ordinary product of functions, $\{f,gh\} = g\{f,h\} + \{f,g\}h$; and the Jacobi identity, $\{f,\{g,h\}\} + \{g,\{h,f\}\} + \{h,\{f,g\}\} = 0$.

Because of all those properties, and being the Poisson bracket an internal operation to the set of functions considered, in the sense that $\{,\}_C : C^\infty(\mathcal{M}_C) \times C^\infty(\mathcal{M}_C) \to C^\infty(\mathcal{M}_C)$, the set of classical observables forms a Poisson algebra under the classical Poisson bracket, which we will denote as:

$$\mathcal{A}_C := (C^\infty(\mathcal{M}_C), \{,\}_C) \ . \tag{1.25}$$

Such Poisson bracket is related to the Poisson bivector Ω_C, inverse of the symplectic form, in the following way:

$$\omega_C(X_f, X_g) = \Omega_C(dg, df) = \{g,f\}_C \quad \forall f,g \in C^\infty(\mathcal{M}_C) \tag{1.26}$$

where Ω_C acting over the correspondent exact one forms df and dg yields a real function given by the Poisson bracket over the associated functions, $\{g, f\}_C$. This is a useful way to introduce the Poisson bracket from a geometric perspective. In the same way ω_C acts over the vector fields X_f, X_g. Such Hamiltonian fields can be rigorously identify seizing its duality to the one forms $X_f = \Omega_C(df, \cdot)$ or, as is commonly done in classical mechanics, as its action over functions, a linear differential operator acting $C^\infty(\mathcal{M}_C)$ given by $X_f \equiv \{\cdot, f\}_C$.

All transformations over phase space that leave the symplectic form invariant (symplectomorphisms), usually physical symmetries, acquire a Hamiltonian representation (at least for manifolds where de Rham's cohomology group is trivial) in terms of a conserved quantity (e.g. for the time translation symmetry, the energy function), in the following sense. Let $X \in \mathfrak{X}(\mathcal{M}_C)$ be a vector field over the classical phase space which represents the infinitesimal generator of a symmetry $\alpha_X : \mathcal{M}_C \to \mathcal{M}_C$, such that its flow α_X realizes such symmetry, then:

$$\forall X \in \mathfrak{X}(\mathcal{M}_C) | \mathcal{L}_X \omega_C = 0 \; \exists f \in \mathcal{A}_C \text{ such that } \mathcal{L}_X g = \{g, f\}_C \; \forall g \in \mathcal{A}_C \; , \tag{1.27}$$

where f is called the generating function of the symmetry and is a conserved quantity under it, while $\mathcal{L}_X$ is the Lie derivative under X, which is equivalent to the directional derivative ∇_X for scalar functions, like g in the definition. This means that, for any physical observable, we can represent its transformation under a symplectomorphism with the Poisson bracket with its generating function.

In particular, for the dynamics, being f_H the energy function generating the symmetry "time translations", its infinitesimal action over any observable is given by:

$$\frac{dg}{dt} = \{g, f_H\}_C \forall g \in \mathcal{A}_C \; , \tag{1.28}$$

which particularizes to Hamilton's equations of motion for when g is identified with the canonical coordinates, Q_i, P^i.

Geometric formulation of quantum mechanics

In [70] an analogous formalism to the one introduced above, based on symplectic geometry, is developed for quantum mechanical systems. In this section, we summarize such formalism.

In ordinary quantum mechanics, the quantum states are vectors is a Hilbert space, $\Psi \in \mathcal{H}$. This Hilbert space, its scalar product and the states, already contain all the ingredients necessary for the geometric formulation of quantum mechanics. Although the construction described by Kibble [70] is basis-agnostic and valid for finite and infinite-dimensional spaces, in order to gain intuition on the construction, we will summarize

firstly the easier coordinate-based approach introduced by Heslot [64] for finite dimensional Hilbert spaces.

Let $\{\Psi_i \in \mathcal{H}\ \forall i \in [1, d_Q] \mid \langle \Psi^i | \Psi^j \rangle = \delta_{ij}\}$ be a basis of the Hilbert space $\mathcal{H}$ of dimension d_Q. Let us now consider the coordinates $c_i := \langle \Psi | \Psi_i \rangle$ of the quantum state $\Psi \in \mathcal{H}$. Such coordinates can be decomposed into real (q_i) and imaginary parts (p_i) such that:

$$\Psi = \sum_{j=1}^{d_Q} (q_j + i p_j) \Psi_j \ . \tag{1.29}$$

The state can be characterized, therefore, by the vector $V_\Psi := (q_1, \cdots q_{d_Q}, p_1, \cdots p_{d_Q})^t \in \mathcal{M}_Q$, defining in this way the quantum phase space $\mathcal{M}_Q = \mathbb{R}^{d_Q} \times \mathbb{R}^{d_Q}$, isomorphic to $\mathcal{H}$. As it is a linear space, the set of tangent vectors defined on $\mathcal{M}_Q$ define a set which is isomorphic to $\mathcal{M}_Q$. This manifold has a complex structure, J_Q, a $(1,1)-$tensor reproducing the multiplication by the imaginary unit i over the Hilbert space, $\mathcal{H}$. Naturally, acting over a vector of $\mathcal{M}_Q$, can be represented as a matrix which can be defined by blocks as:

$$J_Q V_\Psi := \begin{pmatrix} 0_{d_Q} & -\mathbb{I}_{d_Q} \\ \mathbb{I}_{d_Q} & 0_{d_Q} \end{pmatrix} \begin{pmatrix} q_1 \\ \vdots \\ q_{d_Q} \\ p_1 \\ \vdots \\ p_{d_Q} \end{pmatrix} = \begin{pmatrix} -p_1 \\ \vdots \\ -p_{d_Q} \\ q_1 \\ \vdots \\ q_{d_Q} \end{pmatrix}, \tag{1.30}$$

which is just reproducing the fact that the real part of a coordinate of $i\Psi$ is minus the imaginary part of the one of Ψ, and the imaginary part of a coordinate of $i\Psi$ is the real part of Ψ. Furthermore, we can define a symplectic structure $\omega_Q := dp^i \wedge dq_i$, which, acting on two vectors on $\mathcal{M}_Q$ represented by their coordinates on the vector basis $\partial_{q_i}, \partial_{p_i}$, can be represented matricially as:

$$\omega_Q(V_{\Psi_a}, V_{\Psi_b}) = \begin{pmatrix} q_1^a \\ \vdots \\ q_{d_Q}^a \\ p_1^a \\ \vdots \\ p_{d_Q}^a \end{pmatrix}^t \begin{pmatrix} 0_{d_Q} & -\mathbb{I}_{d_Q} \\ \mathbb{I}_{d_Q} & 0_{d_Q} \end{pmatrix} \begin{pmatrix} q_1^b \\ \vdots \\ q_{d_Q}^b \\ p_1^b \\ \vdots \\ p_{d_Q}^b \end{pmatrix} = \sum_{i=1}^{d_Q} (p_i^a q_i^b - q_i^a p_i^b) \ . \tag{1.31}$$

The scalar product of two vectors in the Hilbert space can be written in this coordinates as:

$$\langle \Psi_a | \Psi_b \rangle = \sum_{i=1}^{d_Q} \bar{c}_i^a c_i^b = \sum_{j=1}^{d_Q} \left(q_j^a q_j^b + p_j^a p_j^b - i \left(p_j^a q_j^b - q_j^a p_j^b \right) \right) \ . \tag{1.32}$$

This scalar product can be reproduced at the tensorial level, as the scalar product of any Hilbert space is a Hermitian form, which we will denote by h_Q. From its coordinate version

in eqs. (1.31, 1.32), we realize that the imaginary part of h_Q is given by the symplectic structure ω_Q. On the other hand, combining ω_Q and J_Q, (1.31, 1.30) in coordinates, we find that the real part of h_Q is given by μ_Q defined as $\mu_Q(V_{\Psi_a}, V_{\Psi_b}) := \omega_Q(J_Q V_{\Psi_a}, V_{\Psi_b})$. Precisely, if μ_Q is a Riemannian metric over the vector space (real, symmetric, defining a positively defined norm), we state that the complex and symplectic structures are in Kahler compatibility, and we denote the manifold of quantum states provided with this triad of compatible structures, $(\mathcal{M}_Q, J_Q, \omega_Q, \mu_Q)$, a Kahler manifold [70].

With these considerations, dispensing with the particular choice of coordinates above, the following tensorial representation of the scalar product is immediately shown to be equivalent to eq. (1.32):

$$\langle \Psi_a | \Psi_b \rangle = h_Q(V_{\Psi_a}, V_{\Psi_b}) := \omega_Q(J_Q V_{\Psi_a}, V_{\Psi_b}) + i\omega_Q(V_{\Psi_a}, V_{\Psi_b}) \ . \tag{1.33}$$

On the other hand, as is the case of the complex structure J_Q, linear self-adjoint operators over the Hilbert space are seen as $(1,1)-$ tensors that can be represented by real matrix-like operators. Their expectation values, therefore, are quadratic functions on the variables q_j, p_j:

$$\langle \Psi | \hat{A} \Psi \rangle = \begin{pmatrix} q_1 \\ \vdots \\ q_{d_Q} \\ p_1 \\ \vdots \\ p_{d_Q} \end{pmatrix}^t \begin{pmatrix} A_{qq}^{11} & \cdots & A_{qq}^{1d_Q} & A_{qp}^{11} & \cdots & A_{qp}^{1d_Q} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ A_{qq}^{d_Q 1} & \cdots & A_{qq}^{d_Q d_Q} & A_{qp}^{d_Q 1} & \cdots & A_{qp}^{d_Q d_Q} \\ A_{pq}^{11} & \cdots & A_{pq}^{1d_Q} & A_{pp}^{11} & \cdots & A_{pp}^{1d_Q} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ A_{pq}^{d_Q 1} & \cdots & A_{pq}^{d_Q d_Q} & A_{pp}^{d_Q 1} & \cdots & A_{pp}^{d_Q d_Q} \end{pmatrix} \begin{pmatrix} q_1 \\ \vdots \\ q_{d_Q} \\ p_1 \\ \vdots \\ p_{d_Q} \end{pmatrix} = \sum_{u,v=q,p} A_{uv}^{ij} u_i v_j \tag{1.34}$$

These quadratic functions, more generally introduced later, constitute a representation of the quantum algebra of observables. The inverse of the symplectic structure, ω_Q, defines a Poisson tensor, Ω_Q. The action of this Poisson tensor over exact 1-forms $\Omega_Q(df, d_g)$ is given by the bidifferential operator over the associated functions $\{f, g\}_Q$, which is the geometric way of introducing the quantum Poisson bracket $\{,\}_Q$. This crucial object, written in coordinates, is given by:

$$\{f, g\}_Q := \partial_{q_i} f \partial_{p^i} g - \partial_{p^i} f \partial_{q_i} g \ . \tag{1.35}$$

It can be shown that this Poisson structure, that is analogous to the one of classical mechanics, reproduces the Lie bracket of operators (given by the imaginary unit times their commutator) for the quadratic functions representing the expectation value of self-adjoint operators:

$$\{\langle \Psi | \hat{A} \Psi \rangle, \langle \Psi | \hat{B} \Psi \rangle, \}_Q = \frac{-i}{\hbar} \langle \Psi | [\hat{A}, \hat{B}] \Psi \rangle \ . \tag{1.36}$$

In this way, we have an analogous formulation to classical mechanics for quantum observables.

Keeping in mind this illustrative case based on real and imaginary coordinates, we will now expand on these concepts following the coordinate-free approach of [70]. In general, the Hilbert space $\mathcal{H}$ can be decomposed into two copies of a *real* vector space which we will denote by $\mathcal{N}_R$ (for example, 2-integrable real functions, for $L^2_{\mathbb{R}}(\Sigma, d\text{Vol}_\Sigma)$, or the q's and p's manifolds, isomorphic to $\mathbb{R}^{d_Q}$, of [64]) The cartesian product manifold $\mathcal{N}_R \times \mathcal{N}_R$ can be provided with a Kähler structure, the triad formed by a complex structure J_Q, a symplectic form ω_Q and a Riemannian metric μ_Q, which fulfil the compatibility relation:

$$\mu_Q(V, W) = \omega_Q(J_Q V, W) \quad \forall V, W \in \mathcal{N}_R \times \mathcal{N}_R \,. \tag{1.37}$$

Consequently, two of such structures determine the third one uniquely. The resulting Kähler manifold is isomorphic to the original Hilbert space:

$$\mathcal{M}_Q := (\mathcal{N}_R \times \mathcal{N}_R, \omega_Q, \mu_Q) \cong \mathcal{H} \,. \tag{1.38}$$

We will call $\mathcal{M}_Q$ the quantum phase space, which is a vector space. In fact, the inner product $\langle , \rangle$ of the Hilbert space $\mathcal{H}$ is seen as an Hermitian 2-form in this framework, where ω_Q is its imaginary part and μ_Q its real part. Let V_Ψ denote the vector in $\mathcal{M}_Q$ that represents through the isomorphism the quantum state in the Hilbert space, $\Psi \in \mathcal{H}$. Then:

$$\langle \Psi_1, \Psi_2 \rangle = \frac{1}{2} \left(\mu_Q(V_{\Psi_1}, V_{\Psi_2}) + i\omega_Q(V_{\Psi_1}, V_{\Psi_2}) \right) \forall \Psi_1, \Psi_2 \in \mathcal{H}. \tag{1.39}$$

Given this isometry, to alleviate the notation we will in the following denote the vectors in the quantum phase space $\mathcal{M}_Q$ directly by the same character as the quantum state they represent in the Hilbert space, Ψ, and the Hermitian form by $\langle , \rangle$.

Regarding physical observables, in quantum mechanics they are represented by self-adjoint operators over the Hilbert space, denoted by $\mathcal{O}_H(\mathcal{H})$, which form a Lie algebra under the $i\times$commutator:

$$\frac{-i}{\hbar}[\hat{A}, \hat{B}] \in \mathcal{O}_H(\mathcal{H}) \quad \forall \hat{A}, \hat{B} \in \mathcal{O}_H(\mathcal{H}) \,. \tag{1.40}$$

In the context of the geometric formulation, the operators (which we will still denote by $\hat{A}$) are seen as real (1,1)-tensors acting over the vectors $V \in \mathcal{M}_Q$, the self-adjointness property means $[\hat{A}, J_Q] = 0$ and $\omega_Q(V_{\Psi_1}, \hat{A}V_{\Psi_2}) = \omega_Q(\hat{A}V_{\Psi_1}, V_{\Psi_2})$, while the Lie bracket for self-adjoint operators has the imaginary unit i substituted by the complex structure, J_Q.

Such set of operators can in turn be represented by the quadratic functions over the Hilbert space, denoted by, $\mathcal{F}_2(\mathcal{H})$ (or as $\mathcal{F}_2(\mathcal{M}_Q)$, in its geometric representation) given by the expectation value of the Hermitian operators:

$$\mathcal{F}_2(\mathcal{H}) := \{ f_A : \mathcal{H} \to \mathbb{R} | f_A = \langle \Psi, \hat{A}\Psi \rangle \quad \forall \hat{A} \in \mathcal{O}_H(\mathcal{H}) \} \,. \tag{1.41}$$

Over such set of functions, one can define a Poisson bracket, $\{,\}_Q$ in order to reproduce the Lie-bracket of the Hermitian operators:

$$\{f_A, f_B\}_Q = \frac{-i}{\hbar}\langle\Psi|[\hat{A},\hat{B}]|\Psi\rangle \tag{1.42}$$

which, naturally fulfils antisymmetry, Jacobi identity and bilinearity as the Lie bracket did, and Leibniz for the completion of $\mathcal{F}_2(\mathcal{H})$ under the ordinary product of functions. It is immediate to show that $\mathcal{F}_2(\mathcal{H})$ forms a Poisson algebra under $\{,\}_Q$, which we will denote as the quantum algebra of observables:

$$\mathcal{A}_Q := (\mathcal{F}_2(\mathcal{H}), \{,\}_Q) \tag{1.43}$$

We must remember that all these properties can analogously be expressed for $\mathcal{M}_Q$ in terms of J_Q and ω_Q, so we are using the notation indistinctly . As happened in classical mechanics, such Poisson bracket is associated to the inverse of the (sometimes weakly defined as in [70]) symplectic form ω_Q (which we remind to be the imaginary part of the Hermitian product), through the same relations as in the classical case. Consequently, a symmetry (equivalently, a symplectomorphism) with infinitesimal generator $X_Q \in \mathfrak{X}(\mathcal{M}_\mathcal{Q})$ over the quantum phase space, induces an infinitesimal transformation over the quantum algebra of observables $\mathcal{A}_Q$ that can be represented (in complete analogy with the classical case) through the Poisson bracket with its generating function $f_A \in \mathcal{A}_Q$:

$$\mathcal{L}_{X_Q} g_B = \{g_B, f_A\}_Q \quad \forall g_B \in \mathcal{A}_Q \tag{1.44}$$

For the particular case of the dynamics, the energy function is given by the expectation value (in this case restricted to normalized states, $\langle\Psi|\Psi\rangle = 1$, to avoid the usual division by the norm of the state) of the Hamiltonian operator, inducing the usual quantum dynamics for expectation values of self-adjoint operators:

$$f_H := \langle\Psi|\hat{H}\Psi\rangle \Rightarrow \frac{d}{dt} f_A = \{f_A, f_B\}_Q = \frac{-i}{\hbar}\langle\Psi|[\hat{A},\hat{H}]|\Psi\rangle \tag{1.45}$$

In order to recover Schrödinger's equation of motion for the quantum states $\Psi \in \mathcal{H}$, given that it cannot be identified with an element of $\mathcal{F}_2(\mathcal{H})$, we have two options.

The first path requires the extension of the action of the Poisson bracket to be a bi-derivative operator over any pair of differentiable functions over $\mathcal{H}$, which requires a proper definition of the functional derivatives $\dfrac{\delta}{\delta\Psi(x)}$ and $\dfrac{\delta}{\delta\bar{\Psi}(x)}$. Note that when writing $\Psi(x) \in \mathcal{H}$ we are making the usual identification of the Hilbert space with complex 2-integrable functions $L^2(\Sigma, d\text{vol}_\Sigma)$ with domain a certain finite-dimensional manifold Σ. A possible solution to make sense of these functional derivatives is the truncation of the Hilbert space to be a finite dimensional manifold (which is natural in the context of molecular simulations, as one has to perform the simulations on a finite number of quantum levels anyway), and then use the Poisson bracket defined in [64] as in (1.35), permitting the definition

of standard differential calculus. Another (more cumbersome) solution is the definition of Fréchet differential calculus over infinite dimensional manifolds in a convenient setting [5, 7, 84]. Both approaches have been used (either explicitly or implicitly) in the articles of this compendium, the latter being unavoidable in the case of quantum field theory in curved spacetime studied in [5]. Under this path, once we have made proper sense of the functional derivatives, operationally we may work with the generalization to functional derivatives of Wirtinger's approach (see [86, 87] for Wirtinger's operators, and [7] for their generalization to infinite dimensional manifolds):

$$\frac{\delta\Psi(x')}{\delta\Psi(x)} = \frac{\delta\bar{\Psi}(x')}{\delta\bar{\Psi}(x)} = \delta(x-x') \text{ and } \frac{\delta\bar{\Psi}(x')}{\delta\Psi(x)} = \frac{\delta\Psi(x')}{\delta\bar{\Psi}(x)} = 0, \tag{1.46}$$

where the δ distributions must be taken with respect to the measure under consideration for the scalar product defining the L^2-space (which, in this thesis, will be Lebesgue for finite dimensional domain, as in the electronic example above, and a proper Gaussian measure in the infinite dimensional case).
Once this is done, one can extend the Poisson bracket to act over any $f, g \in C^\infty(\mathcal{H})$ as $\{f,g\}_Q = \int dx \frac{\delta}{\delta[\Psi(x)}f\frac{\delta}{\delta\Psi(x)]}g$ and therefore, the Hamiltonian field defined by $\{\cdot, f_H\}_Q$ can yield Schrödinger equation when acting over the identity over Ψ (either in x-basis or in any other):

$$\frac{d\Psi}{dt} = \{\Psi, f_h\}_Q = \frac{-i}{\hbar}\hat{H}\Psi\ . \tag{1.47}$$

This is the path we will follow in [5].

The second path to recover Schrödinger dynamics is perhaps simpler, as it avoids issues of differential calculus, and is based on the usual path to reach von Neumann's equation, but presented in the current geometric formalism. We firstly pick an orthonormal basis $\{\sigma_i | \operatorname{Tr}(\sigma_i\sigma_j) = \delta_{i,j}\}$ for the space of self-adjoint operators $\mathcal{O}_H(\mathcal{H})$ over the Hilbert space (such as properly normalized Pauli matrices and identity, in dimension 2). Then, we consider the projection of the pure quantum state Ψ in each of the elements of such basis, $\Psi_i = \langle\Psi|\sigma_i\Psi\rangle$, which is already an element of the quadratic functions belonging to $\mathcal{A}_Q$, so the quantum Poisson bracket can directly act over it with the original definition. The dynamics of such objects yield:

$$\frac{d\Psi_i}{dt} = \{\Psi_i, f_H\}_Q = \frac{-i}{\hbar}\langle\Psi|[\sigma_i, \hat{H}]\Psi\rangle = \frac{-i}{\hbar}\operatorname{Tr}(\hat{\rho}_\Psi[\sigma_i, \hat{H}])\ , \tag{1.48}$$

where we have substituted the expectation value by the trace with respect to the representation of the density matrix of the pure state associated to Ψ, whose representation as a self-adjoint operator under the trace can be defined by $\hat{\rho}_\Psi := \sum_i \Psi_i\sigma_i$. Using the cyclic property of the trace, it can be shown that $\operatorname{Tr}(\hat{\rho}_\Psi[\sigma_i, \hat{H}]) = \operatorname{Tr}(\sigma_i[\hat{H}, \hat{\rho}_\Psi])$. By definition,

$$\frac{d}{dt}\hat{\rho}_\Psi := \sum_i \frac{d\Psi_i}{dt}\sigma_i = \frac{-i}{\hbar}\sum_i \operatorname{Tr}(\sigma_i[\hat{H}, \hat{\rho}_\Psi])\sigma_i = \frac{-i}{\hbar}[\hat{H}, \hat{\rho}_\Psi], \tag{1.49}$$

recovering von Neumann's equation for the density matrix from the dynamics of the quadratic functions Ψ_i. Given that $\hat{\rho}_\Psi$ represents a pure state, we know that its evolution, completely determined by the Hamiltonian field $\{, f_H\}_Q$, is equivalent to Schrödinger's equation for $\Psi \in \mathcal{H}$. Although the differential path is more versatile, this approach already introduces a relevant feature regarding statistical mechanics: the dynamics of the density matrix (which later will be a statistical mixture) can be obtained in this geometric picture as usually, from the adjoint of the evolution operator which dictated the dynamics of the self-adjoint operators representing physical observables.

With these summarized descriptions of geometric quantum and classical mechanics, we may proceed to a joint geometric description of quantum-classical systems.

Geometric formulation of simple hybrid systems

The hybrid phase space, can be described in most cases (such as in Ehrenfest dynamics [63, 69]) using the cartesian product of the classical and quantum phase space:

$$\mathcal{M}_H := \mathcal{M}_C \times \mathcal{M}_Q \ . \tag{1.50}$$

This manifold can in turn be provided with a hybrid symplectic structure ω_H in the following way. Let $\pi_C : \mathcal{M}_H \to \mathcal{M}_C$ be the canonical projection over the classical subspace, i.e. $\pi_C(\vec{\mathbf{Q}}, \vec{\mathbf{P}}, V_\Psi) = (\vec{\mathbf{Q}}, \vec{\mathbf{P}}) \in \mathcal{M}_C$. Analogously, the canonical projection over the quantum subspace $\pi_Q : \mathcal{M}_H \to \mathcal{M}_Q$ acts as $\pi_Q(\vec{\mathbf{Q}}, \vec{\mathbf{P}}, V_\Psi) = V_\Psi \in \mathcal{M}_Q$. With these two objects, given the triviality of the manifold $\mathcal{M}_H$, we can perform the pullback with respect to the correspondent projections (denoted by $\pi_C^\star, \pi_Q^\star$) of the symplectic structures already present in each submanifold. This defines the hybrid symplectic structure in the following sense:

$$\omega_H := \pi_C^\star(\omega_C) + \pi_Q^\star(\omega_Q) \tag{1.51}$$

which will be related, as in the previous cases, with a Poisson bracket over physical observables. As shown in one of the articles of this compendium [4], such algebra of observables can be formally defined as:

$$\mathcal{A}_H := \mathcal{A}_C \otimes \mathcal{A}_Q \ . \tag{1.52}$$

In more traditional approaches [69], one first considers the space of self-adjoint operators over the Hilbert space isomorphic to the quantum submanifold $\mathcal{M}_Q$, allowing a smooth parametric dependence of such operators on the classical variables $(\vec{\mathbf{Q}}, \vec{\mathbf{P}})$. We call these objects *hybrid operators*. Formally, they may be described as sections over a fibration $\tau : \mathcal{F}_O \to \mathcal{M}_C$ with base $\mathcal{M}_C$ and fiber $\mathcal{O}_H(\mathcal{H})$ (thus, $\mathcal{F}_O$ is locally trivialized into $\mathcal{M}_C \times \mathcal{O}_H(\mathcal{H})$), such that any hybrid operator $\hat{A}(Q, P)$ belongs to the space $\Gamma(\mathcal{F}_O)$ of such sections:

$$\hat{A}(Q, P) \in \Gamma(\mathcal{F}_O) \ . \tag{1.53}$$

This is just a fancy way of stating that once a particular classical point $\xi \in \mathcal{M}_C$ is provided, a concrete self-adjoint operator over $\mathcal{H}$ is obtained,

$$\begin{aligned} \hat{A}(Q,P) &: \mathcal{M}_C \to \mathcal{O}_H(\mathcal{H}) \\ \xi &\to A(Q,P)|_\xi \in \mathcal{O}_H(\mathcal{H}) \ , \end{aligned} \tag{1.54}$$

and that the dependence of the hybrid operator on $\mathcal{M}_C$ is smooth. We remind that $\mathcal{O}_H(\mathcal{H})$ is the space of self-adjoint operators over the Hilbert space $\mathcal{H}$ to which the quantum states Ψ belong.

For example, the Hamiltonian operators introduced in eqs. 1.15,1.14, governing Ehrenfest's dynamics belong to this space of hybrid operators, being both differentiable in Q, P and, for each value of $Q, P \in \mathcal{M}_C$, self-adjoint operators over the Hilbert space of electronic wave functions.

This set of hybrid operators can be represented, as in the quantum case, as quadratic functions over the quantum phase space (while keeping its C^∞-nature over the classical variables) through the expectation value structure on normalized vectors, $\langle\Psi|\Psi\rangle = 1$.

We will refer to this set of functions as hybrid observables, which we will denote as $\mathcal{F}_{2Q}(\mathcal{M}_H)$ to make explicit that the quadracity is only on the quantum degrees of freedom. It can be formally defined as:

$$\mathcal{F}_{2Q}(\mathcal{M}_H) := \{f_A(\xi) : \mathcal{M}_H \to \mathbb{R} \quad | \quad f_A := \langle\Psi|\hat{A}(\xi)\Psi\rangle \quad \forall \hat{A}(\xi) \in \Gamma(\mathcal{F}_O)\} \ . \tag{1.55}$$

In a sense, this sews the two notions of physical observables introduced for the classical ($C^\infty(\mathcal{M}_C)$) and quantum case ($\mathcal{F}_2(\mathcal{H})$). On the one hand, these hybrid observables keep the differentiability with respect to classical variables without additional restrictions in that regard (although they auxiliarily depend on Ψ). Besides, once evaluated on any particular classical data the hybrid observables are regarded as expectation values with respect to Ψ of self-adjoint operators over $\mathcal{H}$. As in the previous cases, the inverse of the hybrid symplectic form as defined above is ultimately related to a hybrid Poisson bracket over the hybrid observables (regarded as specific functions over $\mathcal{M}_H$), which act as:

$$\{f_A, f_B\}_H = \{f_A, f_B\}_C + \{f_A, f_B\}_Q \quad \forall f_A, f_B \in \mathcal{F}_{2Q}(\mathcal{M}_H) \ . \tag{1.56}$$

It turns out that $\mathcal{F}_{2Q}(\mathcal{M}_H)$ does not form an algebra under the Poisson bracket, because, in the latter equation, the term

$$\{f_A, f_B\}_C = \langle\Psi|\partial_{[Q_i}\hat{A}(\xi)|\Psi\rangle\langle\Psi|\partial_{P^i]}\hat{B}(\xi)|\Psi\rangle \tag{1.57}$$

does not belong to $\mathcal{F}_{2Q}(\mathcal{M}_H)$, where we are reusing the notation introduced in (1.24) for the Poisson bracket. In general, this expression is not quadratic over $\mathcal{M}_Q$, but quartic. In turn, $\{\{f_A, f_B\}_C, f_C\}_C$ is order 6 on $\mathcal{M}_Q$, and so on. This feature, arising here as a mathematical intricacy with no apparent immediate physical implication that crucially

modifies the nature of observables and has deep consequences in the definition of out-of-equilibrium hybrid statistical mechanics, as it will be explained later.

At this level, the definition of a hybrid Poisson algebra requires the completion of $\mathcal{F}_{2Q}(\mathcal{M}_H)$ under the ordinary product, defining:

$$\bar{\mathcal{F}}_{2Q}(\mathcal{M}_H) := \{\prod_{i=1}^{k} f_{A_i} \quad \forall k \in \mathbb{N}\,, \quad \forall f_{A_i} \in \mathcal{F}_{2Q}(\mathcal{M}_H)\} \tag{1.58}$$

in this case, indeed $\{,\}_H : \bar{\mathcal{F}}_{2Q}(\mathcal{M}_H) \times \bar{\mathcal{F}}_{2Q}(\mathcal{M}_H) \to \bar{\mathcal{F}}_{2Q}(\mathcal{M}_H)$ and therefore, the Poisson algebra of hybrid observables is defined as:

$$\mathcal{A}_H := (\bar{\mathcal{F}}_{2Q}(\mathcal{M}_H), \{,\}_H) \tag{1.59}$$

Note that this algebra is the same as the one that would be defined from the completion of the original $\mathcal{F}_{2Q}(\mathcal{M}_H)$ by considering all the possible functions that result of any application of the Poisson brackets.

Two subcases of these observables with easy interpretation are:

- Exclusively classical observables are given by the expectation value of an operator of the type
$$\hat{A}_C(\xi) = f(\xi)\hat{\mathbb{I}} \in \Gamma(\mathcal{F}_O) \quad f(\xi) \in C^\infty(\mathcal{M}_C)\,, \tag{1.60}$$
i.e. a differentiable classical function times the identity operator over the quantum Hilbert space. Once the expectation value is taken,
$$f_{A_C(\xi)} = f(\xi)\langle\Psi|\Psi\rangle = f(\xi) \tag{1.61}$$
where we have made use of $\langle\Psi|\Psi\rangle = 1$, which, in the case of Ehrenfest dynamics, holds at all times. Therefore, it is common to represent $f_{A_C(\xi)}$ (and even $\hat{A}_C(\xi)$ if the notation is oversimplified) with $f(\xi)$ uniquely as is the case of the kinetical energy of the nuclei K_n and the potential energy V_n defined above, just before eq. (1.15). In this sense, for variations restricted to the submanifold of norm 1 for the quantum states, these classical observables depend on ξ, but not on Ψ.

- Exclusively quantum observables are, on the other hand, characterized by the expectation value of an operator $\hat{A}_Q$ which lacks a dependence on ξ, $\partial_{Q_i}\hat{A}_Q = \partial_{P^i}\hat{A}_Q = 0$. The expectation value $\langle\Psi|\hat{A}_Q\Psi\rangle$ is thus an observable dependent on Ψ, but not on ξ. An example of these observables is the expectation value of the kinetic energy of the electron $\hat{K}_e$ as defined above, or the electron-electron interaction potential V_q.

In contrast, generic hybrid observables are of the type of the expectation value of the interaction potential $\langle\Psi|V_{qc}(Q)|\Psi\rangle$, whose dependence on both kinds of variables is unavoidable.

Resuming the former discussions on the Hamiltonian representation of symplectomorphisms for quantum and classical mechanics, it is immediate to show that they generalize trivially to the hybrid case. In that sense, a particular relevant element of the hybrid Poisson algebra is the hybrid energy function:

$$f_{H(\xi)} := \langle\Psi|\hat{H}(\xi)\psi\rangle \in \mathcal{A}_H \tag{1.62}$$

where $\hat{H}(\xi)$ can be identified with (1.15), the hybrid operator governing the dynamics. In the same spirit as in the quantum case, $f_{H(\xi)}$ is the generating function of the hybrid dynamics. Consequently, the Hamiltonian field

$$X_H = \{\cdot, f_H\}_H \tag{1.63}$$

realizes the time evolution. In particular, for any quadratic function,i.e. $\forall f_A \in \mathcal{F}_{2Q}(\mathcal{M}_H)$:

$$\frac{d}{dt}f_A = \{f_A, f_H\}_H = \partial_{[Q_i}\langle\Psi|\hat{A}(\xi)\Psi\rangle\partial_{P^i]}\langle\Psi|\hat{H}(\xi)\Psi\rangle + \frac{-i}{\hbar}\langle\Psi|\left[\hat{H}(\xi), \hat{A}(\xi)\right]\Psi\rangle\ . \tag{1.64}$$

This may be extended to the whole $\mathcal{A}_H$ straightforwardly through the use of Leibniz's identity. A key feature of the geometric formulation of hybrid systems is the Hamiltonian nature of the field generating the dynamics, which makes evident the symplectomorphic nature of time evolution:

$$\mathcal{L}_{X_H}\omega_H = 0\ . \tag{1.65}$$

Lastly, Ehrenfest's hybrid equations of motion are easily derived, just by making the same construction as in the quantum and classical cases. For the e.o.m. of the classical variables, we choose classical observables assigned to the identity over each classical canonical coordinate Q_i, P^i. For the quantum one, we may extend the Poisson bracket to act outside $\mathcal{A}_H$ in order to act on the function over $\mathcal{M}_H$ selecting the quantum state (in which case we make use of the differential nature of the Poisson vector, as in the quantum case). Analogously, we could also recover the quantum equation of motion through the derivation of von Neumann's equation for the pure density matrix as the adjoint operator to the one defining the dynamics of operators, as in the quantum case. In any case, once properly defined, the e.o.m. given by

$$\frac{d}{dt}Q_i = \{Q_i, f_H\}_H = \{Q_i, f_H\}_C \tag{1.66}$$

$$\frac{d}{dt}P^i = \{P^i, f_H\}_H = \{P^i, f_H\}_C \tag{1.67}$$

$$\frac{d}{dt}\Psi = \{\Psi, f_H\}_H = \{\Psi, f_H\}_Q \tag{1.68}$$

are equivalent to eqs. (1.5,1.6,1.7) of Ehrenfest's dynamics.

This whole construction has been realized for a trivial fiber bundle given by the product manifold of the classical and quantum phase spaces. We anticipate that more general hybrid

manifolds, not necessarily based on the cartesian product manifold, but on a generic fibration with base (almost) the classical phase space and fiber the quantum one, even provided with a non-trivial connection, may be necessary to capture correctly the phenomenology of more complex systems. In particular, in the last article of this compendium, such general fibration structure is introduced and shown to be mandatory for a consistent coupling of QFT to classical gravity [5]. While formal similarities can still be found, some crucial results are fundamentally different, for example, $\frac{d}{dt}\Psi = \{\Psi, f_H\}_Q$ is no longer fulfiled.

Having defined the hybrid phase space $\mathcal{M}_H$, the hybrid algebra of observables $\mathcal{A}_H$ regarded as certain functions over $\mathcal{M}_H$, we can proceed to the definition of hybrid statistical ensembles.

1.3 Statistical mechanics

In this section, we will restrict the discussion to finite dimensional manifolds, which requires finite dimensional Hilbert space of the quantum subsystem, for the sake of simplicity. This approximation is often physically justified, as it is the natural framework in molecular dynamics simulations – or in any simulation, for that matter –, the main field of application of statistical and thermodynamical hybrid systems. In such systems, due to the finite memory and computational power, the Hilbert space is truncated, allowing for only a finite number of energy levels. This truncation can either be done through a discretization of the domain of the wave functions (a lattice approach), or through the truncation of a basis of functions of L^2. In any case, the construction for infinite dimensional manifolds can be performed by following an approach analogous to [88] for the quantum subsystem. The geometry of infinite dimensional hybrid systems is deeply explored in the fifth article presented in this thesis [5] in the context of QFT and, more abstractly, in [7, 8]. In order to define the statistical mechanics, the only extra subtlety is the proper definition of the measure over the infinite dimensional quantum phase space, which must be done differently to the case of finite dimensional systems.

Proceeding now to the definition of hybrid ensembles, the key idea we must keep from the previous section is that Ehrenfest dynamics is described as a Hamiltonian system over a symplectic manifold, $\mathcal{M}_H$. Any such symplectic manifold of finite dimension d has a natural volume form $d$vol over it, defined as:

$$d\text{vol} := \omega \wedge \overset{\text{d times}}{\cdots} \wedge \omega \ . \tag{1.69}$$

We will briefly introduce these concepts in the case of classical and quantum statistical mechanics, for an easier understanding of the hybrid case.

We must make a last general remark before properly commencing this section, and

it is in regards to the notion of entropy used. Throughout this thesis we will follow an approach based on the definition *à la* Gibbs of ensemble and entropy. The Boltzmannian picture (where the entropy can be associated to a microstate ξ, in terms of the volume of the space of microstates that macroscopically look the same as ξ) can be found in [89] both for classical and quantum statistical mechanics. Their combination would make up for a Boltzmannian picture of statistical hybrid systems, analogous to the one followed in the first article of this compendium in the Gibbsian approach.

Brief summary of classical statistical mechanics

For the classical phase space $\mathcal{M}_C$ introduced above, which is naturally finite dimensional, the symplectic volume form is given by

$$d\mathrm{vol}_C := \omega_C \wedge \overset{6\mathrm{N\ times}}{\cdots} \wedge \omega_C \equiv dQ_1 \cdots dQ_n dP^1 \cdots dP^n \,. \tag{1.70}$$

The classical observables are functions in $C^\infty(\mathcal{M}_C)$. Generic statistical states are described by a distribution over the classical phase space $\mathfrak{F}_C \in D'(\mathcal{M}_C)$. Without loss of generality for physical applications, we may represent such distribution with respect to the symplectic volume as a definite positive density of weight 1 denoted by F_C.[3] This means, that for any observable f defined as a differentiable function of compact support, its expectation value $E_F(f)$ under the probability measure associated to $\mathfrak{F}$ can be written as:

$$E_F(f) := \mathfrak{F}_C(f) = \int\limits_{\mathcal{M}_C} d\mathrm{vol}_C F_C(\xi) f(\xi)\ \forall f \in C^\infty_C(\mathcal{M}_C) \mid \int\limits_{\mathcal{M}_C} d\mathrm{vol}_C F_C(\xi) = 1 \tag{1.71}$$

We have characterized a mathematical statistical mixture over $\mathcal{M}_C$ through the density $F_C(\xi)$, but the key question is: does this constitute a physical statistical ensemble? The answer is in the positive, as there is a one-to-one correspondence between independent statistical events and the points over the classical phase space. Therefore, two classical events are mutually exclusive simply if they are represented by different points over phase space. Thus, $F_C(\xi)$, being a density of weight 1 over $\mathcal{M}_C$, is a proper probability density for the physical states.

The statistical average $\langle f \rangle_C$ of a classical observable $f \in \mathcal{A}_C$ can be computed as usual:

$$\langle f \rangle_C =: \int\limits_{\mathcal{M}_C} d\mathrm{vol}_C F_C(\xi) f(\xi) \quad \forall f \in \mathcal{A}_C \,, \tag{1.72}$$

[3] Note that a density of weight 1 is defined to be differentiable, and therefore, some distributions, such as Dirac's delta, cannot be represented as densities. Nevertheless, functions that are both differentiable and integrable (over $\mathcal{M}_C$) are dense over the space of densities, so we always have an arbitrarily close approximation to F_C with a well behaved object, regarding integro-differential calculus. For example, the Schwartz space, whose best known orthonormal basis are Hermite functions, is dense in $L^1(\mathcal{M}_C)$.

where we recall that $\mathcal{A}_C$ is the classical Poisson algebra of observables. Regarding the time evolution of the probability densities: remembering that the classical observables evolved as $d_t f = \mathcal{L}_{X_H} f$ for the Hamiltonian field $X_H = \{, f_H\}_C$, we may define the dynamics of such statistical averages induced by such Hamiltonian microdynamics:

$$d_t\langle f\rangle_C =: \int\limits_{\mathcal{M}_C} d\mathrm{vol}_C F_C(\xi)\mathcal{L}_{X_H} f = -\int\limits_{\mathcal{M}_C} \mathcal{L}_{X_H}(d\mathrm{vol}_C F_C(\xi))f = -\int\limits_{\mathcal{M}_C} d\mathrm{vol}_C \mathcal{L}_{X_H}(F_C(\xi))f \tag{1.73}$$

where, in the first equality we have omitted a null total derivative and in the second equality we have made use of Liouville's theorem $\mathcal{L}_{X_H} d\mathrm{vol}_C = 0$, given the Hamiltonian nature of the dynamics and the symplecticity of the volume form.

This formulation of Liouville's theorem may be easier to understand in the case of a finite time translation, where $f(\xi(t))$ would represent the evolution of the functions (if they do not depend explicitly on time). Then, for each value of t, a change of variables in the integral can be performed. As the evolution of Hamiltonian dynamics is a symplectomorphism, the volume element can not change in time. Consequently, the integral representing the expectation value of $f(\xi(t))$ under the original distribution becomes equal to the integral of the value of the density $F_c(\xi(-t))$ times the value of the function at original time $f(\xi(0))$, i.e.

$$\int_{\mathcal{M}_C} dvol F(\xi(-t))f(\xi(0)) = \int_{\mathcal{M}_C} dvol F(\xi(0))f(\xi(t)) \tag{1.74}$$

For this particular property we can refer to chapter 2 of [90] (Lemma at the bottom of page 39)

Given that such relation must hold for any observable $f \in \mathcal{A}_C$, we realize that, in terms of the Liouvillian operator $-\mathcal{L}_{X_H}$, the dynamics of classical ensembles can be represented as:

$$d_t F_C(\xi) = -\mathcal{L}_{X_H} F_C = \{f_H, F_C\}_C \,, \tag{1.75}$$

associated to the adjoint of the evolution operator (which acted over the observables) acting over distributions, taken into account the constant nature of the volume form.

Finally, Gibbs entropy, usually associated to thermodynamical entropy, can be constructed as the following function of the probability density:

$$S_C := \int\limits_{\mathcal{M}_C} d\mathrm{Vol}_C F_C(\xi)\log(F_C(\xi))\,. \tag{1.76}$$

This function is left invariant under the action of the Liouvillian operator: the Liouville Hamiltonian dynamics preserves the Gibbs entropy for classical systems.

Brief summary of quantum statistical mechanics

The usual route to defining quantum statistical systems is based on von Neumann's density matrix formalism. Let us consider a quantum state $\Psi \in \mathcal{H}$ and its associated projector over Hilbert space, $\hat{P}_\Psi := |\Psi\rangle\langle\Psi|$, (note that the construction assumes normalized states, $\langle\Psi|\Psi\rangle = 1$, to avoid division by the norm). The scalar product of this projector with another self-adjoint operator $\hat{A}$ representing a physical magnitude yields the statistical expectation value over such single quantum state, Ψ:

$$\langle\Psi|\hat{A}|\Psi\rangle = \mathrm{Tr}(\hat{P}_\Psi \hat{A}). \tag{1.77}$$

Then, the quantum statistical state, dual to the self-adjoint operators, defined by $\mathrm{Tr}(\hat{P}_\Psi \cdot) : \mathcal{O}_H((H) \to \mathbb{R}$ can be represented by a self-adjoint operator itself and such representation is called density matrix. This will be particularly relevant in Koopman's formalism of hybrid systems developed in [4].

Thus, most of the time, one represents the quantum statistical system as a density matrix (in this example, the projector $\hat{P}_\Psi$ itself is a pure statistical state) and invoke the scalar product for the operators (in terms of the trace) in order to obtain expectation values. This is the quantum equivalent to representing a distribution under a measure (where the role of the measure is now played by the trace) in terms of a probability density of weight 1.

In any case, the example considered above, represents a *pure* density matrix, as it is constructed with the projector over a single element in Hilbert's space $\Psi \in \mathcal{H}$. If we consider a statistical mixture of projectors with probabilities $1 \geq \lambda_i \geq 0$, like in the following definition:

$$\hat{\rho} := \sum_i \lambda_i \hat{P}_i \mid \sum_i \lambda_i = 1 \tag{1.78}$$

we have a generic density matrix, which is dubbed *mixed* state if it populates with non-null probability at least two different projectors. The statistical expectation values of a physical magnitude, represented as by a self-adjoint operators $\hat{A}$, can be defined as:

$$\langle A\rangle_Q := \mathrm{Tr}(\hat{\rho}\hat{A}) \tag{1.79}$$

Following the construction made at the end of the section about the geometric picture of quantum mechanics, and taking into account the linearity of the density matrix with respect to the projectors, one straightforwardly derives von Neumann's equation:

$$d_t\hat{\rho} = \frac{-i}{\hbar}[\hat{H}, \hat{\rho}]\ . \tag{1.80}$$

This is the adjoint to Heisenberg's dynamics for operators. Of course, von Neumann's definition of ensemble through the density matrix takes appropriate care of the notion of

quantum exclusivity of events: two quantum events are mutually exclusive if their representation as vectors in the Hilbert space are orthogonal:

$$\text{Event } i \text{ and event } j \text{ are mutually exclusive} \Leftrightarrow \mathrm{Tr}(P_i P_j) = \langle \Psi_i, \Psi_j \rangle = 0 \ . \tag{1.81}$$

This notion is key to the definition of quantum thermodynamical entropy, usually agreed to be von Neumann's entropy:

$$S_Q = Tr\left(\hat{\rho}\log(\hat{\rho})\right) \ , \tag{1.82}$$

which is left invariant under von Neumann's dynamics [91].

Nevertheless, there is a different picture of quantum ensembles that is usually not considered in standard literature. This picture is particularly convenient for the later introduction of hybrid statistical systems. In complete analogy with classical statistical mechanics, we may consider the symplectic manifold $\mathcal{M}_Q$ and the symplectic volume over it (restricted here to finite dimensional systems, d_Q being the dimension of $\mathcal{M}_Q$):

$$d\mathrm{Vol}_Q := \omega_Q \wedge \overset{d_Q \text{ times}}{\cdots} \wedge \omega_Q \ . \tag{1.83}$$

For illustrative purposes, a construction of such volume form in terms of coordinates for a finite dimensional $\mathcal{M}_Q$ can be found in [69]. It firstly considers an orthonormal basis $\{\Psi_i\}$ over the Hilbert space $\mathcal{H}$, and choosees as coordinates for $\mathcal{M}_Q$ the real ($q_i := \mathrm{Re}(\langle \Psi | \Psi_i \rangle)$) and imaginary parts ($p_i := \mathrm{Im}(\langle \Psi | \Psi_i \rangle)$) of the coordinates of the quantum state in such basis, $\Psi = (q_j + ip_j)\Psi^j$. It can be seen that, in such basis, $\omega_Q = \sum\limits_j dp_j \wedge dq_j$, and consequently $d\mathrm{Vol}_Q = \prod\limits_j dp_j dq_j$, in analogy to the classical case.

Nevertheless, we will keep a coordinate-free narrative to keep a general framework. The next step is considering a (positive definite) probability distribution $\mathfrak{F}_Q : C^\infty(\mathcal{M}_Q) \to \mathbb{R}$, such that $\mathfrak{F}_Q(1) = 1$. Therefore, as in the classical case, it can be represented as a positive definite density of weight 1, F_Q, under an integration measure, assigning a probability density to each region in quantum phase space $\mathcal{M}_Q$ or, equivalently, to each vector $\Psi \in \mathcal{H}$. Note that this construction is not yet accounting in any way for orthogonality representing exclusivity of events.

We may now consider a quadratic function $f_A = \langle \Psi | \hat{A} | \Psi \rangle$ over the Hilbert space given by the expectation value of a self-adjoint operator $\hat{A} \in \mathcal{O}_H(\mathcal{H})$ as the functional representation of a physical magnitude. In analogy to the classical case, its statistical expectation value can be expressed as:

$$\langle f_A \rangle_Q = \int\limits_{\mathcal{M}_Q} d\mathrm{vol}_Q F_Q(\Psi) f_A(\Psi) \quad \forall f_A \in \mathcal{A}_Q \ . \tag{1.84}$$

It can be shown that, following this prescription, F_Q yields the same statistical averages using eq. (1.84) as the density matrix $\hat{\rho}$ using (1.79). Both descriptions of the quantum

ensemble are related in the following way:

$$\hat{\rho} := \int_{\mathcal{M}_Q} d\mathrm{vol}_Q F_Q(\Psi)\hat{P}_\Psi \ . \tag{1.85}$$

This can be interpreted as an extension to the continuum of eq. (1.78), assigning to the density matrix the linear combination of the projectors over every element Ψ of the Hilbert space weighted with the probability density $F_Q(\Psi)$. Note that this definition of $\hat{\rho}$ in terms of F_Q is just the statistical average of a linear function on the projectors, $\hat{P}_\Psi$, thus characterizing the first statistical moment (on projectors) of the distribution associated to F_Q. Therefore, any other probability density with the same first moment but different higher order moments, would yield the same density matrix and the same expectation values for the elements of $\mathcal{A}_Q$, but different expectation values for generic functions (more than quadratic) over $\mathcal{M}_Q$. Consequently, eq. (1.85) defines an equivalence class of all the probabilty density distributions defining the same density matrix:

$$[F_Q]_{\hat{\rho}} := \left\{ F_Q \in D(\mathcal{M}_Q) \quad | \quad \hat{\rho} := \int_{\mathcal{M}_Q} d\mathrm{vol}_Q F_Q(\Psi)\hat{P}_\Psi \right\} \ . \tag{1.86}$$

We can further extend the formal analogy with classical mechanics and make use of the Hamiltonian definition of quantum dynamics, introduced in the previous section, to derive, by means of Liouville's theorem, the dynamics of quantum statistical ensembles. Therefore, when computing the dynamics of statistical averages, we may perform a total derivative and, leaving the symplectic volume form invariant under the Lie derivative along the quantum Hamiltonian field $X_H = \{\cdot, \langle\Psi|\hat{H}\Psi\rangle\}_Q$, we can reproduce the same results as in the classical case:

$$d_t\langle f_A\rangle_Q = \int_{\mathcal{M}_Q} d\mathrm{vol}_Q F_Q \mathcal{L}_{X_H} f_A = -\int_{\mathcal{M}_Q} d\mathrm{vol}_Q \mathcal{L}_{X_H}(F_Q) f_A \quad \forall f_A \in \mathcal{A}_Q \tag{1.87}$$

$$\Rightarrow d_t F_Q = -\mathcal{L}_{X_H}(F_Q) \ . \tag{1.88}$$

This Liouvillian dynamics can be shown to be equivalent to von Neumann's equation for the density matrix using eq. (1.85) due to a key feature of quantum dynamics: its linearity. Such linearity can be used through the computation of the evolution of the first momentum on the projectors of F_Q (which is precisely $\hat{\rho}$), which can be shown to be:

$$d_t \int_{\mathcal{M}_Q} \mathcal{F}_Q \hat{P}_\Psi d\mathrm{vol}_Q = -\int_{\mathcal{M}_Q} \mathcal{L}_{X_H}\mathcal{F}_Q \hat{P}_\Psi d\mathrm{vol}_Q = \frac{-i}{\hbar}\int_{\mathcal{M}_Q} \mathcal{F}_Q[\hat{H}, \hat{P}_\Psi] \quad \text{which is linear on } \hat{P}_\Psi. \tag{1.89}$$

From this equation, von Neumann's equation follows immediately. Nevertheless, if $\mathcal{L}_{X_H}$ had induced any non-linearity (a quadratic or higher order power of $\hat{P}_\Psi$ in this last equation) the dynamics for the density matrix would depend on higher order moments of

F_Q. Therefore, given that $\hat{\rho}$ is only the first moment on projectors of F_Q, the evolution of $\hat{\rho}$ would need further statistical information to be properly defined, a fact that would take us beyond the density matrix formalism. That extra statistical information would arise from higher order moments of F_Q, breaking the equivalence class (1.86), and therefore, each different F_Q defining the same density matrix could yield different dynamics for $\hat{\rho}$. This will be the root cause of a very puzzling aspect of hybrid statistical systems, identified in [51], which will be treated later.

This leads us to posing the same question as in the classical case: does F_Q properly represent a physical quantum statistical ensemble, in the same way that the density matrix does? We must remain skeptical, as the answer is not so clear as before.

On the positive side, we can recover the density matrix formalism, the correct statistical dynamics (as long as we have linear microdynamics) and the correct statistical averages of physical observables. Still, F_Q contains way more information than is necessary to describe a physical state, as it overcounts statistical correlated events. This is due to the lack of a mechanism to take into account the orthogonality defining exclusivity of events. Consequently, a definition of the entropy based on the translation of eq. (1.76) to this quantum case would be incorrect: it would not reproduce von Neumann's entropy for the associated density matrix.

Despite this caveat, this formalism has some appealing mathematical features, such as the analogy with classical statistical mechanics and the identification of Liouville's theorem. These will be particularly useful for the joint description of quantum and classical statistical mechanics, introduced in the following section.

Hybrid statistical systems and thermodynamics

Generalizing the formalism based on distributions over symplectic manifolds, in the case of hybrid systems we can work with the symplectic volume element constructed in terms of ω_H, as defined in (1.51):

$$d\mathrm{vol}_H := \omega_H \wedge \overset{6N+d_Q \text{ times}}{\cdots} \wedge \omega_H = d\mathrm{vol}_C d\mathrm{vol}_Q \tag{1.90}$$

where $d\mathrm{vol}_C$ and $d\mathrm{vol}_Q$ are the ones defined analogously for their respective symplectic forms.

With this natural volume form over the hybrid phase space, a statistical mixture of microstates can be described once again as a positive definite density of weight 1 over $\mathcal{M}_H$, denoted by $F_{QC}(\xi, \Psi)$, such that:

$$\int_{\mathcal{M}_H} d\mathrm{vol}_H F_{QC}(\xi, \Psi) = 1 \ . \tag{1.91}$$

This can be decomposed into a marginal classical probability density $F_C(\xi)$, and a conditional quantum one $F_{Q-\text{cond}}(\Psi;\xi)$ defined as:

$$F_C(\xi) := \int_{\mathcal{M}_Q} d\text{vol}_Q F_{QC}(\xi,\Psi) \tag{1.92}$$

$$F_{Q-\text{cond}}(\Psi;\xi) := \frac{F_{QC}(\xi,\Psi)}{F_C(\xi)} \text{ if } F_C \neq 0\,. \tag{1.93}$$

The definition is completed considering $F_{Q-\text{cond}}(\Psi;\xi) = 0$ if $F_C(\xi) = 0$.

In analogy to the quantum case, one can define a hybrid density matrix $\hat{\rho}(\xi)$ from the distribution, through the statistical average of the projectors over Hilbert space. This represents the first quantum moment of the distribution regarding the projectors (second moment if $\Psi \in \mathcal{H}$ or $(q,p) \in \mathcal{M}_Q$ are used instead):

$$\hat{\rho}(\xi) := \int_{\mathcal{M}_Q} d\text{vol}_Q F_{QC}(\xi,\Psi)\hat{P}_\Psi \;\forall \xi \in \mathcal{M}_C\,. \tag{1.94}$$

In this context, the normalization condition, instead of being just $\text{Tr}(\hat{\rho}) = 1$, is given by:

$$\int_{\mathcal{M}_C} d\text{vol}_C \text{Tr}(\hat{\rho}(\xi)) = 1 \tag{1.95}$$

As in the quantum case, we can define the equivalence class of the set of hybrid probability densities over $\mathcal{M}_H$ yielding the same hybrid density matrix as:

$$[F_{QC}]_{\hat{\rho}(\xi)} := \left\{ F_{QC} \in D(\mathcal{M}_H) \quad | \quad \hat{\rho}(\xi) := \int_{\mathcal{M}_Q} d\text{vol}_Q F_Q(\Psi)\hat{P}_\Psi \right\}\,. \tag{1.96}$$

This approach to hybrid statistical ensembles is the main subject of study in the first article of this compendium [1]. The rest of this section summarizes the main results of the article.

The construction is based on the definition of a notion of mutual exclusivity for two elements in hybrid phase space, $(\xi_1,\Psi_1),(\xi_2,\Psi_2) \in \mathcal{M}_H$:

$$(\xi_1,\Psi_1) \text{ represents a mutually exclusive event to } (\xi_2,\Psi_2) \Leftrightarrow \xi_1 \neq \xi_2 \;\; or \;\; \langle\Psi_1|\Psi_2\rangle = 0\,. \tag{1.97}$$

This is properly captured in the definition of $\hat{\rho}(\xi)$, and lays the foundations for a consistent definition of hybrid entropy:

$$\begin{aligned} S_H &:= \int_{\mathcal{M}_C} d\text{vol}_C \text{Tr}\left(\hat{\rho}(\xi)\log(\hat{\rho}(\xi))\right) \\ &= \int_{\mathcal{M}_C} d\text{vol}_C F_C(\xi)\log(F_C(\xi)) + \int_{\mathcal{M}_C} d\text{vol}_C F_C(\xi)\text{Tr}\left(\hat{\rho}_\xi\log(\hat{\rho}_\xi)\right)\,. \end{aligned} \tag{1.98}$$

As shown in the second equality, this definition can be decomposed into a marginal classical Gibbs entropy for $F_C(\xi)$ and the average (under $F_C(\xi)$) of a conditional von Neumann entropy for the conditional density matrix, $\hat{\rho}_\xi := F_C^{-1}(\xi)\hat{\rho}(\xi)$. This ensures the correct classical and quantum limiting behavior for uncoupled and uncorrelated hybrid statistical systems. In [1], we also apply a maximum entropy procedure subject to the following fixed statistical average of the energy. Such constraint is implemented as

$$\int\limits_{\mathcal{M}_C} d\mathrm{vol}_C \mathrm{Tr}(\hat{\rho}(\xi)\hat{H}(\xi)) - E = 0\,, \tag{1.99}$$

where $\hat{H}(\xi) \in \Gamma(\mathcal{F}_O)$ is the hybrid operator representing the total energy of the system. The result of this maximum entropy principle can be defined as the hybrid canonical ensemble:

$$\hat{\rho}_{HCE}(\xi) = \frac{e^{-\beta\hat{H}(\xi)}}{Z_{HCE}} \quad \text{with} \quad Z_{HCE} := \int\limits_{\mathcal{M}_C} d\mathrm{vol}_C \mathrm{Tr}\left(e^{-\beta\hat{H}(\xi)}\right) \quad \text{and} \quad \beta = (k_B T)^{-1}\,, \tag{1.100}$$

from which the definition of the temperature of the ensemble immediately follows.

Notice that in this section about hybrid statistical systems, and in [1], we do not make any consideration about the dynamics, an therefore the conclusions should be valid for any hybrid model. Instead, we save the discussion about the dynamics for another article in this compendium, [3], later summarized in this introduction.

Nevertheless, it is remarkable to point out that some previous approaches in the literature [92] were misguided by the Hamiltonian nature of Ehrenfest dynamics, that conserves the quadratic function $f_H = \langle\Psi|\hat{H}(\xi)|\Psi\rangle$, and, following an approach *à la* Balescu [67] to statistical mechanics (where dynamical visitation and stability of probability densities over phase space under the Hamiltonian field play a prominent role in the definition of thermodynamical ensembles), considered that the hybrid canonical ensemble should be given by the following density over the hybrid phase space:

$$F_{HCE-\mathrm{Gibbs}}(\xi,\Psi) = \frac{e^{-\beta f_H(\xi,\Psi)}}{Z_{QC-HCE}} \quad \text{with} \quad Z_{QC-HCE} := \int\limits_{\mathcal{M}_H} e^{-\beta f_H(\xi,\Psi)}\,. \tag{1.101}$$

Such ensemble is thermodinamically inconsistent, as it maximizes Gibbs entropy for the density F_{QC}, which incorrectly accounts for hybrid exclusive events, instead of a proper definition of hybrid entropy. Furthermore, the thermodynamics magnitudes that can be derived from it (such as the free energy, the internal energy, or the thermodynamic entropy) are non-additive [93], and its thermodynamical limit (big dimensional systems) leads to a divergence of the energy of the system [94].

Therefore, the contributions of the first article of this compendium dissipated this long-standing confusion about the thermodynamical ensembles for hybrid systems, which were

considered inconsistent because of this ill-defined canonical ensemble. Nevertheless, given that the best understood benchmark of hybrid systems are molecular dynamics simulations, endorsed by the biggest and most prolific community working with hybrid systems, the question about the hybrid canonical ensemble would not be completely satisfactory if regarded solely from this *ensemblist* position. In the context of hybrid dynamics, ensembles are reproduced through an *ergodicist* position: time-averaging over the solution curve to hybrid dynamics coupled to a classical thermostats is the dominating approach (as in [69, 92, 94], and many others). The following section is devoted to this issue and summarizes the results of the second article of this compendium.

1.3.1 Ergodic hypothesis, phase space visitation for thermostatted trajectories and hybrid canonical ensemble

In [94], it is shown that the time averages at long times of the integral curves of Ehrenfest dynamics coupled to a classical thermostat yield some puzzling results, despite apparently constituting an ergodic system:

- The mean energy of the quantum subsystem consistently exceeds the thermal energy associated to a given temperature of the classical bath driving the dynamics.
- Such energy is an increasing function on the number of quantum states (dimension of the Hilbert space) and diverges as the number of quantum levels approaches infinite (which is interpreted as the thermodynamical limit, constructed to the tensor product of several finite dimensional quantum systems).

It was shown that the visitation over phase space associated to such thermal dynamics gradually approaches the ill-behaved Gibbsian hybrid canonical ensemble, defined in eq. (1.101).Experimentally, the following finite version of a limit can be reproduced. For arbitrary levels of precision ϵ, there exists a finite time of simulation t_0 such that the statistical averages under the wrong HCE of any physical magnitude (represented by a hybrid operator $\hat{A}(\xi) \in \Gamma(\mathcal{F}_O)$) are compatibly approximated by any time average of longer duration than t_0 over the classically thermostated trajectory, $\gamma(t) = (\xi(t), \Psi(t))$. We can state such result as follows. There exists a time $t_0 > 0$ such that the time average of any observable $\hat{A}(\xi)$ over any solution curve to (1.1,1.2,1.3) plus a thermostat, from $t = 0$ to $t_f > t_0$, is compatible with the expectation value yielded by the Gibbs ensemble, under a given finite resolution ϵ:

$$\forall \epsilon \in \mathbb{R} \;\; \forall \hat{A}(\xi) \in \Gamma(\mathcal{F}_O) \;\; \forall \xi(t), \Psi(t) \text{ solutions to (1.1,1.2,1.3) plus thermostat} \quad \exists t_0 \in \mathbb{R}_+ |$$
$$\left\| \int_0^{t_f} dt \; \langle \Psi(t) | \hat{A}(\xi(t)) \Psi(t) \rangle - \int_{\mathcal{M}_H} d\mathrm{Vol}_H \frac{e^{-\beta f_H(\xi,\Psi)}}{Z_{HCE-\mathrm{Gibbs}}} \langle \Psi | \hat{A}(\xi) \Psi \rangle \right\| \leq \epsilon \quad \forall t_f > t_0 \; , \quad (1.102)$$

or equivalently:

$$\lim_{t_f\to\infty}\int_0^{t_f} dt\langle\Psi(t)|\hat{A}(\xi(t))\Psi(t)\rangle \to \int_{\mathcal{M}_H} d\mathrm{Vol}_H \frac{e^{-\beta f_H(\xi,\Psi)}}{Z_{HCE-\mathrm{Gibbs}}}\langle\Psi|\hat{A}(\xi)\Psi\rangle \ , \tag{1.103}$$

whose strict proof would require very elusive results of ergodic theory. Note that the hybrid statistical model is, mathematically, a classical Hamiltonian system, described with Liouville's equation. On the other hand, the classical thermostats were invented to produce precisely the detailed balance visitation that reproduces Gibbs ensemble, if one assumes the ergodic hypothesis. Thus, it is not surprising to recover Gibbs ensemble also in this hybrid case, when thermostatted only classically.

This formulation allows us to identify the root cause of the problem: it is precisely the difference between the role of the parameter β in such ensemble and the one for the truly thermodynamical β, weighting exclusive events in the HCE (as defined in eq.(1.100)), what yields a wrong temperature and an incorrect thermal visitation for the quantum subsystem, with the aforementioned non-additivity of thermodynamical magnitudes.

Nevertheless Ehrenfest dynamics is computationally effective and easy to implement, classical thermostats are well characterized, and the ergodic hypothesis for finite times typically works well. It could therefore be a useful tool, if it did not produce this wrong visitations of phase space. In order to keep its utility and reproduce the correct thermodynamical ensembles, in the second article of this memoir [2], we address this issue and introduce a way to correct time averages in order to recover the correct thermodynamical averages. The procuedure is illustrated with a numerical example for a hybrid model of dimer dynamics.

The key contribution of this work is the redefinition of the time average procedure, incorporating a rescaling function $g_A(\xi,\Psi)$ for each averaged observable, such that:

$$\begin{aligned}&\forall\epsilon\in\mathbb{R}\ \forall\hat{A}(\xi)\in\Gamma(\mathcal{F}_O)\exists t_0\in\mathbb{R}_+|\\ &\|\int_0^{t_f} dt\ g_A(\xi(t),\Psi(t))\langle\Psi(t)|\hat{A}(\xi(t))\Psi(t)\rangle - \int_{\mathcal{M}_C} d\mathrm{Vol}_C \mathrm{Tr}\left(\hat{\rho}_{HCE}(\xi)\hat{A}(\xi)\right)\| \leq \epsilon \quad \forall t_f > t_0 \ ,\end{aligned} \tag{1.104}$$

allowing to effectively substitute phase space integrals by time averages along the solution curve to thermostatted Ehrenfest dynamics.

Usually, microdynamics relate to statistical mechanics in two ways. The first one, in terms of the ergodic hypothesis, has already been explored in this section. which summarized the results of [2]. The second one, is the induction of statistical dynamics over the densities characterizing statistical ensembles, through Liouville's theorem in the case of Hamiltonian dynamics. The third article of this compendium tackles this problem, and

the aforementioned nuances related to it. The next section contextualizes the work and summarizes its main results.

1.3.2 Hybrid Liouville's theorem and its consequences

In [63], the Hamiltonian formalism of hybrid mechanics is used to derive statistical dynamics for the density distribution over hybrid phase space, F_{QC}, introduced above. As in the classical and quantum cases, by use of Liouville's theorem, the symplectic volume is left invariant, and the dynamics for the density is driven by the Liouvillian operator:

$$\frac{dF_{QC}(\xi,\Psi)}{dt} = \{f_H, F_{QC}(\xi,\Psi)\}_H \tag{1.105}$$

where we recall that $f_H = \langle\Psi|\hat{H}(\xi)\Psi\rangle$. It is also shown in [63] that, if the dynamics for ensembles is factorizable into classical and quantum densities, $F_{QC}(\xi,\Psi) = F_C(\xi)F_Q(\Psi)$, and there is no interaction between both subsystems, one can write correct Liouville equations both for F_C and F_Q, and keep the factorization. In such case, the dynamics for F_Q is linear in projectors, as they follow the same quantum statistical dynamics as in eq. (1.89). In consequence, von Neumann's equation for the density matrix of the quantum subsystem can be derived, and F_C follows the classical Liouville equation. Even though this property may seem trivial, and for the Hamiltonian formulation of Ehrenfest's dynamics it is indeed immediate, it is an important (and, regarding the Literature, rather discriminating) consistency test of hybrid statistical dynamics.

However, for interacting quantum-classical systems, as the ones described by the total Hamiltonian operator $\hat{H}(\xi)$ in eq.(1.15), it is shown that an extension of the algebra of observables is necessary, as explained in eq. (1.58), to incorporate the non-linearities on the quantum projectors arising from the classical Poisson bracket, $\{f_A, f_H\}_C$. In consequence, the dynamics of F_{QC}, representing the dual to the hybrid observables, must incorporate such non-linearities, too.

This issue is deeply analyzed by Buric *et al.* [51]. The results of that study, adapted to the language of this thesis, can be summarized as:

- In order to be consistent with Liouvillian dynamics, the hybrid statistical ensemble must be represented by a probability density on the hybrid phase space (in contrast to the density matrix description accounting for hybrid exclusive events introduced above, natural for the definition of entropy and thermodynamical magnitudes).

- Each distribution with the same first moment on quantum projectors determines the same quantum density matrix for the quantum subsystem, arriving thus to the equivalence class $[F_{QC}]\hat{\rho}(\xi)$ as defined in eq. (1.96).

- The evolution of hybrid statistical mixtures cannot be written, in general, solely in terms of $\hat{\rho}(\xi)$, but requires the use of the hybrid probability density, reproducing Liouville's dynamics.
- Different initial $F_{QC}(\xi, \Psi, t_0) \in [F_{QC}]\hat{\rho}(\xi, t_0)$ yielding the same hybrid density matrix $\hat{\rho}(\xi, t_0)$ at initial time t_0, evolve to yield different hybrid density matrices. In consequence, member of the same equivalence class are not really *physically* equivalent, contrarily to the case of (ordinary, linear) quantum mechanics.

This last point is recovered in our work [3]. Following the notation used throughout this memoir, and using Liouville's equation for F_{QC}, it can be understood from the following equation:

$$\begin{aligned} d_t\hat{\rho}(\xi) &= \int_{\mathcal{M}_Q} d\mathrm{Vol}_Q\{f_H, F_{QC}(\xi,\Psi)\}H\hat{P}_\Psi \\ &= \frac{-i}{\hbar}[\hat{H}(\xi), \hat{\rho}(\xi)] + \int_{\mathcal{M}_Q} d\mathrm{Vol}_Q\{\mathrm{Tr}(\hat{P}_\Psi\hat{H}(\xi)), F_{QC}(\xi,\Psi)\}_C\hat{P}_\Psi\,. \end{aligned} \tag{1.106}$$

The last term, that involves the classical Poisson bracket, is non-linear on $\hat{P}_\Psi$, and is therefore the root cause of the splitting of the equivalence class $[F_{QC}]\hat{\rho}(\xi)$ under the dynamics.

This is difficult to reconcile with the usual notion of physical observable in hybrid systems, given by the quadratic functions defined as the expectation value of hybrid operators $\mathcal{F}_{2Q}(\mathcal{M}_H)$. If those were the only true physical observables in hybrid systems, all initial ensembles in the equivalence class $F_{QC,t_0} \in [F_{QC}]\hat{\rho}(\xi, t_0)$ would be indistinguishable: there would not exist any possible physical measurement whose result could not be characterized by the hybrid density matrix. However, such ensembles would evolve to yield different physical ensembles with measurable physical magnitudes distinguishing them. Thus, such difference in the evolution would apparently depend on inaccessible variables.

As a consequence, the extension of the hybrid algebra of observables (1.58), which was introduced as a mathematical trick for the definition of a proper Poisson algebra (1.59), arises here as a physical feature of the theory. The statistical average of these extended magnitudes cannot be captured by the usual hybrid density matrices, which is why, in [51], they choose the most general description of statistical ensemble as probability densities over the hybrid manifold.

In the third paper of this compendium, [3], we reanalyze all these issues and recover the density matrix formalism, although in a generalized manner that allows us to capture the k-th order moments of F_{QC} in terms of a density matrix. Such generalized density matrices are the key mathematcal objects of the paper, and are defined as:

$$\hat{\rho}^{(k)}(\xi) := \int_{\mathcal{M}_Q} d\mathrm{Vol}_Q F_{QC}(\xi)\hat{P}_\Psi \otimes \overset{k}{\cdots} \otimes \hat{P}_\Psi \forall k \in \mathbb{N}\,, \tag{1.107}$$

which serves as a substitute of eq. (1.106).

As will be seen in [3] , this formalism allows us to consider the expectation value of generic observables in (1.59). Their dynamics can be directly derived from Liouville's equation for $F_{QC}(\xi, \Psi)$ as the following set of linearly coupled differential equations:

$$d_t\hat{\rho}^k(\xi) := \frac{-i}{\hbar}[\hat{H}, \hbar\rho^k(\xi)] + \mathrm{Tr}_1\left(\{\hat{H}(\xi) \otimes^{\overset{k+1}{\cdots}} \mathbb{I}, \hat{\rho}^{k+1}(\xi)\}_C\right) , \tag{1.108}$$

where Tr_1 denotes the partial trace over the first subspace of the tensor product. This dynamics allows us to identify in which way the higher order moments of F_{QC} affect the evolution of $\hat{\rho}(\xi)$, characterizing precisely how the elements of $[F_{QC}]\hat{\rho}(\xi)$ split apart under the evolution. This splitting is illustrated with some statistical dynamical simulations for a simple hybrid model, as well as its effects over physical observables.

Additionally, an effective approach is proposed to be able to truncate the dynamics of the generalized density matrices up to a certain power, with potential applications in simulations of out-of-equilibrium hybrid statistical systems.

Lastly, this formalism has a natural definition of entropy at each level $\hat{\rho}^k(\xi)$, generalizing the results of [1] to the statistical ensembles adapted to higher order observables. In this line, this formalism would theoretically ease the identification of the correct representation of a hybrid ensemble as F_{QC}. Doing so in terms of its quantum statistical moments allows us to follow some physically sensible criterium, such as the conservation of the total entropy. As this feature occurs naturally for isolated systems under classical (under Liouville's dynamics) or quantum (under von Neumann's equation) statistical dynamics, it is natural to expect a similar behavior for hybrid systems.

Nevertheless, the specific relation of the entropies for different orders (denoted by k in $\hat{\rho}^k(\xi)$) is still missing. Consequently, the consistency requirements between thermodynamical magnitudes as introduced in [1] and this algebraic Liouvillian approach are still a matter of study.

To address these difficulties, and try to find compatible statistical dynamics and thermodynamics, we introduce a new mathematical formalism in the fourth work of this compendium [4]. This will be the last article in this memoir about statistical systems. It generalizes Koopman's formalism of classical statistical mechanics [95, 96] to hybrid systems. The following section introduces the context of this work and summarizes its results.

1.3.3 Koopman's formalism for hybrid $C^\star$ algebras

Indeed, Koopman's formalism has recently regained interest in the context of hybrid systems, as it allows for a rigorous mathematical characterization of both the dynamics and the statistical magnitudes [95, 96]. In the search of a unified description of classical and

quantum mechanics, this approach is complementary to the geometrical formulation of hybrid systems in terms of a hybrid phase space: instead of making the quantum subsystem *look like* classical mechanics, we are disguising the classical one as quantum, through its description in terms of Hilbert spaces.

The fourth article of this compendium [4], starts with a thorough review of Koopman's formalism, originally introduced in [97], that we briefly summarize here. Let us consider a classical statistical dynamical system defined by a probability density F_C on a classical phase space subject to a Liouville equation, as introduced in section 1.3. With these prerequisites, the key features of Koopman's formulation of classical mechanics are the following:

- It rewrites the classical ensemble denoting a probability density, $F_C : \mathcal{M}_C \to \mathbb{R}_+$, as the modulus squared $F_C = \bar{\Psi}_C \Psi_C$ of a wave function $\Psi_C \in L^2(\mathcal{M}_C)$, and promotes such wave function to represent the state of the statistical classical system.

- Regarding the Liouvillian dictating the dynamics of the classical probability density, $d_t F_C = -X_H(F_C)$, its symplectomorphic nature is exploited to reinterpret it as the infinitesimal generator of unitary transformations U_t over $L^2(\mathcal{M}_C)$. Stone's theorem is invoked to identify the self-adjoint operator L such that $U_t = e^{-iLt}$. Such operator defines the dynamics for Ψ_C and is shown to be related to the Liouvillian as:

$$i d_t \Psi_C = L\Psi_C := -iX_H(\Psi_C) = -i\left(\frac{\partial}{\partial[Q_i} f_H(Q,P)\frac{\partial}{\partial P^i]}\Psi_C\right) . \tag{1.109}$$

- Regarding operators characterizing physical observables, given the classical nature of the system, they are constructed as multiplicative operators on Q_i, P^i. Note that this is natural, since in the usual picture they are just (densely approximated by) polynomials over $\mathcal{M}_C$, and the L^2 space of Koopman's construction has the whole classical phase space as its domain. This is in striking contrast to the usual picture of quantum mechanics, where one restricts the domain of the wave functions to a Lagrangian submanifold [98] of the classical phase space (usually, the positions). In such case, we are forced to characterize, through the quantization procedure $\mathcal{Q}$, the variables left outside of the manifold (usually, the momenta) as derivative operators over the L^2 (defining tangent fields over its domain). In other words, while in usual quantum mechanics $\mathcal{Q}(x) = x$ and $\mathcal{Q}(p) = -i\hbar\partial_x$, in Koopman's formulation of classical mechanics the quantization is trivial, $\mathcal{Q}(Q_i) = Q_i$ and $\mathcal{Q}(P^i) = P^i$.

  Nevertheless, this quantization map can be extended to include the corresponding quantum-momenta operators to Q_i, P^i, denoted by Π_{Q_i} Π_{P^i}, which shall not be confused with the classical momenta P^i. This would imply an extension of the classical phase space to contain $(Q_i, P^i, \Pi_{Q_i}, \Pi_{P^i}) \in \mathcal{M}_{C-\text{extended}}$ through the definition of a cotangent bundle to the original $\mathcal{M}_C$, which is provided with a canonical

symplectic form. Then, in the quantization procedure the system is restricted to the Lagrangian submanifold consisting of the original classical phase space. Therefore, the quantization of the new momenta operators will be of derivative nature, $\mathcal{Q}(\Pi_{Q_i}) = -i\partial_{Q_i}$, $\mathcal{Q}(\Pi_{P^i}) = -i\partial_{P^i}$, appropriately defined to be self-adjoint operators over $L^2(\mathcal{M}_C, d\text{Vol}_C)$. However, the algebra of classical physical observables will still be the multiplicative subalgebra consisting of quantization of polynomials on Q_i, P^i, while the quantization of polynomials containing any quantum momenta will be considered to be external elements to the subalgebra of physical observables.

- This means that they form a commutative subalgebra $\mathcal{A}_C$ (multiplicative operators always commute), and therefore, the Heisenberg picture of Koopman's description, where the operator L governs the dynamics of the algebra of operators, has a crucial difference: L, being derivative, does not belong to the classical commutative algebra of multiplicative operators over $L^2(\mathcal{M}_C)$. In turn, the dynamics for the classical algebra of observables must be regarded as an outer-automorphism generated by $L : \mathcal{A}_C \to \mathcal{A}_C$. This outer automorphism was given by the Poisson bracket, and therefore it is a linear combination of the operators ∂_{Q_i} and ∂_{P^i}, which represent the quantization of the extended-momenta $\mathcal{Q}(\Pi_{Q_i})$ and $\mathcal{Q}(\Pi_{P^i})$. Hence, L belongs to the extended algebra of operators containing quantum momenta.

Another key ingredient constuction of this work is the notion of states over the $C^\star$-algebras that characterize both classical and quantum observables, which is generalized to hybrid systems. Using the GNS construction [99, 100], once we choose a state (i.e., an element of the dual of the algebra), the hybrid $C^\star$-algebra can be represented as self-adjoint linear operators over the tensor product of the Koopmanian Hilbert space and the quantum mechanical one, $\mathcal{O}_H\left(L^2(\mathcal{M}_C, d\text{Vol}_C) \otimes \mathcal{H}_Q\right)$, with the additional restriction introduced above: the functional representation of the operators on the classical variables can only be multiplicative, not derivative. This implies a hybrid Lie bracket structure, given by the trivial commutativity of operators in the classical sector, and the Lie bracket regarding the quantum one.

The hybrid statistical states, therefore, following Gleason's theorem [101], must be given by a hybrid density matrix, $\hat{\rho}_H$, which in general can be a mixed state and presents entanglement between the classical and quantum sectors. The key developments of the fourth article of this compendium can then be summarized in the following points:

- We construct the hybrid statistical state as a density matrix $\hat{\rho}_H$. This object looks apparently fully quantum in both the classical subsector and the quantum one, as they are described in Koopmanian and standard quantum mechanical pictures, respectively. Nevertheless, it acts as the dual to the hybrid $C^\star$ algebra of operators defined as the tensor product of classical and quantum ones, $\mathcal{A}_H := \mathcal{A}_C \otimes \mathcal{A}_Q$. Given

that the classical algebra of operators is commutative, the nature of observables and associated states is still hybrid, even if the density matrix picture is formally shaped as in full quantum mechanics. Thus, any hybrid observable, regarded as an element $\hat{A} \in \mathcal{A}_H$ has its expectation value computed as $\mathrm{Tr}(\hat{\rho}_H \hat{A})$, which reproduces accurately the expectation value under a classical distribution for purely classical observables.

- It is shown that such hybrid Koopman-von Neumann density matrix has an associated entropy given by von Neumann's entropy, which is also shown to accurately reproduce the hybrid notion of entropy introduced in [1]: $S_{vN}(\hat{\rho}_H) = S_H(\hat{\rho}(\xi))$, for the non-Koopmanian notion of hybrid density matrix $\hat{\rho}(\xi)$ introduced in (1.94).

- General hybrid statistical dynamics are characterized in compatibility with physical and mathematical requirements. In particular, it is shown that unitary dynamics cannot capture the physics of interacting systems, as they are unable to produce any backreaction of the quantum subsystem into the classical one. This constitutes a formal characterization of a well known feature of hybrid dynamics: as was shown in [69] and further studied in [3], the *backreaction* is a source of non-linearity in the usual picture of hybrid systems. It implies the loss of unitarity of the evolution regarding the quantum subsystem. Therefore, the more general notion of unitarity applied to the hybrid Koopman-von Neumannn state $\hat{\rho}_H$ is also compromised if the hybrid dynamics present backreaction of the quantum part on the classical one.

This opens a new avenue for research on the compatibility of thermodynamics and dynamics of hybrid systems, as their relationship can be easily characterized in the picture of hybrid Koopman-von Neumann density matrices. Their properties are already being explored beyond unitary dynamics (e.g. under the statistical dynamics given by a hybrid Lindblad's equation), in order to capture more physical phenomena. More work is required in this formalism to characterize the set of hybrid dynamics that allow for a consistent thermodynamical behavior, such as the preservation of the hybrid canonical ensemble.

With this, we conclude our summary on the contributions of these works to hybrid statistical mechanics and thermodynamics. The following section changes topic and is devoted to the last article contained in this thesis, [5], which generalizes the geometrical formulation of hybrid systems to field theories.

1.4 Hybrid systems for field theories

The vast majority of hybrid systems rigorously studied in the literature are made of a finite dimensional classical submanifold (such as positions and momenta for a set of particles) and a subsystem of *ordinary quantum mechanics*, described by a Hilbert space which is either finite dimensional or isomorphic to an $L^2(\Sigma, dx)$ space, where the domain of the wave

functions, Σ, is a finite dimensional manifold (for example, square integrable functions over $\mathbb{R}^{3n}$, for n particles over a three dimensional spatial manifold). This is the convenient setting for the study of molecular dynamics, most non-relativistic solid-state physics, and, in general, any framework that does not require quantum field theory.

The aim of the fifth article of this memoir and the purpose of this section is the introduction of a geometric formalism for hybrid field theoretical systems, applied to quantum field theory coupled to a dynamic curved spacetime. Such hybrid system must have as classical variables the metric tensor field chosen in the Eisnteinian picture of General Relativity (in fact, as we will see, some other tensors related to it), while the quantum variables will be some wave functionals $\Psi(\phi)$, whose domain must be the space of fields $\phi \in \mathcal{M}_\phi = \mathcal{N}'(\Sigma)$, denoting in this way distributions over the spatial (or spacetime, depending on the approach) manifold Σ. We will now summarize the geometric formalisms of both General Relativity (GR) and Quantum Field Theory (QFT), as they are the main ingredients. The main applications of such theory are the study of those systems where the backreaction of quantum fields on the geometry of spacetime, and in turn the subsequent influence of such change on the propagation of the fields themselves is relevant. For example, the study of early universe cosmology where quantum effects are relevant, Hawking radiation and its coupled black hole evaporation, particle creation in curved spacetime such as the Unruh effect and the quantum effects preventing, perhaps, the formation of singularities on spherically symmetric shells of matter gravitational collapse, within others.

1.4.1 General Relativity and its Hamiltonian formulation

In all physical theories, the symmetry groups play a crucial role in understanding the underlying structure of the theory, allowing the construction of an invariant action functional from which we can derive the whole theory. The symmetry group of a theory is thus constituted by all the mathematical transformations that leave the equations of the theory invariant. In the case of general relativity, the symmetry group is the diffeomorphism group of spacetime, which encompasses all possible coordinate transformations of spacetime.

This symmetry group is thus the final consolidation of two ubiquitous notions in the history of physics. Firstly, the freedom to choose any coordinate system (in the case of GR, to describe the geometry of spacetime) without changing the physical content of the theory. This notion ultimately leads to the principle of general covariance, which states that the laws of physics should be formulated in a way that is independent of the choice of coordinates, ensuring that physical predictions do not rely on any particular reference frame.

Secondly, the diffeomorphism symmetry is intimately connected to the conservation laws in general relativity. The equations of motion in general relativity can be derived

from the principle of least action, which must be invariant under diffeomorphisms. Noether's theorem relates continuous symmetries to conserved quantities, and in the case of diffeomorphism symmetry, it gives rise to a plethora of well known conserved quantities: such as energy, momentum and angular momentum.

In the original theory of gravitation introduced by Einstein in 1915, gravity is described as the curvature of spacetime $\mathcal{M}$ caused by the distribution of mass and energy. The fundamental variable encoding the geometry of spacetime is the metric tensor $g_{\mu\nu}$, with signature $(-,+,+,+)$ (time distances are negative, space distances are positive). The choice of this tensorial object, in terms of which we can define a connection and the associated covariant derivatives for any vector field, will be key for the implementation of the GR symmetry group.

The spacetime manifold, sometimes called the manifold of events (characterized by a location in space and time), combines three spatial dimensions of space with a temporal one, and it does not have in general a preferred time-direction. The metric tensor defines the distances (and angles) between infinitesimally neighboring points or tangent vectors in $\mathcal{M}$, thus providing a scalar product for vectors. Any vector field v^μ whose local scalar product with itself is negative, $g_{\mu\nu}(x)v^\mu(x)v^\nu(x) \leq 0 \quad \forall x \in \mathcal{M}$, is called a time-like vector field and defines a valid direction for a causal time evolution. In the same sense, if it is positive, the vector is dubbed space-like (its integral curves relating events that are causally disconnected) and if it is exactly zero, it is dubbed light-like or null (only light or equivalently fast particles can relate the events belonging to its integral curves).

Being a $(0,2)$ symmetric tensor over a 4-dimensional manifold, $g_{\mu\nu}$ can be written in coordinates as a symmetric matrix with 16 components, only 10 of them being independent. The way this tensor is related to the distribution of mass and energy of matter is through Einstein's field equations:

$$G_{\mu\nu}(X^\alpha) = \kappa T_{\mu\nu}(X^\alpha) - \Lambda g_{\mu\nu}(X^\alpha) \quad \forall X^\alpha \in \mathcal{M} \tag{1.110}$$

where the LHS corresponds to Einstein's tensor $G_{\mu\nu} := R_{\mu\nu} + \frac{1}{2}Rg_{\mu\nu}$, constructed in terms of the Ricci tensor $R_{\mu\nu}$ and its trace $R := g^{\mu\nu}R_{\mu\nu}$, both constructed in terms of $g_{\mu\nu}$ and its associated Levi-Civita connection. On the other hand, Λ represents the dark energy or the cosmological constant, a natural curvature of spacetime, treated as a constant in this work which can always be included given its invariance under diffeomorphisms.

Lastly, $T_{\mu\nu}$ is the stress energy tensor of the matter theory (in the absence of matter, this term is null), which can be defined as $T_{\mu\nu} = \frac{-2}{\sqrt{|g|}}\frac{\delta}{\delta g_{\mu\nu}}S_M$, with S_M being the action functional for the matter degrees of freedom, constructed in a way that is invariant under diffeomorphisms. Note that, rigorously, $\frac{\delta}{\delta g_{\mu\nu}}$ represents the Frèchet functional derivative with respect to the tensor components, considered as functionals of the space-time

coordinates. For example, for a massive free scalar field, the invariant action is given by:

$$S_M[\phi] := \int_{\mathcal{M}} d^4X\sqrt{|g|}\frac{1}{2}\left(g^{\mu\nu}\frac{\partial}{\partial X^\mu}\phi\frac{\partial}{\partial X^\nu}\phi + m^2\phi^2\right) \tag{1.111}$$

where the square root of the absolute value of the determinant of the metric $\sqrt{|g|}$ in the volume element ensures its invariance under coordinate transformations, while the contraction of the derivatives of the field with the metric provides the kinetic term with said invariance. The associated energy tensor is given by:

$$T_{\mu\nu} := \frac{-2}{\sqrt{|g|}}\frac{\delta}{\delta g^{\mu\nu}}S_M = -\frac{\partial}{\partial X^\mu}\phi\frac{\partial}{\partial X^\nu}\phi + g_{\mu\nu}\frac{1}{2}\left(g^{\alpha\beta}\frac{\partial}{\partial X^\alpha}\phi\frac{\partial}{\partial X^\beta}\phi + m^2\phi^2\right) , \tag{1.112}$$

where all the tensors and scalars are local on the local coordinates X^α, but the dependence is not written explicitly to avoid cumbersome expressions.

Hilbert-Einstein action

In the same way the stress-energy tensor is derived from the action for matter fields, S_M, Einstein's tensor can be derived from the Hilbert-Einstein action S_G, which is given by

$$S_G := \frac{1}{2\kappa}\int_{\mathcal{M}} d^4X\sqrt{|g|}(R - 2\Lambda) , \tag{1.113}$$

so that $G_{\mu\nu} + \Lambda g_{\mu\nu} = \dfrac{2\kappa}{\sqrt{|g|}}\dfrac{\delta}{\delta g^{\mu\nu}}S_G$. Note that the original H-E action presented in [102] has been corrected to contain the gravitational constant. Consequently, Eintein's field equations can be derived from a least action principle from the sum of both actions:

$$\frac{2\kappa}{\sqrt{|g|}}\frac{\delta}{\delta g^{\mu\nu}}\left(S_G + S_M\right) = 0 \Rightarrow G_{\mu\nu} + \Lambda g_{\mu\nu} = \kappa T_{\mu\nu} . \tag{1.114}$$

This Lagrangian procedure is profoundly rooted in the covariant formalism, where there is no preferred time direction. The objective of this section, and of the fifth article included in this thesis, is the substitution of the classical matter appearing in the stress-energy tensor by a quantum field theory for matter, but instead of using the covariant formalism, we rewrite the theory in a Hamiltonian fashion. Nevertheless, in the Hamiltonian formalism the time direction appears as unique, so the laws of physics in such formalism apparently do not fulfil the general covariance principle. This issue is solved in the Hamiltonian formulation of General Relativity known as geometrodynamics introduced by Hojman, Kuchar and Teitelboim in [103], which is based on the Arnowitt-Deser-Misner formalism, introduced in [104] in the late 1950s.

The ADM formalism and geometrodynamics

The ADM formalism provides a way to decompose Einstein's field equations into a set of evolution equations and constraints, which simplifies the study of the gravitational field

allowing for a dynamical picture, instead of a covariant one.

In order to do so, spacetime is divided into a sheaf of three-dimensional spatial slices, which is formally characterized by a foliation of $\mathcal{M}$ in terms of spacelike hypersurfaces, with each hypersurface corresponding to a specific moment in time, for a consistent (but arbitrary) definition of time as a function $\tau : \mathcal{M} \to \mathbb{R}$. Consequently, this foliation allows us to split the spacetime metric tensor $g_{\mu\nu}$ into its spatial and temporal components, at each hypersurface. The spatial part is also a metric tensor h_{ij}, in this case Riemannian and over a three dimensional spatial manifold, accounting for the first fundamental form of each hypersurface. This 3-metric will play the role of the generalized positions in the Hamiltonian formalism of gravity. The associated momenta are related through a Legendre transform to the extrinsic curvature K_{ij} of the hypersurface, which dictates the change of h along the normal vector to the leaf, playing (almost) the role of the velocities. On the other hand, the time sector of this decomposition of $g_{\mu\nu}$ defines the so called lapse function N and shift vector N^i, which relate the evolution of the spatial slices through time and act as Lagrange multipliers for the constraints of the theory. For an introductory picture of the ADM formalism, an accessible source is the eleventh chapter of Padmanabhan's book, [105], while the Hamiltonian construction in terms of Poisson brackets is more clearly presented in the thorough review made in the first sections of [103]. Instead of introducing the Hamiltonian picture of Eisnteinian gravity, which is carefully reviewed in the fifth article of this memoir, [5], in this introduction we will familiarize with ADM's formalism in a way that allows us to keep the analogy with the more traditional mechanical systems. Firstly, we introduce the Lagrangian formalism, obtaining the equations of motion through a least action principle. The key aspects of the construction are the following:

1. To have a notion of time, one can always choose an arbitrary function $\tau : \mathcal{M} \to \mathbb{R}$ such that their $\tau(X^\mu) = s$ constitutes a general plane equation defining the hypersurface Σ_s whose normal vector field $n_\mu = \dfrac{\partial \tau}{\partial X^\mu}$ is always time-like. The label s will play the role of the time coordinate in this construction. The s-parametric family of hypersurfaces fills a globally hyperbolic spacetime, so that $\mathcal{M} \simeq \{\Sigma_s \quad \forall s \in \mathbb{R}\}$. An important feature of the construction is that the choice of foliation is made arbitrarily, so the physics must not depend on such construction.

2. Having assigned the meaning of time to s, we may as well choose some arbitrary spatial coordinates x^i for each hypersurface Σ_s. In this way, we can make use of the parametric equations for the hypersurface, $X^\mu = X^\mu(x^i, s)$, so that we can write the tensorial objects over Σ_s in coordinates for this chart. In particular, the metric tensor for spacetime, $g_{\mu\nu}$, which induces a 3-metric $h_{ij}(x, s)$ over each Σ_s defining distances and angles for the vectors over such hypersurface, which in the chosen coordinates can be defined as follows:

$$h_{ij}(x, s) = g_{\mu\nu}(X^\alpha(x, s)) \frac{\partial X^\mu(x, s)}{\partial x^i} \frac{\partial X^\nu(x, s)}{\partial x^j} \tag{1.115}$$

Associated to the s-label playing the role of time, there exists an evolution vector field E that accounts for the change from one hypersurface to the infinitesimally neigbouring one, as $\frac{d}{ds}$. Making use of the parametric equations it can be defined as:

$$E := \frac{dX^\mu(x,s)}{ds} \ . \tag{1.116}$$

In turn, such vector can be decomposed into a normal direction and three tangential directions to the hypersurface, given by $n^\mu_s = g^{\mu\nu}\frac{\partial \tau}{\partial X^\nu}$ and $t^\mu_i := \frac{\partial X^\mu}{\partial x^i}$ respectively. Projecting E onto such directions (through the use of the scalar product defined by $g_{\mu\nu}$), allows us to identify the size of the change of the hypersurface (from a current one to an infinitesimally neighbouring one) in said normal and tangential directions. This defines the so called Lapse function N (component of E in the normal direction) and shift vector N^i (components of E in each tangential direction), as follows:

$$N(x,s) := g_{\mu\nu}(\frac{dX^\mu(x,s)}{ds}n^\nu(x,s) \quad \text{and} \quad N^i(x,s) := g_{\mu\nu}\frac{dX^\mu(x,s)}{ds}t^\nu_j(x,s)h^{ij}(x,s) \ . \tag{1.117}$$

Therefore, given that from an initial hypersurface Σ_s the vector field E can, by definition, span the whole foliation of spacetime through its flow α^s_E, and, given that such vector field is uniquely defined in terms of the Lapse function and shift vector over the whole spacetime, the choice of such parameters is equivalent to the choice of a foliation.

3. Having defined the first fundamental form, $h_{ij}(x,s)$, we may ask for the second fundamental form, which is the change of h_{ij} along the normal direction to the hypersurface $\vec{n}_s$, defining thus the extrinsic curvature of the hypersurface Σ_s as proportional to the Lie derivative of the tensor h_{ij} along the flow of the vector field $\vec{n}_s$:

$$K_{ij} := \frac{1}{2}\mathcal{L}_{\vec{n}_s}h_{ij} \ . \tag{1.118}$$

With some convoluted geometrical relation[105], it can be shown to be:

$$K_{ij} = \frac{1}{2N}\left(D_\beta N_\alpha + D_\alpha N_\beta - \partial_s h_{ij}\right) \tag{1.119}$$

where we are making use of the projection of the 4-covariant derivative on the hypersurface Σ_s, for the tangent vectors to the hypersurface, defined as:

$$D_\beta V_\alpha = h^i_\beta h^j_\alpha \nabla_i X_j \ \forall \vec{V} \text{ such that } V_\alpha n^\alpha = 0 \ , \tag{1.120}$$

In turn, this definition provides us with a notion of spatial covariant derivative, associating D with the Levi-Civita connection for the 3-metric h. In terms of such connection we may define, as usual, the Riemann tensor ${}^{(3)}R^i_{jkl}$ of h, which measures the non-commutativity of two of such covariant derivatives. Over tangent vectors, such non-commutativity is related to the Ricci identity, as usual:

$$\forall v \in T(\Sigma_s), \ (D_iD_j - D_jD_i)v^k = R^k_{lij}v^l \tag{1.121}$$

4. In terms of these objects, it can be shown that the Hilbert-Einstein action introduced in (1.113) can be rewritten (up to surface terms) as:

$$S_G := \frac{1}{2\kappa}\int_{s_0}^{s_f}\int_{\Sigma_s} d^3x N\sqrt{h}\left[{}^{(3)}R(h) + K_{ij}K^{ij} - K^a_a K^b_b - 2\Lambda\right] , \tag{1.122}$$

where ${}^{(3)}R(h)$ is the scalar of curvature for the Riemannian 3-metric h. We must realize that Hilbert-Einstein Lagrangian was given solely by $\sqrt{g}(R(g) - 2\Lambda)$, which is identified as the only term that is invariant under diffeomorphisms being no more than quadratic on derivatives of g. But it has a difficult interpretation in terms of the common structures of classical mechanics such as potential and kinetic energies. Contrarily, in the case of the ADM presentation of the action, the invariance under diffeomorphisms is not self-evident, but has some boons regarding its interpretation in analogy with classical mechanics. For example, $K_{ij}K^{ij} - K^a_a K^b_b$ has the shape of a kinetic energy term for the $(2,0)-$tensor field K_{ij}, which in turn can be formally related with the velocity of the generalized position given by the 3-metric h_{ij}. Furthermore, ${}^{(3)}R(h)$ appears as a function solely of h, and contains only spatial derivatives of it, so can be interpreted as a potential energy term for h.

Armed with this interpretation, we may perform a Legendre transform to identify the geometrodynamic conjugate momentum to h_{ij} in terms of the extrinsic curvature as:

$$\pi^{ij}_h := \frac{\partial L_{ADM}}{\partial \dot{h}_{ij}} = -\frac{1}{2\kappa}\sqrt{h}(K^{ij} - Kh^{ij}) \tag{1.123}$$

which allows us to rewrite the action in a Hamiltonian way:

$$\begin{aligned} S_G = \int_{s_0}^{s_f}\int_{\Sigma_s} d^3x \left(\pi^{ij}(x,s)\frac{d}{ds}h_{ij}(x,s) - N(x)\mathcal{H}(h,\pi;x) - N^i(x)\mathcal{H}_i(h,\pi;x)\right) \quad \text{where} \\ \mathcal{H} := G_{ijkl}\pi^{ij}\pi^{kl} - (2\kappa)^{-1}\sqrt{h}(R - 2\Lambda) \text{ and } \mathcal{H}_i := -2D_j(h_{i\alpha}\pi^{\alpha j}) . \end{aligned} \tag{1.124}$$

where $G_{ijkl} := h_{ik}h_{jl} + h_{il}h_{jk} - h_{ij}h_{kl}$ is the Wheeler-DeWitt metric, which in turn induces a metric over the manifold of 3-Riemannian metrics. These functions $\mathcal{H}, \mathcal{H}_i$ of geometrodynamic positions and momenta, are usually called *superhamiltonian* and *supermomenta* respectively (collectively denoted *supermagnitudes*) and we anticipate that they will play a central role in the Hamiltonian theory. We may note that in this formalism, the Lapse function $N(x)$ and the coordinates of the shift vector $N^i(x)$ appear in a non-derivative way. This means that the action does not account for the dynamics of such objects and, therefore, must be external parameters which play the role of Lagrange multipliers for the theory. In fact, analyzing the shape of the action, the Hamiltonian function of the theory can be easily identified solely in terms of such Lagrange multipliers contracted with the supermagnitudes:

$$H_G = \int_{\Sigma_s} d^3x \left(N(x)\mathcal{H}(h,\pi;x) + N^i(x)\mathcal{H}_i(h,\pi;x)\right) \tag{1.125}$$

5. The Hamilton's equations of such action for s are derived from a extreme action principle as:

$$\frac{d}{ds}h_{ij}(x) = \frac{\delta H}{\delta \pi_h^{ij}(x)} = 2N(x)G_{ijkl}(x)\pi_h^{kl}(x) - 2N^{\alpha}(x)D_j(h_{\alpha i}(x)) \tag{1.126}$$

and

$$\begin{aligned}\frac{d}{ds}\pi_h^{ij}(x) = -\frac{\delta H}{\delta h_{ij}(x)} = N(x)\sqrt{h}(\ {}^{(3)}G^{ij}(h) - \Lambda h_{ij}) - \sqrt{h}D^{\alpha}D^{\beta}N(x) \\ -N(x)\frac{\delta G_{ijkl}}{\delta h_{ij}(x)}(\pi^{ij}\pi^{kl}) - \frac{\delta(N^{ix}\mathcal{H}_{ix})}{\delta h_{ij}(x)}\end{aligned} \tag{1.127}$$

where ${}^{(3)}G^{ij}(h)$ is Einstein's tensor for the 3-metric h. On the other hand, the extreme action principle with respect to N and N^i, which appear as Lagrange multipliers, yields the constraints:

$$\mathcal{H} = 0 \quad \text{and} \quad \mathcal{H}_i = 0 \tag{1.128}$$

This set of equations with constraints are equivalent to Einstein's equations without matter. While the dynamical equations are explicitly non-covariant, the constraints ensure the covariance of their solutions.

6. In order to include matter sources, this transformation (from a covariant formalism to a Hamiltonian one) can be equivalently performed on the matter sector. For example, for the scalar field we only need to identify $\phi(x)$ as the restriction of the covariant field solutions $\phi(X^{\mu})$ to the submanifold Σ_s (being scalar, it is just their value over the hypersurface), and define their associate momentum π_{ϕ} through a Legendre transform of the action. In this way, the action introduced in (1.111) can be rewritten as:

$$\begin{aligned}S_M = \int_{s_0}^{s_f}\int_{\Sigma_s} d^3x \left(\pi_{\phi}(x)\frac{d}{ds}\phi(x) - N(x)\mathcal{H}^M(x) - N^i(x)\mathcal{H}_i^M(x)\right) \quad \text{where} \\ \mathcal{H}^M(x) = \frac{1}{2}\sqrt{h}\left(h^{-1}\pi_{\phi}^2 + h^{ij}\partial_{x^i}\phi\partial_{x^j}\phi + m^2\phi^2\right) \quad \text{and} \quad \mathcal{H}_i^M(x) = \pi_{\phi}\partial x^i\phi\end{aligned} \tag{1.129}$$

Given that the total theory was derived from the sum of actions, the total supermagnitudes (denoted here by a T superindex) can be derived as the sum of the matter and gravitational ones:

$$\mathcal{H}^T(x) := \mathcal{H}^M(x) + \mathcal{H}(x) \quad \text{and} \quad \mathcal{H}_i^T(x) := \mathcal{H}_i^M(x) + \mathcal{H}_i(x) \tag{1.130}$$

which constitute the local generators of the dynamics for the whole theory of matter and gravity, defining a total Hamiltonian $H^T := N^x\mathcal{H}_x^T + N^{ix}\mathcal{H}_{ix}^T$, where the repeated x subindex implies integration over Σ_s. In this sense, for any differentiable function

of all the variables $F(h, \pi_h, \phi, \pi_\phi)$, its dynamics are given by:

$$\frac{d}{ds}F(h,\pi_h,\phi,\pi_\phi) = \int\limits_\Sigma d^3x \left(\frac{\partial F}{\partial h_{ij}(x)}\frac{\partial H}{\partial \pi^{ij}(x)} - \frac{\partial F}{\partial \pi^{ij}(x)}\frac{\partial H}{\partial h_{ij}(x)} + \frac{\partial F}{\partial \phi(x)}\frac{\partial H}{\partial \pi_\phi(x)} - \frac{\partial F}{\partial \pi_\phi(x)}\frac{\partial H}{\partial \pi_\phi(x)} \right) , \tag{1.131}$$

which, in particular for $F = h$ and $F = \pi_h$, yields a system of coupled differential equations equivalent to Einstein's field equations coupled to an energy momentum tensor accounting for the presence of matter. This equivalence is only true under the superhamiltonian and momenta constraints, which, naturally, in the presence of matter are given by $\mathcal{H}^T(x) = \mathcal{H}_i^T(x) = 0$.

Departing from this approach, Hojman, Kuchar and Teitelboim regained the term *geometrodynamics*, coined by Wheeler in the early 60's, to denote the Poissonian formalism of Eisnteinian gravity developed in [103]. The main contribution of their work is the axiomatic derivation of these equations and constraints without departing from the Hilbert-Einstein action, but from first principles.

Their formalism is thoroughly reviewed in [5], the last article of this compendium, as it is a cornerstone in the development of the hybrid theory of gravitation and quantum matter. Therefore, instead of reviewing it here once again, we will provide some physical insight by connecting all the physical requirements and principia claimed in [103] with their mathematical consequences in the formalism, so that the later reading of [5] is more intuitive. Let us proceed.

- Instead of considering the diffeomorphism group as the symmetry group of the theory, Hojman *et al.* search for a Hamiltonian representation of Dirac's group of hypersurface deformations in the Lorentzian spacetime $\mathcal{M}$, originally introduced in [106, 107], where their symplectomorphic nature is identified. The idea is that a foliation is a smooth path along the space of possible spatial hypersurfaces $\Sigma_s \subset \mathcal{M}$. Therefore, departing from an initial hypersurface Σ_0 and smoothly changing its shape is equivalent to the whole foliation. Such smooth changes of shape can be infinitesimally generated by two kinds of deformations of the hypersurface. The first one is given by normal deformations, $D_0(x)$, analogous to poking with a finger a rubber balloon surface embedded in three spatial dimensions, but along the normal vector n^μ at the point $x \in \Sigma_s$ of the 3-dimensional hypersurface embedded in Lorentzian spacetime. The second kind is constituted of tangential stretchings, $D_i(x)$, which interpretation, extending the analogy, can be grasped as pinching the rubbery surface in two infinitesimally adjacent points around a point $x \in \Sigma_s$ aligned with the tangent vector t_i^μ and pulling apart. The integral versions of these last ones, the tangential ones, are

generic diffeomorphisms solely of spatial nature, internal to the spatial hypersurface Σ_s. For the relation between both symmetry groups, which, under the given constraints are equivalent for all physical purposes in General Relativity, the original reference is [108].

- In general, two different local deformations of a hypersurface do not commute, but instead, the infinitesimal generators form a Lie algebra (technically, an algebroid) as follows

$$[D^x_\mu, D^{x'}_\nu] = c^{\zeta;x,x'}_{\mu\nu;x''}(h) D^{x''}_\zeta \ , \tag{1.132}$$

  where the greek letters μ, ν, ζ go from 0 to 3, and the repetition of lower and upper discrete indices, as for ζ, implies Einstein summation convenction, while continuous indices, denoted by x, x', x'', denote the point of application in Σ_s, and its contraction implies integration. In this way, D^x_0 would denote an infinitesimal normal deformation at the point $x \in \Sigma_s$, and $D^{x'}_i$ a tangential one along t^μ_i at a different point x'. Lastly, $c^{\zeta;x,x'}_{\mu\nu;x''}(h)$ plays the role of the structure constant, although it is a function of the 3-metric h_{ij}, so it is called structure function, and we anticipate that it is local on x'' (i.e., constructed as a linear combination of $\delta(x - x'')$ and $\delta(x' - x'')$).

  The objective of [103] is to find a Hamiltonian representation of this infinitesimal local generators D^x_μ as functions $f^x_\mu(h_{ij}, \pi^{ij}_h)$ over the manifold $\mathcal{M}_G$ of 3-metrics and their associated momenta, so the Hamiltonian field they constitute is reproduced under a geometrodynamical Poisson bracket $\{,\}_G : C^\infty(\mathcal{M}_G) \times C^\infty(\mathcal{M}_G) \to C^\infty(\mathcal{M}_G)$. Besides, such generating functions must close under the Poisson bracket with the same structure functions as Dirac's algebra, $\{f_\mu(x), f_\nu(x')\}_G = c^{\zeta;x,x'}_{\mu\nu;x''}(h) f^{x''}_\zeta$ to be an appropriate representation of it. This is equivalent to the symplectemorphic nature of Dirac's group and constitutes the *representation postulate* of [103].

- These generating functions must be found without referring to a particular action. Instead, given that the tangential deformations are spatial diffeomorphisms over a given leaf, the local generators must reproduce the Lie derivative along the tangent vectors t_i. Given that the content on an initial hypersurface is completely known ($h_{ij}(x, s = 0)$ is initial data $\forall x \in \Sigma_0$), the relations for h_{ij} and π^{ij} along t_i can be derived from geometric relations. This constitutes the *initial data reshuffling* postulate, which mathematically implies $\mathcal{L}_{t_i(x)} F = \{F, f^x_i\}_G \quad \forall F \in C^\infty(\mathcal{M}_G)$, allowing to identify straightforwardly the generating functions of the tangential deformations with the supermomenta of ADM's formalism, $f_i(x) := \mathcal{H}_i(x)$.

- Some more physically sensible postulates, such as *locality* for the dynamics for h_{ij} (given its relation with the extrinsic curvature, which is a purely geometrical relation), the *evolution rule* stating that whole geometric content of spacetime is the solution to a continuous set of linear combinations (the coefficients stating the size of each one)

of tangential and normal deformations, and the *reversibility* condition for the generation of spacetime (time-reversed spacetime are generated with the same generating functions, but with negative coefficients), together with the representation postulate introduced above (giving a particular Poisson bracket with $f_i(x)$ of the tangential deformations, already known), are enough to determine the generating function of the normal deformation, which is found to be precisely the superhamiltonian function of ADM's formalism, $f_0(x) = \mathcal{H}(x)$.

- The last ingredient for this construction is the implementation of the *path independence principle*. This principle states that the geometric content of a final hypersurface Σ_{s_f}, resulting from the evolution through subsequent hypersurface deformations from an original one Σ_{s_0}, must be independent of the path followed in the space of possible intermediates for hypersurfaces (or equivalently, of the sequence of deformations applied Σ_{s_0}, as long as it yields the desired final shape Σ_{s_f}). This encodes the original idea of this summary about the arbitrariness of the choice of foliation not affecting physical data. Mathematically, this is implemented through the first class constraints for physical data given by $\mathcal{H} = 0$ and $\mathcal{H}_i = 0$, reaching the same set of equations with constraints as in the Hamiltonian presentation of ADM's formalism, but without requiring general covariance, nor an extreme action principle. Instead, the theory is constructed solely as the symplectomorphic representation of Dirac's group, which is a more fundamental approach.

- The theory can be extended to contain matter sources following the geometrodynamical analogue to the equivalence principle, which mathematically implies that the total generating functions of the hypersurface deformations are the sum of the purely gravitational one and the matter one, which is allowed to depend on h_{ij}, but not on its derivatives, nor on π_h^{ij}. As in the purely gravitational case, such generating functions for the matter case can be identified with the matter supermagnitudes.

This completes the contextualization of the Hamiltonian picture of General Relativity, which will constitute the classical part of the hybrid field theory constructed in [5]. Even though we have focused on Eisnteinian gravity, with had only quadratic kinetic terms in the action, the Hamiltonian formulation can be generalized to a wide range of theories of gravity as long as they are covariantly constructed in its origin or fulfil the principia stated of [103]. For example, $f(R)$ theories *à la* Brans-Dicke are provided with equivalent Hamiltonian formulation under the Palatini formalism in [109].

However, these generalizations only contemplated classical matter sources. The hybrid Hamiltonian system encompassing QFT matter sources coupled to gravity in the context of geometrodynamics remains an unexplored domain within the existing literature. Addressing this notable absence, the fifth article of this thesis executes a systematic construction of both the mathematical tools, further developed in[7, 8], as well as the physical theory

itself and delves into its possible phenomenological implications. A crucial prerequisite for delving into the construction of hybrid geometrodynamics is the knowledge of QFT in curved spacetime, and its Hamiltonian formulation. Nevertheless, all the quantum systems introduced previously in this memoir where not quantum field theoretical. In order to bridge this knowledge gap, we proceed with the review of some key aspects of QFT in curved spacetime, aiming to provide the reader with the necessary tools for the understanding of [5].

In order to do so, instead of reviewing the mainstream picture of QFT in Minkowskian spacetime some canonical references are [110, 111], and its traditional generalization to curved spacetime (to which Wald's book [112] is devoted), we will follow a different formulation more suitable for a Hamiltonian formulation and, thus, easily adaptable to be part of the hybrid system. This alternative formulation is called the Schrödinger functional picture of QFT and it presents strong formal similarities with ordinary quantum mechanics, which allows for a more graspable mathematical analogy with the geometric formulation of quantum mechanics reviewed above. A rigorous introduction to this functional representation, although in the context of algebraic QFT and based on slightly different mathematical tools, can be found in [113].

1.4.2 The Schrödinger functional picture of quantum field theory

Schrödinger wave functional (SWF) picture of QFT emerged as arguably the most natural generalization of the well established formalism of ordinary quantum mechanics. This formalism exhibits a complete analogy, where a wave functional denoted by $\Psi[\phi]$ (where the domain variables, $\phi \in \mathcal{M}_\phi(\Sigma)$, are configuration fields over the hypersurface Σ with convenient analytical properties [84] resides within a Hilbert space $L^2(\mathcal{M}_F)$, (or multiple spaces, as we will explore further in [5]) and its temporal evolution is governed explicitly by the Schrödinger functional equation:

$$\frac{d}{dt}\Psi[\phi] = \frac{-i}{\hbar}\hat{H}[\phi]\Psi[\phi] \tag{1.133}$$

where the Hamiltonian operator is a self-adjoint linear operator over the Hilbert space. Note that, in this case, the representation of such operator is given by functionals of the fields ϕ, of multiplicative nature for the potential terms (as ϕ plays the role of x in ordinary quantum mechanics) and functional derivatives with respect to ϕ in the case of the kinetic terms (such derivatives arise from the quantization of the field-momenta as in the ordinary case, but their functional nature require a careful definition).

Nevertheless, in the early times of the development of QFT, the manifest invariance of the equations under symmetry groups such as Lorentz transformations (and, later, general diffeomorphsims) were very much *en vogue*. This hindered the development of the Schrödinger wave functional formalism in favor of the mainstream approach, as the

Schrödinger wave functional equation is manifestly not covariant, given the prominent role played by time.

Besides, the viability of computing relevant phenomenology through S-matrix perturbative calculations, having a standardized recipe for regularization and renormalization of the Hamiltonian and other relevant magnitudes (which SWF lacked at the time), skyrocketed the popularity of the perturbative theory introduced by Feynmann, based on the expansion of his path integral approach. Consequently, the interest in the mathematical properties of QFT which are most naturally presented in Schrödinger's picture, such as its geometric structures or the rigorous definition of the integro-differential calculus tools used in its construction, paled in comparison to the feverish race in reproducing experimental results of particle physics experiments, which, understandably, would dominate the theoretical physics community for decades.

Despite the predictive power of the mainstream formulation of QFT, it was well known and acknowledged by the community that some long-standing issues with ill-defined objects were lurking in the most fundamental definitions of the theory, which were only tolerated as long as there was a way to circumvent the problem and arrive to the predictive power of the calculations. One of the most unsettling aspects was Feynmann's path integral formulation, which is still regarded as a cornerstone of the construction of QFT, but historically has been considered not rigourous, mainly (but not only) because it requires an integral over the space of all possible paths (continuous or not) that a field may follow from initial to final state in time (weighted with the exponential of imaginary unit times the classical action of such field path). Such integral was originally considered respect to a Lebesgue-like measure, which does not exist over the space of field paths because of its infinite-dimensional nature (see, for example, reference [114] for an introductory discussion on this issue in this context). [4]

These, and many other puzzling properties, are avoided in the Schrödinger wave functional picture as long as the functional spaces are correctly identified from the beginning in order to have properly defined integro-differential calculus. It was not until the mid 80's when the formalism regained interest, as a result of Symanzik proof of the renormalizability of the theory in [118] and the subsequent foundational work reproducing bosonic and fermionic theories well studied in the mainstream approach, such as Jackiv's [119]. In the late 90's the formalism was extended to curved spacetime, being Long and Shore's work,

[4] This formal issue was later solved using the tools of stochastic calculus, developed originally for Brownian motion. In this line, the space of paths can be provided with a well defined notion of measure, a Wiener measure (see [115, 116] for the mathematical construction and its physical applications, respectively), which, under an imaginary redefinition of time, $\tau = it$, allows for a new formalism, denoted Feynman-Kac formula, introduced in [117]. This most rigorous approach, although cumbersome in measure theory and infinite dimensional calculus, in the end leads to a framework which is easily relatable to the SWF formalism.

[120], the canonical reference. The SWF picture in curved spacetime is further explored in [121], where it is also related to the conventional approach based on Fock spaces. In this context, for general curved spacetimes some of the boons of the mainstream formulation of QFT, based on Fock space, seem to crumble. It is mostly due to the time dependence of the vacuum state which forms the ground-state of the Hilbert space in reference to which all the excitations conforming Fock space are constructed. Intuitively, the time dependence can be grasped as a mere parametric dependence of the Hamiltonian operator: as the vacuum state is an eigenstate of the Hamiltonian operator which depends on the metric, which, in turn, is time-dependent in curved spacetime, such state inherits the dependence through the metric on time. This picture is common in [120], as it is intuitive and allows for illustrative argumentation. Nevertheless, its validity, if constructed as naively as presented here, is limited to finite dimensional manifolds for the fields, and the argument must be carefully extended through a projective limit to the infinite dimensional manifold that characterize the true field theory. More sophisticated ways of introducing this dependency, based on the metric-dependence of the quantization procedure and the nature of Wiener measures over the field manifold is followed in [121–123] based on Asthekar's work, reference [124].

On the other hand, the particle interpretation of the conventional picture of QFT, usually based on the irreducible representations of the Poincaré group, can not play any special role in generic spacetimes that are not asymptotically flat, and therefore, a generic formalism in terms of wave functionals (instead of asymptotic states for the S-matrix) seems more appropriate. Besides, the fulfilment under the conventional picture of Wald's axioms for QFT in curved spacetime (see [112] and [125]) is difficult without modifications. On the other hand, the SWF picture arises naturally from a semiclassical limit of canonical quantum gravity (as in [23]). Therefore, Schrödinger wave functional picture is particularly useful for discussing the quantization of fields in curved spacetime and even allows for the extension of the framework to the quantization of the gravitational variables, in the context of quantum gravity. Nevertheless, despite its formal advantages and the rigorous definition of its technical ingredients, it is a mathematically challenging approach, and consequently other formalisms like the path integral approach will remain sovereign of practical calculations in QFT in Minkowskian spacetime, when the curvature of spacetime can be neglected.

The most compelling argument for its use in the context of this thesis is that it naturally admits a Hamiltonian structure and a straightforward definition of a Poisson algebra of observables, with easy identification of the generating function of hypersurface deformations at the quantum level. This allows for the construction of the hybrid theory of classical gravity and quantum matter in a compatible way, without worrying with the lack of explicit diffeomorphism invariance, as the constraints of the *path independence principle* can be implemented at the hybrid level. The key aspects of the SWF picture are presented here in

a way that highlights the analogy with ordinary quantum mechanics and its Hamiltonian formulation, to provide the reader with a smooth transition from the molecular context reviewed above to the field theoretical one.

In ordinary quantum mechanics, the Schrödinger wave function provides the quantum state in the Hilbert space $|\Psi\rangle \in \mathcal{H}$ with a functional representation, $\Psi(x) = \langle x|\Psi\rangle$, through its projection on the eigenstate of the position operator $\hat{x}|x\rangle = x|x\rangle$. This wave function, in turn, belongs to the square integrable functions over the space of positions (which we will denote by a generic finite dimensional manifold $\mathcal{M}_x$), so that $\Psi(x) \in L^2(\mathcal{M}_x, dL_x)$, where dL_x is Lebesgue measure over $\mathcal{M}_x$. Therefore, the Schrödinger wave function representation is just an isomorphism between the square integrable functions and the Hilbert space, $L^2(\mathcal{M}_x, dL_x) \sim \mathcal{H}$. In this case, we can choose a different measure, for example a Gaussian measure

$$d\mu_\Delta := dL_x \frac{e^{-\frac{1}{2}x^i(\Delta^{-1})_{ij}x^j}}{\sqrt{2\pi \mathrm{det}(\Delta)}} \tag{1.134}$$

with covariance matrix Δ^{ij}, and the space of square integrable functions under such measure would still be isomorphic to the same Hilbert space, and, in turn, to the Lebesgue-based functional space:

$$L^2(\mathcal{M}_x, d\mu_\Delta) \sim \mathcal{H} \sim L^2(\mathcal{M}_x, dL_x) \tag{1.135}$$

and the equality would hold for any valid covariance matrix, i.e. $\forall\Delta$.

In the Schrödinger wave functional picture, the procedure is equivalent, but instead of having its domain given by the finite dimensional manifold $\mathcal{M}_x$ accounting for the possible outcomes of the measurement of the positions, it has the manifold of fields, $\mathcal{M}_\phi$, which is infinite dimensional. This manifold of fields, in a classical field theory, must be given by the set of smooth and integrable functions over the hypersurface Σ, with respect to the measure $d^3x\sqrt{h}$ (or any suitable measure, e.g. Gaussian measures). These properties and the suitability of the functional space to perform global analysis requires the classification of the functions under nuclear-Fréchet spaces (see [84]), denoted by $\mathcal{N}$, which can be given, for example, by functions of the Schwartz class or differentiable functions of compact support, $C^\infty_C(\Sigma)$, as detailed in [5, 7]. If that had to be the domain for the wave functionals, we should be able to define square integrable functions over such manifold, $\mathcal{L}_2(\mathcal{N}, D\mu)$.

Nevertheless, an appropriate notion of measure $D\mu$ does not exist over such nuclear-Fréchet spaces, $\mathcal{N}$, so integrability is not well defined. Thus, in order to properly define the Schrödinger wave functionals, we must consider a bigger space as their domain: the strong dual space to the classical fields, $\mathcal{N}'$, which is still nuclear, and, in general, contains the distributions over Σ. Over such space, the existence of a measure $D\mu$ is ensured [7, 8, 84]. Such distributions are not necessarily representable by smooth functions which were contained in $\mathcal{N}$. In fact, $\mathcal{N}'$ contains infinitely more elements than the ones that are related to $\mathcal{N}$, such as Dirac's delta distribution over Σ. Therefore, while for Hilbert spaces

we have the Riesz representation theorem providing an isomorphism between a Hilbert space and its dual space, $\mathcal{H} \sim \mathcal{H}'$, for the nuclear Fréchet space (representing the fields here), its dual is not isomorphic to the original space. Instead only a (dense) subset of it, $\mathcal{F}$, fulfils the isomorphism: $\mathcal{N} \sim \mathcal{F} \subset \mathcal{N}'$. This feature will be relevant in the mathematical construction of hybrid geometrodynamics in [5].

Thus, the domain of the Schrödinger wave functional $\Psi[\phi]$ is given by the distributions $\mathcal{N}'$, (strong) dual to the classical conception of fields, which can be provided with a certain measure $D\mu$. This allows us to extend the formalism of ordinary quantum mechanics in order to represent a quantum state by a wave functional belonging to the square integrable functions in the following sense:

$$\Psi[\phi] \in L^2(\mathcal{N}', D\mu) \ . \tag{1.136}$$

Note that Lebesgue measure is not properly defined over the space of field (as happened for Feynmann's path integral), but instead we can define a Gaussian measure as $D\mu$ which is defined without referencing to the Lebesgue measure, but, following Minlos theorem [126], through its characteristic functional [5]:

$$\int_{\mathcal{N}'} D\mu(\phi) e^{i(\rho_x \bar{\phi}^x + \bar{\rho}_x \phi^x)} = e^{-\bar{\rho}_x \Delta^{xy} \rho_y} \tag{1.137}$$

which allows us to identify Δ^{xy} with the covariance of the Gaussian measure, as considered in [5] and carefully reviewed in [7, 8].

An example of a quantum state, integrable under such measure could be, for example, $\Psi[\phi] = f_x \phi^x$, which contracts a coefficient function f_x with the field distribution ϕ^x over Σ, which can be interpreted as a one-particle state. On the other hand, $\Psi[\phi] = 1$ is considered the vacuum state with respect to the measure $D\mu$.

As in quantum mechanics, restricting to polynomial functionals on the field variables and its momenta for simplicity, physical magnitudes can be represented as linear self-adjoint operators over $L^2(\mathcal{N}', D\mu)$, of multiplicative nature (if they are a result of the quantization of a polynomial solely on the field configurations, ϕ) or derivative nature (if the polynomial contained field momenta, π_ϕ). The derivative must be made covariant with respect to the measure $D\mu$ for the operator to be self-adjoint. As anticipated at the beginning of this section, the dynamics of the Schrödinger functional follow the Schrödinger equation:

$$\frac{d}{dt}\Psi[\phi] = \frac{-i}{\hbar}\hat{H}[\phi]\Psi[\phi] \ . \tag{1.138}$$

Historically, the framework has been applied to static or stationary spacetimes, and thus, the notion of time could be associated to the label s of a foliation of spacetime given by the

[5] In this definition of characteristic functional an holomorphic picture is followed, where the field distributions ϕ are considered complex and $\bar{\phi}$ denotes its complex conjugate. The real case is analogously defined, but with real covariance matrix and domain.

time-like killing vector field, which is identified with its normal vector field. Nevertheless, in the construction of hybrid geometrodynamics spacetime must remain completely generic, and therefore, while the role of time will still be played by the hypersurface label s, the foliation can be arbitrarily chosen and thus, there is no preferred notion of time.

As we saw in the case of standard quantum mechanics, the solutions to the Schrödinger equation can be rewritten in a Hamiltonian framework, where the Poisson bracket for any two differentiable functions over the space of wave functionals, $f, g \in C^\infty(L^2(\mathcal{N}', D\mu))$ is given by

$$\{f, g\}_Q = \frac{-i}{\hbar} \int_{\mathcal{N}'} D\mu(\phi) \frac{\delta}{\delta[\Psi(\phi)} f \frac{\delta}{\delta\bar{\Psi}(\phi)]} \,, \tag{1.139}$$

where the functional derivatives can be defined in a Fréchet sense, on a dense submanifold of the Hilbert space of quantum fields, given that Hida functions (which conform a Fréchet space) are dense in the square integrable funtions. As it happened in the case of ordinary quantum mechanics, for the functions given by the expectation values of self-adjoint operators, this Poisson structure reproduces the Lie bracket of operators:

$$\{\langle\Psi|\hat{A}\Psi\rangle, \langle\Psi|\hat{B}\Psi\rangle\}_Q = \frac{-i}{\hbar}\langle\Psi|[\hat{A}, \hat{B}]\Psi\rangle \tag{1.140}$$

and therefore, such set of functions constitute a Poisson algebra for $\{,\}_Q$, in complete analogy to $\mathcal{A}_Q$. Within this algebra, the generating function of the dynamics is given by:

$$f_H := \langle\Psi|\hat{H}(\phi)\Psi\rangle = \int_{\mathcal{N}'} D\mu(\phi)\bar{\Psi}(\phi)\hat{H}(\phi)\Psi(\phi) \tag{1.141}$$

Therefore, for any functional over the quantum space of functionals, $F \in C^\infty(L^2(\mathcal{N}', D\mu))$, its evolution is defined by:

$$\frac{d}{ds}F = \{F, f_H\} \,, \tag{1.142}$$

The essential ingredients required for constructing hybrid geometrodynamics from a physical perspective are now in place. The approach, as detailed in article [5], involves the consistent integration of the Hamiltonian picture of SWF as the material sources for the geometrodynamical description of classical gravity.

Hybrid theory

The combination of these two frameworks, while preserving the spirit of the formalism introduced so far, requires slight technical modifications of Schrödinger wave functional picture that generalize the framework consistently to arbitrary foliations of generic spacetimes. One striking difference, which is however a cornerstone of the construction, is that, instead of considering a single measure, $D\mu$, a parametric family $[D\mu]$ of Gaussian measures

must be considered:

$$[D\mu] := \{D\mu_\xi \in \text{Meas}(\mathcal{N}') \,|D\mu_\xi \text{ is Gaussian with } \Delta^{x,y}(\xi)\ \forall \xi = (h, \pi_j, N, N^i) \in \mathcal{M}_G \times \mathcal{M}_N\} \tag{1.143}$$

where $\Delta^{x,y}(\xi)$ is a parametric family of covariances over the space of fields, and the parameters, represented by ξ are precisely given by the possible geometric content of the hypersurfaces Σ. In particular, the set of possible 3−metrics h_{ij} and their associated momenta π_h^{ij} conform the manifold $\mathcal{M}_G$, while we have denoted the set of all lapse functions and shift vectors by $\mathcal{M}_N$. Given this dependence of the scalar product on ξ, we cannot have a single Hilbert space for the quantum states, but a different one for each different geometric content, implying that the quantum manifold must be different at each point of $\mathcal{M}_G \times \mathcal{M}_N$. Therefore, in order to connect the different L^2 spaces, the hybrid phase space cannot be constructed by a single copy of the quantum manifold and a single copy of the gravitational manifold in an uncorrelated way, but a non trivial fibration must be constructed.

This implies a crucial difference with ordinary hybrid systems: instead of the trivial bundle given by the Cartesian product of the classical and quantum phase spaces, $\mathcal{M}_C \times \mathcal{M}_Q$, which in eq. (1.50) constituted the hybrid phase space in the geometric formulation of non-field theoretical Ehrenfest systems, we now have a non trivial fibration, $\mathcal{F}$ where the fiber is given by the quantum phase space, containing these different L^2 spaces given by the ξ-parametric family of Gaussian measures, while the manifold of gravitational variables is on the base. Nevertheless, *locally*, i.e. at each point of the gravitational manifold h, π_h, N, N^i, this hybrid phase space is still isomorphic to the Cartesian product $\mathcal{M}_G \times L^2(\mathcal{N}', D\mu)$.

Such fibration is provided with a connection, materializing the non-trivial structure of the tangent bundle to this hybrid manifold. This allows us to see how the change of gravitational variables induce a change on the quantum state, providing with a notion of parallel transport of quantum states along the fibration from one functional representation, inside an L^2 space given by $D\mu_{\xi_1}$, to a different one, inside a different L^2 space with a different measure, $D\mu_{\xi_2}$.

Another crucial difference with ordinary hybrid systems, is, of course, that both manifolds, $\mathcal{M}_C$ and $\mathcal{M}_Q$, will be infinite dimensional, as so will be the domain of the Schrödinger wave functional. This requires careful definitions of derivatives and measures for integration in order to provide the geometric structures, such as the Poisson bracket. Nevertheless, the final result is that, once the intricacies have been sorted out by a proper characterization of the functional spaces, calculus can be performed without further nuances for physical applications. All these mathematical technicalities related with functional spaces and infinite dimensional calculus, despite playing a crucial role in the construction and having been mentioned when necessary, have not been further expanded in this introduction in favour of a more clear presentation of the key physical ideas. Nevertheless, they are explained

in [5], where, in turn, further mathematical details are relegated to the subsequent works, in [7, 8], which lay mathematical scaffolding for the construction of the physical theory in [5]. A comprehensive reference for Fréchet calculus and differential geometry in infinite dimensional manifolds could be, for example, [127], while a more accessible review of this issues with more immediate applications in theoretical physics can be found in [84].

In this thesis, to arrive to a description of classical gravity coupled to quantum matter, we have chosen a novel avenue for the construction of the hybrid theory, which can be encompassed under the picture of bottom-up approaches. Dispensing with the covariant formulation, but adopting the Hamiltonian structure of geometrodynamics both for gravitational and quantum degrees of freedom, we can formulate a Hamiltonian hybrid system with analogue geometric structures to the ones of section 1.2. Despite the non-covariant picture, physical symmetries of the system, given by the *path independence principle*, which is the foliated-spacetime analogue to general covariance, are recovered through the introduction of constraints.

Nevertheless, other approaches to arrive to a joint description of classical gravity and quantum field theoretical matter had previously been introduced in the literature. The novelty and implications of the work developed in [5] cannot be fully apprehended without contextualizing the work in relation to these previous approaches, reviewing their faults and their boons, which we proceed to summarize.

- In the line of the top-down approach (as explained for the derivation of Ehrenfest dynamics following Bornemann's work, [68]), one can depart from a full-quantum system of quantum gravity plus matter, factorize the system in two subsystems, one for gravitational degrees of freedom, the other one for quantum matter (which can be correlated with the gravitational states) and force the self consistent field approximation which allows us to perform a semiclassical limit solely over the gravitational submanifold.

  Most contributions in this line have been made assuming the canonical approach to quantum gravity [25, 128] and then deriving a semiclassical limit for the gravitational subsystem, coupled to matter (and, many times, also to quantum perturbations to classical gravity) as in [24]. The states in canonical quantum gravity are formally analogous to the SWF picture of QFT, where the wave functional $\Psi[h, \phi]$ belongs to a certain L^2 space with domain the space of 3-metrics, h_{ij} and matter fields, collectively denoted by ϕ. The quantization procedure for a constrained Hamiltonian system, as is geometrodynamics, requires the quantization of the constraints. In particular, canonical quantum gravity requires the quantization of the superhamiltonian and supermomenta constraints for the total supermagnitude, as introduced in eq. (1.130). This leads to the cornerstone of quantum gravity: Wheeler-DeWitt equation, given

by

$$\hat{H}^T \Psi[h, \phi] = 0 \, , \tag{1.144}$$

where $\hat{H}^T$ is the quantization of the total Hamiltonian given by the contraction of the supermagnitudes with any lapse function and shift vector. This equation implies the imposibility of evolution for the wave functional of the universe, resulting in an adynamical theory: a lack of time in a completely quantum universe. In this context, the truncation of a WKB expansion, in analogy to Maslov's procedure of stationary phase, allows to recover a notion of time relative to the semiclassical paths resembling classical Hamiltonian gravity. Over such paths, the quantum perturbations and matter fields may be provided with a notion of evolution [23]. Indeed, when matter is present in the theory, an effective theory with quantum field theoretical matter can be recovered taking into account the appropriate WKB decomposition of quantum perturbations to gravity (see [24]).

The main objection to this approach is the lack of current falsifiability of the full quantum theory of gravitation (for which we have a plethora of candidates), which makes the viability of the whole top down perspective unclear, as the more fundamental theory is far from being verifiable experimentally, potentially resulting, *a priori*, in several effective theories as a result of the semiclassical limit.

The bottom-up approach followed in [5] avoids these issues, as it does not require a theory of quantum gravity, but instead uses minimal ingredients which are well tested experimentally: QFT and General Relativity. In this line, the theory has a more resilient construction, as the limiting phenomenology for each subsystem is just the properly falsified one for each of these ingredients. Instead of speculating into the unfalsifiable terrain of Planck scales or making further assumptions, hybrid geometrodynamics provides with a joint description of two well-stablished theories under a common mathematical formalism.

Nevertheless, from a theoretical point of view, it would be interesting to check whether or not the partial semiclassical limit for the different full quantum theories yield equivalent hybrid dynamics to the bottom up approach followed in [5], so that we can check the viability of the full quantum theory through its compatibility with a suitable hybrid effective theory obtained without assumptions on the nature of the full quantum realm.

- Another possibility explored in the literature, which can also be classified as a bottom up approach, roots in the modification of the covariant construction of General Relativity to include the backreaction of quantum matter onto classical gravity. The contruction relies on a sensible substitution in Einstein's field equations of the energy-momentum tensor $T_{\mu\nu}$ by a suitable object that represents how quantum matter acts as a source of curvature for classical gravity. This approach leads to the introduction,

attributed to Moller and Rosenfeld (see [129] and [130] respectively) of the so called semiclassical Einstein's equations:

$$G_{\mu\nu} = \kappa\langle\Psi(\phi)|\hat{T}_{\mu\nu}\Psi(\phi)\rangle \tag{1.145}$$

where $\hat{T}_{\mu\nu}$ is the quantization of the classical stress energy tensor, whose expectation value is taken under Ψ, the wave functional over the fields ϕ representing the quantum state of matter.

From the theoretical standpoint this approach has a major drawback: this way to couple quantum matter with gravitation was neither introduced as a formal derivation from a more general theory nor as a result of compatibility requirements between the mathematical structures of both theories in play, but as an heuristic guess.

On the other hand, from a practical point of view, many difficulties arise when considering $\hat{T}_{\mu\nu}$. As Robert Wald argued in [131], in general, the energy tensor operator is not renormalizable without violating some of Wald's axioms for backreaction of QFT in curved spacetime (analyzed in [125]), either by losing its covariance $\nabla^{\mu}\langle\Psi|\hat{T}_{\mu\nu}|\Psi\rangle \neq 0$ (which violates the third axiom and would lead to inconsistencies between Bianchi identities for $G_{\mu\nu}$ and Einstein's semiclassical equations), or, if this issue is solved, inducing a trace anomaly which leads to higher orders derivatives of the metric (violating the fifth axiom) and thus, introducing the necessity of the addition of an arbitrary fundamental length scale. Even though later developments where able to partially overcome some of these issues, recent analysis, such as [132], show that the current status of the theory still presents several conceptual and computational problems, being practically unsolvable in most physically relevant scenarios.

Besides, some *Gedankenexperimenten* in the literature have provided with phenomenolically ill situations, natural of this mean-field approach for the sources. For example, a quantum state that constitutes a mass or energy distribution equally concentrated around two distant points in space, for the same time, leads to an effect on curvature as if an effective mass distribution was picked around the mid-point, which *a priori* is empty space. Instead of considering it a complete failure of the theory, if this criticism (which can be in fact extended to any mean field approach) actually holds experimentally, should be interpreted as a reminder that the theory can be of effective nature, and its application is perhaps limited to not very delocalized, not very massive or energetic quantum states (in other words, small spatial width for the mass energy distribution under the quantum state is required for the validity of the theory). Contrarily, in [5], the construction is made carefully local even though the mean field approach is also taken. The quantum states populate the field distributions $\phi \in \mathcal{N}'$. Therefore, $|\Psi(\phi)|^2$ assigns a probability (under a suitable measure $D\mu$) to a whole field configuration ϕ over the manifold, not to the spatial distribution

of matter. For any local observable, $F(\phi(x))$, its value is given by the average over all the field configurations weighted with probability distribution $D\mu|\Psi(\phi)|^2$ of the function F evaluated on the value, $\phi(x)$, of each field configuration ϕ on the point x of the hypersurface, Σ:

$$\langle \Psi(\phi), F(\phi(x))\Psi(\phi)\rangle = \int_{\mathcal{N}'} D\mu(\phi)\bar{\Psi}(\phi)F(\phi(x))\Psi(\phi)\ . \tag{1.146}$$

In this sense, it appears that this thought experiment actually does not apply to the hybrid geometrodynamical formalism, but further research on the actual phenomenology of the theory will elucidate to what extent non-localities arise.

The primary objective of this introductory chapter was to contextualize the research endeavor of this thesis, offering an overview of the state of the art of the field. Additionally, essential mathematical elements have been introduced in order to ease the understanding of the articles, while providing a cohesive narrative that connects all of them. The ensuing chapters exclusively feature the articles themselves, constituting the core of this memoir.

Chapter 2

Statistical Mechanics

This chapter comprises the following four articles on statistical mechanics of hybrid systems:

- J. L. Alonso, C. Bouthelier-Madre, A. Castro, J. Clemente-Gallardo, and J. A. Jover-Galtier. Entropy and canonical ensemble of hybrid quantum classical systems. *Physical Review E*, **102**, 4 2020. [1]
- J. L. Alonso, C. Bouthelier-Madre, A. Castro, J. Clemente-Gallardo, and J. A. Jover-Galtier. About the computation of finite temperature ensemble averages of hy-brid quantum-classical systems with molecular dynamics. *New Journal of Physics,* **23**, 063011, June 2021. [2]
- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, D. Martínez-Crespo, and J. Pomar. Effective nonlinear Ehrenfest hybrid quantum-classical dynamics. *The European Physical Journal Plus*, **138** 2023. [3]
- C. Bouthelier-Madre, J. Clemente-Gallardo, L. González-Bravo, and D. Martínez-Crespo. Hybrid Koopman $C^\star$-formalism and the hybrid quantum-classical master equa- tion. *Journal of Physics A*, **56** 2023. [4]

2.1 Article:
Entropy and canonical ensemble of hybrid quantum classical systems

Entropy and canonical ensemble of hybrid quantum classical systems

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(Received 7 April 2020; revised 14 April 2020; accepted 16 September 2020; published 14 October 2020)

In this work we generalize and combine Gibbs and von Neumann approaches to build, for the first time, a rigorous definition of entropy for hybrid quantum-classical systems. The resulting function coincides with the two cases above when the suitable limits are considered. Then, we apply the MaxEnt principle for this hybrid entropy function and obtain the natural candidate for the hybrid canonical ensemble (HCE). We prove that the suitable classical and quantum limits of the HCE coincide with the usual classical and quantum canonical ensembles since the whole scheme admits both limits, thus showing that the MaxEnt principle is applicable and consistent for hybrid systems.

DOI: 10.1103/PhysRevE.102.042118

I. INTRODUCTION

Hybrid quantum-classical (QC) systems are the natural approximation to those quantum systems containing some degrees of freedom that can be well approximated as classical variables. This possibility arises when there are two different energy or mass scales, as it happens, for instance, in molecular and condensed matter systems where the nuclei are heavy and slow, while the electrons are light and fast. Hybrid models have also been proposed to explain the measurement process [1,2]: the measurement device is modeled as a classical system coupled to the quantum system to be measured. In field theory, hybrid quantum-classical systems have also been considered as candidates to describe quantum matter fields interacting with a (classical) gravitational field, as a semiclassical approximation or even a fundamental theory (see Refs. [3,4]).

The correct mathematical formalism for the dynamics and statistics of these hybrid models is not obvious. Two different points of view can be taken. On the one hand, a practical one: the construction of a hybrid theory that approximates, as closely as possible, the full quantum dynamics of the problem. Such methods can be applied to a very large array of problems in condensed matter and molecular physics and chemistry, as nonadiabatic processes play a fundamental role [5–9]. On the other hand, a fundamental, theoretical point of view: the construction of a mathematically and physically consistent theory for hybrid systems, according to different demands of consistency [1,10–27], independently of how well it may approximate the full quantum dynamics. This second approach is compulsory when the full quantum dynamics is not known, as in the case of a system of quantum matter fields interacting with gravity. In any case, it is not clear what is the best possible dynamics from any of those two points of view. Here, we assume the second one, and add to the discussion on the construction of a mathematically consistent and physically motivated hybrid theory.

The focus of this work is on the statistical mechanics of hybrid systems, *regardless of the dynamics* chosen for their description. In particular, we consider two open questions: first, what is the correct definition of the entropy of a hybrid system? And then, given this definition, can we use the MaxEnt formalism and obtain the canonical ensemble of a hybrid system, as we do for classical or quantum ones? Apparently, these are purely fundamental questions, but their answers are crucial for many applications, in particular, for the *ab initio* modeling of molecules and materials and their numerical simulation methods at finite temperature (for example, see Refs. [28–33]). We determine, in a simple way, the equilibrium ensemble that the numerical methods must reproduce and the entropy function they must consider.

The structure of the paper is as follows. In Sec. II we will first discuss the proper definition of the hybrid entropy function. Then, in Sec. III we will derive the hybrid canonical ensemble (HCE) as the one that maximizes this entropy, subject to the constraint of a given expectation value for the energy (MaxEnt principle). The resulting ensemble had been perhaps implicitly assumed before, but few times explicitly spelled, and never, to our knowledge, derived from the general principle of entropy maximization. We will also briefly discuss some relevant properties of the resulting ensemble.

Finally, in Sec. IV we will summarize our main conclusions.

II. THE ENTROPY OF A HYBRID QC SYSTEM

A correct statistical mechanical definition of any system departs from the definition of a sample space: a set of

statistically independent states, i.e., a basis of mutually exclusive events (MEE), which can be unequivocally characterized by the results of an experiment. Let us start by recalling the basic definitions in the purely classical or purely quantum cases.

In classical systems, a basis of MEEs is simply the phase space $\mathcal{M}_C$, the set of all positions and momenta of the classical particles: $\mathcal{M}_C = \{(Q, P) \mid Q \in \mathbb{R}^n,\ P \in \mathbb{R}^n\}$, where n is the number of classical degrees of freedom. Any point in this phase space defines an exclusive event from any other event. Observables are real functions on this $\mathcal{M}_C$. Statistical mechanics for classical systems can then be described by using *ensembles* on this phase space, i.e., (generalized)[1] probability distribution functions (PDFs) F_{C}

In quantum systems, the states are rays of a Hilbert space $\mathcal{H}$, i.e., the analogous to the classical phase space is the projective space, $\mathcal{M}_Q = \mathcal{P}\mathcal{H}$. We will represent its points as the projectors on 1-dimensional subspaces of the Hilbert space $\hat{\rho}_\psi = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle}$, with $|\psi\rangle \in \mathcal{H} \setminus \{\vec{0}\}$. Even though all of the states in $\mathcal{M}_Q$ are physically legitimate, they are not mutually exclusive. Indeed, if the system has been measured to be, with probability one, in a state $\hat{\rho}_{\psi_1}$, the probability of measuring it to be in other state $\hat{\rho}_{\psi_2}$ is not zero, unless they are orthogonal: $\hat{\rho}_{\psi_1}, \hat{\rho}_{\psi_2}$ are MEE only if $\langle\psi_1 \mid \psi_2\rangle = 0$. As a consequence, considering generalized probability density functions F_{Q} over the Hilbert space (or over the projective space of rays) to define ensembles, following the classical analogy, results in overcounting the same outcome for a hypothetical experiment in a nontrivial way. One way to see this clearly is that many different F_{Q} can correspond to exactly the same ensemble (i.e., they are physically indistinguishable). The correct way to get a sample space of MEEs is therefore considering a basis of orthogonal events. From this idea, von Neumann [34] derived the density matrix formalism, which contains all the physically relevant statistically nonredundant information in a compact way. A density matrix can be obtained from a PDF F_{Q} in the quantum state space as

$$\hat{\rho}[F_{\mathrm{Q}}] = \int \mathrm{d}\mu_Q(\hat{\rho}_\psi) F_{\mathrm{Q}}(\hat{\rho}_\psi)\hat{\rho}_\psi, \tag{1}$$

where we represent by $d\mu_Q$ the volume element on $\mathcal{M}_Q$. Analogously, in the following, we will represent by $d\mu_C$ the volume element on $\mathcal{M}_C$.

We move on now to QC theories. Despite the various proposals referenced above, one can perhaps establish a common denominator. The classical part is described by a set of position $Q \in \mathbb{R}^n$ and momenta $P \in \mathbb{R}^n$ variables, that we will hereafter collectively group as $\xi = (Q, P)$. The quantum part is described by a complex Hilbert space $\mathcal{H}$. Observables are Hermitian operators on $\mathcal{H}$, and they may depend parametrically on the classical variables, $\hat{A}(\xi) : \mathcal{H} \to \mathcal{H}$. Those observables defined on the classical subsystem are just ξ-functions times the identity, i.e., $\hat{A}(\xi) = A(\xi)\hat{I}$; those observables defined on the quantum subsystem only are operators that lack the ξ-dependence.

[1]We introduce the adjective *generalized* to refer to the set of generalized functions (or distributions) and include, for instance, Dirac δ functions.

We are going to consider two different approaches to the definition of the entropy, one based on the usual approach to classical systems, and another one inspired by the quantum case.

A. A Gibbs-entropy for hybrid systems?

The formal similarities of one of the best known hybrid dynamical models, Ehrenfest dynamics, with the classical one (see Refs. [18,27] for details) may lead to consider hybrid systems as formally closer to classical than to quantum dynamics. Indeed, Ehrenfest dynamics can be given a Hamiltonian structure (see Refs. [27,35]) in terms of

(1) a Hamiltonian function constructed as

$$f_H(\xi, \hat{\rho}_\psi) = \mathrm{Tr}(\hat{H}(\xi)\hat{\rho}_\psi) = \frac{\langle\psi|\hat{H}(\xi)\psi\rangle}{\langle\psi|\psi\rangle}, \tag{2}$$

(2) and a Poisson bracket obtained as the combination of the Poisson bracket of classical mechanics and the canonical Poisson bracket of quantum systems (see Refs. [36,37]).

This fact makes Ehrenfest dynamical description of hybrid system formally analogous to a classical Hamiltonian dynamical system. When considering the definition of hybrid statistical systems, we can then consider a hybrid (generalized) PDF F_{H} defined over the hybrid phase space $\mathcal{M}_H = \mathcal{M}_C \times \mathcal{M}_Q$, in an analogous manner to the definition of classical statistical systems. The Hamiltonian nature of the dynamics allows to define a Liouville equation for F_{H} in a straightforward manner (see Refs. [18,27]).

Within that framework, it is also tempting to borrow the notion of entropy from classical statistical mechanics and define a Gibbs-like function associated with the density function F_{H} in the following form:

$$S_{\mathrm{G}}[F_{\mathrm{H}}] = -k_B \int_{\mathcal{M}_H} d\mu_H(\xi, \rho_\psi) F_{\mathrm{H}}(\xi, \rho_\psi) \log[F_{\mathrm{H}}(\xi, \rho_\psi)], \tag{3}$$

where k_B represents the Boltzman costant and $d\mu_H$ represents the volume element on $\mathcal{M}_H$ which can be written in terms of the classical and quantum volume elements as $d\mu_H = d\mu_C \wedge d\mu_Q$.

Notice that this entropy function is well defined for classical systems, where the points of phase-space correspond to mutually exclusive events. Therefore, when considering S_{G} we are adding all points of the phase space $\mathcal{M}_H$ as if they were mutually exclusive. Thus, we treat them as classical statistical systems, where being at a given point in phase space excludes the possibility of being at a different point. Hence, we are not weighting correctly the quantum subsystems from the physical point of view, ruining the function ability to measure physical information for the hybrid system.

Despite this fact, this entropy function has been implicitly assumed several times when considering hybrid or even purely quantum statistical systems (see Refs. [27,38–40]), when defining the so called Schrödinger-Gibbs (SG) ensemble or the corresponding Schrödinger microcanonical ensemble. Thus, SG represents a canonical ensemble where the probability density is written by assigning to each state the Gibbs weight associated with the expectation value of the Hamiltonian, instead of the operator itself. But the bad physical

properties of S_G lead to very strange and un-physical properties for the corresponding thermodynamic functions. In particular, this was the case when the Schrödinger-Gibbs ensemble was analyzed in Ref. [41]. Nonetheless, notice that S_G is a mathematically consistent entropy function, despite the unphysical properties of the Statistical Mechanics it defines.

B. Gibbs–von Neumann entropy

From our analysis above, it is clear that the straightforward extension of Gibbs classical entropy function to hybrid systems leads to inconsistencies because the points of hybrid phase space do not define mutually exclusive events as the classical phase space points do. To do statistical mechanics in a consistent way with the nature of its quantum subsystem, one must reconsider the notion of mutually exclusive events, and combine the classical and the quantum notions of MEE. The combined hybrid phase space is now $\mathcal{M}_H = \mathcal{M}_C \times \mathcal{M}_Q$. But, we must consider that two hybrid states $(\xi_1, \hat{\rho}_{\psi_1}), (\xi_2, \hat{\rho}_{\psi_2}) \in \mathcal{M}_H$ represent MEEs if and only if $\xi_1 \neq \xi_2$ or $\langle\psi_1|\psi_2\rangle = 0$.

The next step is to define a probability distribution on the set of MEEs of $\mathcal{M}_H$. Following von Neumann idea and the mathematical construction of Gleason theorem [42], we can build a hybrid density matrix to represent the hybrid probability in a consistent way. As the physical properties of the hybrid system, in general, combine the states of $\mathcal{M}_C$ and $\mathcal{M}_Q$ (for instance, the total energy of the system), we cannot expect both sets to be independent from the probabilistic point of view. Nonetheless, we can assume that we can simultaneously measure any classical observable and any hybrid observable of the form $\hat{A}(\xi)$. This fact permits to define the conditional probabilities $p(a|\xi)$: the probability of measuring an eigenvalue a of operator $\hat{A}(\xi)$, given that the classical subsystem is at state $\xi \in \mathcal{M}_C$. The probabilities associated to the hybrid measurement can then be decomposed into the marginal probability associated to the classical phase space, $F_C(\xi)$, and the conditional probabilities associated to the measurement of $\hat{A}(\xi)$, given ξ:

$$p(a, \xi) = F_C(\xi) p(a|\xi). \tag{4}$$

For these quantum conditional probabilities $p(a|\xi)$, all the requirements of Gleason's theorem [42] apply, and one may therefore define, at each ξ point, a density matrix $\hat{\rho}^\xi$. It provides the probabilities of measuring an eigenvalue a of observable $\hat{A}(\xi)$, given ξ, through the usual Born rule: $p(a|\xi) = \mathrm{Tr}[\hat{\rho}^\xi \hat{\pi}_a(\xi)]$, where $\hat{\pi}_a(\xi)$ is the projector onto the eigen-subspace associated to a. From this, we can define the *hybrid density matrix* as the ξ-dependent matrix:

$$\hat{\rho}(\xi) = F_C(\xi)\hat{\rho}^\xi, \tag{5}$$

such that $p(a, \xi) = \mathrm{Tr}[\hat{\rho}(\xi)\hat{\pi}(a)]$. Notice that, strictly speaking, Gleason theorem ensures the existence and uniqueness of the density matrix $\hat{\rho}^\xi$ only for Hilbert spaces of dimension at least 3. However, the recent developments based on positive-operator-valued measures (POVM) (see, for instance, Refs. [43,44]) allow to prove a more general formulation of Gleason theorem for quantum states which is valid in dimension 2, but in that case the construction is not based on orthogonality of the rank-one projectors but on a more global set of *effects*.

In conclusion, the probability distribution on the set of MEEs of hybrid states can be written as a family of quantum density operators parameterized by the classical degrees of freedom, $\hat{\rho}(\xi)$. For each ξ, $\hat{\rho}(\xi)$ is a self-adjoint and nonnegative operator, which is normalized on the full hybrid sample space:

$$\int_{\mathcal{M}_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}[\hat{\rho}(\xi)] = 1. \tag{6}$$

This is an immediate consequence of the normalization of $F_C(\xi) = \mathrm{Tr}\hat{\rho}(\xi)$ [$\int_{\mathcal{M}_C} d\mu_C(\xi)F_C(\xi) = 1$] and of $\hat{\rho}^\xi$ ($\mathrm{Tr}\hat{\rho}^\xi = 1$). Given a hybrid state determined by the classical point ξ [which has probability $\mathrm{Tr}\hat{\rho}(\xi)$], and a quantum state represented by the projector $\hat{\pi}$, the probability of measuring the system to be in that state is given by $\mathrm{Tr}[\hat{\rho}(\xi)\hat{\pi}]$. These ξ-dependent density matrices have already been used before, for example, by Aleksandrov [25], or obtained by taking the partial classical limit in the Wigner transformation of the full quantum density matrix, in the quantum-classical Liouville equation method [26].

Let us consider now how to define the entropy of these hybrid states. For any bivariate distribution $p(x, y)$ of two sets of random variables (X, Y), the entropy $S(p)$ decomposes as

$$S(p) = S(p_X) + \sum_x p_X(x) S(p_{Y|x}), \tag{7}$$

where $p_X(x) = \sum_y p(x, y)$ is the marginal distribution of X, and $p_{Y|x}$ is the conditional probability of Y given x. This general result must be applicable to the decomposition Eqs. (4) and (5). Therefore, the entropy of the hybrid system must be equal to the sum of the (classical) entropy (S_C) of the marginal classical distribution $F_C(\xi)$ and the average, over $F_C(\xi)$, of the (von Neumann) entropy associated to the conditional probability ρ^ξ, i.e.,

$$S[\hat{\rho}(\xi)] = \overbrace{-k_B \int_{\mathcal{M}_C} d\mu_C(\xi) F_C(\xi) \log(F_C(\xi))}^{S_C(F_C)} + \int_{\mathcal{M}_C} d\mu_C(\xi) F_C(\xi) \underbrace{[-k_B \mathrm{Tr}(\hat{\rho}^\xi \log \hat{\rho}^\xi)]}_{S_{\mathrm{vN}}(\hat{\rho}^\xi)}. \tag{8}$$

It is immediate then to rewrite this as

$$S[\hat{\rho}(\xi)] = -k_B \int_{\mathcal{M}_C} \mathrm{d}\mu_C(\xi)\ \mathrm{Tr}[\hat{\rho}(\xi)\log\hat{\rho}(\xi)], \tag{9}$$

which is our proposal for the hybrid QC entropy. To the best of our knowledge, this is the first rigorous proposal of an entropy function for a hybrid quantum-classical system. If the classical subsystem is pure [i.e., $F_C(\xi) = \delta(\xi - \xi_0)$], then the classical entropy vanishes and the entropy above reduces to von Neumann entropy. Analogously, when the quantum state is pure and independent of the classical state, the von Neumann entropy of ρ^ξ vanishes, and the expression above reduces to the classical entropy function. Therefore, the entropy function Eq. (9) combines the classical and quantum information in a consistent way, and has the correct classical and quantum limits.

III. THE MAXENT PRINCIPLE FOR HYBRID QC SYSTEMS

A. MaxEnt principle for the hybrid entropy function

The maximum entropy principle is one of the standard procedures to derive the canonical ensemble at both the classical or the quantum level. First, one must assume that the system is in equilibrium. Then, one can find the canonical ensemble as the solution of the MaxEnt problem: given a certain thermodynamic system and an entropy function S, find the equilibrium ensemble which maximizes S among those with a fixed value of the average energy $E = \langle \hat{H}(\xi) \rangle$.

In the following, we will prove that *the canonical ensemble that results of this maximization, for the hybrid case, is given by*

$$\hat{\rho}_{\mathrm{HCE}}(\xi) = \frac{e^{-\beta \hat{H}(\xi)}}{Z_{\mathrm{HCE}}(\beta)}, \tag{10}$$

$$Z_{\mathrm{HCE}}(\beta) = \int_{\mathcal{M}_C} \mathrm{d}\mu_C(\xi)\, \mathrm{Tr}(e^{-\beta \hat{H}(\xi)}), \tag{11}$$

where $\hat{H}(\xi)$ is the Hamiltonian [typically decomposed into a classical and a quantum part, as $f_H^c(\xi)\hat{I} + \hat{H}_Q(\xi)$], $Z_{\mathrm{HCE}}(\beta)$ is the partition function, and β is a constant, determined by the choice of E, that is used to define the (inverse of the) temperature. Note that this ensemble had been perhaps implicitly assumed before, but seldom explicitly written [45] and, to our knowledge, never derived. Notice that the orthogonal projectors of its spectral decomposition coincide with those of the adiabatic basis.

The problem can be addressed as a constrained optimization problem: find the density matrix that maximizes S in Eq. (9), subject to the following constraints:

$$C_N[\hat{\rho}(\xi)] := \int_{\mathcal{M}_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\hat{\rho}(\xi)] - 1 = 0, \tag{12}$$

$$C_E[\hat{\rho}(\xi)] := \int_{\mathcal{M}_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\hat{\rho}(\xi)\hat{H}(\xi)] - E = 0. \tag{13}$$

These can be incorporated *via* Lagrange multipliers, defining the full optimization functional to be

$$\mathcal{S} := S - \lambda_N C_N - \lambda_E C_E. \tag{14}$$

Without loss of generality, let us work in the (ξ-dependent) basis of eigenstates of the Hamiltonian (the *adiabatic* basis). First, we will consider the optimization over a reduced set of density matrices: those which are diagonal in this adiabatic basis. The terms in Eq. (14) then read

$$S[\{\rho_{ii}\}] = -k_B \int_{\mathcal{M}_C} d\mu_C(\xi) \sum_i \rho_{ii}(\xi) \log(\rho_{ii}(\xi)), \tag{15}$$

$$C_N[\{\rho_{ii}\}] = \int_{\mathcal{M}_C} d\mu_C(\xi) \sum_i \rho_{ii}(\xi) - 1, \tag{16}$$

$$C_E[\{\rho_{ii}\}] = \int_{\mathcal{M}_C} d\mu_C(\xi) \sum_i H_i(\xi)\rho_{ii}(\xi) - E. \tag{17}$$

Taking derivatives and setting them to zero leads immediately to

$$\rho_{ii}(\xi) = Z_{\mathrm{HCE}}(\beta)^{-1} e^{-\beta H_i(\xi)}, \tag{18}$$

where $\beta = \frac{\lambda_E}{k_B}$.

We consider now a general density matrix $\hat{\tilde{\rho}}(\xi)$, whose nondiagonal elements may be nonzero, fulfilling the two constraint Eqs. (12) and (13). Since it is Hermitian with nonnegative eigenvalues, it satisfies Klein's lemma [46]:

$$-\mathrm{Tr}[\hat{\tilde{\rho}}(\xi) \log(\hat{\tilde{\rho}}(\xi)] \leqslant -\sum_i \tilde{\rho}_{ii}(\xi) \log[\tilde{\rho}_{ii}(\xi)], \tag{19}$$

where $\tilde{\rho}_{ii}(\xi)$ are its diagonal elements (the equality only holds if it is actually diagonal). As the constraint Eqs. (12) and (13) in the adiabatic basis only depend on the diagonal elements of $\hat{\rho}(\xi)$, we may conclude that for any nondiagonal density matrix that fulfills the constraints there exists a diagonal one (defined to be the one whose diagonal entries are the same) that also fulfills the constraints and has a larger entropy. The global maximum, therefore, has to be found among the diagonal ones, and is the one given in Eq. (18). This concludes the proof.

B. Properties of the HCE

Let us now check that the ensemble thus defined fulfills some very natural requirements:

(1) *Additivity*. If two systems are in the canonical ensemble equilibrium at the same temperature, then they must also be at equilibrium when we consider them to form a single system with two (independent) subsystems. Extensive variables as the energy and entropy must be additive.

This can be proven for the HCE in the following way. If $\hat{H}_1(\xi_1)$ and $\hat{H}_2(\xi_2)$ are the Hamiltonians of both systems, then the combined one is

$$\hat{H}(\xi) = \hat{H}_1(\xi_1) \otimes \hat{\mathbb{I}}_2 + \hat{\mathbb{I}}_1 \otimes \hat{H}_2(\xi_2), \tag{20}$$

where $\xi = (\xi_1, \xi_2)$.

As the two terms of Eq. (20) trivially commute,

$$e^{-\beta \hat{H}(\xi)} = e^{-\beta \hat{H}_1(\xi_1)} \otimes e^{-\beta \hat{H}_2(\xi_2)}, \tag{21}$$

and because of this,

$$\int_{\mathcal{M}_{C_1} \times \mathcal{M}_{C_2}} d\mu_C(\xi_1, \xi_2) \mathrm{Tr}\, e^{-\beta \hat{H}(\xi)} = \int_{\mathcal{M}_{C_1}} d\mu_C(\xi_1) \mathrm{Tr}\, e^{-\beta \hat{H}_1(\xi_1)} \int_{\mathcal{M}_{C_2}} d\mu_C(\xi_2) \mathrm{Tr}\, e^{-\beta \hat{H}_2(\xi_2)}. \tag{22}$$

Thus, we can just write

$$\hat{\rho}(\xi) = \hat{\rho}_1(\xi_1) \otimes \hat{\rho}_2(\xi_2). \tag{23}$$

This factorization of $\hat{\rho}(\xi)$ immediately implies the additivity of the internal energy Eq. (13) and of the entropy Eq. (9).

(2) The classical canonical ensemble, which maximizes Gibbs entropy, is recovered when only one quantum energy state exists.

(3) The quantum canonical ensemble, which maximizes von Neumann entropy, is recovered when only one classical point is allowed.

(4) If the QC coupling is turned off (the quantum Hamiltonian $\hat{H}_Q$ is independent of the classical variables and *vice versa*), then the HCE becomes the product of the classical and quantum canonical ensembles, which maximize the sum of their respective entropies independently.

C. Dynamics

Another extra condition that an equilibrium ensemble must obviously verify is missing in the previous list: stationarity under the dynamics of the microstates. However, up to now we have disregarded the dynamics, and derived the canonical ensemble from very broad assumptions, freed from dynamical arguments. The dynamics is neither relevant for the definition of the entropy function nor affects directly the solution of the MaxEnt condition. For instance, $\mathrm{MaxS_G}$ defines the MaxEnt solution for the entropy function S_{G} [Eq. (3)], independently of the dynamics of the microstates we consider. The existence of dynamics having it as an equilibrium point would be an extra requirement for the definition of a thermodynamical ensemble.

On the other hand, we also proved above that the MaxEnt solution of the true hybrid entropy function Eq. (9) is the HCE. This implies that the only possible ensemble which can be considered to represent the canonical ensemble of a hybrid system is the HCE. Is there a dynamics that makes it also stationary? Trivially, the commutator with $\hat{H}(\xi)$ (i.e., a generalized von Neumann equation) does, but many others may also be possible. We will analyze this issue in a forthcoming publication.

IV. CONCLUSIONS

It has been the purpose of this paper to shed some light into the issue of the entropy and the canonical equilibrium expression for hybrid systems. We have first discussed the definition for the entropy of an ensemble of hybrid systems. We have done it by making very general assumptions on the hybrid theory, but without any consideration for the particular dynamics. We have considered two different alternatives, one based on probability densities on the hybrid phase space and another based on projectors and the notion of hybrid mutually exclusive events. The first case leads to a Gibbs-like function which treats the hybrid system as a direct analog of a classical system. We have shown how that entropy function assigns the wrong weight to hybrid events and because of this fails to produce a physically meaningful Thermodynamics. The second proposal departs from the information-theory definition of entropy, and carefully considers the principle of mutually exclusive events. The resulting hybrid entropy function weights correctly the hybrid exclusive events and defines a physically consistent thermodynamical entropy.

Then, we have derived the HCE as the one that fulfills the MaxEnt principle with respect to the hybrid entropy function, using it for the first time for hybrid quantum-classical systems. Furthermore, we verified that the HCE reproduces the classical and quantum cases when the suitable limits are considered. Hence, we can claim that the MaxEnt principle is applicable and consistent for hybrid quantum-classical systems.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Floria and Prof. Zueco for their very useful suggestions. Partial financial support by MINECO Grant No. FIS2017-82426-P is acknowledged. C.B. acknowledges financial support by Gobierno de Aragón through the grant defined in ORDEN IIU/1408/2018.

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2.2 Article:

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New Journal of Physics
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Published in partnership with: Deutsche Physikalische Gesellschaft and the Institute of Physics

OPEN ACCESS

RECEIVED
9 February 2021

REVISED
16 April 2021

ACCEPTED FOR PUBLICATION
20 April 2021

PUBLISHED
7 June 2021

PAPER

About the computation of finite temperature ensemble averages of hybrid quantum-classical systems with molecular dynamics

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Keywords: molecular dynamics, Ehrenfest dynamics, hybrid quantum classical dynamics, hybrid canonical ensemble, finite temperature, ergodic trajectories

Supplementary material for this article is available online

Abstract

Molecular or condensed matter systems are often well approximated by hybrid quantum-classical models: the electrons retain their quantum character, whereas the ions are considered to be classical particles. We discuss various alternative approaches for the computation of equilibrium (canonical) ensemble averages for observables of these hybrid quantum-classical systems through the use of molecular dynamics (MD)-i.e. by performing dynamics in the presence of a thermostat and computing time-averages over the trajectories. Often, in classical or *ab initio* MD, the temperature of the electrons is ignored and they are assumed to remain at the instantaneous ground state given by each ionic configuration during the evolution. Here, however, we discuss the general case that considers both classical and quantum subsystems at finite temperature canonical equilibrium. Inspired by a recent formal derivation for the canonical ensemble for quantum classical hybrids, we discuss previous approaches found in the literature, and provide some new formulas.

1. Introduction

Molecular dynamics (MD) [40] is conventionally considered to be the theoretical description of molecular or condensed matter systems that assumes the nuclei to be classical particles. Therefore, these move according to Newton's equations, in the presence of their mutual interaction and of a force that somehow approximates the electron influence. In its traditional formulation (*classical* MD), the forces are parameterised in some analytical expressions that have been carefully developed over the years, and the numerical problem amounts to the propagation of a purely classical Hamiltonian system with a predefined potential function. The so-called *ab initio* or *first-principles* MD [31] substitutes those analytical force definitions by the *on the fly* calculation of the quantum electronic structure problem, that provides the forces on the ions due to the electrons in a more precise—yet more costly—manner. Still, a first principles MD simulation also consists in the integration of a purely classical problem, even though one needs to use quantum mechanics to obtain the forces at each time step. In both classical and first principles MD, the electrons are usually assumed to remain in their ground state, *adiabatically* adapting to the ions as they move. Therefore, both the classical MD and the (Born–Oppenheimer ground-state) first-principles MD are

not, strictly speaking, hybrid quantum-classical dynamics. These methods have been widely employed for both equilibrium and out-of-equilibrium problems.

In the equilibrium case, when studying a system in, e.g., the canonical ensemble, one is normally not interested in the particular trajectory followed by a microstate, but on the ensemble average values of a given property. The MD simulations are then used to compute the multi-dimensional integrals that define those averages, by substituting them with time-averages over dynamical trajectories of the system—typically, coupled to a *thermostat* [45]. But in any case, despite the finite temperature, normally the electrons are assumed to be frozen in the ground state. This may be a very good approximation if the electronic excited state energies are far higher than the thermal energies at that temperature. Yet in many circumstances those excited states cannot be ignored.

Out of equilibrium, this may in fact happen very frequently. For example, when dealing with photo-chemistry, that naturally involves electronic excitations. This situation calls for a *non-adiabatic* extension of the previous MD concept, that allows for 'live' electrons: the dynamics must be that of a true hybrid quantum-classical model, in which both classical and quantum particles evolve simultaneously through a set of coupled equations. Two prototypical examples of truly hybrid dynamics are Ehrenfest equations [11] and surface hopping [46] (in this latter case, the electronic motion is stochastic and consists of 'jumps' between the adiabatic eigenstates).

In equilibrium, one may also need to lift the approximation of ground state electrons, if the temperature is high enough that the thermal population of the excited states is not negligible. This is the situation discussed in this article. In molecular physics this may happen rarely, but in condensed matter, the metallic or near metallic systems naturally call for a computation of ensemble averages that acknowledges the non-zero population of electronic excited states at non-zero temperature, even if low. In any case, this situation begs the questions: what are the canonical ensemble averages for observables of hybrid systems, and can one compute them using MD? The standard procedure used within classical or adiabatic first principles MD is no longer directly applicable if one is simultaneously propagating nuclei and electrons. The idea of assuming ergodicity and attaching a thermostat to the dynamics, a concept designed for purely classical systems, is dubious at best.

This issue has been addressed by performing MD propagating only the classical nuclei, but somehow incorporating the electronic temperature in the definition of the forces, instead of deriving them by merely assuming the electrons to be in the ground state. One possible route, based on the use of density-functional theory, was theorised by Alavi *et al* [3]. Their method was based on the use of density-functional theory (DFT) [13] to solve for the electronic structure problem. In particular, on the finite temperature extension of DFT (FTDFT) [33, 39], that substitutes the ground-state energy functional by a free energy functional. Then, to perform first principles MD at finite temperature, the forces used to propagate the classical ions are given by the gradient of this free energy functional. In essence, this is the same idea that underlies the approach given in references [9, 10], except that in this latter case the formulation is general, and not tied to DFT. The fact that the electronic free energy—considered at fixed nuclear configurations—can be viewed as an effective classical Hamiltonian from which the hybrid quantum-classical partition function can be computed was already found by Zwanzig [47]. DFT is in fact the most common electronic structure method for the purpose of performing *ab initio* MD. The inclusion of electronic temperature effects is therefore usually managed with some form of FTDFT. In practice, this procedure consists of using a Fermi–Dirac distribution for the population of the Kohn–Sham orbitals that constitute the fictitious auxiliary non-interacting system employed to substitute the true interacting many-electron problem. The resulting density is used to compute the ionic forces, in lieu of the ground-state density. The procedure should be completed with the use of temperature-dependent exchange-and-correlation functionals, but this is often ignored, as the development of these functionals has proved to be very difficult.

In this work, we discuss this and other possible routes to obtain the rigorous canonical ensemble averages through the use of thermostatted MD. The goal is to establish a clear theoretical link between the definition of hybrid ensemble averages and the manners that one can use to compute them using some form of MD with a thermostat. The basic idea consists of generating an ensemble with some form of MD, even if the generated ensemble is wrong, and then using a reweighting formula to compute the right averages. From the analysis, it emerges that, in fact, various possibilities exist. The dynamics for the classical particles moving on the free energy surface will be shown to be a very particular case of this general class. The relative efficiency of the various options may depend on the particular system and choice of electronic structure method. The idea of performing wrong or fictitious dynamics, and then correcting with some reweighting procedure, has been used in the past in the field of MD mostly with the objective of accelerating rare events—see for example references [17, 23]. In this work we extend the same idea to the simulation of hybrid quantum-classical systems.

In section 2 we present the expressions for the ensemble averages that constitute the target of the current work. Section 3 discusses the possibility of computing these using a hybrid quantum-classical non-adiabatic MD such as Ehrenfest dynamics. Although the naïve computation of time-averages over thermostatted Ehrenfest dynamics trajectories lead to wrong results (as already noted in earlier works [32, 34, 35]), we discuss ways to correct this issue. Section 4 discusses approaches based on classical-only MD propagations.

2. The canonical ensemble of hybrid quantum-classical systems

We start by recalling which are the ensemble averages that we are addressing in this work.

The first step should be to clarify the mathematical description of a hybrid model, an issue that is not at all obvious, as demonstrated by the various proposals that have been put forward, and by the discussions about their internal consistency [1, 2, 4, 12, 15, 18–20, 22, 25, 27, 28, 36–38, 42–44]. We will however assume the following very broad assumptions. The classical part is described by a set of position $Q \in \mathbb{R}^n$ and momentum $P \in \mathbb{R}^n$ variables, that we will hereafter collectively group as $\xi = (Q, P)$. Normally, they correspond to N particles, such that $n = 3N$ in three dimensions. The quantum part is described by a complex Hilbert space $\mathcal{H}$. The observables of the full hybrid system are Hermitian operators on $\mathcal{H}$ that may depend parametrically on the classical variables, $\hat{A}(\xi) : \mathcal{H} \to \mathcal{H}$. Some observables may refer only to the classical subsystem; in that case they are just ξ-functions times the identity, i.e. $\hat{A}(\xi) = A(\xi)\hat{I}$. If, on the contrary, they refer to the quantum subsystem only, they are operators that lack the ξ-dependence. In any other case, a hybrid observable couples the quantum and classical parts to each other. The most important one is the Hamiltonian $\hat{H}(\xi)$. Although its precise form is not important for the following discussion, as an example we write here the typical definition of this Hamiltonian for a set of N_e quantum electrons and N nuclei:

$$\hat{H}(Q,P) = \left(\sum_{I=1}^{N} \frac{\vec{P}_I^2}{2M_I}\right)\hat{I} + \hat{H}_e(Q). \tag{1}$$

The first term is the kinetic energy of the classical particles, whereas the second part is

$$\hat{H}_e(Q) = \sum_{i=1}^{N_e} \frac{\hat{\vec{p}}_i^2}{2m_e} + \hat{V}_{en}(Q) + V_{nn}(Q)\hat{I}, \tag{2}$$

where the first term is the kinetic electronic operator, the second term is the electron–nucleus interaction potential, and the last (purely classical) term is the nucleus–nucleus interaction potential.

Ensembles of hybrid quantum-classical systems can be described [4, 5, 25] by ξ-dependent density matrices, $\hat{\rho}(\xi)$, normalized as:

$$\int \mathrm{d}\mu(\xi)\ \mathrm{Tr}\ \hat{\rho}(\xi) = 1. \tag{3}$$

These fully characterize the ensemble, i.e. they permit to obtain the probabilities associated to any measurement. For example, the probability associated to finding the classical subsystem at ξ, *and* measuring a for observable $\hat{A}(\xi)$, is given by $\mathrm{Tr}\,[\hat{\rho}(\xi)\hat{\pi}_a(\xi)]$, where $\hat{\pi}_a(\xi)$ is the projector associated to the eigenvalue a of $\hat{A}(\xi)$. Or, the probability density associated to the classical subsystem, regardless of the quantum part, is given by $F_C(\xi) = \mathrm{Tr}\ \hat{\rho}(\xi)$. Likewise, given any observable $\hat{A}$, the ensemble average is given by:

$$\langle \hat{A} \rangle_{\hat{\rho}} = \int \mathrm{d}\mu(\xi)\ \mathrm{Tr}\left[\hat{A}(\xi)\hat{\rho}(\xi)\right]. \tag{4}$$

One route to the definition of equilibrium ensembles is the principle of maximization of entropy. Recently, we argued [5] that the proper definition of entropy for a hybrid quantum-classical system must be:

$$S[\hat{\rho}] = -k_B \int \mathrm{d}\mu(\xi)\,\mathrm{Tr}\left[\hat{\rho}(\xi)\log\ \hat{\rho}(\xi)\right]. \tag{5}$$

Likewise, we also showed that the maximization of this entropy, subject to the constraint of a given value for the average energy, leads to the *hybrid canonical ensemble*:

$$\hat{\rho}_{HC}(\xi) = \frac{1}{Z_{HC}(\beta)} \mathrm{e}^{-\beta\hat{H}(\xi)}, \tag{6}$$

$$Z_{HC}(\beta) = \int \mathrm{d}\mu(\xi)\,\mathrm{Tr}\ \mathrm{e}^{-\beta\hat{H}(\xi)}. \tag{7}$$

Therefore, the canonical ensemble average of any observable is:

$$\langle \hat{A} \rangle_{\mathrm{HC}}(\beta) = \frac{1}{Z_{\mathrm{HC}}(\beta)} \int \mathrm{d}\mu(\xi)\, \mathrm{Tr}\left[\hat{A}(\xi) \mathrm{e}^{-\beta \hat{H}(\xi)}\right]. \tag{8}$$

The computation of these averages is challenging. First, depending on the model and quantum level of theory used, the calculation of the traces, that in principle require all excited states, can be problematic. But, more importantly, the integral over the classical phase space is difficult because of its very large dimensionality ($6N$ for N classical particles in 3D).

This latter problem is of course akin to the one encountered when studying purely classical systems. It is therefore natural to ask whether it is possible to circumvent it by doing some form of MD.

3. The failure of Ehrenfest dynamics, and some ways to correct it

One possibility that immediately comes to mind is the use of a hybrid quantum-classical MD, such as Ehrenfest's, and attaching a thermostat in order to simulate the presence of a bath that would permit to generate the canonical ensemble along the trajectory. In other words, replicating the procedure invented for 'standard' MD, but using a hybrid dynamics that requires the explicit propagation of the electrons.

It was soon realized, however, that this procedure leads to wrong ensemble averages [32, 34, 35]. In the following, we will reexamine this fact in the light of the Hamiltonian character of Ehrenfest dynamics. This analysis will help to understand the correction procedures that in fact permit to use this dynamics to obtain the true ensemble averages.

3.1. Fast recap of Hamiltonian dynamics

Let us first recap the basics of Hamiltonian theory. A system can be characterized by providing a phase space $\mathcal{M}$ of even dimension $2n$. The Poisson bracket is an operation defined over functions in this phase space (the observables), which in the canonical coordinates $(q, p) \in \mathcal{M}$ reads:

$$\{A, B\} = \sum_{i=1}^{n} \left[\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i}\right]. \tag{9}$$

The dynamics is determined by the definition of a Hamiltonian function H: the equations of motion for the coordinates q_i or p_i of any state in $\mathcal{M}$ are $\dot{q}_i = \{q_i, H\}$ and $\dot{p}_i = \{p_i, H\}$, or equivalently, as they are more often encountered, in the form of Hamilton's equations:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \tag{10}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{11}$$

If there is no certainty about the system state, instead of a single point, one must use a probability distribution $\rho(q, p, t)$ defined over the phase space, also known as an ensemble. This distribution may change in time, according to Liouville's equation:

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}. \tag{12}$$

The entropy of any ensemble can be computed as (hereafter, we will group all variables q, p as y):

$$S[\rho] = -k_{\mathrm{B}} \int \mathrm{d}\mu(y) \rho(y) \log\, \rho(y). \tag{13}$$

The maximization of this entropy over all possible ensembles subject to the constraint of a given Hamiltonian ensemble average or energy, $\langle H \rangle_\rho = \int \mathrm{d}\mu(y) H(y) \rho(y)$, leads to the canonical ensemble [41]:

$$\rho_{\mathrm{CC}}(y) = \frac{1}{Z_{\mathrm{CC}}(\beta)} \mathrm{e}^{-\beta H(y)}, \tag{14}$$

$$Z_{\mathrm{CC}}(\beta) = \int \mathrm{d}\mu(y) \mathrm{e}^{-\beta H(y)}. \tag{15}$$

Here, $\beta = \frac{1}{k_{\mathrm{B}} T}$ is inversely proportional to the temperature T, 'CC' stands for 'classical canonical', $Z_{\mathrm{CC}}(\beta)$ is the partition function, and the integrals extend over all phase space. This is an equilibrium ensemble, lacking the time-dependence because it is stationary: $\{H, \rho_{\mathrm{CC}}\} = 0$.

The averages, for any observable A, over this canonical ensemble are then given by:

$$\langle A\rangle_{\mathrm{CC}}(\beta) = \frac{1}{Z_{\mathrm{CC}}(\beta)} \int \mathrm{d}\mu(y)\mathrm{e}^{-\beta H(y)}A(y). \tag{16}$$

The obvious numerical difficulty of computing these very high-dimensional integrals can then be circumvented by integrating a single dynamical trajectory, and using the ergodic hypothesis to identify a time average with the phase space integral:

$$\langle A\rangle_{\mathrm{CC}}(\beta) = \lim_{t_f\to\infty} \frac{1}{t_f}\int_0^{t_f} \mathrm{d}t\, A(y^\beta(t)), \tag{17}$$

where $y^\beta(t)$ is a trajectory obtained by solving the equations of the motion, modified with a thermostat, i.e.:

$$\dot{y}_i^\beta = \{y_i^\beta, H\} + X_i^\beta(t). \tag{18}$$

Here, we have symbolically added to the Poisson bracket $\{\cdot,\cdot\}$ a thermostat $X_\beta(t)$ (it may represent Langevin's stochastic term [29, 45], a Nose–Hoover chain [30], etc.)

3.2. Schrödinger dynamics as a Hamiltonian system

The theory summarized in subsection 3.1 can be applied to any Hamiltonian dynamics—for example, to Schrödinger's equation, which despite its quantum character, is a 'classical' Hamiltonian system from a mathematical perspective. We summarize this fact here—for the mathematical conditions and functional spaces (both finite and infinite dimensional) on which this formalism can be applied, see [16, 26]; in [24], one can follow the standard approach that is summarized here.

Indeed, Schrödinger's equation ($\hbar = 1$ is assumed throughout this paper),

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle, \tag{19}$$

is easy to rewrite as a set of Hamiltonian equations. First, one expands the wavefunction in an orthonormal basis $\{\varphi_i\}_i$, and rewrites Schrödinger's equation for the coefficients $c_i = \langle\varphi_i|\psi\rangle$:

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} c_1\\ c_2\\ \vdots\\ c_n\end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n}\\ H_{21} & \ddots & \ddots & H_{2n}\\ \vdots & \ddots & \ddots & \vdots\\ H_{n1} & \dots & \dots & H_{nn}\end{pmatrix}\begin{pmatrix} c_1\\ c_2\\ \vdots\\ c_n\end{pmatrix}, \tag{20}$$

where H_{ij} are the elements of the Hamiltonian matrix $H_{ij} = \langle\varphi_i|\hat{H}|\varphi_j\rangle$. We define a set of 'position' and 'momenta' variables by taking the real and imaginary parts of this coefficients, respectively: $c = \frac{1}{\sqrt{2}}(q + \mathrm{i}p)$. One may then show [24, 26] that equation (19) is equivalent to

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \tag{21}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{22}$$

i.e. Hamiltonian's equations, defining $H(q,p)$ as the expectation value of $\hat{H}$ for the wavefunction determined by the (q,p) coefficients: $H(q,p) = \langle\psi(q,p)|\hat{H}|\psi(q,p)\rangle$. Note that these 'position' and 'momentum' variables should not be given any particular physical meaning, forcing any analogy with classical mechanics.

The Poisson bracket can then be defined in the usual way (equation (9)). We will use the notation $\{\cdot,\cdot\}_Q$ for this Poisson bracket defined in this new 'quantum' phase space, $\mathcal{M}_Q$, defined by the variables (q,p). The system dynamics then reduces to:

$$\dot{f} = \{f, H\}_Q, \tag{23}$$

for any function f defined in $\mathcal{M}_Q$. For the particular case of the coordinate functions q and p, one obtains the Hamilton equations above. Taking into account the dependence of $\psi(q,p)$, they are entirely equivalent to Schrödinger's equation (see [24, 26] for details).

Gibbs canonical ensemble associated with the expectation value of the energy $H(q,p)$, equation (14), is stationary under the dynamics, and in principle one could attach one of the typical classical-type thermostats to Schrödinger equation, and produce this ensemble through a trajectory. If one did that,

however, the resulting ensemble averages would be wrong, because Gibbs ensemble is not the true quantum canonical ensemble, which is defined through a density matrix as:

$$\hat{\rho}_{\mathrm{QC}} = \frac{1}{Z_{\mathrm{QC}}(\beta)} \mathrm{e}^{-\beta \hat{H}}, \tag{24}$$

$$Z_{\mathrm{QC}}(\beta) = \mathrm{Tr}\ \mathrm{e}^{-\beta \hat{H}}. \tag{25}$$

This is the density matrix that maximizes the von Neumann entropy,

$$S[\hat{\rho}] = -k_{\mathrm{B}}\ \mathrm{Tr}(\hat{\rho}\ \log\ \hat{\rho}), \tag{26}$$

which is the real entropy of a quantum system, and not equation (13), from which the classical canonical ensemble is derived. It is obvious that the fact that the 'thermostatted' Schrödinger dynamics does not produce the correct thermal averages is not a defect of Schrödinger equation, but results of the erroneous application of a technique invented for classical systems to quantum ones.

3.3. Ehrenfest dynamics as a Hamiltonian system

Ehrenfest dynamics, usually introduced as a partial classical limit of the full-quantum dynamics [11], constitutes also a Hamiltonian system, as shown for example in [6, 7, 11]. We summarize here this fact.

We consider a hybrid quantum-classical system, as defined in section 2. The classical variables $\xi = (Q, P)$ define a classical phase space $\mathcal{M}_{\mathrm{C}}$, whereas the quantum variables $\eta = (q, p)$, associated to a wavefunction $\psi(\eta)$ as explained above, define a quantum phase space $\mathcal{M}_{\mathrm{Q}}$. We may put these together and define a full, hybrid phase space:

$$\mathcal{M} = \mathcal{M}_{\mathrm{C}} \times \mathcal{M}_{\mathrm{Q}}. \tag{27}$$

Furthermore, we may define a Poisson bracket for functions defined on this full hybrid space by adding the two classical and quantum brackets, defined over the ξ and η variables, respectively:

$$\begin{aligned} \{A, B\}_{\mathrm{H}} &= \{A, B\}_{\mathrm{C}} + \{A, B\}_{\mathrm{Q}} \\ &= \sum_i \left(\partial_{Q_i} A \partial_{P_i} B - \partial_{P_i} A \partial_{Q_i} B\right) + \sum_i \left(\partial_{q_i} A \partial_{p_i} B - \partial_{p_i} A \partial_{q_i} B\right). \end{aligned} \tag{28}$$

Thus, the classical bracket derivates only with respect to the classical coordinates (Q, P), and the quantum bracket with respect to the quantum ones (q, p). It is a well known result of Poisson geometry that the addition of two brackets in a Cartesian product results in a bracket that fulfills all the necessary properties.

Finally, given any hybrid observable $\hat{A}(\xi)$, we may define a real function over $\mathcal{M}$ as:

$$A(\eta, \xi) = \langle \psi(\eta) | \hat{A}(\xi) | \psi(\eta) \rangle. \tag{29}$$

If, in particular, we consider the Hamiltonian operator $\hat{H}(\xi)$, which is dependent on the classical degrees of freedom ξ, the hybrid dynamics is generated by the function $H(\eta, \xi) = \langle \psi(\eta) | \hat{H}(\xi) | \psi(\eta) \rangle$ and the Poisson bracket:

$$\dot{\xi}_i = \{\xi_i, H\}_{\mathrm{H}} = \{\xi_i, H\}_{\mathrm{C}}, \tag{30}$$

$$\dot{\eta}_a = \{\eta_a, H\}_{\mathrm{H}} = \{\eta_a, H\}_{\mathrm{Q}}, \tag{31}$$

where in the last equality of both lines the classical and quantum nature of ξ and η respectively has been invoked to make use of $\{\xi, f\}_{\mathrm{Q}} = \{\eta, f\}_{\mathrm{C}} = 0\ \forall\ f \in C^{\infty}(\mathcal{M})$.

One may further expand those equations: for the hybrid Poisson bracket acting on the classical variables ξ_i, one has:

$$\dot{\xi}_i = \{\xi_i, H\}_{\mathrm{C}} = \sum_j \left((\partial_{Q_j} \xi_i) \langle \psi | \partial_{P_j} \hat{H}(\xi) | \psi \rangle - (\partial_{P_j} \xi_i) \langle \psi | \partial_{Q_j} \hat{H}(\xi) | \psi \rangle \right). \tag{32}$$

If one then considers the cases $\xi_i = Q_k$ or $\xi_i = P_k$ separately, one arrives to Newton's-like equations for Q_i, P_i:

$$\dot{Q}_k = \langle \psi | \frac{\partial \hat{H}}{\partial P_k} | \psi \rangle, \tag{33}$$

$$\dot{P}_k = -\langle \psi | \frac{\partial \hat{H}}{\partial Q_k} | \psi \rangle. \tag{34}$$

On the other hand, the dynamical equation of the quantum variables,

$$\dot{\eta}_a = \{\eta_a, H(\xi,\eta)\}_Q, \tag{35}$$

is exactly the same as equation (23), but with a dependence of the Hamiltonian operator on the classical variables. Therefore, this equation, as it was shown in the previous section for the quantum-only case, is equivalent to Schrödinger's equation for $\psi(\eta)$—although one must maintain that parametric dependence of the Hamiltonian operator on the classical variables $\xi = Q, P$:

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = -\mathrm{i}\hat{H}(Q,P)|\psi\rangle. \tag{36}$$

Equations (33), (34) and (36) are Ehrenfest's equations for a hybrid model. From our previous analysis of the classical and the quantum case, it becomes clear that they compose a Hamiltonian system with the Poisson bracket defined as in equation (28). Perhaps the form given in equations (33), (34) and (36) is still not the most recognizable; if one uses the Hamiltonian defined in equations (1) and (2) for a set of electrons and nuclei, one gets:

$$\dot{\vec{Q}}_I = \frac{\vec{P}_I}{M_I} \tag{37}$$

$$\dot{\vec{P}}_I = -\langle\psi|\vec{\nabla}_I\hat{H}_\mathrm{e}(Q)|\psi\rangle, \tag{38}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = -\mathrm{i}\hat{H}(Q,P)|\psi\rangle. \tag{39}$$

Allured by the Hamiltonian character of this set of equations, one may be tempted to consider the Gibbs equilibrium ensemble, equation (14), to be the hybrid canonical one. In terms of the quantum-classical variables, it reads:

$$\rho_{\mathrm{CC}}(\eta,\xi) = \frac{1}{Z_{\mathrm{CC}}(\beta)}\mathrm{e}^{-\beta H(\eta,\xi)}, \tag{40}$$

$$Z_{\mathrm{CC}}(\beta) = \int \mathrm{d}\mu(\xi)\mathrm{d}\mu(\eta)\ \mathrm{e}^{-\beta H(\eta,\xi)}. \tag{41}$$

It is also a stationary ensemble in the hybrid case. The averages over this ensemble would be the ones obtained if one attaches a thermostat tuned to temperature $T = \frac{1}{k_\mathrm{B}\beta}$ to Ehrenfest dynamics, propagates a trajectory $(\eta^\beta(t), \xi^\beta(t))$, and computes the time averages:

$$\begin{aligned}\langle A\rangle_{\mathrm{CC}}(\beta) &= \lim_{t_f\to\infty}\frac{1}{t_f}\int_0^{t_f}\mathrm{d}t\, A(\eta^\beta(t),\xi^\beta(t)) \\ &= \frac{1}{Z_{\mathrm{CC}}(\beta)}\int \mathrm{d}\mu(\xi)\mathrm{d}\mu(\eta)A(\eta,\xi)\mathrm{e}^{-\beta H(\eta,\xi)}.\end{aligned} \tag{42}$$

For example, one practical way to proceed is to use Langevin's dynamics (although there are various other thermostat definitions that have been invented over the years), that essentially consists in substituting the equation for the force (38) by:

$$\dot{\vec{P}}_I = -\langle\psi|\vec{\nabla}_I\hat{H}_\mathrm{e}(Q)|\psi\rangle - \beta\gamma\frac{\vec{P}_I}{M_I} + \vec{\eta}_I(t), \tag{43}$$

where $\vec{\eta}_I(t)$ are stochastic Gaussian processes that must verify:

$$\langle\vec{\eta}_I(t)\rangle = 0, \tag{44}$$

$$\langle\eta_{I\alpha}(t)\eta_{J\beta}(t')\rangle = 2\gamma\delta_{IJ}\delta_{\alpha\beta}\delta(t,t'). \tag{45}$$

The α, β indices run over the three spatial dimensions; see for example reference [45] for details. In any case, the values thus obtained are *not* the ensemble average values that one would wish to obtain, given above in equation (8), hence the previously documented numerical failure of this approach—see for example references [32, 34, 35]. It should be noted, however, that this fact by itself should not be considered a failure of Ehrenfest dynamics—inasmuch as the same fact noted above for the quantum case cannot be considered a failure of Schrödinger equation. It results, once again, of the erroneous application of a technique invented for purely classical systems to hybrid ones, that contain some quantum variables.

A correct statistical-mechanical definition of a system requires the definition of a sample space, i.e., a basis of mutually exclusive events, which can be unequivocally characterized by the results of an experiment (see [5, 8, 14, 21]). The underlying reason behind the difference between classical and hybrid (or quantum) ensembles is that, in classical systems, all points in the phase space are mutually exclusive, whereas they are not in the quantum and hybrid case. Indeed, in classical mechanics, two different points of the phase space represent statistical events which are mutually exclusive: if the system is at state ξ, one cannot measure it to be at state ξ'. One may then define an entropy function using the classical phase space as sample space (i.e. a space that contains mutually exclusive events), and its maximization, subject to a fixed ensemble energy, leads to the classical Gibbs canonical ensemble.

In contrast, in quantum mechanics, two different states of the Hilbert space are not always mutually exclusive: if the system is at state ϕ, the probability of measuring it to be at ϕ' is not zero, unless the two states are orthogonal, $\langle\phi|\phi'\rangle = 0$. Therefore, using the standard theory of probability, we should consider only orthogonal states to represent events (see sections 4.5 and 4.6 of [21]). This consideration led von Neumann and others to the introduction of the concept of density matrix in order to define a statistical ensemble—and to the definition of an entropy based on these objects, whose maximization results in the quantum canonical ensemble.

This precaution about the exclusivity of events must also be taken in the hybrid case—a fact that is discussed at more length in reference [5]. The points of the hybrid phase space are not mutually exclusive unless their quantum parts are orthogonal, or their classical parts are different. It should be noticed, however, that the MD procedure (and in particular the thermostats) produces a visitation of the phase space that disregards this fact. Thus, a MD trajectory visits (assuming ergodicity) all points in a hybrid phase space, assigning to each one a Boltzmann weight, and therefore producing a purely *classical* canonical ensemble that does not take into account the non-exclusivity of hybrid events.

3.4. Corrected averages for Ehrenfest dynamics

Nevertheless, equation (42) can be useful, as we will show now. The thermostatted Ehrenfest dynamics does sample the phase space, and it generates an ensemble, even if wrong. One may then apply a reweighting procedure—essentially, modifying the averaging in the time integral—and obtain the correct hybrid ensemble averages. This can be done in fact in several ways.

The first thing to notice is that equation (42) holds for any function $g(\eta, \xi)$ on $\mathcal{M}$, not only on the ones that result of a hybrid observable as $A(\eta, \xi) = \langle\eta|\hat{A}(\xi)|\eta\rangle$. Then one may ask the question: for any hybrid observable $\hat{A}$, can one find a function $g_{\hat{A}}(\eta, \xi)$, such that:

$$\langle\widehat{A}\rangle_{\mathrm{HC}}(\beta) = \langle g/A\widehat{A}\rangle_{\mathrm{CC}}(\beta)\,? \tag{46}$$

If so, one could then perform the dynamics and use equation (42) with $g_{\hat{A}}$ in order to obtain $\langle g_{\hat{A}}\rangle_{\mathrm{CC}}(\beta)$, and therefore the *true* hybrid ensemble average $\langle\hat{A}\rangle_{\mathrm{HC}}(\beta)$.

The answer is positive, and there is not only one, but many possible functions that can be used. In the following, we consider two examples:

(a) Equation (46) holds if $g_{\hat{A}}$ is defined as:

$$g_{\hat{A}}(\eta, \xi) = \mu(\beta)\mathrm{e}^{\beta H(\eta,\xi)}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi)}\hat{A}(\xi)\right], \quad \text{where} \tag{47}$$

$$\mu(\beta) = \frac{Z_{\mathrm{CC}}(\beta)}{(\int \mathrm{d}\mu(\eta))Z_{\mathrm{HC}}(\beta)}. \tag{48}$$

The computation of the normalization factor $\mu(\beta)$ may seem problematic, but it can be obtained from the dynamical trajectory, in the following way: for each $g_{\hat{A}}$, we define an 'unnormalized' function

$$\tilde{g}_{\hat{A}}(\eta, \xi) = \frac{g_{\hat{A}}(\eta, \xi)}{\mu(\beta)} = \mathrm{e}^{\beta H(\eta,\xi)}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi)}\hat{A}(\xi)\right], \tag{49}$$

such that $\langle g_{\hat{A}}\rangle_{\mathrm{CC}}(\beta) = \mu(\beta)\langle\tilde{g}_{\hat{A}}\rangle_{\mathrm{CC}}(\beta)$.

On the other hand, we know that for the identity operator, $\langle\hat{I}\rangle_{\mathrm{HC}}(\beta) = 1$, and therefore:

$$\langle g_{\hat{I}}\rangle_{\mathrm{CC}}(\beta) = \mu(\beta)\langle\tilde{g}_{\hat{I}}\rangle_{\mathrm{CC}}(\beta) = \langle\hat{I}\rangle_{\mathrm{HC}}(\beta) = 1. \tag{50}$$

Thus, we may compute $\mu(\beta)$ as $1/\langle\tilde{g}_{\hat{I}}\rangle_{\mathrm{CC}}(\beta)$, and $\langle\tilde{g}_{\hat{I}}\rangle_{\mathrm{CC}}(\beta)$ can be obtained from a dynamics propagation, i.e.:

$$\frac{1}{\mu(\beta)} = \lim_{t_f\to\infty}\frac{1}{t_f}\int_0^{t_f}\mathrm{d}t\, g_{\hat{I}}(\eta^\beta(t), \xi^\beta(t)). \tag{51}$$

Summarizing, a final formula that permits to compute the hybrid ensemble averages is:

$$\langle \hat{A} \rangle_{\mathrm{HC}}(\beta) = \frac{\lim\limits_{t_f\to\infty} \int_0^{t_f} \mathrm{d}t\, \mathrm{e}^{\beta H(\eta^\beta(t),\xi^\beta(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi^\beta(t))}\hat{A}(\xi^\beta(t))\right]}{\lim\limits_{t_f\to\infty} \int_0^{t_f} \mathrm{d}t\, \mathrm{e}^{\beta H(\eta^\beta(t),\xi^\beta(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi^\beta(t))}\right]}. \tag{52}$$

Therefore, the procedure consists of performing a thermostatted Ehrenfest dynamics, and computing the previous time integrals over the obtained trajectory $(\eta^\beta(t), \xi^\beta(t))$. One obvious difficulty lies in the computation of the traces over the quantum Hilbert space, whose difficulty depends on the level of theory used to deal with the quantum electronic problem.

(b) Equation (46) also holds if $g_{\hat{A}}$ is defined as:

$$g_{\hat{A}}(\eta,\xi) = \lambda(\beta)\sum_\alpha \delta(\eta - \eta_\alpha(\xi))A_{\alpha\alpha}(\xi), \tag{53}$$

$$\lambda(\beta) = \frac{Z_{\mathrm{CC}}(\beta)}{Z_{\mathrm{HC}}(\beta)}, \tag{54}$$

where $\eta_\alpha(\xi)$ are the adiabatic states:

$$\hat{H}(\xi)|\eta_\alpha(\xi)\rangle = E_\alpha(\xi)|\eta_\alpha(\xi)\rangle, \tag{55}$$

and

$$A_{\alpha\alpha}(\xi) = \langle\eta_\alpha(\xi)|\hat{A}(\xi)|\eta_\alpha(\xi)\rangle. \tag{56}$$

The difficulty due to the computation of the $\lambda(\beta)$ factor can be solved in a similar way to the method used in the previous case, leading to the following final formula:

$$\langle \hat{A} \rangle_{\mathrm{HC}}(\beta) = \frac{\lim\limits_{t_f\to\infty} \int_0^{t_f} \mathrm{d}t\, \sum\limits_\alpha \delta(\eta^\beta(t) - \eta_\alpha(\xi^\beta(t)))A_{\alpha\alpha}(\xi^\beta(t))}{\lim\limits_{t_f\to\infty} \int_0^{t_f} \mathrm{d}t\, \sum\limits_\alpha \delta(\eta^\beta(t) - \eta_\alpha(\xi^\beta(t)))}. \tag{57}$$

This formula avoids the need to compute all the electronic excited states, necessary for the traces present in equation (52). In exchange, it contains a probably worse numerical difficulty: the presence of the delta functions. The interpretation of these is the following: during the trajectories, one should not count in the average the state that is being visited, unless the trajectory passes by an eigenstate of the Hamiltonian (a state of the adiabatic basis). In other words, apart from the normalization factor given by the denominator, this formula is a modification of the straightforward average given in equation (42), that discards all states except for the adiabatic eigenstates.

That correction is easy to understand intuitively. Let us first rewrite the hybrid canonical ensemble density matrix,

$$\hat{\rho}_{\mathrm{HC}}(\xi) = \frac{1}{Z_{\mathrm{HC}}(\beta)}\mathrm{e}^{-\beta\hat{H}(\xi)}, \tag{58}$$

in terms of its spectral decomposition for each ξ:

$$\hat{\rho}_{\mathrm{HC}}(\xi) = \frac{1}{Z_{\mathrm{HC}}(\beta)}\sum_\alpha \mathrm{e}^{-\beta E_\alpha(\xi)}\hat{\eta}_\alpha(\xi), \tag{59}$$

where $E_\alpha(\xi)$ are the eigenvalues, and $\hat{\eta}_\alpha(\xi)$ the projectors on the eigenspaces of the Hamiltonian $\hat{H}(\xi)$ (we assume, for simplicity, that there is no degeneration; otherwise one would just need to use an orthogonal basis for each degenerate subspace). Now, this expression can be written in terms of a (generalized) probability distribution function in $\mathcal{M}$, as:

$$\rho_{\mathrm{HC}}(\eta,\xi) = \frac{1}{Z_{\mathrm{HC}}(\beta)}\sum_\alpha \delta(\eta - \eta_\alpha(\xi))\mathrm{e}^{-\beta E_\alpha(\xi)}. \tag{60}$$

This distribution determines $\hat{\rho}_{\mathrm{HC}}(\xi)$, since:

$$\hat{\rho}_{\mathrm{HC}}(\xi) = \int \mathrm{d}\mu(\eta)\rho_{\mathrm{HC}}(\eta,\xi)\frac{|\eta\rangle\langle\eta|}{\langle\eta|\eta\rangle}. \tag{61}$$

By comparing equation (60) with equation (40), it becomes clear that the error that this latter equation does is counting all possible states, whereas the true hybrid ensemble only counts the states in the adiabatic basis. Of course, one could choose a different basis, but the point is that the 'classical' Gibbs distribution (40) overcounts the quantum states. For a deeper discussion on this issue, we refer the reader to reference [5].

In order to implement this procedure numerically, one should of course use some finite representation of the delta functions, giving them a non-zero width. It is unclear, however, that this would lead to an efficient scheme, since the propagation would probably have to be very long in order to obtain an accurate sampling of the quantum states.

4. Approaches that do not require the propagation of the electrons

The use of Ehrenfest dynamics to compute the ensemble averages, as described in the previous section, has a notable caveat: it requires the explicit propagation of the electrons. The time scale associated to the electronic movement is very small (of the order of attoseconds), which makes hybrid MD schemes computationally intensive due to the need of a very fine time step.

In this section, we show how this problem can be circumvented by making use of dynamics that do not explicitly propagate the electrons, such as ground-state Born–Oppenheimer MD—including the necessary correction to account for the hot electrons, or the dynamics based on the electronic free energy surface that has already been used in the past. In this way, we frame these approaches into the theoretical setup described above.

Let us suppose that we perform a MD for the classical particles, based on a Hamiltonian function $\mathcal{H}(\xi)$ (to be specified below). In this case, the dynamics is not hybrid: the propagation equations involve only the classical particles, moving under the influence of $\mathcal{H}(\xi)$. The ergodic assumption, if it holds, permits to compute:

$$\langle g\rangle_{\mathrm{CC}}(\beta) = \frac{1}{Z_{\mathrm{CC}}(\beta)}\int \mathrm{d}\mu(\xi)\mathrm{e}^{-\beta\mathcal{H}(\xi)}g(\xi) = \lim_{t_f\to\infty}\frac{1}{t_f}\int_0^{t_f}\mathrm{d}t\, g(\xi^\beta(t)), \tag{62}$$

for any function $g(\xi)$. Notice that the classical canonical ensemble that we are using now refers to the classical degrees of freedom ξ only, as opposed to the one used in the previous section, that included the quantum ones.

In the same manner as we did in the previous section, one may wonder the following: for a given hybrid observable $\hat{A}(\xi)$, does there exist some function $g_{\hat{A}}(\xi)$ such that

$$\langle\hat{A}\rangle_{\mathrm{HC}}(\beta) = \langle g_{\hat{A}}\rangle_{\mathrm{CC}}(\beta)\,? \tag{63}$$

Once again, the answer is affirmative, and in more ways than one. One obvious possibility, analogous to the first one used for Ehrenfest dynamics, is:

$$g_{\hat{A}}(\xi) = \mu(\beta)\mathrm{e}^{\beta\mathcal{H}(\xi)}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi)}\hat{A}(\xi)\right], \tag{64}$$

$$\mu(\beta) = \frac{Z_{\mathrm{CC}}(\beta)}{Z_{\mathrm{HC}}(\beta)}. \tag{65}$$

As it happened in the previous section, the calculation of the normalization factor $\mu(\beta)$ does not require of the explicit computation of the partition functions (that may be impractical), but may result from the MD propagation itself, using the identity $\langle\hat{I}\rangle_{\mathrm{HC}}(\beta) = 1$. Using this fact and the same procedure shown in the previous section, one arrives to the final formula:

$$\langle\hat{A}\rangle_{\mathrm{HC}}(\beta) = \lim_{t_f\to\infty}\frac{\int_0^{t_f}\mathrm{d}t\,\mathrm{e}^{\beta\mathcal{H}(\xi^\beta(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi^\beta(t))}\hat{A}(\xi^\beta(t))\right]}{\int_0^{t_f}\mathrm{d}t\,\mathrm{e}^{\beta\mathcal{H}(\xi^\beta(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}(\xi^\beta(t))}\right]}. \tag{66}$$

This formula is very similar to equation (52). However, the trajectory $\xi^\beta(t)$ to be used here must be obtained through a thermostatted classical-only MD determined by a Hamiltonian function $\mathcal{H}(\xi)$, in contrast to the hybrid quantum-classical Ehrenfest dynamics used in the previous section. The Hamiltonian function $\mathcal{H}(\xi)$ is in fact arbitrary, although a bad choice for this object could lead to a very bad convergence with respect to the total propagation time t_f—since using the ergodic hypothesis requires an accurate sampling of phase space. Two options that immediately come to mind are:

(a) Using the electronic free energy:

$$\mathcal{H}(\xi) = F(\xi;\beta) = -\frac{1}{\beta}\log \mathrm{Tr}\, \mathrm{e}^{-\beta\hat{H}(\xi)}. \tag{67}$$

This actually permits to simplify equation (66) into a very appealing form:

$$\langle \hat{A}\rangle_{\mathrm{HC}}(\beta) = \lim_{t_f\to\infty}\frac{1}{t_f}\int_0^{t_f} \mathrm{d}t\ \langle \hat{A}(\xi^\beta(t))\rangle_Q, \tag{68}$$

where at each classical phase space point in the trajectory one must compute the quantum ensemble average:

$$\langle \hat{A}(\xi)\rangle_Q = \frac{\mathrm{Tr}\left[\hat{A}(\xi)\mathrm{e}^{-\beta\hat{H}(\xi)}\right]}{\mathrm{Tr}\,\mathrm{e}^{-\beta\hat{H}(\xi)}}. \tag{69}$$

Equation (68) reminds of the usual MD ergodic averaging formula, just substituting the observable value by the thermal quantum average. In fact, if the observable that one is interested in is purely classical, $\hat{A}(\xi) = A(\xi)\hat{I}$, the formula is identical:

$$\langle A\rangle_{\mathrm{HC}}(\beta) = \lim_{t_f\to\infty}\frac{1}{t_f}\int_0^{t_f} \mathrm{d}t\ A(\xi^\beta(t)). \tag{70}$$

Therefore, for purely classical observables, if one uses the electronic free energy instead of the ground-state adiabatic energy as the Hamiltonian driving the ionic movement, the resulting MD provides the hybrid canonical averages using the 'standard' ergodic average. If the observable is itself hybrid, one must compute at each point during the trajectory the quantum thermal average.

This propagation of the classical variables following the electronic free energy surface underlies the scheme put forward by Alavi *et al* [3], although in that work the procedure is tightly tied to the use of FTDFT as the scheme that handles the electronic structure problem (computation of the free energy, and of its gradients). The same concept was also suggested by some of the current authors in references [9, 10].

(b) Using the ground-state Born–Oppenheimer energy:

$$\mathcal{H}(\xi) = E_0(\xi). \tag{71}$$

In this case we would just need to do the usual ground-state Born–Oppenheimer MD, which has the advantage of being a very well known and tested technique, for which plenty of codes and tools exist. In order to obtain the hybrid ensemble averages that do not ignore the electronic temperature, however, one must use the averaging formula (66), which for this case can be transformed into:

$$\langle \hat{A}\rangle_{\mathrm{HC}}(\beta) = \lim_{t_f\to\infty}\frac{\int_0^{t_f}\mathrm{d}t\sum_\alpha \mathrm{e}^{-\beta\Omega_\alpha(\xi^\beta(t))}A_{\alpha\alpha}(\xi^\beta(t))}{\int_0^{t_f}\mathrm{d}t\ \sum_\alpha \mathrm{e}^{-\beta\Omega_\alpha(\xi^\beta(t))}}, \tag{72}$$

where α runs over all the adiabatic eigenstates, and

$$\Omega_\alpha(\xi) = E_\alpha(\xi) - E_0(\xi) \tag{73}$$

are the electronic excitations.

On top of the usual ground-state Born–Oppenheimer MD, the added difficulty here would be the computation of these excitations, which may be more or less demanding depending on the level of theory used to model the many-electron problem.

Note that if the observable $\hat{A}(\xi)$ is actually a classical observable $A(\xi)\hat{I}$, this scheme can also be rewritten as:

$$\langle A\rangle_{\mathrm{HC}}(\beta) = \lim_{t_f\to\infty}\frac{\int_0^{t_f}\mathrm{d}t\, A(\xi^\beta(t))\mathrm{e}^{-\beta F(\xi^\beta(t);\beta)-E_0(\xi^\beta(t))}}{\int_0^{t_f}\mathrm{d}t\,\mathrm{e}^{-\beta F(\xi^\beta(t);\beta)-E_0(\xi^\beta(t))}}. \tag{74}$$

Here, we also write the formula in terms of the free energy. Computationally, the difference with respect to the previous approach given in formula (70) is that one does not need the gradients of the free energy, necessary in the previous approach for the computation of the forces in the dynamics.

All previous formulas have assumed that the thermostat is fixed to the target temperature. However, the dynamics can be performed at a different temperature (a technique that has been used in MD to probe larger regions of configuration space in less simulation time), as long as the reweighting corrects for this.

Take, for example, formula (66), that we repeat here for convenience, although we now use two different temperatures β and β':

$$\langle \hat{A} \rangle_{\mathrm{HC}}(\beta) = \frac{\lim\limits_{t_f\to\infty} \int\limits_0^{t_f} \mathrm{d}t\, \mathrm{e}^{\beta' \mathcal{H}(\xi^{\beta'}(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta \hat{H}(\xi^{\beta'}(t))} \hat{A}(\xi^{\beta'}(t))\right]}{\lim\limits_{t_f\to\infty} \int\limits_0^{t_f} \mathrm{d}t\, \mathrm{e}^{\beta' \mathcal{H}(\xi^{\beta'}(t))}\ \mathrm{Tr}\left[\mathrm{e}^{-\beta \hat{H}(\xi^{\beta'}(t))}\right]}. \tag{75}$$

In this formula the temperature dependence is twofold:

(a) The temperature used to define the thermostat, which appears in the β' labeling the trajectories $\xi^{\beta'}(t)$. This should be equal to the temperature used for defining the re-weighting factors, i.e. the inverse Boltzmann weight $\mathrm{e}^{\beta' \mathcal{H}(\xi^{\beta'}(t))}$.

(b) The 'target' temperature, that is the one that should be used in the exponent of the un-normalized hybrid canonical ensemble density matrix, appearing inside the trace, $\mathrm{e}^{-\beta \hat{H}}$.

These two temperatures can be different, and formula (75) still holds. In practical applications, this would permit to obtain hybrid canonical ensemble averages at different temperatures β by computing a single thermostatted trajectory at a fixed 'ergodic temperature' β'. The main motivation to use this procedure is saving computation time, as only one trajectory needs to be computed, and the results at different temperatures are obtained by post-processing this one trajectory. Furthermore, once one has the thermostatted dynamics, the computation of the ensemble averages at different temperatures using formula (75) can be easily parallelized, either using a core for each different temperature, or even dividing the post-processing of the original trajectory in different sections.

This can also be done when using Ehrenfest dynamics, and formulas (52) and (57) above. It does not hold, however, if one uses formulas (68) or (70) for the dynamics on the free energy surface, since they rely on a cancellation that is only achieved if the two temperatures are equal (two temperatures can also be used when doing the dynamics on the free energy, but one would then need to compute the free energy at those two temperatures). Note also that, in practice, this procedure cannot be indefinitely extended to any temperature range, since the ergodic visitation will not be effective unless the two temperatures are similar.

A higher temperature trajectory will provide a wider visitation of the whole phase space in less time, which in principle would imply faster approximation to the ergodic limit. This could be used to obtain low temperature ensemble averages in less simulation time. Indeed, using artificially high temperatures has been used to be able to observe rare events in MD simulations in the past. Notice, however, that a high temperature trajectory will necessarily be less dense in the relevant phase space areas. This might have the opposite effect, and lead to a bad convergence, specially if the two temperatures are too different. In general, for a particular problem, it cannot be determined beforehand which of the two effects would prevail

Summarizing, the previous formulas permit to use well known MD techniques and obtain canonical averages that correctly account for the electronic temperature. Looking, for example, at equation (74), the procedure entails two steps:

(a) One first performs a standard first principles MD simulation using, for example, the common technique based on ground-state DFT.

(b) Then, either on the fly as the trajectory is being generated, or later in a post-processing procedure, one computes the electronic free-energy at the trajectory points, using the finite-temperature DFT extension. With such information, one can use equation (74) to correct the time averages that, without this averaging method, would fail to converge to the real canonical ensemble.

This scheme can be applied on top of trajectories obtained previously, had they been saved. Note that, for the reasons explained above, one may recycle trajectories obtained with ground-state BOMD at some (nuclear only) temperature, to compute ensemble averages at various different global temperatures. This may be an advantage over the procedure implied by equation (70) (MD with forces computed on the electronic free-energy surface), as in that case one trajectory must be generated at each temperature. Finally, of course DFT need not be the method to be used for the computation of the forces—and the finite temperature DFT need not be the procedure to obtain the free energy, as one may use for example TDDFT to compute the electronic excitations and apply formula (72).

4.1. Numerical example

We finish with a numerical demonstration of the validity of the formulas given above, using a simple model and the very last of the presented schemes: 'standard' ground-state Born–Oppenheimer MD with a correction formula. Thus, we consider a simple dimer model, using the internuclear distance Q as the only

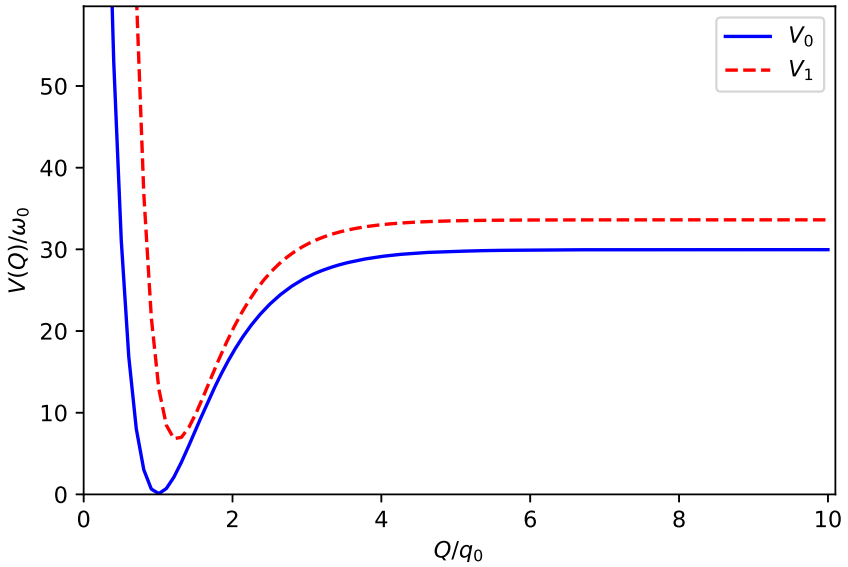

Figure 1. Electronic potential energy curves of the modeled dimer (in units of the ground state vibrational frequency ω_0): ground state (blue) and first excited state (dashed red), as a function of the dimer length (in units of the ground state equilibrium distance).

classical position variable (being P the corresponding momentum), and the subspace generated by the two lowest electronic adiabatic states as the quantum space. Furthermore, we consider that these two adiabatic states correspond to Morse potentials. Hence, the Hamiltonian operator ruling the hybrid dynamics can be written, in the basis of its eigenstates, as:

$$\widehat{H}(Q,P) = \frac{P^2}{2m}\widehat{\mathbb{I}} + \begin{pmatrix} V_0(Q) & 0 \\ 0 & V_1(Q) \end{pmatrix}, \tag{76}$$

where m is the dimer reduced mass, and the Morse potentials are given by:

$$V_i(Q) = D_i(1 - \mathrm{e}^{-b_i(Q-q_i)})^2 + \Delta_i. \tag{77}$$

The parameters defining the Morse potential for the ith energy level $V_i(Q)$ have an easy interpretation: Δ_i is a global shift that sets the value of the curve at its minimum; q_i the position at that minimum ($V_i(Q = q_i) = \Delta_i$); D_i defines how quickly the potential ascends for $Q > q_i$, and also determines the value of the gap between the minimum (Δ_i) and the big Q limit of the potential: $\lim_{Q\to\infty} V_i(Q) = \Delta_i + D_i$. Lastly, b_i defines how narrow the well is, how sharply it grows when $Q \to 0$, and also how rapidly it reaches the plateau for $Q > q_i$. The vibrational frequency associated to each potential well is given by $\omega_i = \sqrt{\frac{2b^2D}{m}}$. Figure 1 depicts these potential energy curves[6].

Using ground-state Born–Oppenheimer MD means that the classical degrees of freedom follow the Hamiltonian system defined by the function:

$$\mathcal{H}(Q,P) = E_0(Q,P) = \frac{P^2}{2m} + V_0(Q). \tag{78}$$

The system is coupled to a Langevin thermostat, at the temperature given by $T = \frac{1}{k_B\beta}$. This dynamics provides an ergodic curve over the classical phase space with a visitation weight given by the Boltzmann factor $\mathrm{e}^{-\beta E_0(Q,P)}$. Using the corrected averaging procedure defined by equation (72), we can obtain the hybrid canonical ensemble averages. Although this formula is valid for any observable, we chose to compute the average value of the length of the dimer, a purely classical observable: $\hat{A}(Q,P) = Q\hat{I}$.

Figure 2 shows the results. As the model is particularly simple, we can display both the exact values (i.e. the hybrid canonical ensemble averages computed by performing the direct integration in phase space, using equation (8)), and the values produced by using the time-averages over the dynamics. In this latter case, we display both the corrected averages, that result from formula (72), and the ergodic averages using

[6] We supply, as supporting information (https://stacks.iop.org/NJP/23/063011/mmedia), a computational notebook containing all the code that generates the results displayed in the article. It also contains all the chosen parameter values.

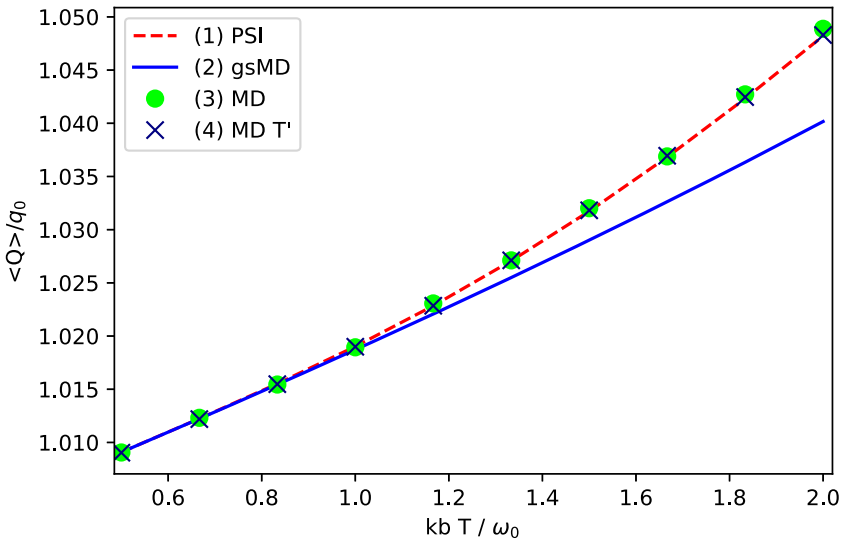

Figure 2. Ensemble average dimer length, $\langle Q \rangle_{\mathrm{HC}}(\beta)$, in units of the ground state equilibrium length q_0, as a function of temperature, calculated via: (1) direct integration in the phase space, labeled PSI; (2) ground-state MD without the correction, i.e. ignoring the electronic temperature, labeled gsMD; (3) ground-state MD with the application of the correcting average formula (72), labeled MD; (4) ground-state MD at a single temperature ($T' \sim 1.35\omega_0/k_{\mathrm{B}}$) for the thermostat with the application of the correcting average formula (75) for the whole range of temperatures of the target HCE.

ground-state MD, which corresponds to the purely-classical canonical ensemble average. It is clear how the proposed reweighting formula yields the correct numbers.

We stress that, in the procedure presented above, the computation of the ergodic trajectory is an indirect way to perform phase space integrals over the classical phase space. In principle, any infinite ($t_f \to \infty$) ergodic trajectory could be used as a basis to apply the corrected averaging procedure, as long as the implicit distribution over the phase space that results of the dynamics is compensated in the time averages: the use of the ground-state potential energy surface to generate the dynamics is one of the possible many choices. This only holds if the trajectory provides a dense enough visitation of the phase space.

However, in practice, the simulations provide only finite-time trajectories and, therefore, the visitation of phase space is not dense. The effectiveness of a given dynamics will depend on what regions of phase space it probes more frequently. Some thermostatted MD trajectories will be more cost-effective than others, if they visit more frequently the regions of the phase space that are relevant to the target distribution.

In our example, the target distribution is the hybrid canonical ensemble, and one should choose a dynamics that is likely to force the system to spend time on its high probability regions. This is not the only factor to consider, however. For example, it is likely that Ehrenfest dynamics fulfills this condition, but the cost of propagating Ehrenfest equations is high, due to the need to propagate the electrons. Likewise, it may happen that using the free energy as the driving Hamiltonian is costly due to the requirement of computing its gradients with respect to the classical degrees of freedom in order to obtain the forces. A dynamics that requires longer times t_f to achieve the convergence of the time average can be however computationally cheaper if the cost of performing the propagation itself is lower. We consider that ground-state MD can be a good compromise, specially at low temperatures, but the analysis strongly depends on the particular model, the electronic structure method, etc.

Finally, the blue crosses in figure 2 (marked as MD T′) are the results obtained by performing a single trajectory at a fixed temperature T', and then correcting appropriately for each different temperature. We have chosen $T' \sim 1.35\omega_0/k_{\mathrm{B}}$, corresponding to the sixth data point in the figure, as it is in the middle of the temperature range that we want to probe. The accuracy seems to be slightly better than the results obtained by performing different trajectories at different temperatures. This should not be taken as a general rule: we have performed convergence analysis with both methods and we cannot conclude that the use of the different-temperature method always leads to more precise averages for equal total propagation time. Note, however, than the single-trajectory method may be more advantageous as the computation time saved by not computing the multiple trajectories at different temperatures can be used to converge better the single trajectory with respect to its total propagation time.

5. Conclusions

We have examined the problem of computing the canonical ensemble averages through MD calculations, for hybrid quantum classical systems (typically, quantum electrons and classical nuclei in molecular or condensed matter physics and chemistry). If the temperature is high enough so that the electronic excited states cannot be ignored, performing ground state Born Oppenheimer MD and computing the ergodic averages on the generated trajectories does not yield the correct ensemble averages.

The fact that one cannot assume that the electrons are inert, adiabatically adapting to the ground state, naturally seems to demand for a truly hybrid dynamics, such as Ehrenfest's. However, the addition of a thermostat to these equations, followed by the computation of the resulting observable time-averages, does not produce the right averages either. The quantum character of part of the electrons cannot be handled by the standard MD + thermostat procedure, designed to produce essentially classical equilibrium ensembles.

Nevertheless, performing a thermostatted dynamics, be it Ehrenfest, or a purely classical one such as ground state MD, does generate a trajectory (i.e. an ensemble) in phase space that can be reweighted in order to obtain the true hybrid averages. This amounts to correcting the time averaging formulas. It has been the purpose of this work to examine here the various options that exist, setting them in a common language. The procedure can be followed using Ehrenfest dynamics, which is a hybrid dynamics, but can also be followed using classical-only dynamics driven by, for example, the ground-state Born–Oppenheimer Hamiltonian. Likewise, this framework does include, as a particular case, the possibility of performing the nuclear dynamics on the Hamiltonian that results of considering the electronic free energy. In this case, if one is interested in computing averages of purely classical observables, the time averages do not require correction, as the factors cancel out. The suitability of any of these procedures over the others depends on the particular model and level of theory used to handle the electronic structure problem.

Acknowledgments

The authors acknowledge financial support by MINECO Grant FIS2017-82426 P. CB acknowledges financial support by Gobierno de Aragón through the Grant defined in ORDEN IIU/1408/2018.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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2.3 Article:
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Eur. Phys. J. Plus (2023) 138:649
https://doi.org/10.1140/epjp/s13360-023-04266-w

THE EUROPEAN PHYSICAL JOURNAL PLUS

Regular Article

Effective nonlinear Ehrenfest hybrid quantum-classical dynamics

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Received: 17 February 2023 / Accepted: 6 July 2023

Abstract The definition of a consistent evolution equation for statistical hybrid quantum-classical systems is still an open problem. In this paper, we analyze the case of Ehrenfest dynamics on systems defined by a probability density and identify the relations of the nonlinearity of the dynamics with the obstructions to define a consistent dynamics for the first quantum moment of the distribution. This first quantum moment represents the physical states as a family of classically-parametrized density matrices $\hat{\rho}(\xi)$, for ξ a classical point; and it is the most common representation of hybrid systems in the literature. Due to this obstruction, we consider higher order quantum moments, and argue that only a finite number of them are physically measurable. Because of this, we propose an effective solution for the hybrid dynamics problem based on approximating the distribution by those moments and representing the states by them.

1 Introduction

It is an accepted fact that the most accurate physical theories describing Nature are quantum. Nonetheless, it is also well known that ab-initio full quantum theories are not useful from the practical point of view, because of their complexity. One of the choices is then to approximate the full quantum model by a simpler one where as many degrees of freedom as possible are modeled as classical systems. The paradigmatic example of this situation is the model of a molecule. Based on the application we have two options: either to consider all the degrees of freedom as classical (this is the case in most frequent molecular dynamics simulation methods), or to create a hybrid quantum-classical model where only the valence electrons, responsible of the chemical properties of the molecule, are modeled as quantum objects, the rest of degrees of freedom being represented by classical variables. In this second case, we define a more accurate description of the chemical properties, with a much simpler model than the full-quantum one. Nonetheless, the definition of an accurate hybrid dynamical system is not an easy task. There exist several approaches to define hybrid dynamical models for molecular systems (see, for instance, [1] for a recent review). We can classify them based on different properties, but, attending only to the definition of the dynamics, we may consider, among others:

- those based on hybrid dynamics on the space of hybrid states [2–8],
- those which are algorithmic (see [9, 10])
- or others obtained as suitable limit equations of the full-quantum dynamics [11–15].

If we enlarge our scope and consider other hybrid dynamical models, we can also find those considering the problem of measurements of quantum systems with classical devices [16, 17] and other type of systems (see [18–21] and references therein).

One of the most common choices is the Ehrenfest dynamics, where it is simple to track the accuracy of the hybrid model with respect to the original full quantum one within a semiclassical description [22]. Ehrenfest equations represent a dynamical system defined on the cartesian product of the classical and quantum phase spaces $M_C \times M_Q$. This hybrid phase space contains the hybrid pure states, i.e., those states where the classical and the quantum degrees of freedom are completely determined. Our group proved [5] that this system admits a Hamiltonian description with a suitable hybrid Poisson bracket and a hybrid Hamiltonian function, which combines the classical and the quantum energies. Nonetheless, molecular systems do not usually have completely determined dynamical states since initial conditions are impossible to fix. Therefore, a statistical description appears to be the most reasonable one. In [5] we also used the Hamiltonian structure of Ehrenfest equations to define a statistical model having Ehrenfest equations as dynamics for the microstates. In this statistical description, the state of the system is defined as a probability distribution on the hybrid phase-space following a Liouville equation. This is a consistent mechanism to define a statistical mechanical system associated to a well-defined thermodynamics (see [23]).

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Published online: 25 July 2023

In the last years, several relevant applications of this scheme have been published [6, 7] but also some limitations have appeared. Among them, the most relevant one may be the difficulty to write an entropy function and the corresponding notion of canonical ensemble [24] or, in more general terms, of an equilibrium thermodynamics with a well-defined temperature.

Our goal in this paper is a careful analysis of the origin of these difficulties, and a discussion of possible solutions and their implications. From the mathematical point of view, the problems are associated with the incompatibility of the notion of hybrid state as a probability density on the phase space and the definition of hybrid entropy, which require an alternative notion of state. Instead of the probability density described above, entropy can be formulated by considering its first quantum moment, which defines the type of hybrid state which has been used extensively since the early eighties (see [25]) and is used in many of the references presented above. But the challenge is to define a consistent master equation for this object, since the Liouville equation of the probability density does not preserve the first moment of the density. We will see this property in detail, and define a series of equations for the different moments which are equivalent to the Liouville equation for the probability distribution. Nonetheless, depending on the physical situation, not all the moments are necessary to define the physically relevant averages and their evolutions. For those situations where only a finite number of them are physically relevant, just a finite system of equations characterize the evolution of the quantum moments and an effective nonlinear master equation can be defined. This is the main result of the paper.

It is important to remark that the properties of the Hamiltonian structure of the microstate dynamics, such as having two independent symplectic or Poisson structures (as Ehrenfest dynamics), is the true origin of these properties. The particular Hamiltonian function, and hence the detailed properties of the dynamics are not that relevant. Hence, most of the conclusions of our paper shall be true in any Hamiltonian system sharing independent structures for the classical and quantum subsystems.

The scheme of the paper is as follows. First, in Sect. 2 we will summarize the construction of the Hamiltonian structure for Ehrenfest equations and its statistical extension. We will discuss that its Hamiltonian nature implies that only a finite number of quantum moments of the hybrid distribution are physically measurable. Then, Sect. 3 analyzes the properties of the different definitions of the hybrid statistical state and justifies why Liouville equation cannot be restricted to any of the quantum moments. The reason for that is the nonlinearity introduced in Ehrenfest equations by the classical degrees of freedom. Nonetheless, we can encode the full Liouville equation in a series of coupled differential equations of the full set of moments. But since only a finite number of moments are physically meaningful, we can approximate the behavior of Liouville equation by a finite number of those differential equations, suitably adapted. This is the main result of the paper. Finally, Sect. 4 summarizes the main contributions of the paper and discusses future lines of research based on them.

2 Ehrenfest dynamics: from pure states to distributions

2.1 Ehrenfest equations on pure states

Let us consider first the problem of Ehrenfest dynamics for pure states. We assume then that the state of the hybrid system is characterized by a pair $(\xi,\ \rho_\psi)$, where $\xi = (\mathbf{q},\ \mathbf{p}) \in M_C$ is a point on the classical phase space and ρ_ψ specifies the pure state of a quantum system by a one-dimensional projector determining a point in the complex projective space $\mathcal{PH}$ of a certain Hilbert space $\mathcal{H}$. Ehrenfest equations define a set of coupled differential equations describing the evolution of these degrees of freedom as

$$\begin{aligned} \dot{q}^k =& \frac{p^k}{M} \\ \dot{p}^k =& -\frac{\partial \mathrm{Tr}(\rho_\psi \hat{H}(\xi))}{\partial q^k} \\ i\,\dot{\rho}_\psi =& [\hat{H}(\xi), \rho_\psi] \end{aligned} \tag{1}$$

where $\hat{H}(\xi)$ represents the quantum energy as a self-adjoint family of operators on $\mathcal{H}$ parametrized by the classical degrees of freedom written in Darboux coordinates $q^k,\ p_j$ for $j,\ k = 1, \ldots n$ for the $2n$–dimensional symplectic manifold M_C (see [26] for the definition of these concepts). The simplest image for this operator is the electronic Hamiltonian for the valence electrons of a molecular system which depends on the positions of the charges of the protons and inner electrons of the atoms which are modeled by the classical degrees of freedom. In [22] it is proved that this system of equations defines a dynamical system whose solutions approximate the solutions of the Schrödinger equation for a full-quantum molecular Hamiltonian, the accuracy depending on the ratio of the masses of the quantum and the classical particles and the ratio of the width of the nuclear wave-packet with respect to the natural length of the problem.

The classical phase space M_C is assumed to be endowed with a symplectic form ω_C. Hence, its functions $C^\infty(M_C)$ can be endowed with a canonical Poisson bracket $\{\cdot,\ \cdot\}_C$. On the other hand, the quantum degrees of freedom correspond to the points of the set of pure density matrices of a quantum system (which we will denote in the following as M_Q), which being a Kähler manifold, is also endowed with a canonical Poisson structure $\{\cdot,\ \cdot\}_Q$ (for details see [27–29]). For the sake of simplicity we will consider that the quantum system is finite dimensional, and hence that M_Q is a finite dimensional Kähler manifold. From the point of view of

applications, this is not a serious constraint, since numerical simulation, which is usually the final goal of the hybrid model, requires a finite dimensional system.

In conclusion, we can endow the set of functions of the hybrid phase space $M_C \times M_Q$ with a Poisson structure by combining the classical and the quantum brackets (for simplicity, we will fix $\hbar = 1$ in the following) obtained from the symplectic forms on M_C and M_Q:

$$\{\cdot,\cdot\}_H := \{\cdot,\cdot\}_C + \{\cdot,\cdot\}_Q. \tag{2}$$

From the results in [5], it is immediate to prove that Ehrenfest equations can be given a Hamiltonian description with respect to the hybrid Poisson bracket $\{\cdot,\ \cdot\}_H$ and the Hamiltonian function

$$f_{\hat{H}(\xi)} := \mathrm{Tr}\Big(\rho_\psi (H_C(\xi)\hat{\mathbb{I}} + \hat{H}(\xi))\Big), \tag{3}$$

where we represent as $H_C(\xi)$ the general expression of the energy of the classical degrees of freedom (in Eqs. (1) it would reduce to just the classical kinetic term but more general situations with arbitrary classical potentials can also be considered); and $\hat{\mathbb{I}}$ represents the identity operator.

Thus, the integral curves of the Hamiltonian vector field

$$X_{f_H} := \{\cdot, f_H\}, \tag{4}$$

correspond to the solutions of Ehrenfest equations. The dynamics preserves the purity of the quantum states but it is nonlinear in general, because of the classical degrees of freedom (the term $H_C(\xi)$ in Eq. (3)). For more details see [5, 6].

2.2 Ehrenfest dynamics for statistical systems

2.2.1 The general case

From the definition of the hybrid Hamiltonian, we can consider the general notion of hybrid observable, representing the physical magnitudes written in terms of the classical and quantum degrees of freedom. Generally speaking, we can think at the hybrid observables as the tensor product of the C^*-algebra of classical functions and the C^*-algebra of quantum operators. For technical reasons, we will ask the classical functions to have compact support for integrals to be well defined. In practical applications, most frequently computer simulations, this does not seem to be a strong requirement. If we use the geometrical formulation described in [5], we can consider that the space of hybrid observables can be represented by the functions on $M_C \times M_Q$ which correspond to a pair of classical and quantum observables, i.e., functions of the form

$$f_{\hat{A}(\xi)} := \mathrm{Tr}\Big(\hat{\rho}_\psi \hat{A}(\xi)\Big). \tag{5}$$

In [5] we proved that it is possible to define a statistical mechanical formalism for hybrid systems by introducing a measure in this set of observables. If we take a reference measure $\mathrm{d}\mu_{QC}$ on the hybrid phase space (for instance, the symplectic volume), the chosen measure can be written as a probability density function $F_{QC}(\xi,\ \rho_\psi)$ with respect to it, defining the average of a certain magnitude $\hat{A}(\xi)$ as

$$\langle \hat{A}(\xi)\rangle := \int_{M_C\times M_Q} \mathrm{d}\mu_{QC}(\xi,\rho_\psi) F_{QC}(\xi,\rho_\psi) f_{\hat{A}(\xi)}. \tag{6}$$

Naturally, the measure must be well defined and therefore the density must satisfy that

$$F_{QC} \geq 0; \qquad \int_{M_C\times M_Q} \mathrm{d}\mu_{QC}(\xi,\rho_\psi) F_{QC} = 1. \tag{7}$$

2.2.2 The first quantum moment

Notice, though, that in physical terms, only the first quantum moment of F_{QC} is necessary to determine the average value of a hybrid observable of the form of Eq. (5). Indeed, the first quantum moment of F_{QC} determines a family of quantum operators indexed by the classical variables ξ in the form:

$$\hat{\rho}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi) F_{QC}(\xi,\rho_\psi)\rho_\psi, \tag{8}$$

where $\mathrm{d}\mu_Q$ is a measure on M_Q (for instance, the quantum symplectic volume). Average values of hybrid observables can then be computed as

$$\langle \hat{A}(\xi)\rangle = \int_{M_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}\Big(\hat{\rho}(\xi)\hat{A}(\xi)\Big), \tag{9}$$

where $d\mu_C$ is a measure on M_C (for instance, the classical symplectic volume) and then $d\mu_{QC} = d\mu_Q d\mu_C$. Notice that we use the term *quantum moment* since, considering a basis for states ρ_ψ, the coordinates of $\hat{\rho}(\xi)$ correspond, precisely, to the moments of the probability distribution F_{QC} considered as a function of the coordinates of the quantum projectors.

Furthermore, from the mathematical point of view, we can relate this first quantum moment with the marginal and conditional probabilities of the original density F_{QC}. As a bivariate hybrid measure, we can consider its classical marginal probability and the corresponding quantum conditional one:

- The classical marginal probability $F_C(\xi)$ can be obtained as

$$F_C(\xi) = \mathrm{Tr}\hat{\rho}(\xi) = \int_{M_Q} d\mu_Q(\rho_\psi) F_{QC}(\xi, \rho_\psi). \tag{10}$$

- The quantum conditional probability for a classical value $\xi \in M_C$ is a purely quantum distribution. We can consider it to be a distribution over the quantum phase space with some density $F^{\mathrm{cond}}_\xi(\rho_\psi)$ on the quantum phase space M_Q. As such, Gleason theorem [30] ensures that there exists a well-defined quantum density matrix $\hat{\rho}_\xi$ which is able to determine the average value of any quantum observable (for a fixed value of the classical variable ξ).

As it was explained in [24], standard probability theory allows us to write the operator $\hat{\rho}(\xi)$ as the product of these two objects, i.e.,

$$\hat{\rho}(\xi) = F_C(\xi)\hat{\rho}_\xi. \tag{11}$$

Notice that the resulting object is not normalized as a density matrix, since

$$\mathrm{Tr}\hat{\rho}(\xi) = F_C(\xi); \qquad \int_{M_C} d\mu_C(\xi)\mathrm{Tr}\hat{\rho}(\xi) = 1. \tag{12}$$

This operator $\hat{\rho}(\xi)$ is the usual representation of a hybrid state in the literature, since the early eighties [25]; and it is the usual choice in most of the references we presented in the Introduction. Notice, though, that from the probabilistic point of view, it just represents an element of the dual space to the set of hybrid observables of the form of Eq. (5). If we consider the C^*–algebra defined by the operators of that type, operator $\hat{\rho}(\xi)$ defines a state for such an algebra. From this point of view, this first quantum moment of F_{QC} is the only relevant part of the probability distribution if we restrict the physical magnitudes to functions of the form (5), since higher moments do not contribute to any average value. Hence we can define an equivalence relation in the space of hybrid measures by the first moment: two hybrid measures represent the same physical state if and only if their first quantum moments coincide.

Furthermore, this first moment $\hat{\rho}(\xi)$ is also able to capture the mutual exclusivity of hybrid events (see [24]). Indeed, notice that the points of the hybrid phase-space $M_C \times M_Q$ do not represent mutually exclusive events from the probabilistic point of view, as it happens with a classical manifold. While a classical system at a point ξ_1 cannot be at the same time at point ξ_2 (the probabilities of one case and the other are independent hence), it is not incompatible for a quantum system to be at point ρ_{ψ_1} and at point ρ_{ψ_2} unless $\langle \psi_1, \psi_2 \rangle = 0$ (probabilities are not independent then). From that point of view, representing a hybrid state with the density F_{QC} makes very difficult to define a hybrid entropy function (which requires of a correct representation of independent events which, as we just argued, is not achieved on $M_C \times MQ$). The first moment representation $\hat{\rho}(\xi)$, on the other hand, represents well the independence of hybrid events (as von Neumann entropy does for quantum systems) and allows us to define a well-behaved entropy function. From it, we can also use the MaxEnt principle to define a consistent notion of canonical ensemble and therefore a mechanism to make finite-temperature numerical simulations of hybrid systems (see [24, 31] for details).

2.2.3 Considering dynamics: the necessity of higher order moments

From a static point of view, the picture above is perfect. For the natural set of hybrid observables, we can consider a state corresponding to a probability density F_{QC} on the hybrid phase space $M_C \times M_Q$, but only the first quantum moment is necessary to define averages of physical magnitudes. That first moment also allows us to define a consistent notion of hybrid entropy. The problem arises when we want to consider a dynamical framework for statistical averages or even to equilibritum thermodynamics.

In this paper, we are going to consider Ehrenfest dynamics as the candidate for the dynamics of the statistical microstates. It is immediate to verify that dynamical Eq. (1) defines also a dynamics on the set of hybrid magnitudes, which can be written by means of the Hamiltonian vector field X_{f_H}. Indeed, we can write:

$$\frac{\mathrm{d}}{\mathrm{d}t} f_{\hat{A}(\xi)}(t) = X_{f_{\hat{H}(\xi)}} f_{\hat{A}(\xi)} := \{f_{\hat{A}(\xi)}, f_{\hat{H}(\xi)}\}_H. \tag{13}$$

Clearly, a function of the form $f_A(\xi, \rho_\psi; t) := f_A(\xi(t), \rho_\psi(t))$ where $(\xi(t), \rho_\psi(t))$ is a solution of Ehrenfest equations, is itself a solution of Eq. (13) with initial condition $f_A(\xi, \rho_\psi; 0) = f_A(\xi, \rho_\psi)$. Therefore, the system has solutions, and we can consider the time-dependence of statistical averages

$$\langle \hat{A}(\xi) \rangle(t) := \int_{M_C \times M_Q} d\mu_{QC}(\xi, \rho_\psi) F_{QC}(\xi, \rho_\psi) f_{\hat{A}(\xi)}(t), \tag{14}$$

and define out-of-equilibrium statistical mechanics of hybrid systems.

But it is important to realize that hybrid observables of the form (5) do not define a Poisson subalgebra for the hybrid Poisson bracket (2). Indeed, given $f_{\hat{A}(\xi)}$ and $f_{\hat{B}(\xi)}$ defined as Eq. (5), in general there exists no function $f_{\hat{D}(\xi)}$ of the form (5) such that

$$f_{\hat{D}(\xi)} = \{f_{\hat{A}(\xi)},\, f_{\hat{B}(\xi)}\}_H = \{f_{\hat{A}(\xi)},\, f_{\hat{B}(\xi)}\}_C + \{f_{\hat{A}(\xi)},\, f_{\hat{B}(\xi)}\}_Q.$$

This property can be proved immediately since the classical bracket $\{f_{\hat{A}(\xi)},\, f_{\hat{B}}(\xi)\}_C$ defines a function which is quadratic in the quantum degrees of freedom while the quantum bracket $\{f_{\hat{A}(\xi)},\, f_{\hat{B}(\xi)}\}_Q$ is still linear. Just those hybrid magnitudes which depend only on the classical or on the quantum degrees of freedom are closed under the bracket. After a straightforward computation, and choosing Darboux coordinates $\xi = (\mathbf{q},\, \mathbf{p}) = \{(q^k,\, p_j)\}_{k,\, j=1,\ldots,n}$ for M_C we obtain that:

$$\{f_{\hat{A}(\xi)}, f_{\hat{B}(\xi)}\}_C = \sum_k \left(f_{\partial_{q^k}\hat{A}(\mathbf{q},\mathbf{p})} f_{\partial_{p_k}\hat{B}(\mathbf{q},\mathbf{p})} - f_{\partial_{q^k}\hat{B}(\mathbf{q},\mathbf{p})} f_{\partial_{p_k}\hat{A}(\mathbf{q},\mathbf{p})} \right) \tag{15}$$

and

$$\{f_{\hat{A}(\xi)}, f_{\hat{B}(\xi)}\}_Q = f_{[\hat{A},\hat{B}](\xi)}, \tag{16}$$

where

$$[\hat{A}, \hat{B}](\xi) = -i(\hat{A}(\xi)\hat{B}(\xi) - \hat{B}(\xi)\hat{A}(\xi)). \tag{17}$$

Therefore, we can write that

$$\{f_{\hat{A}(\xi)}, f_{\hat{B}(\xi)}\}_H = \sum_k \left(f_{\partial_{q^k}\hat{A}(\mathbf{q},\mathbf{p})} f_{\partial_{p_k}\hat{B}(\mathbf{q},\mathbf{p})} - f_{\partial_{q^k}\hat{B}(\mathbf{q},\mathbf{p})} f_{\partial_{p_k}\hat{A}(\mathbf{q},\mathbf{p})} \right) + f_{[\hat{A},\hat{B}](\xi)}, \tag{18}$$

i.e, we obtain a combination of quantum-linear functions and quantum-quadratic ones. Clearly, successive brackets will increase further the quantum-degree.

From the physical point of view, this relation implies that, even if it is Hamiltonian, the dynamics on the space of observables cannot be restricted to quantum-linear functions of the form of Eq. (5). Nonetheless, hybrid energy is conserved, since $\{f_{\hat{H}(\xi)}, f_{\hat{H}(\xi)}\}_H = 0$.

If we average this expression with the density F_{QC}, we can write that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}(\xi)\rangle(t) &= \int_{M_C\times M_Q} \mathrm{d}\mu_{QC}(\xi,\rho_\psi) F_{QC}(\xi,\rho_\psi)\{f_{\hat{A}(\xi)}, f_{\hat{H}(\xi)}\}_H \\ &= \langle f_{\partial_{q^k}\hat{A}} f_{\partial_{p_k}\hat{H}}\rangle - \langle f_{\partial_{q^k}\hat{H}} f_{\partial_{p_k}\hat{A}}\rangle - \langle f_{[\hat{A},\hat{H}](\xi)}\rangle. \end{aligned} \tag{19}$$

Notice that in this expression the requirement of the extension of the algebra is explicit, since we need the average values of pointwise products of the elements of the algebra. Only the last term belong to it. If we write it as an equation on the density F_{QC}, the last term affects only its first moment, i.e.,

$$\begin{aligned} \langle f_{[A,H](\xi)}\rangle &= \int_{M_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}\Big(\hat{\rho}(\xi)[\hat{A}(\xi), \hat{H}(\xi)]\Big) \\ &= \int_{M_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}\Big([\hat{H}(\xi), \hat{\rho}(\xi)]\hat{A}(\xi)\Big). \end{aligned} \tag{20}$$

But the other two cannot be written as a function of the first moment only, and higher order moments are required. Indeed, we can write the average value of the product of the functions $f_{\hat{A}(\xi)}$ and $f_{\hat{B}(\xi)}$ as

$$\langle f_{\hat{A}(\xi)} f_{\hat{B}(\xi)}\rangle = \int_{M_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}\Big(\hat{\rho}^{\otimes 2}(\xi)(\hat{A}(\xi)\otimes\hat{B}(\xi))\Big), \tag{21}$$

where $\hat{\rho}^{\otimes 2}(\xi)$ is the second quantum moment of the density F_{QC}, defined as

$$\hat{\rho}^{\otimes 2}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi) F_{QC}(\xi,\rho_\psi)\rho_\psi\otimes\rho_\psi. \tag{22}$$

Analogously, the average value of the product of k functions $f_{\hat{A}_j(\xi)}$ is obtained as

$$\langle f_{\hat{A}_1(\xi)}\cdots f_{\hat{A}_n(\xi)}\rangle = \int_{M_C} \mathrm{d}\mu_C(\xi)\mathrm{Tr}\Big(\hat{\rho}^{\otimes k}(\xi)(\hat{A}_1(\xi)\otimes\cdots\otimes\hat{A}_k(\xi))\Big), \tag{23}$$

where

$$\hat{\rho}^{\otimes k}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi) F_{QC}(\xi,\rho_\psi)\overbrace{\rho_\psi\otimes\cdots\otimes\rho_\psi}^{k} \tag{24}$$

represents the k-th quantum moments of the distribution F_{QC}.

In conclusion, in order to consider Eq. (13) as a dynamical system on the hybrid algebra, the algebra itself must be enlarged. As each classical bracket increases the order of the quantum degrees of freedom by one, clearly we must consider all polynomial functions in ρ_ψ and arbitrary classical dependence as the minimal Poisson algebra generated by hybrid functions of the form (5). At each level, higher and higher quantum moments of the distribution are required to compute the average values of the extended functions. Indeed, if we consider the series of derivatives of order k with respect to time of the average value $\langle\hat{A}(\xi)\rangle(t)$, we can write it as a function of different terms depending on all the moments $\hat{\rho}^{\otimes j}(\xi)$ up to order $k+1$ evaluated on different combinations of $\hat{A}(\xi)$ and $\hat{H}(\xi)$:

$$\frac{\mathrm{d}^k}{\mathrm{d}t^k}\langle\hat{A}(\xi)\rangle(t) = F\Big(\hat{\rho}^{\otimes 0}(\xi), \ldots, \hat{\rho}^{\otimes k+1}(\xi), \hat{A}(\xi), \hat{H}(\xi)\Big). \tag{25}$$

Hence, for a finite range of time $(t_0,\ t_0+\Delta t)$, the behavior of an average value $\langle\hat{A}(\xi)\rangle(t)$ can be approximated to arbitrary precision by a finite number of quantum moments of the distribution F_{QC}. Notice that the particular time scale and the precision depends on the particular observable $\hat{A}(\xi)$. In any case, by considering a finite time range we see that the concept of hybrid observable changes. Time introduces correlations between the classical and quantum subsystems and the nonlinear evolution makes that correlation measurable in the time-dependence of the average values. We can see that in Eq. (19). If we want to consider a linearized time dependence in $\langle\hat{A}(\xi)\rangle$, we need to compute average values of pairs of quantum operators.[1] The time range which can be approximated by a finite number of time derivatives may depend on the observable we consider. But for any observable, there will be a certain time scale where the behavior of the system can be approximated to any precision with a sufficiently high order of quantum moments. As the application of our model will be a numerical simulation of the system at a certain time scale, this finite number of moments should be enough to characterize the state of the system. In the following sections we will learn to write the dynamics of the quantum moments and thus the dynamics of the physical macrostate for the relevant time range.

3 Hybrid states and dynamics

3.1 Writing a dynamics for the physical states

Let us consider now how to define an equation to write the evolution of the average value $\langle\hat{A}(\xi)\rangle$ given by (14) as an evolution equation on the physical state. Following [23] we can associate a Liouville equation to the probability density and define the curve on the space of probability densities which reproduces the evolution of the average values $\langle\hat{A}(\xi)\rangle(t)$, i.e.,

$$\langle\hat{A}(\xi)\rangle(t) = \int_{M_C\times M_Q} \mathrm{d}\mu_{QC}(\xi,\rho_\psi)F_{QC}(\xi,\rho_\psi;t)f_{\hat{A}}(\xi), \tag{26}$$

where $F_{QC}(\xi,\ \rho_\psi;t)$ is the solution of the master equation. In [5] we proved that because the dynamics is Hamiltonian we can obtain a dynamical equation for the density F_{QC} as the Liouville equation

$$\frac{\mathrm{d}F_{QC}}{\mathrm{d}t} = \{f_{\hat{H}(\xi)}, F_{QC}\}_H. \tag{27}$$

This equation translates the microstate dynamics to the full probability density. Nonetheless, if we are interested in the behavior of average values of physical magnitudes for a certain time scale, we know that not all the density is required, only a few of its quantum moments. Hence, we are going to study now how can we write the effect of Ehrenfest dynamics on those moments.

3.2 The initial problem: the dynamics of the first quantum moment

Let us consider now the first moment of the distribution F_{QC}, i.e., the family of operators $\hat{\rho}(\xi)$. We can consider Liouville equation for the density and re-write it in terms of the first moment:

$$\begin{aligned}\frac{\mathrm{d}\hat{\rho}(\xi)}{\mathrm{d}t} &= \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi)\{f_H, F_{QC}\}_H(\xi,\rho_\psi)\rho_\psi \\ &= [\hat{H}(\xi),\hat{\rho}(\xi)] + \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi)\{f_H, F_{QC}\}_C(\xi,\rho_\psi)\rho_\psi.\end{aligned} \tag{28}$$

[1] Notice that the analysis done here for time evolution can be repeated for any transformation requiring to introduce the necessary infinitesimal generator, that in this case is the Hamiltonian. This justifies extending the hybrid algebra to products of arbitrary operators, as any operator can be used to define a transformation of the system.

As the time dependence of average values can be written as a result of dynamics written on the space of operators or on the space of states,

$$\langle \hat{A} \rangle(t) = \begin{cases} \int_{M_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\hat{\rho}(\xi;t)\hat{A}(\xi)] \\ \int_{M_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\hat{\rho}(\xi)\hat{A}(\xi;t)] \end{cases}, \tag{29}$$

Equation (28) must satisfy

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{A}(\xi) \rangle = \int_{M_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\dot{\hat{\rho}}(\xi)\hat{A}(\xi)] = -\int_{M_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}[\hat{\rho}(\xi)\dot{\hat{A}}(\xi)], \tag{30}$$

where the dot represents the tangent vector of each respective curve (on states or on operators). Notice that, by definition,

$$\hat{\rho}(\xi;t) := \int_{M_Q} \mathrm{d}\mu_q(\rho_\psi) F_{QC}(\xi, \rho_\psi; t)\rho_\psi . \tag{31}$$

Therefore, we can conclude that the properties of the first quantum moment will be preserved (normalization, positivity, etc.), if the solution of the Liouville equation defines a curve of well-defined probability densities.

As we saw in the previous section, the set of linear functions of the form f_A is not closed under the hybrid Poisson bracket. This has an important impact on the Liouville equation (27). Indeed, a master equation for the density F_{QC} which captures the dual behavior of the dynamics of the hybrid observables (which does not have linear functions as a Poisson subalgebra) cannot be restricted to the first quantum moment, which is only able to capture the linear (quantum) functions of the form (5). If we must include quantum polynomial functions of orders higher than one (i.e., objects of the form $f_A f_H$), higher quantum moments of the distribution F_{QC} must be considered. But then the equivalence relation given by the first moment is broken: two measures having identical first quantum moments may evolve in different ways and produce different hybrid states for each value of time, depending on the higher quantum moments. Let us consider this issue in some detail in a particular example.

Example 1 As we saw above, there exist many densities F_{QC} with the same first quantum moment. Let us see now that the nonlinearity of Ehrenfest equations makes impossible to write Ehrenfest dynamics in terms $\hat{\rho}(\xi)$ in a consistent way.

Let us now construct a particular hybrid system with Ehrenfest dynamics, with an ad-hoc Hamiltonian and density matrix. We will then find a one-parameter family of different densities with the same first moment $\hat{\rho}(\xi)$ and see that the tangent vector defined by each density is different. More in particular:

1. We consider one classical degree of freedom, $M_C \equiv \mathbb{R}^2$ and $\xi \equiv (R,\ P)$.
2. We choose a two-level system as the quantum subsystem. Therefore, the space of projectors is:

$$M_Q = \{\rho_\psi \mid \rho_\psi \in \mathrm{Herm}(2) = \mathrm{span}_{\mathbb{R}}\{\sigma_0,\ \sigma_1,\ \sigma_2,\ \sigma_3\},\ \rho_\psi^2 = \rho_\psi,\ \mathrm{Tr}(\rho_\psi) = 1\}$$

   with $\{\sigma_i\}_{i=1}^3$ being the Pauli matrices and σ_0 the identity. The usual description of this space in quantum mechanics is *the Bloch sphere*. It can be proved that M_Q as defined above is bijective to $S^2 = \{x^2 + y^2 + z^2 = 1 \mid x,\ y,\ z \in \mathbb{R}\} \subset \mathbb{R}^3$, with coordinates $\{x = \mathrm{Tr}[\sigma_1\rho_\psi],\ \ y = \mathrm{Tr}[\sigma_2\rho_\psi],\ \ z = \mathrm{Tr}[\sigma_3\rho_\psi]\}$, which will be called *Bloch coordinates*, denoted by a subscript $\mathcal{B}$.
3. The Hamiltonian of the system is defined as

$$\hat{H}(\xi) = \hat{H}(R,P) = \frac{1}{2}(R^2 + P^2)\mathbb{I}_2 + E_1(R,P)\hat{\pi}_1(R,P) + E_2(R,P)\hat{\pi}_2(R,P) \tag{32}$$

   where $\hat{\pi}_k \in M_Q$ are classical-point-dependent projectors: $\hat{\pi}_1(R,\ P) = (\sin R,\ 0,\ \cos R)_{\mathcal{B}}$ and $\hat{\pi}_2(R,\ P) = (-\sin R,\ 0,\ -\cos R)_{\mathcal{B}}$. Note that they are orthogonal by construction. The two energy levels E_k are:

$$E_1(R,\ P) = \frac{1}{1+R^2} \qquad E_2(R,\ P) = E_1(R,\ P) + 1 + 0.1R^2 .$$

4. The hybrid density matrix is defined as

$$\hat{\rho}(\xi) = F_C(\xi)\lambda(\xi)\,\hat{\pi}_1(\xi) + F_C(\xi)(1-\lambda(\xi))\,\hat{\pi}_2(\xi)$$

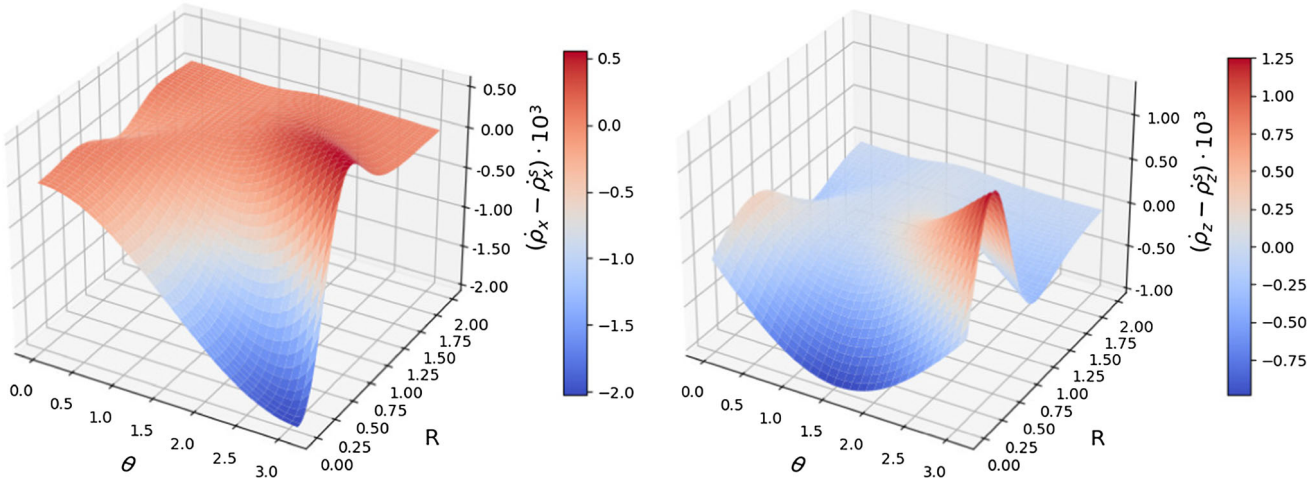
   with $\lambda(R,\ P) = \frac{2}{\pi}\mathrm{atan}\left(R^2 + P^2\right)$, $F_C(R,\ P) = \frac{1}{2\pi}\exp\left(-\frac{R^2+P^2}{2}\right)$ and with projectors defined as, $\hat{\pi}_1(R,\ P) = (\sin a,\ 0,\ \cos a)_{\mathcal{B}}$ and $\hat{\pi}_2(R,\ P) = (-\sin a,\ 0,\ -\cos a)_{\mathcal{B}}$, where $a = \mathrm{atan}\left(R^2 + P^2\right)$.

Finally, we define a family of densities F_{QC}^{θ} in terms of the arbitrary parameter $\theta \in \mathbb{R}$. Consider a decomposition of the matrix $\hat{\rho}(\xi)$ as sum of projectors

$$\hat{\rho}(\xi) = \sum_k \lambda_k(\xi)\hat{\pi}_k(\xi), \qquad \hat{\pi}_k(\xi)^2 = \hat{\pi}_k(\xi). \tag{33}$$

It is immediate to prove that the density

$$F_{QC}(\xi, \rho_\psi) = \sum_k \lambda_k(\xi)\delta(\rho_\psi - \hat{\pi}_k(\xi)), \tag{34}$$



(a) x-coordinate, $\frac{1}{2}\mathrm{Tr}(\dot{\rho}(\xi)\sigma_1)$. (b) z-coordinate, $\frac{1}{2}\mathrm{Tr}(\dot{\rho}(\xi)\sigma_3)$.

Fig. 1 Difference of x and z components of $\dot{\rho}(\xi)$ for different values of the classical parameter R and θ

has $\hat{\rho}(\xi)$ as first moment. We can consider a family of the decompositions choosing the coordinates of one projector to be $(\sin\theta, 0, \cos\theta)_{\mathcal{B}}$, and solving the geometric problem in the Bloch sphere to find the other projector and the corresponding weights. Thus, we construct the θ-dependent family of densities F^{θ}_{QC} having the same first quantum moment. For each density, consider Eq. (28) and represent the corresponding tangent vector as a function of the parameter θ. We present graphically the results in Fig. 1. We observe that the x and z coordinates of $\hat{\rho}(\xi)$ (in the Bloch basis) depend of the arbitrary parameter.

As expected, we verify that the dynamics of the first quantum moment depend on the parameter θ and therefore that the dynamics of the first moment is not well defined. Hence, we see that different density dynamics are possible for a given $\hat{\rho}(\xi)$, depending on elements which are not physically observable, *a priori*, at the (quantum) linear level. Notice that the origin of the problem is the nonlinearity of Ehrenfest dynamics, which defines a different evolution for the two different quantum states coupled to the same classical point ξ. Had we considered a pure quantum system with unitary evolution, or even an uncoupled hybrid system, the evolution would be well defined because of the linearity of the pure quantum evolution. Let us see now how the dynamics can be determined when considering higher order moments.

3.3 The dynamics of higher quantum moments

We have seen above how at the linear level, we have part of the information of the full Liouville equation, although not all. Nonetheless, Eq. (28) is enough to read the behavior of the two marginal distributions $F_C(\xi) = \mathrm{Tr}\hat{\rho}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q F_{QC}(\xi, \rho_\psi)$ and $\hat{\rho} = \int_{M_C} \mathrm{d}\mu_C(\xi)\hat{\rho}(\xi)$. Indeed, marginalizing one of the variables makes one of the two brackets to vanish, and that produces:

$$\frac{\mathrm{d}}{\mathrm{d}t}F_C(\xi) = \mathrm{Tr}\Big(\{\hat{H}(\xi), \hat{\rho}(\xi)\}_C\Big), \tag{35}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = \int_{M_C} \mathrm{d}\mu_C(\xi)[\hat{H}(\xi), \hat{\rho}(\xi)]. \tag{36}$$

These two equations coincide with those obtained from different approaches to hybrid quantum-classical dynamics, such as [12, 25], where Ehrenfest equations were not considered. This is a remarkable result, since it ensures that, at least at first order, the evolution of pure classical or pure quantum magnitudes behave the same as in those other approaches even for coupled quantum-classical systems.

What about the full hybrid (i.e., non-marginalized) behavior? Can we read any useful properties from Liouville equation? Indeed, we can. We saw above that writing Ehrenfest dynamics on the physical states requires of higher order quantum moments to be able to capture the effects of the nonlinearity and the non-closeness of the Poisson algebra. Dynamics written on the first moment only is not well defined, as the nonlinearity of the dynamics makes it dependent on the choice of the decomposition of the quantum operator at each classical point. In this section, we will see that the dynamics of each moment depends on the next one; the Liouville equation being thus equivalent to an infinite series of differential equations, one for each $\hat{\rho}^{\otimes k}(\xi)$.

Let us consider again the definition of the k-th moment given in Eq. (24). By construction, they are operators on the Hilbert space $\bigotimes_{j=1}^{k}\mathcal{H}_j$. We can define partial traces if we average over some of those copies, since $\mathrm{Tr}\rho_\psi = 1$ and hence $\mathrm{Tr}_p\overbrace{\rho_\psi\otimes\cdots\otimes\rho_\psi}^{k} = \overbrace{\rho_\psi\otimes\cdots\otimes\rho_\psi}^{k-p}$ for $p \leq k$. It is immediate then that

$$\mathrm{Tr}_p\hat{\rho}^{\otimes k}(\xi) = \hat{\rho}^{\otimes k-p}(\xi), \tag{37}$$

where the zeroth order moment corresponds to the marginal classical density

$$\mathrm{Tr}_k\hat{\rho}^{\otimes k}(\xi) = \hat{\rho}^{\otimes 0}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi)F_{QC}(\xi,\rho_\psi) = F_C(\xi). \tag{38}$$

Despite of the symmetric nature of the expressions involving the points ρ_ψ in the following we will consider traces of different operators, and will denote as Tr_1 the trace acting always on the first one

$$\mathrm{Tr}_1(A\otimes B) = \mathrm{Tr}(A)B. \tag{39}$$

In an analogous way, the expression is extended to arbitrary traces Tr_k.

Using these relations, it is immediate to re-write Eq. (19) as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}(\xi)\rangle(t) =& \langle f_{\partial_{q^k}A}f_{\partial_{p_k}H}\rangle - \langle f_{\partial_{q^k}H}f_{\partial_{p_k}A}\rangle - \langle f_{[A,H]}\rangle \\ =& \int_{M_C}\mathrm{d}\mu_C(\xi)\mathrm{Tr}([\hat{A},\hat{H}]\hat{\rho}(\xi)) + \int_{M_C}\mathrm{d}\mu_C(\xi)\sum_k \mathrm{Tr}\Big(\Big(\partial_{[q^k}\hat{A}\otimes\partial_{p_k]}\hat{H}\Big)\hat{\rho}^{\otimes 2}(\xi)\Big),\end{aligned}$$

where $\partial_{[q^k}\hat{A}\otimes\partial_{p_k]}\hat{H} = \partial_{q^k}\hat{A}(\xi)\otimes\partial_{p_k}\hat{H}(\xi) - \partial_{q^k}\hat{H}(\xi)\otimes\partial_{p_k}\hat{A}(\xi)$.

From that expression, and using the compact support of the classical functions, we can read the time derivative of the first quantum moment as

$$\dot{\hat{\rho}}(\xi) = [\hat{H}(\xi),\hat{\rho}(\xi)] + \mathrm{Tr}_1\Big(\Big\{\hat{H}(\xi)\otimes\mathbb{I},\hat{\rho}^{\otimes 2}(\xi)\Big\}_C\Big), \tag{40}$$

where $\dot{\hat{\rho}}(\xi)$ is defined by Eq. (28). Analogously, we can define the time derivative of any moment $\dot{\hat{\rho}}^{\otimes k}(\xi)$ as a function of $\hat{\rho}^{\otimes k}(\xi)$ and $\hat{\rho}^{\otimes k+1}(\xi)$.

$$\dot{\hat{\rho}}^{\otimes k}(\xi) = [\hat{H}^k(\xi),\hat{\rho}^{\otimes k}(\xi)] + \mathrm{Tr}_1\left(\left\{\hat{H}(\xi)\otimes\overbrace{\mathbb{I}\otimes\cdots\otimes\mathbb{I}}^{k},\hat{\rho}^{\otimes k+1}(\xi)\right\}_C\right), \tag{41}$$

where

$$\hat{H}^k = \overbrace{\hat{H}(\xi)\otimes\mathbb{I}\otimes\cdots\otimes\mathbb{I}}^{k} + \cdots + \overbrace{\mathbb{I}\otimes\cdots\otimes\mathbb{I}\otimes\hat{H}(\xi)}^{k} \tag{42}$$

In this way, we find a system of differential equations for all the quantum moments $\{\hat{\rho}^{\otimes k}(\xi)\}_{k=0,\ldots,}$ which is equivalent to the Liouville equation for the density F_{QC} (Eq. (27)).

3.4 An effective equation

As we saw above, only a finite number of quantum moments are necessary to recover the behavior of the average value of physical observables for finite time intervals. Notice, though, that when we make the approximation for a certain time range, the approximated solution of the dynamics of the hybrid observables $\hat{A}(\xi;t)$ defines a different dynamics for the average values $\langle\hat{A}(\xi)\rangle(t)$. As in each case the average values involve a finite number of quantum moments, we can define different dynamics on the space of states with the corresponding Eq. (41). But there is a problem to do that: the dynamics of the k-th quantum moments, depends on the $k+1$-th one and therefore it is not possible to solve the equation for a certain k without the solution to the next level. Nonetheless, as the time scale is only able to capture the k-first moments, it is not possible to do any measurement or sequence of measurements which depend on those degrees of freedom. Hence, as the $(k+1)$-th moment cannot be known, we may consider an effective dynamical equation for $\hat{\rho}^{\otimes k}(\xi)$ where the value of $\hat{\rho}^{\otimes k+1}(\xi)$ represents the minimum knowledge on the system compatible with the physical constraints. In order to do that, we must introduce a suitable notion of entropy.

In [24] we introduce a notion of hybrid entropy for the first quantum moment $\hat{\rho}(\xi)$. We built it based on the bivariate distribution that the first moment represents, and the corresponding factorization in marginal and conditional probabilities. That factorization makes sense for any of the quantum moments $\hat{\rho}^{\otimes k}(\xi)$, which, on the other hand, happens to be formally analogous to $\hat{\rho}(\xi)$ with the only difference of being an operator on the product Hilbert space $\bigotimes_{j=1}^{k}\mathcal{H}$:

- the marginal probability of the bivariate probability distribution represented by $\hat{\rho}^{\otimes k}(\xi)$ corresponds to the classical density

$$F_C(\xi) = \mathrm{Tr}_k \hat{\rho}^{\otimes k}(\xi) = \int_{M_Q} \mathrm{d}\mu_Q(\rho_\psi) F_{QC}(\xi, \rho_\psi). \tag{43}$$

- The corresponding quantum conditional probability $\mathcal{P}(\rho_\psi \mid \xi)$ is the probability of a pure quantum system (the classical degrees of freedom ξ are fixed). As such, Gleason theorem [30] ensures that a well-defined density matrix $\hat{\rho}_\xi^{\otimes k}$ (i.e., a trace class, normalized and non-negative self-adjoint operator on $\bigotimes_{j=1}^k \mathcal{H}$) must exist to represent it.

This representation allows to implement the exclusivity of hybrid events in a simpler way, since it incorporates automatically the orthogonality of the mutually exclusive quantum events (as the usual density matrix does). See [24] for a more detailed discussion.

By using this factorization, we can adapt the construction of the hybrid entropy in [24]. As the entropy for the state $\hat{\rho}^{\otimes k}(\xi)$ must be written as the sum of the entropy of the marginal distribution (43) and the classical average of the entropy of the conditional one we obtain

$$\begin{aligned} S\left[\hat{\rho}^{\otimes k}(\xi)\right] &= -k_B \int_{M_C} \mathrm{d}\mu_C(\xi) F_C(\xi) \log F_C(\xi) - k_B \int_{M_C} \mathrm{d}\mu_C(\xi) F_C(\xi) \mathrm{Tr}_k\left(\hat{\rho}_\xi^{\otimes k} \log \hat{\rho}_\xi^{\otimes k}\right) \\ &= -k_B \int_{M_C} \mathrm{d}\mu_C(\xi) \mathrm{Tr}_k\left(\hat{\rho}^{\otimes k}(\xi) \log \hat{\rho}^{\otimes k}(\xi)\right). \end{aligned} \tag{44}$$

This function represents the entropy of the hybrid system modeled by the k-th quantum moment. Using this entropy function, we may consider searching for the state $\hat{\rho}^{\otimes k+1}(\xi)$ which maximizes the entropy subject to some constraints to use in the right hand side of Eq. (41). The natural constraint is asking this first unknown moment to produce the last known one by trace, i.e., we will search for a $k+1$ moment such that

$$\mathrm{Tr}_1 \hat{\rho}^{\otimes k+1}(\xi) = \hat{\rho}^{\otimes k}(\xi), \tag{45}$$

where $\hat{\rho}^{\otimes k}(\xi)$ is the moment whose dynamics is being defined. The unknown components of the moment are thus only the degrees of freedom being integrated out by the trace. As it is not possible to determine that information by any measurement, we select the state with the maximum possible entropy for those degrees of freedom to act as a source for the dynamical equation. In the following we shall represent as $\hat{\rho}^{\otimes k}_{\mathrm{MaxEnt}}(\xi)$ the state which maximizes the entropy with constraint (45).

Notice that we are using the MaxEnt formalism from the point of view of information (see [32]), and not as it is usually done when trying to identify thermodynamical ensembles. Those thermodynamical problems can also be considered, though. The entropy function would be the same, but depending on the problem, other constraints would be considered. For instance, we may study the state which maximizes entropy (44) while keeping the normalization and the average value of the Hamiltonian $\hat{H}(\xi)$ fixed. This would produce the candidate to model the canonical ensemble in our context, as we considered in [24] for the case of the first moment. In a similar way we may consider a microcanonical ensemble $\hat{\rho}^{\otimes k}_{MCE}(\xi)$. All these situations will be considered in detail in a forthcoming paper.

We conclude thus that this MaxEnt formalism with constraint (45) provides us with a natural candidate to represent the state $\hat{\rho}^{\otimes k+1}(\xi)$ in Eq. (41). As there is no physical measurement which can inform us about the state, we consider it to be the state which maximizes the uncertainty about it, which is precisely $\hat{\rho}^{\otimes k+1}_{\mathrm{MaxEnt}}(\xi)$. Therefore, we can write as effective dynamics for the k-th quantum moments which is the equation:

$$\dot{\hat{\rho}}^{\otimes k}(\xi) = [\hat{H}^k(\xi), \hat{\rho}^{\otimes k}(\xi)] + \mathrm{Tr}_1\left(\left\{\hat{H}(\xi) \otimes \overbrace{\mathbb{I} \otimes \cdots \otimes \mathbb{I}}^{k}, \hat{\rho}^{\otimes k+1}_{\mathrm{MaxEnt}}(\xi)\right\}_C\right). \tag{46}$$

This equation is well defined, since it only depends on the degrees of freedom of the k-th moment (given that the constraint (45) must hold for all times) and can be used to approximate the dynamics of the average values of physical magnitudes in a finite range of times for statistical systems whose microstates follow Ehrenfest dynamics.

Example 2 In order to provide a practical application of our framework, let us consider again the simple example considered above of a system with two dimensional classical phase space and a two level quantum system. Let us assume, for simplicity, that we just consider Eq. (46) the first quantum moment. In that case, we have to identify the solution of Maximal Entropy for the case $k+1=2$. Let us proceed.

First of all, we are going to consider the factorization in marginal and conditional probabilities given by Eq. (11), for $\hat{\rho}(\xi)$ and $\hat{\rho}_\xi^{\otimes 2}$:

$$\hat{\rho}(\xi) = F_C(\xi)\hat{\rho}_\xi; \qquad \hat{\rho}^{\otimes 2}(\xi) = F_C(\xi)\hat{\rho^{\otimes 2}}_\xi. \tag{47}$$

By construction, $\hat{\rho}_\xi$ is written as a combination of the basis $\{\hat{\sigma}_j\}_{j=0,1,2,3}$, and therefore $\hat{\rho^{\otimes 2}}_\xi$ must be written as a combination of the 10-dimensional symmetrical basis $\{\frac{1}{2}(\hat{\sigma}_j \otimes \hat{\sigma}_k + \hat{\sigma}_k \otimes \hat{\sigma}_j)\}_{j\leq k=0,1,2,3}$. The corresponding expressions read:

$$\hat{\rho}_\xi = \sum_{j=0}^{3} \mu_j \hat{\sigma}_j; \tag{48}$$

$$\hat{\rho}_\xi^{\otimes 2} = \mu_{00}\hat{\sigma}_0 \otimes \hat{\sigma}_0 + \frac{1}{2}\sum_{k=1}^{3} \mu_{0k}(\hat{\sigma}_0 \otimes \hat{\sigma}_k + \hat{\sigma}_k \otimes \hat{\sigma}_0) \tag{49}$$

$$+ \frac{1}{2}\sum_{j\leq k=1}^{3} \mu_{jk}(\hat{\sigma}_j \otimes \hat{\sigma}_k + \hat{\sigma}_k \otimes \hat{\sigma}_j), \tag{50}$$

where we can relate these coordinates with the average values with respect to the conditional distribution F_ξ^{cond} of the coordinate functions of the points of M_Q as:

$$\mu_j = \mathbb{E}(\mu_j(\rho_\psi)); \qquad \mu_{jk} = \mathbb{E}(\mu_j(\rho_\psi)\mu_k(\rho_\psi)), \tag{51}$$

$\mu_j(\rho_\psi)$ representing the j-th coordinate of the pure state ρ_ψ with respect to the basis $\{\hat{\sigma}_j\}$.

Furthermore, as $\hat{\rho}_\xi$ and $\hat{\rho}_\xi^{\otimes 2}$ are density matrices, their trace must be normalized. This implies that

$$\mu_0 = \frac{1}{2}, \qquad \mu_{00} = \frac{1}{4}. \tag{52}$$

In this context, constraint (45) implies that

$$2\mu_{0j} = \mu_j, \quad j = 1, 2, 3.$$

Notice, though, that from the definition of $\hat{\rho}^{\otimes 2}(\xi)$ there are also a few relations between the coordinates, to be fulfilled. In particular

- As $\hat{\rho}_\xi$ must be a well-defined density matrix, we know that its purity must be lower or equal to one, i.e.

$$\sum_j \mu_j^2 \leq \frac{1}{2}. \tag{53}$$

- An analogous property holds for $\hat{\rho}_\xi^{\otimes 2}$: its purity must also be lower than one, i.e.,:

$$4\left(\mu_{00}^2 + \frac{1}{2}\sum_k \mu_{0k}^2 + \frac{1}{2}\sum_{i\leq j} \mu_{ij}^2\right) \leq 1 \Rightarrow \sum_k \mu_{0k}^2 + \sum_{i\leq j} \mu_{ij}^2 \leq \frac{3}{8}. \tag{54}$$

- As μ_{jj} is the expectation value of the square of the function $\mu_j(\rho_\psi)$ on M_Q we can easily verify that

$$\mu_{jj} - \mu_j^2 = \mathbb{E}(\mu_j^2(\rho_\psi)) - \mathbb{E}(\mu_j(\rho_\psi))^2 = \mathbb{E}\big((\mu_j(\rho_\psi) - \mu_j)^2\big) \geq 0, \tag{55}$$

  since the variance of the function $\mu_j(\rho_\psi)$ must be positive definite for a well-defined probabilistic system.
- As points $\rho_\psi \in M_Q$ are pure states, $\sum_j \mu_j^2(\rho_\psi) = \frac{1}{2}$ and therefore

$$\sum_{j=1}^{3} \mu_{jj} = \mathbb{E}\left(\sum_j \mu_j^2(\rho_\psi)\right) = \mathbb{E}\left(\frac{1}{2}\right) = \frac{1}{2}. \tag{56}$$

- Analogously, we can verify that, from Cauchy-Schwartz inequality

$$|\mu_{ij} - \mu_i\mu_j| \leq \sqrt{(\mu_{ii} - \mu_i^2)(\mu_{jj} - \mu_j^2)} \tag{57}$$

With these constraints, we search for the MaxEnt solution for the hybrid entropy function (44). The result defines a relation between the free variables of $\hat{\rho}_\xi^{\otimes 2}$ with the other variables, i.e. which depend on those of $\hat{\rho}_\xi$:

$$\mu_{jk} = \mu_{jk}(\mu_l); \qquad j,k = 1,2,3, \quad l = 1,2,3. \tag{58}$$

Computing entropy involves a complicated expression of the logarithm of $\hat{\rho}^{\otimes 2}(\xi)$ (or, analogously, of $\hat{\rho}_\xi^{\otimes 2}$ if we use the marginal-conditional factorization). For the sake of simplicity, instead computing the spectrum of the matrix, we can use Mercator series to approximate it by a polynomial of the traces of the powers of the matrix, i.e.

$$S^{\text{cond}} = -\text{Tr}(\hat{\rho}_\xi^{\otimes 2} \log \hat{\rho}_\xi^{\otimes 2}) \simeq \text{Tr}\left(\hat{\rho}_\xi^{\otimes 2}\left(\left(\mathbb{I} - \hat{\rho}_\xi^{\otimes 2}\right) + \frac{1}{2}\left(\mathbb{I} - \hat{\rho}_\xi^{\otimes 2}\right)^2 + \cdots\right)\right) \tag{59}$$

Keeping only the linear approximation of the entropy, we would obtain

$$S^{\text{cond}} \simeq 1 - \text{Tr}\left(\hat{\rho}_\xi^{\otimes 2}\right)^2 = 1 - 4\left(\mu_{00}^2 + \frac{1}{2}\sum_k \mu_{0k}^2 + \frac{1}{2}\sum_{i\leq j}\mu_{ij}^2\right). \tag{60}$$

Maximizing this function in the region compatible with the constraints above, considering the symmetry between the different group of indices, can be achieved by fixing:

$$\begin{cases} \mu_{0k} = \frac{\mu_k}{2} \text{ for } k = 1,2,3 \\ \mu_{jk} = 0 \text{ for } j \neq k = 1,2,3 \\ \mu_{kk} = \mu_k^2 + \frac{1}{3}\left(\frac{1}{2} - \mathcal{P}(\hat{\rho}_\xi)\right) \text{ for } k = 1,2,3 \end{cases} \tag{61}$$

where $\mathcal{P}(\hat{\rho}_\xi) = \sum_j \mu_j^2$ represents the purity of the state $\hat{\rho}_\xi$. This point can be considered just a simple approximation to the real MaxEnt solution, but it helps us to illustrate how our construction works. Higher order approximations can be implemented with numerical tools on the expansion above.

With the solution of the MaxEnt problem we can write Eq. (46) becomes, written in terms of the coordinates as:

$$\dot{\mu}_0(\xi) = \sum_{k=0}^{3}\{H_k(\xi), \mu_k(\xi)\}_C \tag{62}$$

$$\dot{\mu}_j(\xi) = \sum_{kl} c_{kl}^j \mu_k(\xi) H_l(\xi) + \frac{1}{2}\{H_0(\xi), \mu_j(\xi)\}_C + \sum_{k=1}^{3}\{H_k(\xi), \mu_{jk}(\xi)\}_C, \quad j = 1,2,3 \tag{63}$$

where we used that c_{kl}^j represent the structure constants of $\mathfrak{u}(2)$ in the basis we chose, $\mu_j(\xi) = F_C(\xi)\mu_j$ and $\mu_{jk}(\xi) = F_C(\xi)\mu_{jk}$.

We can see in these equations how classical and quantum degrees of freedom evolve coupled, the marginal classical density $\mu_0(\xi) = F_C(\xi)$ depending on the quantum degrees of freedom $\mu_j(\xi)$, whose evolution is also governed by $\mu_0(\xi)$. Furthermore, from the expressions of Eqs. (61) and (62) and (63), it is immediate to see that the final dynamics of $\hat{\rho}(\xi)$ is nonlinear.

4 Conclusions

In this paper, we have considered the problem of dynamical statistical systems for hybrid quantum-classical systems having Ehrenfest dynamics as microstate dynamics. We have seen how dynamical evolution (or any other type of observable-generated transformation) enlarges the set of physically observable magnitudes since it introduces correlations between the magnitudes of the form $\hat{A}(\xi)$ which are the natural models of hybrid magnitudes. The nonlinearity introduced by the classical subsystem is responsible of that correlation, which produces a progressive enlargement of the hybrid subalgebra. This implies that, while (linear) hybrid observables depend only on the first quantum moment of the distribution, higher quantum moments are required to compute the evolution of the average value of physical observables. For a given time interval and a certain accuracy, only a finite number of those quantum moments are required to approximate the evolution of the average values of arbitrary physical magnitudes. These quantum moments are also useful to implement a consistent notion of hybrid entropy in a simple way since they take the form of a family of density matrices indexed by the classical degrees of freedom, which encode in a simple way the exclusivity of quantum (and hence hybrid) events. In future works, we plan to analyze in detail the implications of these new entropy functions, and some relevant examples of ensembles arising from them, such as the canonical or micro-canonical ensembles. Furthermore, the stability of the resulting distributions with respect to the dynamics can now be studied in a simple way. Following that direction, the analysis of equilibrium thermodynamics of hybrid systems is a feasible objective.

We have also been able to re-write the Liouville Ehrenfest dynamics of the full probability density at the level of the quantum moments. We have obtained a series of coupled differential equations for the set of quantum moments to encode the physical content of Liouville equation. Furthermore, using the fact that only a finite number of quantum moments are required to model the system for finite time intervals, we have considered the problem of defining the dynamics with a finite number of those equations. In order to do that, we need to write the effect of the next moments on the highest one. As those higher moments cannot be determined by physical measurements, we choose to represent those degrees of freedom by the state, compatible with the constraints of the problem, which maximizes the hybrid entropy at that level. With this choice, a well-defined differential equation can be written for the system.

An important consequence of our results is the change it implies at the level of implementing numerical simulations of statistical hybrid systems. We have learned that an accurate description of a statistical hybrid system requires taking into account the correlation between quantum observables mediated by the nonlinear classical subsystem, i.e., the enlargement of the algebra of hybrid observables. This property incorporates into the description more quantum moments which are not required to obtain the initial average values of physical magnitudes, but that are necessary to estimate their evolution. From the point of view of numerical simulation this introduces some difficulties, since incorporating these higher order correlations into the usual simulation methods as the use of independent (pure-state) trajectories is not an easy task. While fixing values of single operators is simple, considering correlations

of several magnitudes represents a new numerical challenge. The issue of knowing the statistical value of the correlations between observables is closely related to the issue of preparation of statistical quantum (in this case, hybrid) states. On the other hand, the preparation of states is very often implemented in simulations through a sampling over quantum phase space of initial conditions that reproduce the average initial values of the characterized observables. Our results show that for non linear dynamics it is not feasible to just approximate the quantum state as a bundle of trajectories with a statistical sampling over quantum phase space of initial conditions, knowing just the expectation value of operators. The main difference with von Neumann's evolution is that such master equation given in terms of $\hat{\rho}$ is linear on quantum projectors and such linearity preserves the original sampling throughout the evolution. In this hybrid case, such sampling must reproduce correlations and higher order observables up to the desired level of precision (associated with $k+1$ in the truncation above), or work directly to the set of k density matrices, characterized through such measurements, to be able to implement the coupled evolution between subsequent powers of quantum projectors in such nonlinear dynamics.

Acknowledgements The authors acknowledge partial finantial support of Grant PID2021-123251NB-I00 funded by MCIN/AEI/10.13039/501100011033 and by the European Union, and of Grant E48-23R funded by Government of Aragón. C.B-M and D.M-C acknowledge financial support by Gobierno de Aragón through the grants defined in ORDEN IIU/1408/2018 and ORDEN CUS/581/2020 respectively.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

Data Availability Statement No Data associated in the manuscript

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2.4 Article:

Hybrid Koopman $C^\star$–formalism
and the hybrid quantum–classical master equation

PAPER

Hybrid Koopman C^*–formalism and the hybrid quantum–classical master equation*

IOP Publishing Journal of Physics A: Mathematical and Theoretical
J. Phys. A: Math. Theor. **56** (2023) 374001 (19pp) https://doi.org/10.1088/1751-8121/aceed5

Hybrid Koopman C^*–formalism and the hybrid quantum–classical master equation*

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Received 4 February 2023; revised 4 August 2023
Accepted for publication 9 August 2023
Published 23 August 2023

Abstract

Based on Koopman formalism for classical statistical mechanics, we propose a formalism to define hybrid quantum–classical dynamical systems by defining (outer) automorphisms of the C^* algebra of hybrid operators and realizing them as linear transformations on the space of hybrid states. These hybrid states are represented as density matrices on the Hilbert space obtained from the hybrid C^*–algebra by the GNS construction. We also classify all possible dynamical systems which are unitary and obtain the possible hybrid Hamiltonian operators.

Keywords: Koopman methods, C^* algebras, hybrid quantum–classical systems

1. Introduction

Hybrid quantum–classical systems are physical models of systems where quantum degrees of freedom interact with classical ones. Their most common application is to approximate full quantum models to simplify them while keeping an accurate model of the most relevant degrees of freedom. The most paradigmatic example are molecular models where most of the degrees of freedom are treated classically while using a quantum system to model the behavior of the most external electrons which are responsible for the chemical properties of the system.

* Contribution to the Special Collection 'Koopman Methods in Classical and Quantum-Classical Mechanics'.
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There are many different approaches to define hybrid dynamical systems for molecular systems (see [47] for a nice review), some of them are based on hybrid dynamics on the space of hybrid states [1, 4–6, 27, 28, 48], others are algorithmic (see [43–45]), others are obtained as suitable limit equations of the full-quantum dynamics [30, 31, 34, 35, 38]. Hybrid dynamical models appear also in other contexts, as those considering the problem of measurements of quantum systems with classical devices [12, 42] and other type of systems (see [19, 20, 26, 37] and references therein). More recently, some new approaches based on Koopman's formalism for classical statistical mechanics have been introduced with several remarkable contributions [8, 22, 23].

Among the different dynamical models, one of the most common is the Ehrenfest model, which can be easily obtained from the original full quantum one within a semiclassical description [9]. Let us use it as a reference example to explain the whole framework. Ehrenfest equations are defined on the Cartesian product of the classical and quantum phase spaces $M_C \times M_Q$, which represent the hybrid pure states. This dynamics can be proved to admit a Hamiltonian description with a suitable hybrid Poisson bracket and a hybrid Hamiltonian function, which combines the classical and the quantum energies. This property can be used to define a dynamical statistical model with Ehrenfest equations as dynamics of the microstates [5]. In this statistical description, the state of the system is defined as a probability distribution on the hybrid phase-space, which follows a Liouville equation defined by a hybrid Hamiltonian function. Thus, the dynamics on the probability density (i.e. the state) is defined as the dual to the dynamics on the space of hybrid observables. This is a natural way to define a consistent statistical mechanical system leading to a well defined thermodynamics (see [7]). This statistical description has relevant applications [4, 6] but also some limitations, as the difficulty to write an entropy function and the corresponding notion of canonical ensemble [3] or, in more general terms, of an equilibrium thermodynamics. From the mathematical point of view, these limitations are associated with the incompatibility of the notion of hybrid state as a probability density on the phase space and the definition of hybrid entropy, which require an alternative notion of state. Indeed, the usual choice to represent the state of the hybrid system is a family of quantum-density-matrix-like operators, parametrized by classical variables. This type of hybrid states has been used extensively since the early eighties (see [2]) and it is used in many of the references presented above. But the challenge is to define a consistent master equation for this object, satisfying that:

- it is inner in the space of hybrid states, i.e. the defining properties of the state such as positiveness, normalization, etc are preserved at all times;
- and it is dual to the dynamics of the observables;

which are the conditions required by the usual construction in Statistical Mechanics (see [7]). This is a complicated task that, to the best of our knowledge, has not been satisfactorily solved yet.

Our aim in this paper is to provide a new solution for this problem by changing our approach: instead of directly looking for possible master equations, we will consider the dynamics on the space of hybrid observables in a different way. First, we will build a hybrid C^*–algebra defined as the tensor product of the classical and the quantum C^*–algebras of observables of each subsystem. This is the same algebra that we would obtain if we model the physical system as a pure quantum one, and then take the classical limit of one of its subsystems. Then, we will borrow Koopman's idea to define dynamics on the space of observables by defining an outer automorphism of the C^*–algebra, and implement that condition on our hybrid observables. In order to do that, we will use the GNS construction [24, 40, 41] to define

a suitable representation of the algebra on a hybrid Hilbert space. In this way, we can impose linearity to the dynamics in a natural way, and make the treatment much more simple. Once the dynamics on the observables is defined, we will build a consistent master equation defining the dynamics of the physical state as the dualized system. In the general case, several conditions must be imposed for the dynamics to be defined on the space of states. In this work, we will consider only the simplest case of unitary dynamics, where these conditions are immediately satisfied, but many others are admissible and will be considered and analyzed in a forthcoming paper.

The structure of the paper is as follows. In section 2 we will consider the mathematical tools which will be used in the rest of the paper. First, we will summarize Koopman's formalism for classical statistical mechanics. Then, we will briefly discuss the notion of C^*–algebra, the GNS construction and the notion of state. Finally, we will present these constructions for the simple cases of the set of observables of classical and quantum systems. With these tools, we will build in section 3 the notion of hybrid C^*–algebra and will characterize their states and the corresponding GNS representation. In section 4 we will use Koopman's idea to define outer automorphisms of the hybrid algebra and discuss all the conditions that the dualized dynamics on the space of hybrid states must satisfy. Then, we will identify the simplest of these dynamics which will define unitary transformations of the GNS–Hilbert space. Finally, in section 5 we will summarize our main conclusions and discuss the analysis of alternative solutions which will be presented in future papers.

2. Mathematical preliminaries

2.1. Koopman formalism for classical statistical mechanics

We will follow [16] in this brief summary. Let us consider a classical statistical system defined on a symplectic manifold (M,ω) of dimension n, through a measure μ defined by a probability density $\rho : M \to \mathbb{R}$, satisfying

$$\mu(M) = \int_M \mathrm{d}\mu = \int_M \rho \,\mathrm{d}\Omega = 1, \qquad \mathrm{d}\Omega = \omega^n.$$

Consider the Hilbert space $\mathcal{L}^2(M)$ defined by square-integrable functions $f : M \to \mathbb{C}$ with respect to the scalar product

$$\langle f_1, f_2 \rangle = \int_M \bar{f}_1 f_2 \mathrm{d}\,\Omega. \tag{1}$$

If we consider thus the state $\psi_\rho \in (\mathcal{L}^2(M), \mathrm{d}\Omega)$ satisfying the condition

$$\rho = \bar{\psi}_\rho \psi_\rho. \tag{2}$$

This object will represent the state of our statistical system in terms of the Hilbert space $\mathcal{L}^2(M)$.

If we consider a Hamiltonian dynamical system X_M on M, it defines a Liouville equation for the probability density ρ in the formalism

$$\dot{\rho} = -X_H(\rho). \tag{3}$$

The corresponding flow $F_t : M \to M$ is a symplectomorphism $F_t^* \omega = \omega$, and therefore it defines a unitary transformation on $\mathcal{L}^2(M)$:

$$U_t(f) = F_t^* f, \qquad \forall f \in C^\infty(M) \subset \mathcal{L}^2(M). \tag{4}$$

The result follows immediately from Liouville theorem and the linearity of the pullback of any differentiable mapping.

Being a unitary transformation, Stone theorem ensures the existence of a self-adjoint operator L satisfying

$$U_t = e^{-iLt}. \tag{5}$$

Being the infinitesimal generator of the Hamiltonian evolution U_t defined above, L must be determined by the Hamiltonian vector field X_H, i.e.

$$L\psi_\rho = -iX_H(\psi_\rho) = -i\left(\frac{\partial H}{\partial q^k}\frac{\partial}{\partial p_k} - \frac{\partial H}{\partial p_k}\frac{\partial}{\partial q^k}\right)\psi_\rho, \tag{6}$$

where (q^k, p_k) represent a chart of Darboux coordinates on M. This unitary operator translates the dynamics to the functions ψ_ρ which thus satisfy

$$i\dot{\psi}_\rho = L\psi_\rho. \tag{7}$$

We can see that the classical wave functions are functions of both positions and momenta, and that the infinitesimal generator of the unitary evolution is a first-order differential operator. It is immediate from these relations to re-obtain in this quantum language the Liouville continuity equation (3) for $\rho = \bar{\psi}_\rho\psi_\rho$.

From the point of view of the operators, notice that q's and p's are analogous variables and therefore the operators having those variables as spectrum ($\hat{Q}$ and $\hat{P}$) must behave as multiplicative operators and hence they must commute. By extension, we can conclude that the whole algebra of classical observables is commutative when realized as linear operators on the Hilbert space. Hence, if we consider the Heisenberg picture on that algebra, we conclude that it is not possible to define an evolution corresponding to the action of the commutator with a Hamiltonian contained in the algebra, i.e. we cannot consider inner automorphisms. On the other hand, if we consider the adjoint action of the Hamiltonian operator (6), we can define a non-trivial evolution on the space of linear operators of $\mathcal{L}^2(M)$. Furthermore, the Hamiltonian (6) is chosen in such a way that the commutative subalgebra corresponding to the classical operators is preserved by the evolution, i.e. the evolution defines an automorphism of the classical subalgebra. Some other dynamics can also be considered, with analogous results on the classical system but small differences in the quantum model (see [29]).

In conclusion, Koopman formalism defines a commutative algebra of operators representing the classical magnitudes, which is represented as a subalgebra of the total space of linear operators of the Hilbert space $\mathcal{L}^2(M)$. Dynamics corresponds to an outer-automorphism of that subalgebra, generated by the Hamiltonian operator (6).

2.2. Operator C^*–algebras and the GNS construction

We will now consider the set of observables of our theory in more detail. In order to do that we are going to consider the C^* algebras containing the set of classical, quantum and hybrid operators. For details on these topics, see [10, 33].

Given a C^*–algebra $\mathcal{A}$, we can consider its dual space $\mathcal{A}^*$ and use the norm on the algebra to define a norm on the dual space. Indeed, given $\omega \in \mathcal{A}^*$, we define its norm as

$$\|\omega\| = \sup\{|\omega(a)|, \|a\| = 1\}. \tag{8}$$

The involution on $\mathcal{A}$ allows also to introduce a notion of positivity for linear functionals, and thus for states. Thus, given $\omega \in \mathcal{A}^*$ we say that it is positive definite if

$$\omega(a^*a) \geqslant 0 \qquad \forall a \in \mathcal{A}. \tag{9}$$

Definition 2.1. A **state** of a C^*–algebra $\mathcal{A}$ is defined as a positive linear functional on $\mathcal{A}$ with norm equal to one.

Finally, GNS construction (see [24, 40, 41]) ensures that given a C^*–algebra $\mathcal{A}$ and a state ω, we can always build a representation π of $\mathcal{A}$ on the set of (bounded) linear operators on a Hilbert space $\mathcal{B}(\mathcal{H})$ where the state is associated to a cyclic vector of $\mathcal{H}$, whose orbit under the representation of $\mathcal{A}$ is dense in $\mathcal{H}$. This result allows us to recover the description of the elements of any C^* algebra as linear operators on a suitable Hilbert space.

Let us see now how this concept allows us to recover Koopman's construction in a simple way, and introduce a treatment of hybrid quantum–classical systems in these algebraic terms.

2.3. Examples: classical and quantum systems

Let us consider two examples which are relevant for us: the set of observables of a classical system, and the set of observables of a quantum one. As the quantum case is simpler and will provide us with some valuable properties, we will consider it first.

2.3.1. The quantum case. Again, for the sake of simplicity we will consider the algebra of bounded operators $\mathcal{B}(\mathcal{H})$ over a Hilbert space $\mathcal{H}$ with respect to composition; and the Hermitian adjoint as the involution $A^* = A^\dagger$. Furthermore, we consider the norm of an operator A

$$\|A\| = \sup\{\|A\psi\|, \quad \psi \in \mathcal{H},\ \|\psi\| = 1\}. \tag{10}$$

Again, it is a well known fact that this set which will be denoted in the following as $\mathcal{A}_Q$ becomes thus a C^*–algebra. Such an algebra contains the set of observables of a quantum system, which corresponds to the subset of self-adjoint operators:

$$L = \left\{A \in \mathcal{A}_Q | A^\dagger = A\right\}. \tag{11}$$

Finally, regarding the set of states of $\mathcal{A}_Q$, it is well known that the set of quantum states is in one-to-one correspondence with the set of density matrices $\mathcal{D}(\mathcal{H})$ on the Hilbert space $\mathcal{H}$:

$$\mathcal{D}(\mathcal{H}) = \left\{\hat{\rho} \in \mathcal{B}(\mathcal{H}) \,|\, \hat{\rho} = \hat{\rho}^\dagger; \hat{\rho} > 0; \mathrm{Tr}\hat{\rho} = 1\right\}. \tag{12}$$

From Gleason theorem (see [25]), we know that with this set we are considering all possible states of a quantum system whose state space corresponds to a Hilbert space $\mathcal{H}$:

Theorem 2.2 (Gleason). *Let $\mathcal{H}$ be a separable Hilbert space with dimension greater than 2 and let μ be a measure defined on the closed subspaces of $\mathcal{H}$. Then, there exists a positive semi-definite self adjoint operator $\hat{\rho}$ of the trace class, satisfying that for any closed subspace $A \subset \mathcal{H}$,*

$$\mu(A) = \mathrm{Tr}(\hat{\rho} P_A),$$

where $P_A : \mathcal{H} \to \mathcal{H}$ is the orthogonal projection of the Hilbert space on A.

This result justifies the use of density matrices to represent the states of any quantum system for it encodes completely the probabilistic nature of the state (remember that the physical magnitudes, being represented by self-adjoint operators, can be written, by means of their spectral decompositions, as real linear combination of those orthogonal projectors).

Going back to the representation of the C^*–algebra, it is also well known that the GNS construction defines an irreducible representation of $\mathcal{A}_Q$ if we select a pure state, and a reducible one if the density matrix is a mixed state (see [21]). The corresponding GNS representation $\pi_Q : \mathcal{A}_Q \to \mathcal{B}(\mathcal{H}_Q)$ is the natural one.

2.3.2. The classical case. For the sake of simplicity we will consider as an example to model the set of physical observables of a classical system the set of compactly supported complex functions on a manifold M_C, $C_c(M_C,\mathbb{C})$, although other possibilities may also be considered with analogous properties. In order to endow this set with a C^*–algebra structure we will use:

- the pointwise algebra $\cdot_C$
- the complex conjugation as involution $f^*(x) = \bar{f}(x)$,
- and the supremum norm $\|f\| = \sup\{|f(x)| \mid x \in M_C\}$.

It is immediate to verify that the set $\mathcal{A}_C = C_c(M_C,\mathbb{C})$ becomes thus a Banach algebra. This algebra can be considered to contain the (bounded) physical observables of a classical system (since the condition on compactness is a technical restriction which does not introduce serious physical limitations).

Finally, let us consider the states of $\mathcal{A}_C$. From the definition, they must correspond to the positive-definite elements of the dual space having norm equal to 1. From the Riesz–Markov representation theorem (see, for instance, [39]), we know that the set of states on $\mathcal{A}_C$ coincides with the set of (Radon) measures on the domain of the classical functions, i.e. given $\omega \in \mathcal{A}_C^*$, there exists a measure μ satisfying

$$\omega(a) = \int_{M_C} \mathrm{d}\mu\, a, \qquad \forall a \in \mathcal{A}_C. \tag{13}$$

If we consider a reference measure on M_C, as it might be the symplectic phase-space volume $\mathrm{d}\Omega$, for most states (i.e. excluding particular cases as the Dirac delta) we can compute the corresponding Radon-Nikodym derivative and obtain thus a density $F_C : M_C \to \mathbb{R}^+$ satisfying

$$\omega(f) = \int_{M_C} \mathrm{d}\Omega\, F_C a, \qquad \forall a \in \mathcal{A}_C. \tag{14}$$

From the physical point of view, states on $\mathcal{A}_C$ correspond then to statistical ensembles on the classical phase space with probability density F_C. This is the starting point of Koopman original proposal, a certain classical probability density. We can reproduce Koopman construction by considering the representation, via GNS construction, of the system on a Hilbert space. It is well known, that the GNS construction for $\mathcal{A}_C$ with state (14) defines the representation $\pi_C : \mathcal{A}_C \to \mathcal{B}(\mathcal{H}_C)$ as a set of multiplicative operators acting on the Hilbert space $\mathcal{H}_C = \mathcal{L}^2(M_C, \mathrm{d}\mu)$, as we saw in section 2.1.

Once on the Hilbert space $\mathcal{H}_C$, we know from Gleason theorem that the state can be written as an element of the set of density matrices $\mathcal{D}(\mathcal{H}_C)$. We can write, in a simple way, the expression of the density matrix on $\mathcal{H}_C$ in terms of the original classical density:

Proposition 2.1. *Consider a classical state ω of the classical C^*–algebra $\mathcal{A}_C$, defined by a probability density function F_C with respect to a measure* $\mathrm{d}\Omega$

$$\omega = F_C \mathrm{d}\Omega,$$

where $d\Omega$ defines the cyclic vector of the GNS representation of $\mathcal{A}_C$. Then, the expression of the density matrix associated with ω by the GNS representation can be written as:

$$\hat{\rho}_C = \int_{M_C} \mathrm{d}\Omega(\xi) \int_{M_C} \mathrm{d}\Omega(\xi') \sqrt{F_C(\xi) F_C(\xi')} |\xi\rangle\langle\xi'|. \tag{15}$$

Proof. Indeed, if we take a function $a(\xi) \in \mathcal{A}_C$, and consider the multiplicative operator $\pi_C(a) = a(\xi)$, it follows

$$\mathrm{Tr}\left(\hat{\rho}_C \pi_C(a)\right) = \int_{M_C} \mathrm{d}\Omega(\xi) \int_{M_C} \mathrm{d}\Omega(\xi') \sqrt{F_C(\xi) F_C(\xi')} \mathrm{Tr}\left(|\xi\rangle\langle\xi'| \pi_C(a)\right).$$

As the classical algebra acts as multiplicative operators on $\mathcal{H}_C$,

$$\mathrm{Tr}\left(|\xi\rangle\langle\xi'| \pi_C(a)\right) = a(\xi)\delta(\xi - \xi'), \tag{16}$$

we obtain that

$$\begin{aligned} \mathrm{Tr}\left(\hat{\rho}_C \pi_C(a)\right) &= \int_{M_C} \mathrm{d}\Omega(\xi) \int_{M_C} \mathrm{d}\Omega(\xi') \sqrt{F_C(\xi) F_C(\xi')} a(\xi)\delta(\xi - \xi') \\ &= \int_{M_C} \mathrm{d}\Omega(\xi) F_C(\xi) a(\xi) = \omega(a), \qquad \forall a \in \mathcal{A}_C. \end{aligned} \tag{17}$$

□

3. The hybrid C^*–algebra

Let us now consider the algebra containing the observables of a hybrid quantum–classical system. As in general the hybrid model is obtained as a suitable partial classical limit of a full-quantum model, a natural candidate corresponds to the tensor product of the two C^*–algebras above, i.e. $\mathcal{A}_H = \mathcal{A}_C \otimes \mathcal{A}_Q$. As we are mostly focused on the application to hybrid quantum–classical physical systems, in the following we will consider only the tensor product of the two examples introduced above, even if many of our conclusions may be of interest for the product of arbitrary commutative and non-commutative C^*–algebras.

3.1. The C^*–algebra structure

The hybrid product is defined in terms of the classical and the quantum products on separable states as:

$$(a \otimes A) \cdot_H (b \otimes B) := (a \cdot_C b) \otimes (A \cdot_Q B), \qquad \forall a, b \in \mathcal{A}_C, A, B \in \mathcal{A}_Q. \tag{18}$$

Let us consider now the involution. On the set of elements of the form

$$f = \sum_k \gamma_k a_k \otimes A_k, \quad \gamma_k \in \mathbb{C}, a_k \in \mathcal{A}_C, A_k \in \mathcal{A}_Q, \tag{19}$$

we can consider the operation (18). This makes it an algebra which we will denote as $\mathcal{A}_H$. On that algebra we can consider the involution

$$f^* = \sum_k \bar{\gamma}_k a_k^* \otimes A_k^\dagger, \tag{20}$$

where a_k^* and $A_k^\dagger$ represent the classical and quantum involutions respectively. Clearly, this makes $\mathcal{A}_H$ an involutive algebra.

Regarding the definition of a norm, a few comments are in order (for a more detailed explanation see, for instance, [11]). In principle, there are different possible norms to be defined on the algebraic tensor product $\mathcal{A}_C \otimes \mathcal{A}_Q$ to make the set a C^*–algebra. But as we are interested in the GNS construction, the most natural candidate seems to be the *spatial norm* defined by the inclusion of $\mathcal{B}(\mathcal{H}_C) \otimes \mathcal{B}(\mathcal{H}_Q)$ in $\mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ and the definition of a representation

$$\pi_H = \pi_C \otimes \pi_Q, \tag{21}$$

with the norm

$$\|f\| = \|\pi_H(f)\|_{\mathcal{B}(\mathcal{H}_C\otimes\mathcal{H}_Q)}. \tag{22}$$

The construction was introduced by Turumaru in [46] and does not depend on the particular representations of the factors. Despite the diversity of possible norms in the general case, as $\mathcal{A}_C$ is a commutative algebra and hence a nuclear one, it is possible to prove that the C^* norm on $\mathcal{A}_C \otimes \mathcal{A}_Q$ is unique (see [11]). Hence, we will keep this construction above as the constitutive definition of the hybrid C^*–algebra structure for $\mathcal{A}_H$.

3.2. Hybrid states

As we saw above for a general C^*–algebra, hybrid states must be positive-definite elements of $\mathcal{A}_H^*$ with norm equal to 1. Obviously, the tensor product of a classical state and a quantum one satisfies these requirements. Hence, we may think in an example of hybrid state as the product of a classical measure $d\mu$ on M_C and a quantum density matrix $\hat{\rho}_Q$. This is a particular case of the representation of hybrid states used in the Literature (see [2–4, 6, 8, 12, 14] and references therein). If we use the GNS representation $\pi_H : \mathcal{A}_H \to \mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ to write them as states on $\mathcal{H}_C \otimes \mathcal{H}_Q$, they become a tensor product of density matrices $\hat{\rho}_C \otimes \hat{\rho}_Q$, i.e. this example turns out to be what in the quantum systems literature is called a simply separable state. From a physical point of view, its most remarkable property is the lack of correlations between the two subsystems, classical and quantum.

More general states of $\mathcal{A}_H$ can be written as in the previous references as a family of quantum operators parametrized by classical variables $\hat{\rho}(\xi)$, satisfying the normalization conditions

$$\int_{M_C} \mathrm{d}\mu(\xi)\mathrm{Tr}\hat{\rho}(\xi) = 1. \tag{23}$$

The action on the elements of $\mathcal{A}_H$ is written as

$$\langle f\rangle = \int_{M_C} \mathrm{d}\mu(\xi) \sum_k \gamma_k a_k(\xi)\mathrm{Tr}(\hat{\rho}(\xi)A_k), \tag{24}$$

for an element $f \in \mathcal{A}_H$ written as equation (19). This is the usual representation of hybrid states in the Literature. As we argued above, the definition of a suitable master equation of hybrid dynamics for this type of system is still an open problem. Next section is entirely devoted to the definition of different possible solutions for it.

In order to obtain a few useful properties of these hybrid states $\hat{\rho}(\xi)$ let us consider their representation as elements of $\mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q)$, i.e. as density matrices. Notice that as the hybrid state defines a measure on $\mathcal{A}_H$, from Gleason theorem [25], there must exist a density matrix $\hat{\rho}_H$ to represent the state of the algebra $\pi_H(\mathcal{A}_H)$ on $\mathcal{H}_C \otimes \mathcal{H}_Q$. The states $\hat{\rho}_H$ must satisfy thus:

$$\langle f\rangle = \int_{M_C} \mathrm{d}\mu(\xi)\mathrm{Tr}(\hat{\rho}(\xi)f) = \mathrm{Tr}(\hat{\rho}_H\pi_H(f)), \quad \forall f \in \mathcal{A}_H. \tag{25}$$

Our main interest in this representation as $\hat{\rho}_H$ is that, as we will see below, it will allow us to write a well defined master equation which captures the hybrid dynamics. The definition of the dynamics is a very difficult task if the state is of the form (25) because of the non-linearity of the classical subsystem dynamics (see [13]), but when realized at the level of the Hilbert space $\mathcal{H}_C \otimes \mathcal{H}_Q$ and as external to the algebra $\pi_H(\mathcal{A}_H)$, it is possible to write it in a simple way. This is why we are interested in this generalization of Koopman classical construction.

Inspired by proposition 2.1, we are going to consider states on $\mathcal{H}_C \otimes \mathcal{H}_Q$ of the form

$$\hat{\rho}_H = \sum_{mm'} \int_{M_C} \int_{M_C} \mathrm{d}\Omega(\xi)\mathrm{d}\Omega(\xi')\rho_{mm'}(\xi,\xi')|\xi,m\rangle\langle\xi',m'|, \tag{26}$$

where $\rho_{mm'}(\xi,\xi') := \sqrt{\langle m \mid \hat{\rho}(\xi) \mid m'\rangle\langle m \mid \hat{\rho}(\xi') \mid m'\rangle}$ and $\{|m\rangle\}$ is a basis for $\mathcal{H}_Q$, which will be assumed to be discrete, for simplicity, (although this is not relevant). For those systems, it is immediate to prove:

Lemma 3.3. *If we consider the marginalized state defined by the trace over $\mathcal{H}_C$ of $\hat{\rho}_H$ we obtain the same state over $\mathcal{H}_Q$ defined marginalizing the state $\hat{\rho}(\xi)$ of $\mathcal{A}_H$, i.e.*

$$\mathrm{Tr}_C(\hat{\rho}_H) = \sum_{mm'} \int_{M_C} \mathrm{d}\Omega(\xi)\langle m \mid \hat{\rho}(\xi) \mid m'\rangle \mid m\rangle\langle m' \mid = \int_{M_C} \mathrm{d}\Omega(\xi)\hat{\rho}(\xi), \tag{27}$$

where Tr_C *stands for the partial trace over $\mathcal{H}_C$, i.e. with that operation we can represent the marginalization of the state $\hat{\rho}_H$. More generally, it can be easily shown that:*

$$\mathrm{Tr}_C(\hat{\rho}_H^k) = \int_{M_C} \mathrm{d}\Omega(\xi)\hat{\rho}(\xi)^k\,, \tag{28}$$

Proof. The proof is completely analogous to the one used in the proof of proposition 2.1 and based on the fact that the trace corresponds to a $\delta(\xi - \xi')$ which produces the expressions above. □

With this result, we can conclude:

Proposition 3.1. *The state $\hat{\rho}_H$ given by equation (26) is the density matrix on $\mathcal{H}_C \otimes \mathcal{H}_Q$ corresponding to the hybrid state $\hat{\rho}(\xi)$.*

Proof. Again, the proof is analogous to the classical case. If we consider separable hybrid observables we can write that

$$\begin{aligned}
\omega(a \otimes A) &= \mathrm{Tr}(\hat{\rho}_H \pi_H(a \otimes A)) \\
&= \int_{M_C \times M_C} \mathrm{d}\Omega_C(\xi)\mathrm{d}\Omega_C(\xi')\mathrm{Tr}\left(\sum_{mm'} \rho_{mm'}(\xi,\xi') \mid \xi,m\rangle\langle\xi',m' \mid \pi_H(a \otimes A)\right) \\
&= \int_{M_C} \mathrm{d}\Omega_C(\xi)\mathrm{Tr}_Q\left(\sum_{mm'} \rho_{mm'}(\xi,\xi) \mid m\rangle\langle m' \mid (a(\xi) \otimes A)\right) \\
&= \int_{M_C} \mathrm{d}\Omega_C(\xi)\mathrm{Tr}_Q\left(\hat{\rho}(\xi)(a(\xi) \otimes A)\right)\,,
\end{aligned} \tag{29}$$

where we wrote that $\pi_C(a) = a(\xi)$, is a multiplicative operator on $\mathcal{H}_C$, and we used the previous lemma for the classical trace. Tr_Q represents the partial trace over $\mathcal{H}_Q$, and we use that $\mathrm{Tr} = \mathrm{Tr}_C\mathrm{Tr}_Q$. The proof for general elements of $\mathcal{A}_H$ of the form (19) is immediate. □

3.3. Hybrid entropy function

An important application of this result is the possibility to relate the von Neumann entropy associated with the state $\hat{\rho}_H$ and the hybrid entropy function introduced in [3]. Indeed, our group introduced a hybrid entropy function for states of the form $\hat{\rho}(\xi)$, based on the analysis of mutually exclusive hybrid events, which reads:

$$S_H[\hat{\rho}(\xi)] = -\int_{M_C} \mathrm{d}\mu(\xi)\mathrm{Tr}\left(\hat{\rho}(\xi)\log\hat{\rho}(\xi)\right). \tag{30}$$

Based on this function, we were also able to identify a candidate for hybrid canonical ensemble, using the MaxEnt formalism. For this state to constitute a valid candidate for a thermodynamical equilibrium ensemble, it is necessary to identify a valid dynamics for the hybrid system, having the MaxEnt solution as a stable equilibrium point. Identifying such a hybrid dynamics is the main motivation for this work. As we argued above, searching for such a dynamics on the set of hybrid states of the form $\hat{\rho}(\xi)$ is a difficult task, since the classical subsystem makes the dynamics nonlinear. Our proposal in this work is to generalize Koopman construction, define the hybrid system on a Hilbert space $\mathcal{H}_C \otimes \mathcal{H}_Q$, and search for possible hybrid dynamics on the set $\mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q)$.

In order to do that, our first task is to prove that we can recover write the hybrid entropy function in terms of the hybrid state $\hat{\rho}_H \in \mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q)$. A natural choice is to consider the well-known von Neumann entropy

$$S_{vN}[\hat{\rho}_H] = -\mathrm{Tr}(\hat{\rho}_H \log \hat{\rho}_H).$$

Lemma 3.2. *Let $\hat{\rho}(\xi)$ be a state for the hybrid algebra $\mathcal{A}_H$ and $\hat{\rho}_H \in \mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ the state of the algebra $\pi_H(\mathcal{A}_H) \in \mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$. Then,*

$$S_{vN}[\hat{\rho}_H] = S_H[\hat{\rho}(\xi)].$$

Proof. As the density matrix is self-adjoint and hence diagonalizable, we can consider its spectral decomposition, where the spectrum is nowhere negative. From the properties of the trace and the definition of the logarithm as a series, we can work directly on the spectrum, and obtain:

$$\begin{aligned} S_H[\hat{\rho}_H] &= -\mathrm{Tr}\left(\hat{\rho}_H \sum_{n=1}^{\infty} (-1)^{n-1} \frac{(\hat{\rho}_H - \mathbb{I})^n}{n}\right) \\ &= \mathrm{Tr}\left(\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{k=0}^{n} \binom{n}{k} \hat{\rho}_H^{k+1} (-1)^{n-k}\right) \\ &= \mathrm{Tr}_Q\left(\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{k=0}^{n} \binom{n}{k} \mathrm{Tr}_C(\hat{\rho}_H^{k+1}) (-1)^{n-k}\right). \end{aligned} \tag{31}$$

Making use of (28), we can substitute the partial trace over the classical part by an integral over phase space, and thus:

$$-S_H[\hat{\rho}_H] = \int_{M_C} \mathrm{d}\Omega(\xi) \mathrm{Tr}_Q\left(\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{k=0}^{n} \binom{n}{k} \hat{\rho}(\xi)^{k+1} (-1)^{n-k}\right) = -S_H[\hat{\rho}(\xi)], \tag{32}$$

which is the hybrid entropy function introduced in [3]. □

This is an important result from the physical point of view, since having an entropy function we can apply MaxEnt formalism to identify the state which maximizes the entropy while keeping the average energy fixed. This allows us to write the canonical ensemble of a hybrid system in this generalized Koopman formalism in a straightforward way. From our analysis above, we conclude that it can be obtained from the result identified in [3] using proposition 3.1. It is important to remark, though, that the MaxEnt computation for the case of $\hat{\rho}_H$ must be done with respect to operator $\pi_H(f_H) \in \pi_H(\mathcal{A}_H)$ associated with the hybrid energy function $f_H \in \mathcal{A}_H$, and not with respect to a Hamiltonian operator defining the dynamics as we saw in the Koopman classical formalism. Such an operator may generate the dynamics, but it does not have a physical meaning as energy of the system since it does not belong to the hybrid algebra. We shall discuss these issues in some detail in the following section.

It is also important to emphasize that the MaxEnt argument is completely independent of the dynamics of the microstates, but it only offers possible candidates to equilibrium ensembles. For these MaxEnt solutions to define actual thermodynamical ensembles, it is necessary to prove that the dynamics of the microstates preserves the solution obtained. Hence, the existence of candidates to equilibrium ensembles defines constraints to the possible dynamics that can be considered on the hybrid system, as we discuss in the next section.

4. Hybrid dynamical systems

4.1. Classical and quantum dynamics

As we saw in section 2.1, Koopman's original construction proved that Liouville evolution equation of a classical statistical system on a phase space M_C can be realized as a unitary one-parameter group of transformations on a suitably defined Hilbert space $\mathcal{H}_C$. In order to do that, a Hamiltonian operator on $\mathcal{H}_C$ which does not belong to the classical (commutative) C^*–algebra which contains the set of physical magnitudes, is required (see [32]). From that unitary group of transformations we can define equivalent dynamical systems on the Hilbert space $\mathcal{H}_C$ (via the Schrödinger equation), on the commutative subalgebra of $\mathcal{B}(\mathcal{H}_C)$ defined by the representation $\pi_C : \mathcal{A}_C \to \mathcal{B}(\mathcal{H}_C)$ (via the Heisenberg equation), or on the set of density matrices $\mathcal{D}(\mathcal{H}_C)$ (via von Neumann equation). All three systems are physically equivalent to the solutions of the Liouville equation on the set of statistical states on M_C, or the equivalent Hamiltonian evolution on the Poisson algebra of classical observables. Notice, though, that the dynamics must be defined on $\mathcal{A}_C$ as an outer automorphism since it is commutative and has a trivial Lie structure. We must add an additional Poisson tensor to the set of functions in $\mathcal{A}_C$ to be able to define the dynamics at the level of the algebra. And therefore the resulting dynamical system defines outer-automorphisms of the C^*–algebra. Nonetheless, this construction is compatible with the C^*–algebra description of the classical system (in terms of $\mathcal{A}_C$) presented above and the corresponding GNS representation $\pi_C : \mathcal{A}_C \to \mathcal{B}(\mathcal{H}_C)$. Thus, when written in the Hilbert space language, dynamics takes the usual form, but with a Hamiltonian which does not belong to $\pi_C(\mathcal{A}_C)$. This corresponds to the usual Koopman's construction. Notice that, in the representation process, the non-linear classical Liouville equation (with a Hamiltonian function in the classical algebra) becomes the linear Heisenberg equation (with a Hamiltonian which does not belong to the subalgebra $\pi_C(\mathcal{A}_C)$) or the linear von Neumann equation for the corresponding density matrix. In a certain way, nonlinearities are 'smoothed' by the representation.

The quantum case is different since the definition of a dynamical system on $\mathcal{A}_Q$ is straightforward using its Lie canonical structure and the corresponding Heisenberg equation. Choosing a self-adjoint Hamiltonian in $\mathcal{A}_Q$ (even if non-bounded, in general), we can define a unitary evolution which can be implemented either at the level of the Hilbert space, at the level of the operator algebra, or at the level of the states, exactly as in the classical case. But finite dynamical transformations correspond to bounded operators and hence inner automorphisms of the Lie structure of $\mathcal{A}_Q$.

4.2. Hybrid dynamics

4.2.1. General considerations. Let us consider now the hybrid case. As we explained above, our final goal is to consider possible dynamics of hybrid states in order to identify those which are useful to model statistical quantum–classical systems. Among those, we will have to check

whether or not they have the hybrid canonical ensemble identified with the MaxEnt formalism as a stable fixed point. If we succeed, we would have found an efficient way to model statistical hybrid system at finite temperature, which is a very relevant situation for molecular simulations. In this paper we will just consider the first problem: how to identify possible hybrid dynamics. We will define the problem and classify the solutions which are unitary, as in the case of classical Koopman dynamics. More general solutions and the evaluation on the hybrid canonical ensemble will be considered in future papers.

We will consider directly the GNS representation of the system and therefore a system characterized by some density matrix $\hat{\rho}_H \in \mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ and the algebra $\pi_H(\mathcal{A}_H) \subset \mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$. The problem of defining a dynamical system directly at the level of the algebra $\mathcal{A}_H$ or its dual, which has received much more attention in the Literature, and its relation with our solution in this paper will be considered in a forthcoming publication. In this paper we will consider the definition of dynamics only at the level of the Hilbert space $\mathcal{H}_C \otimes \mathcal{H}_Q$.

From what we learned in the classical and quantum case, it is clear that we are supposed to build an automorphism of the C^* algebra $\mathcal{A}_H$, or, equivalently, of its image $\pi_H(\mathcal{A}_H) \subset \mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$. This automorphism generalizes Koopman construction to the hybrid case. If the dynamics must act on the classical degrees of freedom in a non-trivial way, it should contain external elements to $\mathcal{A}_C$ (and hence to $\mathcal{A}_H$ when multiplied by quantum operators) and define an external automorphism of the subalgebra $\pi_H(\mathcal{A}_H)$. In this way we define a dynamical system on the space of hybrid physical magnitudes, which preserves the set, unlike what Ehrenfest dynamics was seen to do on $\mathcal{A}_H$ [13].

As a generalization of the classical and quantum cases above, we can ask the dynamics to fulfill the following requirement: it may be defined on the whole $\mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ but it must preserve the subalgebra $\pi_H(\mathcal{A}_H)$. For the sake of simplicity, we will consider only linear systems. Therefore, we will consider a dynamical system of the form

$$\frac{\mathrm{d}\pi_H(f)(t)}{\mathrm{d}t} = \mathcal{L}\pi_H(f)(t), \qquad \forall f \in \mathcal{A}_H, \tag{33}$$

where $\mathcal{L}$ represents a linear super-operator on $\mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$ and satisfies $\mathcal{L}(\pi_C(\mathcal{A}_H)) \subset \pi_C(\mathcal{A}_H)$. In that case, we will write the master equation as an equation on the set of states as:

$$\frac{\mathrm{d}\hat{\rho}_H(t)}{\mathrm{d}t} = \mathcal{L}^\dagger \hat{\rho}_H(t), \tag{34}$$

where $\mathcal{L}^\dagger$ represents the adjoint operator to $\mathcal{L}$. For the sake of simplicity, we assume that the operator $\mathcal{L}$ generates a bounded operator $e^{\mathcal{L}t}$. Nonetheless, this just defines a flow on the dual space to $\mathcal{B}(\mathcal{H}_C \otimes \mathcal{H}_Q)$. Furthermore, we know that the set of density matrices $\mathcal{D}(H_C \otimes H_Q)$ corresponds to just a subset of that dual space (since we impose the conditions on the trace and positivity) and we want the dynamics to preserve that subset. These conditions must also be imposed as restrictions on the dynamical system $\mathcal{L}$. Besides, after our analysis on the hybrid entropy and the equilibrium ensembles, it also makes sense to impose some entropic restrictions to the possible dynamical systems. If we want the hybrid dynamics to represent a microstate dynamics for a physical system, the value of von Neumann entropy on $\hat{\rho}_H(t)$ must be constant in time (if the hybrid system is isolated) or increase (if it is not isolated).

A particularly simple case corresponds to the case of unitary dynamics, where there exists a Hamiltonian operator $\hat{H}$ which allows to write the operator $\mathcal{L}$ as its adjoint action, i.e.:

$$\frac{\mathrm{d}\pi_H(f)(t)}{\mathrm{d}t} = -i\left(\pi_H(f)(t)\hat{H} - \hat{H}\pi_H(f)(t)\right), \quad f \in \mathcal{A}_H. \tag{35}$$

In this case, the dual equation (the corresponding von Neumann equation)

$$\frac{\mathrm{d}\hat{\rho}_H(t)}{\mathrm{d}t} = -i\left(\hat{H}\hat{\rho}_H(t) - \hat{\rho}_H(t)\hat{H}\right), \quad \hat{\rho}_H \in \mathcal{D}(\mathcal{H}_C \otimes \mathcal{H}_Q) \tag{36}$$

is known to preserve the set of density states, since it defines the orbits of the coadjoint action of the evolution operator. Furthermore, in this case it is immediate that a unitary transformation preserves the von Neumann entropy of the state, since it preserves its spectrum. We will analyze the properties of these dynamical systems in the following section.

4.2.2. Conditions on the automorphism of $\pi_H(\mathcal{A}_H)$ I: unitary dynamics. For the sake of simplicity, let us first consider the case of a unitary transformation, i.e. we consider as dynamical equation the adjoint action of a certain Hamiltonian operator $\hat{H}$ (as in equation (35)). As we did above, we can write the Hamiltonian operator without loss of generality as the sum of three terms:

$$\hat{H} = \hat{H}_C \otimes \mathbb{I}_Q + \mathbb{I}_C \otimes \hat{H}_Q + \hat{H}_{CQ}, \tag{37}$$

where again $\hat{H}_C$ represents the energy associated to the classical degrees of freedom, $\hat{H}_Q$ the energy of the quantum ones, while $\hat{H}_{CQ}$ represents the coupling between them.

Written in this form, it is simple to study how to define a (unitary) automorphism of the image of the hybrid algebra $\mathcal{A}_H$. We know that the dependence in the classical degrees of freedom cannot be only on those of $\mathcal{A}_C$, but also on those of $\mathcal{B}(\mathcal{H}_C)$ which do not belong to $\pi_C(\mathcal{A}_C)$. As $\pi_C(\mathcal{A}_C)$ is the (commutative) subalgebra of multiplicative operators on $\mathcal{L}^2(M_C, d\mu)$, we can look for the external operators among those corresponding to the derivation operators, i.e. those representing the quantization of the variables conjugated to those of M_C. From Koopman's construction, we know that the quantization of those variables define suitable operators to define the proper unitary dynamics. For the sake of simplicity, let us consider the case $M_C = \mathbb{R}^{2n}$, and let us denote as Π_{q^k} and Π_{p_j} the conjugated coordinates to q^k and p_j (required to define the quantization from T^*M_C on $\mathcal{H}_C = \mathcal{L}^2(M_C)$). Let us extend the representation mapping π_C to include these functions and define the corresponding operators $\pi_C(\Pi_{q^k})$ and $\pi_C(\Pi_{p_j})$. If we ask the adjoint action of Hamiltonian (37) to preserve the subalgebra $\pi_H(\mathcal{A}_H)$ we must impose the following condition

$$[\pi_H(\mathcal{A}_H), \hat{H}] \subset \pi_H(\mathcal{A}_H). \tag{38}$$

As the action is linear, it is sufficient to impose the condition on separable operators of the form $\pi_C(a) \otimes \pi_Q(A)$; and ask the result to belong to the algebra. Also the coupling term in the Hamiltonian can be supposed to be a linear combination of separable operators on $\mathcal{H}_C$ and $\mathcal{H}_Q$ as $H_{CQ} = \sum_{jk} c_{jk} h^j_C \otimes h^k_Q$, for $c_{jk} \in \mathbb{R}$. As the condition must hold for any hybrid observable, it is immediate to prove that:

- the term $\hat{H}_C$ in the Hamiltonian must be linear in the operators $\pi_C(\Pi_{q^k})$ and $\pi_C(\Pi_{p_j})$ to recover the non-trivial classical dynamics on the classical degrees of freedom. Indeed, as π_C and π_Q are morphisms onto $\mathcal{B}(\mathcal{H}_C)$ and $\mathcal{B}(\mathcal{H}_Q)$ we can write

$$[\pi_C(a) \otimes \pi_Q(A), \hat{H}_C \otimes \mathbb{I}_Q] = [\pi_C(a), \hat{H}_C] \otimes \pi_Q(A). \tag{39}$$

  The condition for $[\pi_C(a), \hat{H}_C]$ to belong to $\pi_C(\mathcal{A}_C)$ implies that $\hat{H}_C$ must be linear in $\pi_C(\Pi_{q^k})$ and $\pi_C(\Pi_{p_j})$. This is analogous to the Koopman's case, which coincides with this one if we fix to zero all other terms in the Hamiltonian.
- Purely quantum terms do not introduce any constraint on the dynamics.

- Finally, the coupling term $\hat{H}_{CQ}$ cannot depend on the operators $\pi_C(\Pi_{q^k})$ and $\pi_C(\Pi_{p_j})$. Indeed, if we consider analytical elements in the hybrid algebra,

$$[\pi_C(a)\otimes\pi_Q(A),\hat{H}_{CQ}] = \sum_{jk} c_{jk}[\pi_C(a)\otimes\pi_Q(A),h_C^j\otimes h_Q^k]$$
$$= \sum_{jk} c_{jk}\left([\pi_C(a),h_C^j]\otimes\pi_Q(A)h_Q^k + \pi_C(a)h_C^j\otimes[\pi_Q(A),h_Q^k]\right). \quad (40)$$

For these terms to belong to $\pi_H(\mathcal{A}_{\mathcal{H}})$, we obtain that

$$[\pi_C(a),h_C^j]\in\mathcal{A}_C \qquad \pi_C(a)h_C^j\in\mathcal{A}_C; \qquad \forall\pi_C(a)\in\pi_C(\mathcal{A}_C), \quad \forall j.$$

This only happens if

$$h_C^j\in\pi_C(\mathcal{A}_C), \qquad \forall j.$$

Hence, we have proved that:

Theorem 4.1. *The only type of Hamiltonian operator of the form of equation (37) which generates a unitary dynamics on $\mathcal{B}(\mathcal{H}_C\otimes\mathcal{H}_Q)$ that defines an outer automorphism of the hybrid subalgebra $\pi_H(\mathcal{A}_H)$ has*

- *a linear dependence on $\pi_C(\Pi_{q^k})$ and $\pi_C(\Pi_{p_j})$ in $\hat{H}_C$ as*

$$\hat{H}_C = \sum_{kj}\left(\alpha_k\pi_C(\Pi_{q^k}) + \beta_j\pi_C(\Pi_{p_j})\right), \quad (41)$$

  where $\alpha_k,\beta_j,\tilde{H}_C\in\pi_C(\mathcal{A}_C)$.
- *The other coefficients must belong to the corresponding subalgebra, i.e. $\hat{H}_Q\in\mathcal{A}_Q,\hat{H}_{CQ}\in\pi_H(\mathcal{A}_H)$.*

The dynamics is non-trivial in the classical degrees of freedom only if $\alpha_k\neq 0$ or $\alpha_j\neq 0$. In order to recover the expression of Koopman's construction, we may write

$$\alpha_k = \pi_C\left(\frac{\partial H_C(q,p)}{\partial p_k}\right), \qquad \beta_j = -\pi_C\left(\frac{\partial H_C(q,p)}{\partial q^j}\right), \quad (42)$$

where the function $H_C(q,p)\in\mathcal{A}_C$ represents the energy of the classical degrees of freedom. With that choice, for a non-interacting system ($H_{CQ}=0$), a separable state of the form $\hat{\rho}_C\otimes\hat{\rho}_Q$ would evolve separately since the evolution operator factorizes. Hence we our construction includes as limit cases the classical and the quantum cases. Any non-trivial interaction (i.e. $H_{CQ}\neq 0$) modifies both terms, and introduces a hybrid behavior. Obviously, in any case, the evolution is Hamiltonian. A similar dynamics is also considered in [29], from a slightly different perspective.

4.2.3. The master equation. Let us consider now the corresponding equation on the set of density matrices. Notice that the immediate consequence of theorem 4.1 above is that if we consider the master equation for the state $\hat{\rho}_H$ defined by von Neumann equation for the same Hamiltonian, we obtain:

$$i\frac{\mathrm{d}\hat{\rho}_H}{\mathrm{d}t} = \sum_{kj}\left[\pi_C\left(\frac{\partial H_C(q,p)}{\partial q^j}\Pi_{p_j} - \frac{\partial H_C(q,p)}{\partial p_k}\Pi_{q^k}\right)\otimes \mathbb{I}_Q, \hat{\rho}_H\right] + [\mathbb{I}_C\otimes\hat{H}_Q,\hat{\rho}_H] + [\hat{H}_{CQ},\hat{\rho}_H], \tag{43}$$

where $H(q,p)\in\mathcal{A}_C$, $\hat{H}_Q\in\pi_Q(\mathcal{A}_Q)$ and $\hat{H}_{CQ}\in\pi_H(\mathcal{A}_H)$ and we used that $\pi_C(\mathcal{A}_C)$ is commutative. By construction, this evolution takes the previous Heisenberg equation to the set of physical states, and being unitary, it defines the corresponding dual unitary action on that space. Hence, the solution must be well defined inside the space of hybrid states since it corresponds to the co-adjoint action of the unitary group. In this way, this construction allows us to write a well defined dynamics on the set of hybrid states.

It is important to notice that, despite the automorphism being external to $\pi_H(\mathcal{A}_H)$, it is completely determined by the hybrid energy via the previous expression. As the dependence must be linear in the momenta Π_{q^k},Π_{p_j}, there is no freedom left in the external degrees to determine the Hamiltonian.

On the other hand, at the formal level the dynamics can be integrated straightforwardly, since it is defined by the evolution operator generated by the Hamiltonian $\hat{H}$. If we assume that the Hamiltonian does not depend on time, the evolution operator corresponds to

$$\hat{U}(t) = e^{-it\hat{H}}, \tag{44}$$

which is a unitary operator on $\mathcal{H}_C\otimes\mathcal{H}_Q$, whose adjoint action on the set of linear operators preserves the subalgebra $\pi_H(\mathcal{A}_H)$. Therefore, its co-adjoint action must preserve the corresponding set of density operators. This case represents the simplest generalization of Koopman construction to the case of hybrid systems.

4.2.4. Conditions on the automorphism of $\pi_H(\mathcal{A}_H)$ II: arbitrary linear dynamics. If we consider arbitrary (bounded) linear dynamics of the form of equation (33), possibilities are much richer. In principle, as we are considering linear subspaces, the condition of being an automorphism for $\pi_H(\mathcal{A}_H)$ implies that the operator generating the automorphism satisfies

$$e^{\mathcal{L}t}(\pi_H(\mathcal{A}_H))\subset\pi_H(\mathcal{A}_H). \tag{45}$$

Furthermore, if the automorphism is not unitary, we need to impose also some conditions on the dual operator $\mathcal{L}^\dagger$ for the master equation to be well defined. In particular we must take into account:

- the evolution must be tangent to the set of density matrices, i.e. define a curve in the space of self-adjoint positive-definite operators. As we can safely assume that the Hilbert space under consideration is separable, we can always choose a numerable basis and turn this space into $\ell^2(\mathbb{N})$ under a unitary isomorphism. Then, the Cholesky decomposition indicates that it is always possible to factor the positive semidefinite density matrix $\rho = LL^\dagger$ with L lower triangular with respect to the order induced in the basis by the isomorphism (see [36]). Hence a simple way to implement this condition may be to impose that

$$e^{\mathcal{L}^\dagger t}(T_1^\dagger T_1) = T_2^\dagger T_2, \tag{46}$$

  for T_1, T_2 arbitrary bounded invertible mappings.
- Furthermore, the trace must be preserved:

$$\mathrm{Tr}\hat{\rho}_H(t) = 1, \quad \forall t \Rightarrow \mathrm{Tr}\left(\frac{\mathrm{d}\hat{\rho}_H(t)}{\mathrm{d}t}\right) = 0. \tag{47}$$

- Finally, if the dynamics is considered as the dynamics of a thermodynamic system, we must ask it to be compatible with the corresponding physical constraints. Thus, von Neumann entropy must be preserved or increased along the solutions (depending on the type of system) and the ensembles which must be of equilibrium (as the hybrid canonical ensemble discussed above) must be fixed points of the dynamics.

In general, the set of admissible dynamical systems may be large. We will explore this set and its properties in a forthcoming paper.

5. Conclusions and outlook

In this paper we have introduced a new framework based on Koopman's construction to study hybrid quantum–classical dynamics. We first consider the set of hybrid operators $\mathcal{A}_H$ defined as the tensor product of the classical and the quantum C^*–algebras. The quantum C^* algebra corresponds to the usual algebra of linear operators of a Hilbert space. As it is well known, it is non-commutative. The classical C^*–algebra is commutative and corresponds to the differentiable functions of the classical phase space. We can consider that it is the result of the classical limit of a quantum algebra. From this point of view we can think on the hybrid algebra as a partial classical limit of an originally full-quantum one.

We can use the usual GNS construction on the hybrid algebra to define a representation of the hybrid observables as a subalgebra of the (bounded) linear operators of a hybrid Hilbert space $\mathcal{H}_C \otimes \mathcal{H}_Q$. The corresponding hybrid states are then realized as regular density matrices on this Hilbert space. We have built explicitly the density matrices from the states of the hybrid algebra, and we have also proved that von Neumann entropy of those density matrices coincides with the notion of hybrid entropy introduced in [3] for the hybrid states. This allows us to import to this framework a relevant physical result as the hybrid canonical ensemble determined in the same paper. Hybrid dynamics is introduced on the algebra as an outer-automorphism of the representation of $\mathcal{A}_H$ on $\mathcal{H}_C \otimes \mathcal{H}_Q$ or, equivalently, as the corresponding dual dynamics on the set of density matrices. We have characterized the conditions of those dynamics, and have classified all possible unitary evolutions satisfying them. Notice, though, that from a physical point of view, the resulting family of unitary dynamics is limited, since it cannot include back-reaction, i.e. the classical subsystem follows a dynamics which does not see the quantum subsystem. A detailed analysis of more general solutions and their properties will be presented in a forthcoming paper. We will also consider the relation with the dynamics written directly at the level of the C^*–algebra and its states, which is the most frequent case in the literature.

Notice that, despite the apparent paradox of treating hybrid classical–quantum systems in a Hilbert space language, it offers several advantages. First, complexity is significantly decreased from an original full-quantum model, since the Hilbert space $\mathcal{H}_C$ representing the classical degrees of freedom is simpler than the original Hilbert space containing all the degrees of freedom, and its operators form a commutative subalgebra. Second, Hilbert space language offers several tools to consider linear dynamics which become non-linear at the classical level (as Koopman dynamics shows). Finally, it also offers the possibility of studying classical–quantum correlations of the statistical ensembles in a simple way, considering the hybrid density matrices. There are also some drawbacks, as the difficulties to consider pure statistical

hybrid states (as it happens in the Koopman's pure classical case). Nonetheless, from a physical point of view, the most common applications of these models correspond to experimental situations where it is impossible to assign precise initial conditions to the physical particles (for instance in a molecular system) and then we consider that missing pure states is not a serious limitation.

Data availability statement

No new data were created or analysed in this study.

Acknowledgments

The authors acknowledge partial financial support of Grant PID2021-123251NB-I00 funded by MCIN/AEI/10.13039/501100011033 and by the European Union, and of Grant E48-23R funded by Government of Aragón. L G B acknowledges that this work has been partially supported by the Madrid Government (Comunidad de Madrid-Spain) under the Multiannual Agreement with UC3M in the line of 'Research Funds for Beatriz Galindo Fellowships' (C&QIG-BG-CM-UC3M), and in the context of the V PRICIT (Regional Programme of Research and Technological Innovation). C B M and D M C acknowledge financial support by Gobierno de Aragón through the grants defined in ORDEN IIU/1408/2018 and ORDEN CUS/581/2020 respectively.

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Chapter 3

Hybrid field theory for gravity and quantum matter

This chapter contains the fifth article presented in this thesis and its supplementary material:

- J. L. Alonso, C. Bouthelier-Madre, J. Clemente-Gallardo, and D. Martínez-Crespo. Hybrid geometrodynamics: A Hamiltonian description of classical gravity coupled to quantum matter. Submitted for publication. [5]

Hybrid Geometrodynamics:
A Hamiltonian description of classical gravity coupled to quantum matter.

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Abstract. We generalize the Hamiltonian picture of General Relativity coupled to classical matter, known as geometrodynamics, to the case where such matter is described by a Quantum Field Theory in Curved Spacetime, but gravity is still described by a classical metric tensor field over a spatial hypersurface and its associated momentum. Thus, in our approach there is no non-dynamic background structure, apart from the manifold of events, and the gravitational and quantum degrees of freedom have their dynamics inextricably coupled. Given the Hamiltonian nature of the framework, we work with the generators of hypersurface deformations over the manifold of quantum states. The construction relies heavily on the differential geometry of a fibration of the set of quantum states over the set of gravitational variables. An important mathematical feature of this work is the use of Hida calculus to define measures over field and differential calculus in order to properly characterize the Schrödinger wave functional picture of QFT. This allows us to relate states within different Hilbert spaces in the case of vacuum states or measures that depend on the gravitational degrees of freedom, as the ones associated to Ashtekar's complex structure. This is achieved through the novel inclusion of a quantum connection for the fibration, which will have profound physical implications. The most remarkable physical features of the construction are norm conservation of the quantum state (even if the total dynamics are non-unitary), the clear identification of the hybrid conserved quantities and the description of a dynamical backreaction of quantum matter on geometry and *vice versa*, which shall modify the physical properties the gravitational field would have in the absence of backreaction.

Keywords: Geometrodynamics, Quantum Field Theory in Curved Spacetime, Backreaction, Hamiltonian field theory. Submitted to: *Class. Quantum Grav.*

1. Introduction

In the pursuit of understanding the fundamental nature of our universe, the need of a holistic description unifying quantum mechanics and general relativity remains one of the greatest challenges in modern theoretical physics. Within this context, the concept of Quantum Gravity (QG) has emerged, aiming to reconcile the quantum behavior of matter with the curvature of spacetime by making quantum the geometry itself. One of the main approaches, inspired by the similarities with quantum mechanics, is Canonical Quantization of Gravity [14]. Such quantization program was the main motivation for the construction of geometrodynamics; the starting point of the quantization process was precisely such Hamiltonian formulation of gravity. In fact, the central result of such canonical quantization is Wheeler–DeWitt equation, resulting from the quantization of the constraints present in geometrodynamics. Because of this, the study of geometrodynamics and its reformulation are still of interest for the community, summarized in [19] from ADM's original approach to the more quantum language of Hamiltonian generators of hypersurface deformations over the space of 3-metrics and their momenta.

Nevertheless, most of Canonical QG phenomenology is far from being falsifiable in a foreseeable future, even when it can be extracted from the *adynamical* Wheeler-deWitt equation. A more humble approach relies on Semiclassical Gravity (SG) theories, which treat matter as quantum states while describing spacetime using classical variables. One example of them is the result of performing a WKB semiclassical limit to Wheeler-deWitt equation [25] (where, even if the gravity is technically still considered quantum, its dynamics follows classical paths over which one may consider quantum corrections). Another well known approach relies on the Moller-Rosenfeld equation, $G_{\mu\nu} = \langle \Psi \mid \hat{T}_{\mu\nu} \mid \Psi \rangle$, where the expectation value of a energy-momentum tensor of a quantum field acts as a source for Einstein's equations.

The crucial question in these approaches is how quantum matter (or in general, quantum degrees of freedom) influences and shapes the classical variables describing the geometry of spacetime. This intricate problem becomes even more complex when one realizes the absence of a unique vacuum state and the consequent ambiguity surrounding the notion of "particle" on curved spacetime. Consequently, finding a mathematically rigorous framework to account for the backreaction of quantum matter on classical spacetime has become a formidable quest, albeit with fundamental phenomenological implications [34]. Of course the backreaction of the matter fields on gravity affects also the propagation of the fields due to the change of the metric, which forces us to find a joint dynamical description to portray this intertwining, even without considering QG and its semiclassical limit, in the spirit of [32, 31].

In this context we situate our work. We are interested in unraveling the extent to which quantum matter fields modify classical general relativity, but, given the greater similitude of geometrodynamical language to quantum mechanics, instead of looking for

a modification of Einstein's equations, we seek the appropriate description of geometrodynamics when the matter is of quantum nature and described in a Hamiltonian way. The main difference with Möller-Rosenfeld equation from this perspective is the dynamical arising, leaf by leaf, of the geometry together with the quantum matter from their coupled evolution along a foliation of spacetime, instead of the usual Einstenian picture of looking at the spacetime and its content as a whole, fulfilling a certain compatibility relation. The price to pay, of course, is the loss of general covariance of the framework. The associated boons is the clarity of the definitions of the conserved quantities and their coupling to gravitational degrees of freedom. Nevertheless, as happened in classical geometrodynamics, covariance is recovered for the solution curves to the dynamics, once the so called hamiltonian and momenta constraints are enforced.

As it happens in the case of classical geometrodynamics, we think that the proposal of this hybrid geometrodynamics can be seen as a previous step to the quantization program, and we think it is still interesting to build the whole formalism of QFT in curved spacetime and gravity under a unified Hamiltonian language. Perhaps, given the difficult falsifiability of the full quantum picture, interesting novel phenomenology already arises at this level. In the same sense as in molecular dynamics, where Ehrenfest's dynamics (describing molecules with classical nuclei and quantum electrons under a coupled Hamiltonian evolution) reproduce with reasonable exactitude the full quantum dynamics thanks to the hierarchical masses and confinement widths between both subsystems, we like to think of hybrid geometrodynamics as an effective theory whose validity will be related to the hierarchy between the gravitational and quantum field scales.
Of course, this idea is not new, and a top-down approach based on a suitable WKB limit from full quantum canonical gravity to QFT coupled to classical geometry has been recently developed in [29], recovering a rigourous picture of QFT in Curved Spacetime. On the other hand, a Hamiltonian picture was developed by Husain and Singh in [22] and [23], characterizing formally the backreaction of QFT on gravity for a Friedman-Roberson-Walker universe and a single foliation of spacetime. Our formalism diverges from theirs both in the mathematical formalism and physical implications, but the spirit is similar. Regarding the formalism, our work aims to provide solid mathematical foundations through a comprehensive characterization of the measure over the space of fields, where the Schrödinger functional (SWF) picture, see [28], will be a cornerstone of our construction. We provide the usual SWF picture with well defined integro-differential calculus based on Hida and Fréchet calculus over infinite dimensional manifolds, which was not considered in previous approaches and avoids some ill-defined properties, such as norm loss or the abuse of notation representing the vacuum as functions when considering the Radon-Nikodym derivative of Gaussian measures with respect to a (non-existent) Lebesgue measure over the infinite dimensional space of fields. This allows us to define probability measures in the context of curved spacetime and relate different physical interpretations under changes of the spatial

geometry, when the vacuum state is dependent on the gravitational degrees of freedom. This dependence, natural from Ashtekar's prescription of complex structure [5], is not present in previous hybrid approaches and constitutes a novelty of our construction. In fact, such dependence makes the whole Hilbert space of quantum states also dependent on the gravitational degrees of freedom, as we will see. It also provides the space of quantum states with a well (although densely) defined symplectic geometry (and, in turn, a proper Poisson bracket) over functionals of infinite-dimensional domain, which was not considered in the Hamiltonian presentation of [23]. Furthermore, a notion of quantum connection is introduced, allowing us to relate unitarily inequivalent theories in different Hilbert spaces through the construction of a non trivial bundle, with base the manifold of gravitational degrees of freedom and fiber the manifold of quantum states. In these mathematical aspects our work differs from previous approaches in the literature. Regarding the physical implications, the quantum connection is a novelty that is in close relation with the phenomenology of Unruh effect, particle creation induced by dynamical spacetimes, inequivalent vacuums and related phenomena. Regarding spacetime considerations, our work provides a more generic framework as it is adapted to arbitrary foliations and generic spacetimes, where the representation of hypersurface deformations and its associated constraints are implemented locally for any foliation in the geometrodynamical spirit of Hojman, Kuchar and Teitelboim's [19]. In this line, our formalism keeps the geometrodynamical physical axioms, such as the *path independence principle* and the *geometrodynamical principle of equivalence*, properly adapted to the current hybrid context. Given the amount of technicalities devoted to the foundational construction of hybrid geometrodynamics and the remarkable length of this paper we will not solve any particular physical example, but illustrative examples (such as those considered in [23, 21]) will be considered in future works.

In order to perform such construction, we will consider first classical geometrodynamics, then, develop a quantum field theory over curved spacetime in a Hamiltonian fashion and couple them in a suitable way to build consistent hybrid geometrodynamics, where the novel notion of quantum connection will come into play. We find that, in order to describe appropriately such quantum field theory over arbitrary dynamical spacetimes, its Hamiltonian picture must be endowed with a novel ingredient, in the form of a quantum connection, that allows us to relate unitarily inequivalent quantizations corresponding to different gravitational backgrounds. As we will show, it turns out that such ingredient, ultimately associated to the parametric family of complex structures defining a set of quantizations, is crucial for the compatibility of hybrid geometrodynamics, further justifying its introduction. Let us get into it.

These ingredients define a Cauchy problem where the initial data must be defined fulfilling certain constraints. In geometrodynamics, such constraints are derived from physical principles, namely the path independence criterium. This criterium can be easily understood: given that the field data contained in a spatial hypersurface should be equal to the one induced by the spacetime field solutions through the foliation map, if some initial field data is evolved from an initial hypersurface through two

different "paths" (sequences of intermediate hypersurfaces), until a same final spatial hypersurface is reached, the field content in such final hypersurface should be the same. To fulfill this integral criterium, it must satisfy its differential form, which is the need of commutativity of the differential generators of different deformations at each hypersurface in each path. Given that the representations generators of hypersurfaces form a non-trivial Poisson algebra, they will only commute if the superhamiltonian and supermomenta are zero on shell. These are the so called hamiltonian and momenta constraints. See [19] for the canonical construction of geometrodynamics.

We can obtain an analogous result from a Lagrangian perspective. In that case, the constraints are derived from an extreme action principle where the Hilbert-Einstein Lagrangian has been written in 3+1 form and Legendre transformed, showing explicit Lagrange multipliers (the lapse N_s and shift $\vec{N}_s$ functions) implementing the foliation as suitable constraints. We will consider spacetime a globally hyperbolic Lorentzian manifold in order to define a proper Cauchy problem in this setting. Notice that, while we will stick to Einstein's General Relativity and its metric description of gravity, any alternative description of gravity should also follow this geometrodynamical framework.

On the other hand, in [19], even though most of the discussion is kept general, the matter sources explicitly considered are classical fields. It is our aim to substitute such classical fields by a quantum theory rewritting QFT in Curved Spacetime in a Hamiltonian formalism where the spacetime itself is not a given background as is the case in [20], but is dynamically coupled to the Quantum Fields. In order to do so, we firsly consider Schrödinger wave functional picture for quantum fields in curved spacetime[28], as it is easily adaptable to the non-covariant Hamiltonian framework as in [17, 24]. Then we promote the geometric variables from a given background to be part of the kinematics, which ultimately will be part of a set of coupled *hybrid equations of motion* of gravitational variables and QFT states, posing a hybrid Cauchy problem.

To rigorously build QFT in curved spacetime in this Hamiltonian nature, we secure our mathematical grounds with tools from infinite dimensional calculus and differential geometry in such framework [2, 3]. As we need to build differential tensors on our manifold of fields (classical and quantum), we will ask that manifold to be defined in such a way that derivatives can be rigorously proved to exist. In this paper we will reduce all the mathematical technicalities to the minimum, addressing the interested reader to the mentioned references in case they need the technical details. Thus, the manifold of classical fields will be assumed to be the dual (see [2, 27] for a careful analysis of the reasons for this choice) to some nuclear-Frechèt space $\mathcal{N}$ of functions defined over a spatial hypersurface Σ (for example, differentiable functions of compact support $\mathcal{N} = C_c^\infty(\Sigma)$ when Σ is compact). This choice ensures the existence of a well-defined differential calculus on the fields phase space. For analogous reasons, quantum wave functions will be modelled using the set of Hida functions ($\mathcal{N}$) that will densely populate the space of quantum pure states, whose domain will be the manifold of classical fields. Being the

set of Hida functions a nuclear-Fréchet space, it allows us to perform Fréchet differential calculus and ultimately, differential geometry. This set of functions will be completed under the choice of a scalar product, which is given by a Gaussian measure $D\mu$ over the space of fields, to form a Rigged Hilbert space $(\mathcal{N}) \subset L^2(\mathcal{N}', D\mu) \subset (\mathcal{N})'$, in analogy to Quantum Mechanics. Such a measure can also be proved to exist in our setting, its properties providing us with many useful tools in QFT (see [2]).

Moreover, such measure is closely related to the quantization procedure (in Corichi et. al. [10], given by the choice of complex structure J_C for the classical space of fields), or to what in the literature is usually referred as the choice of vacuum state. The main difficulty arises from the fact that the quantization procedure or the vacuum state are time dependent, as *a priori* they depend on the leaf 3-metric over the spatial hypersurface, lapse and shift (as J_C does in the static or stationary cases, see [5]). This is a widely known fact in the literature, and yields to notions such as norm loss and quantum completeness [18]. In this line, we consider that this dependence introduces a parametric family of quantizations (or vacuum states associated to different measures) and thus a family of unitarily inequivalent Hilbert spaces. Given that the dynamics along the foliation will necessarily change such geometric parameters, we need a way to relate states (and operators) within inequivalent Hilbert spaces or quantizations. To do so we will introduce, as it is done in [3] for time dependent quantization, a notion based on parallel transport for quantum states along curves over the space of pure geometrodynamical variables. Thus, the quantum states will become sections over a fibration with base the geometrodynamical variables, and a quantum connection will allow us to relate unitarily inequivalent Hilbert spaces. A different notion of quantum connection over a different bundle, but with certain similarities, has been introduced in [9]. In the realm of algebraic quantum field theory, some works, such as [33], have treated the functional picture from the point of view of algebraic QFT, addressing some problems, such as the lack of unitarity of time evolution in the functional picture. The main differences of our approach with such prescriptions of QFT in curved spacetime, even under the consideration of the functional picture, rely precisely on our consideration of a quantum connection, allowing us to relate unitarily inequivalent Hilbert spaces without detriment on the physical interpretation. Besides, our approach is based on a submanifold of field Cauchy data (contrarily to the usual one based on field theoretical solutions), which constitutes the domain of Schrödinger wave functionals. Such submanifold of field Cauchy-data is defined as a suitable set of distributions (over the spatial hypersurface), which is provided with a measure allowing to define square-integrable functions over the space of fields representing the quantum states. To our knowledge, this rigorous treatment of wave functionals based on Hida calculus supposes a novelty in the framework of Schrödinger picture of QFT.

As noted, the Quantum Field theories under consideration will be the result of a certain quantization procedure of a classical field theory. Such classical field theory will be built in a Hamiltonian formalism and, in the spirit of geometrodynamics, the

generating functions of hypersurface deformations over such classical phase space will already fulfill Dirac's closing relations, when joined with the pure geometrodynamical supermagnitudes over a total (geometry plus classical matter) Poisson bracket. This consideration will be key to show that their quantum field theoretical analogues (plus classical gravitation) also reproduce the algebra relations of hypersurface deformations. Note that Schrödinger wave functional picture can be considered (at least at the level of the definition of its dynamics) non-perturbative, and, given that we are only interested in the kinematics of the whole quantum state and its interaction with gravity we do not need to consider yet any regularization or renormalization schemes for QFT in curved spacetime. Nevertheless, a similar analysis to the one in [7, 13] could be carried out in this Hamiltonian framework, although in this case the geometry of spacetime is not known *ab initio*, but constructed simultaneously with the evolution of quantum states.

On the other hand, we maintain the geometrodynamical principle of equivalence as stated in [19] and we consider only the quantization of those theories whose classical matter supermagnitudes only depend locally (not derivatively) on the 3-dim metric tensor h and do not depend on its momentum π_h, nor on the lapse or shift functions. This property is dubbed *ultralocality* [26]. This banishes non-minimally coupled field theories from this scheme, even though a similar analysis could be carried out in that case.

In conclusion, the main result of our work will be the Hamiltonian representation of hypersurface deformations for a hybrid theory of quantum field matter and classical gravitation and the definition of the hybrid constraints that enforce *path independence* as in [19]. In order to do so, if the quantization procedure was dependent on the geometry, lapse and shift, the quantum connection must fulfill some constraints related to the change of the quantization of the symmetry generators.

The structure of the paper is as follows. In the second section, we will introduce the essential mathematical ingredients and notation from geometrodynamics, namely: the notation for the geometry of hypersurfaces and foliations, the closing relations of hypersurface deformations, its representation in phase space and the relations that any matter theory must fulfill as long as it is coupled in a non-derivative way with the 3-metric. For a more detailed presentation of these tools, we address the reader to [11, 12, 19].

We continue with a third section devoted to the Hamiltonian representation of Schrödinger wave functional picture for a leaf dependent quantization procedure, were the section nature of quantum states and the quantum connection are crucial. This construction is based on the mathematical tools developed in [2, 3].

In the fourth one we combine the ingredients from the previous sections, the classical Hamiltonian description of the 3-geometry with the Quantum Field Theory for

matter, to build Hybrid Geometrodynamics. We identify the hybrid generating functions that, under a hybrid Poisson bracket, reproduce the infinitesimal generators of hypersurface deformations over the hybrid algebra of observables. Then, we impose the Hamiltonian and momenta constraints at the hybrid level and have a glance at the hybrid equations of motion. As happened in the hybrid Hamiltonian model for finite dimensional systems defined by Ehrenfest's dynamics [1], the resulting dynamics cannot be unitary because of the non-linearity arising from the backreaction. Nevertheless, the quantum connection provides with norm conservation for the quantum states along the dynamics, even if both the states and the scalar product (or vacuum state) are dependent on the gravitational degrees of freedom.

Lastly, we discuss some physical implications of quantum matter being sources of gravitation constructed in this way and speculate on their phenomenology, in particular in relation with the phenomenon of quantum completeness [18, 4]. In the final Section, we summarize our main results and discuss possible future research lines.

2. A brief summatry of classical geometrodynamics

2.1. Foliations of space-time and hypersurface deformations.

If we consider space-time as a globally hyperbolic spacetime $\mathcal{M}$ with coordinates X^μ, there exists a one parametric family of spatial leaves, $\mathcal{M} \simeq \{\Sigma_s \mid s \in \mathbb{R}\}$ foliating $\mathcal{M}$. Each spatial leaf Σ_s is the image under the s-dependent embedding ε_s of a fixed reference hypersurface Σ, and it is characterized by a hyperplane equation $\tau(X^\mu) = s$, such that each $\varepsilon_s(\Sigma) = \Sigma_s \subset \mathcal{M}$ is a Cauchy surface $\forall s \in \mathbb{R}$. From the hyperplane equation, taking 3 embedding coordinates x^i for Σ, one derives for Σ_s the parametric hyperplane eqs $X^\mu = X^\mu(x, s)$. The Lorentzian metric g of $\mathcal{M}$ induces a Riemannian 3-metric $h_s = \varepsilon_s^\star g$ on each Σ_s, whose coordinates can be defined as:

$$h_{ij}(x, s) = {}^4g_{\mu\nu}(X^\alpha(x, s))\partial_{x^i}X^\mu(x, s)\partial_{x^j}X^\nu(x, s) \tag{1}$$

Each spatial leaf can also be characterized by a time-like normal vector field $\hat{n}_s$ of norm 1, in terms of which we define the second fundamental form $K_{ij}(s) = -\frac{1}{2}\mathcal{L}_{\hat{n}_s}h_{ij}(s)$, where $\mathcal{L}_{\hat{n}_s}$ represents the Lie derivative with respect to the vector field $\hat{n}_s$. With these elements, we define an extrinsic geometry on Σ_s describing how the 3-geometry evolves along the 4-foliation. Thus, we relate the initial coordinates in a 3-surface Σ_s and the coordinates on $\Sigma_{s+\delta_s}$ as a transformation in the normal direction $\hat{n}_s$ to the original hypersurface and a tangential one $\vec{N}$.

In terms of this set of coordinates, the foliation is described as:

$$\frac{d}{ds}X^\mu(s) = N_s(x)n_s^\mu(x) + N_s^i(x)\partial_{x^i}X^\mu(x, s) \tag{2}$$

where the expression in coordinates of the lapse function (obviating the omnipresent

dependence on x) reads:

$$N_s := g_{\mu\nu}(X^\alpha(s)) \left(\frac{d}{ds}X^\mu(s)\right) n_s^\nu, \tag{3}$$

measuring the size of the change in the normal direction. Analogously the coordinates of the shift vector are:

$$N_s^i := g_{\mu\nu}(X^\alpha(s)) \left(\frac{d}{ds}X^\mu(s)\right) \partial_{x^j} X^\mu(s) h_s^{ji} \tag{4}$$

which weights the change in each of the tangential directions associated to ∂_{x^i}.

Both objects can be combined to define an evolution generating vector field E at each hypersurface which encodes the foliation as:

$$E|_{\Sigma_s} = \vec{N}_s + N_s \hat{n}_s \tag{5}$$

We will define for further use the space of lapse and shift functions $(N, N_i) \in \mathcal{M}_N$, which is characterized by four copies (one for the lapse, three for the shifts) of a suitable functional space.

Now, considering an initial data Cauchy surface $\Sigma_0 = \varepsilon_0(\Sigma)$ embedded in $\mathcal{M}$ and E (or lapse and shift $\forall s$), one can span the whole foliation $\{\Sigma_s\}$ equivalent to $\mathcal{M}$ (and all tensors defined at each leaf) when considering its flow α_E^s, so that $\Sigma_s = \alpha_E^s \Sigma_0$. Thus, E characterizes the foliation and relates the embeddings through $\alpha_E^s \circ \varepsilon_0 = \varepsilon_s$.

The role of 4-diffeomorphisms in GR is played in GD by Dirac's group of deformations of a spatial hypersurface embedded in Lorentzian ST (plus constraints). For the relation between both groups see [6].

Identifying an infinitesimal deformation of the hypersurface with the action of $\mathcal{L}_E$ for any N and N^i, we see it can be composed of a normal (lapse-weighted) and tangential deformation (shift weighted). The local generators of such normal deformations (D_n) and stretchings (D_{t_i}) can be written in terms of the local coordinates

$$D_n := n^\mu(x) \frac{\delta}{\delta X^\mu(x)} , \tag{6}$$

$$D_{t_i} := \partial_{x^i} X^\mu(x) \frac{\delta}{\delta X^\mu(x)} , \tag{7}$$

which fulfill the following Lie bracket closing relations:

$$[D_n(x), D_n(x')] = h^{ij}(x) D_{t_j}(x) \delta_{,i}(x, x') - (x \leftrightarrow x') \tag{8}$$

$$[D_{t_i}(x), D_n(x')] = D_n(x) \delta_{,i}(x, x') \tag{9}$$

$$[D_{t_i}(x), D_{t_j}(x')] = D_{t_i}(x') \delta_{,j}(x, x') + D_{t_j}(x') \delta_{,i}(x, x') \tag{10}$$

These closing relations are the key ingredient of GD and play an essential kinematical role, prior to the election of the action or the dynamics themselves. The next step is

providing a phase space representation (for matter and geometry) to the deformations of hypersurfaces, that must fulfill this very same closing relations (c.r.). The importance of the c.r. is such that they can univoquely determine (under some minor physically sensible assumptions) the 3+1 equivalent to Einstenian gravity (without sources) without imposing an action [19].

Such local generators, to provide the infinitesimal deformation of the whole hypersurface, must be integrated over the whole hypersurface with values at s of the lapse and shift functions. For a functional defined over the hypersurface $F[X^\mu(x)] : \Sigma \to \mathbb{R}$, an infinitesimal change of the functional to the neighbouring hypersurface in the foliation is defined by:

$$\frac{\delta F}{\delta s} := \int_\Sigma dx \left(N_s D_n F + N_s^i D_{t_i} F \right) \equiv \mathcal{L}_E F. \tag{11}$$

2.2. Phase space and Hamiltonian deformations.

2.2.1. The gravitational field Given the Hamiltonian nature of deformations of hypersurfaces, they can be risen to the field theoretical phase space defined on it. The objective of this section is the representation over phase space (of matter and geometrical fields) of the generators of deformations of the hypersurface through functions over phase space and the Poisson bracket.

Firstly, one must define a phase space. In the metric description of gravity, the kinematical variables are the Riemannian 3-metric $h_{ij} \in \mathrm{Riem}(\Sigma)$ and its associated momenta $\pi_h \in T^\star(\mathrm{Riem}(\Sigma))|_h$, defined in terms of the extrinsic curvature and seen as a tensor density of weight 1. The Geometrodynamical phase space contains both variables $(h_{ij}, \pi_h^{ij}) \in \mathcal{M}_G$, constructed as a cotangent bundle:

$$\mathcal{M}_G = T^\star \mathrm{Riem}(\Sigma) \sim \mathrm{Riem}(\Sigma) \times \mathrm{Riem}'(\Sigma) \tag{12}$$

locally isomorphic to the Cartesian product of the Riemannian 3-metrics and symmetric (0,2)-tensor densities of weight 1 that we identify as distributions (which we have denoted by $\mathrm{Riem}'(\Sigma)$).

In order to perform differential calculus on $Riem(\Sigma)$, we need a mathematical detour to define the notion of derivative with respect to the metric. The reader interested in these mathematical aspects, although standard in infinite dimensional calculus, is provided with some notes in the supplementary material. Otherwise, one can resume with the reading, assuming that the functional derivatives appearing in eq. (13) can be defined and that, operationally, they work as usual.

This manifold of gravitational variables $\mathcal{M}_G$, where each point is characterized by a pair of 3-metric tensor field h_{ij} and associated momenta distribution π_h^{ij}, is endowed with a Poisson tensor (which is, were proceeds, the weak inverse of the canonical symplectic

form $\omega_g := -dh_{ij;x} \wedge d\pi_h^{ij;x}$) and can be associated to a Poisson bracket over the functions given by:

$$\{f,g\}_G = \int_\Sigma d^3x \delta_{[h_{ij}(x)} f \delta_{\pi_h^{ij}(x)]} g \quad \forall f,g \in C^\infty(\mathcal{M}_G) \tag{13}$$

At an operational level, it is enough to consider that such derivatives are local (here the $\delta(x,x')$ is associated to Lebesgue measure) and independent from each other:

$$\frac{\delta}{\delta\pi^{ij}(x)}\pi^{kl}(x') = \frac{\delta}{\delta h_{kl}(x)} h_{ij}(x') = \delta_{ij}^{kl}\delta(x',x) \quad \text{and} \quad \frac{\delta}{\delta\pi^{ij}(x)} h_{kl}(x') = \frac{\delta}{\delta h_{ij}(x)}\pi^{kl}(x') = 0\,. \tag{14}$$

2.2.2. The matter fields. The classical fibration. This phase space can be extended to contain the matter fields and their associated momenta, for any kind of tensor field ‡. We denote generically by

$$(\phi_1, \cdots, \phi_n, \pi^1, \cdots, \pi^n) \in \mathcal{M}_F \tag{15}$$

the set of all matter fields (either scalar or tensorial, with domain Σ) and their associated momenta (being densities of weight 1, [19]), belonging to the matter manifold $\mathcal{M}_F$. For example, in the case of a scalar field, one may consider the fields in a certain nuclear space (one can check the supplementary material or see [2]), in order to be able to define a differentiable structure on them $\phi \in \mathcal{N}(\Sigma)$ and thus the corresponding cotangent bundle can be written as $\mathcal{M}_F := T^\star\mathcal{N}$. As in the purely geometrodynamical case, one can define a Poisson bracket over the space of functions over this manifold, $C^\infty(\mathcal{M}_F)$, which in turn becomes a Poisson algebra which we will denote by $\mathcal{A}_F$. Operationally it acts, on arbitrary functionals $f, g \in C^\infty(\mathcal{M}_M)$, as:

$$\{f,g\}_M := \delta_{[\phi_{ix}} f \delta_{\pi^{ix}]} g := \delta_{\phi_{ix}} f \delta_{\pi^{ix}} g - \delta_{\phi_{ix}} g \delta_{\pi^{ix}} f\ . \tag{16}$$

To clarify the notation, note that the indices such as i, j, k are discrete indices whose contraction with upper and lower repeated indices is to be seen as Einstein's summation convention. On the other hand, x, y, z represent continuous indices, whose contraction represented by repeated super- and sub-indices implies integration over Σ. In this sense, an object with an upper index represents a density of weight 1, while lower index is assigned to fields over Σ representing points in the linear field manifold but also vectors on it, depending on the case. Using that notation, one must take into account that the field momentum π^{ix} is a density of weight 1. Therefore, to perform the Fréchet functional derivatives one must restrict (though standard, one can check

‡ With analogous considerations as the ones for the purely geometrodynamical variables, *i.e.* functions of compact support, relating the functional-distributional nature through a Gel'fand triple which allows to identify a suitable dense subset of the cotangent bundle to the matter fields which has Fréchet structure and, lastly, taking into account the dense definitiness of the differential structures[2], which can be checked in the supp. material.

the supplementary material) the momenta to belong to a certain dense subset of distributions $\mathcal{N}'$ which is representable under a measure, in the following sense:

$$\{f, g\}_C = \int_\Sigma d^3x \partial_{[\phi_i(x)} f \partial_{\pi^i(x)]} g \ . \tag{17}$$

where $\pi^i(x)$ stands for the local value of the representation of the density $\pi^{i,x}$ under the Lebesgue measure d^3x.

Therefore, the total phase space of geometry and matter denoted as $\mathcal{M}_C$ (where the C stands for classical) is given by the product manifold:

$$\mathcal{M}_C = \mathcal{M}_G \times \mathcal{M}_F \ . \tag{18}$$

For reasons that will become clear later, we will consider also another product manifold,

$$\mathcal{F}_C = \mathcal{M}_N \times \mathcal{M}_G \times \mathcal{M}_F \ , \tag{19}$$

where $\mathcal{M}_N$ contains the lapse and shift degrees of freedom associated with the space-time foliation. $\mathcal{F}_C$ can be considered as a trivial bundle with base manifold $\mathcal{B} = \mathcal{M}_N \times \mathcal{M}_G$ and fiber $\mathcal{M}_F$. We see, thus, that the base manifold contains all the geometrical information of the theory, and the fiber, all the matter information. Notice that $\mathcal{M}_N$, containing the information about the space-time foliation, is different from the other two pieces, as their dynamics are not associated to a particular kinematical structure, but will always be associated to the choice of foliation and thus act as time dependent parameters. Therefore, given the path independence principle, even if some tensors for the matter theory may depend on them (thus, their inclusion in the base of the fibration), we anticipate that physical magnitudes, as well as the Poisson tensors over the gravitational and matter submanifolds, will be independent of $\mathcal{M}_N$.

As we argued above, $\mathcal{M}_C$ can be given a differentiable structure and considered as a representation of the cotangent bundles of the field spaces, both endowed with a canonical Poisson bracket associated with the canonical symplectic forms. The set of infinite differentiable functions $f(\Phi) \in C^\infty(\mathcal{M}_C)$ on this phase space, with the domain variables grouped as $\Phi \in \mathcal{M}_C$, form a Poisson algebra of classical (matter and geometrical) observables, for the total Poisson bracket

$$\{\cdot, \cdot\} : C^\infty(\mathcal{M}_C) \times C^\infty(\mathcal{M}_C) \to C^\infty(\mathcal{M}_C) \tag{20}$$

which is constructed as the sum of the two Poisson brackets of each Poisson submanifold:

$$\{\cdot, \cdot\} = \{\cdot, \cdot\}_G + \{\cdot, \cdot\}_M \tag{21}$$

Such Poisson bracket must fulfill Jacobi, Leibniz, bilinearity and antisymmetry. They are fulfilled immediately given that each PB fulfilled them separately and that they fulfill a certain compatibility condition. We will delve into this condition later, in the

quantum case.

The objective of the geometrodynamical framework is to identify the flow that α_E induces over the space of 3-metric tensor and momenta (and matter fields and associated momenta) and thus, reconstructing all physical information of the Universe within such path. With the former geometric description of the phase space of fields and Poisson brackets, this can be done in a Hamiltonian framework, defining on the phase space of fields a curve parametrized by s, which plays the role of the time for the Hamiltonian system.

Notice that, embracing the GD point of view means forgetting about spacetime, adopting a Hamiltonian view of the Universe as the evolution of a 3-geometry, and interpreting the evolution flow α_E as the deformations of the Cauchy hypersurface Σ_0. In the end, such evolution is translated to the space of fields (including the metric) which are defined on it. This means that, for the geometry, the integral curves of E, defining a certain foliation, is analogous to a curve over $\mathcal{M}_G$, being such curve the $s-$parametrized *history* of the geometry of spacetime.

Now, one has to postulate that that normal and tangential deformations of the hypersurface, being a physical symmetry, must be symplectomorphisms. This leads to the representation axiom of [19], which is imposed together with the compatibility with closing relations and locality of normal deformations of the 3-metric to reproduce its relation with the extrinsic curvature. In essence, what one is assuming is the Hamiltonian nature of the effect over phase space of normal and tangential deformations (locally denoted by $D_n(x)$, $D_{t_i}(x)$). Hence, these vector fields must be the Hamiltonian vector fields associated with certain generating functionals $\mathcal{H}(\Phi), \mathcal{H}_i(\Phi)$, which act on generic functionals $f(\Phi)$ as:

$$D_n(x)f(\Phi) := \{f(\Phi), \mathcal{H}(\Phi(x))\} \quad (22) \qquad D_{t_i}(x)f(\Phi) := \{f(\Phi), \mathcal{H}_i(\Phi(x))\}. \quad (23)$$

We inherit the nomenclature from [19] and refer to the local generating functions $\mathcal{H}$ and $\mathcal{H}_i$ as superhamiltonian and supermomenta.

On the other hand, the Lie bracket closing relations for the generators of the deformations (8),(9) and (10), must be reproduced by the Poisson bracket commutation relations for the supermagnitudes, in order to be proper representations of Dirac's generators. Even without this representation requirement, it can be argued [16] that the supermagnitudes, in order to define a physical evolution related with E, must necessarily fulfill such closing relations. Consequently, the following relations are both a consequence of the kinematics of hypersurface deformations and a requirement for having physical evolution. Thus, they must be enforced prior to the choice of a particular

dynamical theory or action:

$$\{\mathcal{H}_x, \mathcal{H}_{x'}\} = \mathcal{H}^i_x \delta_{,i}(x, x') - \mathcal{H}^i_{x'} \delta_{,i}(x', x) \tag{24}$$

$$\{\mathcal{H}_{ix}, \mathcal{H}_{x'}\} = \mathcal{H}_x \delta_{,i}(x, x') \tag{25}$$

$$\{\mathcal{H}_{ix}, \mathcal{H}_{jx'}\} = \mathcal{H}_{ix'} \delta_{,j}(x, x') + \mathcal{H}_{jx'} \delta_{,i}(x, x') \tag{26}$$

In conclusion, we can define a representation of the Dirac algebra defining the space-time foliation on the phase space of fields, if it is endowed with a Poisson structure. In the following sections we will analyze this construction for the different sets of fields of our theory: the set of classical fields (gravitational and matter), the set of quantum matter fields (assuming a fixed gravitational background), and the set of hybrid quantum-classical fields, when a classical gravitational field and a quantum matter field evolve coupled in the same model. In all cases, the existence of a Poisson structure on the corresponding phase space of fields, will allow us to define the generators of the Dirac algebra at the corresponding level. And therefore we will be able to consider the geometrodynamical formulation of the corresponding theories.

2.3. Identifying the supermagnitudes.

We are now equipped with the kinematical relations the generating functions must fulfill, which will allow us to elucidate their particular shape in the following fashion.
Given that a tangential deformation can be seen as only an *initial data reshuffling* [19], we have access *on leaf* to the result of such deformation. Thus, to identify the supermomenta for any theory it is enough to claim for any variable F in such phase space:

$$\mathcal{L}_{\delta N^k} F = \{F, \mathcal{H}_{kx}\} N^{kx} \tag{27}$$

where $\mathcal{L}_{\delta N^k} F$ represents the Lie derivative along δN^k, encoding the infinitesimal change of F along the flow of a tangential vector field to Σ which characterizes a stretching of it, acting on elements of the field phase space, considered as functions (or distributions) on Σ. As it is argued in [19], the left hand side on the equation can be computed through the use of (7), and the relation above allows us to obtain the expression of the corresponding generating functional $\mathcal{H}_{kx}$, unambiguously (with a degeneracy that disappears once the closing relations for supermomenta (26) are enforced). The main result of this procedure must be that the supermomenta cannot contain powers (higher than 1) of the canonical momenta in order to represent a deformation without extrinsic information to the leaf, as must be the case for said stretching, given that it can be regarded a spacial-on-leaf diffeomorphism.

From such a consistent representation of the generators of tangential deformations, one can find the superhamiltonian by enforcing the remaining closing relations (25) and (24) for the PB. The result is unique under some additional physical considerations

(such as order 2 for the degree on the geometromomenta)[19].

In pure GD (i.e. the matterless case), for metric-based gravity the supermomenta must be:

$$\mathcal{H}_{iG}(h_{ij},\pi^{ij}) = -2D_j\pi_i^j = -2D_j(h_{i\alpha}\pi^{\alpha j}) = -2h_{i\alpha}D_j\pi^{\alpha j} \tag{28}$$

where $D_j = h_{ij}g^{\mu i}\partial_{X^\mu}$. From it, one derives the purely geometrodynamical superhamiltonian to be:

$$\mathcal{H}_G(h_{ij},\pi^{ij}) = \frac{1}{2}\frac{(2\kappa)}{\sqrt{h}}G_{ijkl}\pi^{ij}\pi^{kl} - (2\kappa)^{-1}\sqrt{h}R(h) \tag{29}$$

where $G_{ijkl} := \frac{1}{2\sqrt{h}}\left(h_{ik}h_{jl} + h_{il}h_{jk} - h_{ij}h_{kl}\right)$ is De Witt's metric.

2.4. Matter closing relations.

We will finish this discussion with the main motivation for this review section: remarking how to include matter in the theory in a equivalence-principle-consistent way, and how to obtain the closing relations for the associated matter supermagnitudes. These relations were derived in [19] for Classical matter, but, given its kinematical nature, should be true also for the quantum case which we aim to build in the next Section. In fact, such relations are a must for any matter theory, as long as it has non-derivative coupling with the metric (thus, excluding *a priori* non-minimal coupling terms in the Lagrangian). To do so, we will invoke the GD equivalent to the equivalence principle as in [19], which implies that the total supermagnitudes must be the sum of the pure geometrodynamical magnitudes $\mathcal{H}_{AG}$ and the matter supermagnitudes $\mathcal{H}_{AM}$:

$$\mathcal{H}(x) = \mathcal{H}_G(h,\pi_h;x) + \mathcal{H}_M(h,\phi,\pi;x) \tag{30}$$

$$\mathcal{H}_i(x) = \mathcal{H}_{iG}(h,\pi_h;x) + \mathcal{H}_{iM}(h,\phi,\pi;x) \tag{31}$$

The geometrodynamical equivalence principle also implies that matter supermagnitudes are ultralocal (non-derivative dependence on h and independent of π_h). On the other hand, the pure geometrodynamical generating functions, i.e., those corresponding to the gravitational fields do not depend on the matter fields. Consequently, the purely gravitational supermagnitudes already fulfill the PB closing relations (24),(25) and(26) for $\{,\}_G$, and, of course, are matter independent (null PB under $\{,\}_M$). Thus, given that the total supermagnitudes must fulfill such closing relations for the complete Poisson bracket $\{,\}$, and assuming that $\mathcal{H}_M$ depends on the 3-metric h only locally, it can be seen that matter superhamiltonian fulfills also (24) for $\{,\}_M$, as the former conditions imply:

$$\{\mathcal{H}_G(x),\mathcal{H}_M(x')\}_G + \{\mathcal{H}_M(x),\mathcal{H}_G(x')\}_G = 0 \tag{32}$$

because of locality (on π and h for both derivatives) and antisymmetry.
Regarding the relations that involve supermomenta, on the one hand, as a result of eq.

(27) for classical theories, $\mathcal{H}_{iM}$ does not depend on h, π_h at all, and thus it can be seen that it must fulfill also (26) for $\{,\}_M$, because:

$$\{\mathcal{H}_i(x), \mathcal{H}_{jM}(x')\}_G = 0 \ . \tag{33}$$

On the other hand, to fulfill (25) we need:

$$\{\mathcal{H}_i^G(x), \mathcal{H}^M(x')\}_G + \{\mathcal{H}_i^M(x), \mathcal{H}^M(x')\}_M = \mathcal{H}^M(x)\delta_{,i}(x,x') \ . \tag{34}$$

The crossed gravitational-matter term gives:

$$\{\mathcal{H}_i^G(x), \mathcal{H}^M(x')\}_G = 2h_{i\alpha}(x)D_{x^j}\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)} \tag{35}$$

and thus the matter sector term should provide:

$$\{\mathcal{H}_i^M(x), \mathcal{H}^M(x')\}_M = -2h_{i\alpha}(x)D_{x^j}\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)} + \mathcal{H}^M(x)\partial_{x^i}\delta(x,x') \ . \tag{36}$$

With these closing relations for matter theories coupled in an ultralocal way to the metric we have assured that the total supermagnitudes given by the sum of the geometrical and matter ones fulfill the closing relations of Dirac's generators under the total Poisson bracket. On the other hand, we have assured that they generate the same transformation as the Lie derivative along the shift vector, for a tangential deformation, as in (27). Both conditions together ensure that they are the appropriate generating functions of hypersurface transformations over the whole phase space.

2.5. Classical dynamics and constraints.

Once a foliation of spacetime is chosen, the relations within hypersurfaces is given by the flow α_E. In the 3+1 perspective, from a hypersurface one can access the infinitesimally neighbouring one through a normal deformation and a tangential deformation. Once such deformations are represented in a Hamiltonian way such paths along hypersurfaces are mapped to a path over the phase space of fields, which is the solution to the Hamiltonian dynamics, with the role of time being played by the parameter s:

$$\frac{dF}{ds} = \{F, H\} + \partial_s(N^{\mu x})\frac{\delta}{\delta N^{\mu x}}F + \partial_s F \quad \forall F \in C^\infty(\mathcal{F}_C \times \mathbb{R}) \tag{37}$$

where F is any functional over phase space plus lapse and shift variables, with a possible explicit differentiable dependence on $s \in \mathbb{R}$.
The total Hamiltonian H reproduces E through the contraction of the lapse and shift functions N, N^i, with the corresponding generating functions $\mathcal{H}(x)$, $\mathcal{H}_i(x)$:

$$H(s) = N^x(s)\mathcal{H}_x + N^{ix}(s)\mathcal{H}_{ix} \ . \tag{38}$$

Note that lapse and shift are s dependent functions (each hypersurface with label s relates through E with the neighbouring one, which has a different normal and tangential

deformation to define the next one), and, as such, the formalism is analogue to having an explicitly time dependent Hamiltonian function.

Note also that, making use of eqs. (30) and (31) this Hamiltonian can be decomposed as the sum of a purely geometrodynamical and a matter field Hamiltonian $H(s) = H_G(h, \pi_h, N(s), N^i(s)) + H_M(h, \phi, \pi, N(s), N^i(s))$, such that:

$$H_G(h, \pi_h, N(s), N^i(s)) := N^x(s)\mathcal{H}^G_x + N^{ix}(s)\mathcal{H}^G_{ix} \, , \tag{39}$$

$$H_M(h, \phi, \pi, N(s), N^i(s)) := N^x(s)\mathcal{H}^M_x(h, \phi, \pi) + N^{ix}(s)\mathcal{H}^M_{ix}(h, \phi, \pi) \, . \tag{40}$$

We anticipate that this matter Hamiltonian is the function whose quantization will yield the Hamiltonian operator governing the dynamics at the quantum level.

In the end, the integral curves of the s-dependent Hamiltonian field associated to $\{ \cdot \, , H(s)\}_H$ reproduce over phase space the action of $\alpha_E(s)$ over the hypersurfaces. Once we have the solution to the Cauchy problem the foliation can be undone obtaining physical data over spacetime which must be the same independently of the foliation chosen. In other words, independently of the path followed from one initial hypersurface Σ_0 to a final one Σ_{s_f}, given by the lapse and shift functions $\forall s \in [0, s_f)$, the field content on the final hypersurface must be the same, departing from a given initial Cauchy data. This is introduced in [19] as path independent principle. Naturally, given that the path from an initial hypersurface to a final one is spawned by a continuous set of infinitesimal transformations, independence of the path implies, at the infinitesimal level, commutativity of the associated generators over phase space, for any normal and tangential transformation. In its Hamiltonian representation, for two arbitrary deformations characterized by N^x_A and $\tilde{N}^{x'}_B$ this implies:

$$\{N^x_\mu \mathcal{H}_{\mu x}, \tilde{N}^{x'}_\nu \mathcal{H}_{\nu x}\} = N^x_\mu \tilde{N}^{x'}_\nu \{\mathcal{H}_{\mu x}, \mathcal{H}_{\nu x'}\} \simeq 0 \; \forall \mu, \nu = 0, \cdots, 3, \forall N^x_\mu, \tilde{N}^{x'}_\nu \in C^\infty(\Sigma) \, . \tag{41}$$

where $\simeq$ implies that this constraint holds only *on shell*, *i.e.* once the physical constraints are satisfied. Given that the functions contracting the local generators are arbitrary, the former condition implies that it must hold locally:

$$\{\mathcal{H}_{\mu x}, \mathcal{H}_{\nu x'}\} \simeq 0 \quad \forall \; \mu, \nu = 0, \cdots, 3 \tag{42}$$

Given that the total Poisson brackets of the supermagnitudes fulfill the closing relations (24),(25),(26), which are linearly proportional to the supermagnitudes, the nulity of the closing relations on shell can only by given by the so called Hamiltonian and momenta constraints, which is just the nulity of the total local generators:

$$\mathcal{H}(x) \simeq 0 \quad \text{and} \quad \mathcal{H}_i(x') \simeq 0 \tag{43}$$

These constraints will have their analogue at the hybrid level, for the generating functions for quantum matter and classical geometry, in order to preserve path independence.

3. Quantum Field Geometrodynamics.

Let us consider now that instead of a classical matter field, we have a quantum one. Apparently, it should be possible to adapt the construction above to include this new case, as long as we are able to find a Poisson structure on the space of quantum fields behaving in a similar way to the classical field Poisson bracket. We should transport the previous framework to the case of quantum matter sources, defining a Quantum Phase Space made of Quantum Wave Functionals of the quantized matter fields and provided of a Quantum PB. Our guiding light will be the representation of kinematics of hypersurfaces appropriately for the quantum functionals and thus, the search of quantum supermagnitudes fulfilling the matter closing relations under the Quantum PB.

In this section, we will focus on the construction of the Hamiltonian formalism of quantum field theory for a given background spacetime. Nonetheless, the construction of this Hamiltonian picture is much more complicated than in a trivial foliation of flat spacetime, since the gravitational degrees of freedom have an active role in the construction of the quantization mapping. In turn, those gravitational degrees of freedom have a parametric time (leaf label) dependence, and therefore the ingredients defining quantum theory become different for each hypersurface of the foliation. Hence, when considering the action of the derivative with respect to the gravitational fields on the quantum degrees of freedom, the outcome may be non-vanishing. Thus, a careful analysis of the geometrical properties of the manifold of quantum fields, which, as we will see, will depend on the gravitational degrees of freedom, is necessary before considering the extension of geometrodynamics to the quantum realm. This approach is, to our knowledge, different from the usual construction of QFT in curved spacetime and constitutes the first original contribution of this paper.

3.1. Geometry of classical phase space and quantization.

As it is commonly done in Quantum Mechanics, the set of quantum operators is obtained from classical field theory by a quantization mapping Q of the observables over the field manifold,*i.e.* real functionals over the classical field phase space. On the other hand, the states are suitable representations of the dual of such C^* algebra of operators obtained through Q. Such representations of the states must be adapted to the representation of the operators given by the quantization mapping (considering elements of a certain L^2 over which the operators are self adjoint).

In our construction, we will require of a geometrical description of the quantum fields in terms of Poisson brackets and Hamiltonian dynamics, and therefore, it seems natural to use the geometrical formulation of Quantum Mechanics [24, 17], where these structures are canonical. As a result, our space of quantum states will be endowed with a Kähler structure which will allow for a Hamiltonian description of quantum dynamics.

Furthermore, quantum operators will be described as real sesquilinear functions of the quantum states in the form $F_A(\Psi) = \langle \Psi, A\Psi \rangle$, which form a suitable Poisson subalgebra with respect to the natural Poisson algebra associated with the symplectic tensor of the Kähler structure. In addition, the quantization procedure links the states, operators and geometrical structures of our quantum system to the ones of the classical matter field theory considered for quantization. Thus, we must prepare such classical theory endowing it with some specific geometrical structures.

Firstly, we know that the classical field theoretical phase space is already provided with a symplectic structure,

$$\omega_C = -d\phi_x \wedge d\pi^x \tag{44}$$

regarded as the (weak) inverse of its Poisson tensor. Such symplectic structure, as a tensor, is built independently of the geometrodynamical variables, lapse and shift, which can be mathematically expressed as:

$$\mathcal{L}_{\{,f\}_G} \pi_F^* \omega_C = 0, \quad \text{where} \quad \pi_F^* \omega_C \in (\wedge^2 T^\star(\mathcal{M}_F \times \mathcal{M}_G \times \mathcal{M}_N)) \,, \tag{45}$$

where π_F represents the canonical projection on the cotangent bundle $T^*\mathcal{M}_F$ and the Lie derivative is taken with respect to any Hamiltonian vector field represented by $\{ \cdot , f\}_G$ in the direction of gravitational fields and is assumed to vanish due to the lack of dependence on the gravitational degrees of freedom. Notice that, with this formulation, we have chosen to see ω_C as a two form over the whole manifold, even if it only acts on vectors with components on the matter side, just to define the independence as being constant along any curve that does not change the material data.

This is imposed by the very nature of Hamiltonian dynamics, as the fields ϕ_x, represented as functions, are fundamental kinematical variables, considered independent of any of the geometrical variables, Lapse or shift which we collectively denote by $\xi = (h, \pi_h, N, N^i) \in \mathcal{M}_G \times \mathcal{M}_N$. Analogously, in the usual prescription of Hamiltonian dynamics, its cotangent space contains the momenta, considered as densities of weight 1, and thus independent variables of φ, h, π_h,N, N^i. Thus, having defined such canonical coordinates over the cotangent bundle, from the definition of the symplectic structure in eq. (44), it is clearly ξ-independent. In the following, this crucial property will be referred to as *leaf independence* for any tensor or function fulfilling the same condition as the symplictic form does in eq. (45) .

On the other hand, keeping in mind the objective of geometrodynamics of defining a total Poisson structure for geometry and matter, it is relevant to notice that at least the (h, π_h)-independence of the symplectic structure is very convenient, as it ensures the compatibility of both Poisson brackets and therefore the total Poisson bracket defined in eq. (21) is also a Poisson bracket over $C^\infty(\mathcal{M}_G \times \mathcal{M}_F)$.

Armed with this leaf independent ω_C, we may add a complex structure of our choice, J_C, to form a Kähler structure. Such complex structure has no meaning at the classical level, but prepares the classical field theory for quantization and defines the set of 1-particle states of the quantum field. In fact, all the possible choices of inequivalent quantization (choices of inequivalent vacua and measures) are reduced to the choice of such a classical complex structure [35, 5] whether one works with geometric quantization [30] or with algebraic quantization [10].

Besides, while ω_C was constructed leaf-independently, J_C may be chosen to be ξ-dependent. In fact, in [5], physical arguments are made in the case of stationary space times, in favour of a choice of complex structure over the space of solutions that, when projected over Cauchy data on a given leaf [10], yields precisely a complex structure over $\mathcal{M}_C$ with such dependence.

To include such particular case and more general ones, in this paper we will consider a general quantization procedure dependent on a complex structure that, in turn, may depend smoothly on (h, π_h, N, N^i). This might be seen as a smooth ξ-parametric family of complex structures. Consequently, we will have a different quantization for each $\xi \in \mathcal{M}_G \times \mathcal{M}_N$, making up for a ξ-parametric family of smoothly-related but unitarily-inequivalent quantizations. In ordinary Quantum Mechanics, Stone-von Neumann theorem provides us with unitary equivalence, allowing us identify the representation of the same quantum state within different Hilbert spaces. This is not the case in QFT. Given the unavoidable need of relating different quantizations associated to different hypersurfaces along the foliation, we must introduce another equivalence relation not based on unitary transformations. Based on our geometric approach, we will consider the language of connections and parallel transport.

Notice also that because of the dependence of the quantization process on the gravitational degrees of freedom (3-metric, its momentum and lapse and shift variables), it is natural to consider a fibration $\tau_{\mathcal{F}} : \mathcal{F} \to \mathcal{B}$, where the base manifold is defined as $\mathcal{B} := \mathcal{M}_G \times \mathcal{M}_N$, the total manifold is defined as $\mathcal{F}$ and the fiber $(\mathcal{N})'$ is a suitable functional space (Hida distributions, see [2, 3]) containing all possible Hilbert spaces $L^2(\mathcal{N}', D\mu)$ with respect to different Gaussian measures $D\mu$. Within this framework, we will bind the representation of quantum states to suitable sections of the bundle $\mathcal{F}$, assigning an element of a (possibly different) Hilbert space to each point of the base. As a result, the quantum states will exhibit an explicit dependence on the gravitational degrees of freedom and the nature of their derivative w.r.t. the leaf variables $\xi \in \mathcal{B}$ will be key for the quantum supermagnitudes to fulfill the closing relations of Dirac's group, eqs. (24),(26),(36).

The key motivation to define the states in this way § is precisely the Kähler structure

§ In the particular case of geometric quantization this new section nature of the states (beyond the usual one) arises as early as in the prequantization. The last step to prepare the classical space for a

with which we have provided the phase space of classical fields $\mathcal{M}_F$ and which determines the quantization [35, 5, 10]. A Kähler structure is a triad of tensors given by a symplectic form ω_C, a complex structure J_C (both introduced above) and a Riemannian metric μ_C, fulfilling the following compatibility condition:

$$\mu_C(\cdot,\cdot) = \omega_C(J_C\cdot,\cdot)\,. \tag{46}$$

Note that, given that ω_C as defined in (44) was leaf independent, and that J_C is chosen leaf dependent, μ_C inherits its leaf dependence. Together, they may provide the complexification of $\mathcal{M}_F$ under J_C with a hermitian product $h_C = (\mu_C + i\omega_C)/2$.

The relation with quantization is that such hermitian product is used to define the characteristic functional (analogously, the integral kernel) of a Gaussian measure $D\mu_\xi(\phi)$ over the space of fields (in other texts, the vacuum state) in the following way:

$$\int_{\mathcal{N}'} D\mu_\xi(\phi) e^{(i\bar{\rho}_x\phi^x + i\rho_x\bar{\phi}^x)} = e^{-h_C^{-1}(\bar{\rho},\rho)}\,, \tag{47}$$

where we have chosen complex domain for the measure (this construction is proper of an holomorphic picture, but it can be related with the real Schrödinger picture straightforwardly through a Segal-Bargmann transform [2]). This characterizes the Gaussian measure $D\mu_\xi$ univocally, becoming the quantum heir of the leaf dependence of the classical complex structure J_C.
In turn, this measure will provide the scalar product of the usual Hilbert space characterizing the QFT constructed over the space of classical fields, $L^2_{\mathrm{Hol}}(\mathcal{N}', D\mu_\xi)$, where the subindex stands for "holomorphic", following the example above. For any two elements $\Psi_1, \Psi_2 \in L^2_{\mathrm{Hol}}(\mathcal{N}', D\mu_\xi)$, its scalar product is then defined as:

$$\langle \Psi_1, \Psi_2 \rangle_\xi = \int_{\mathcal{N}'} D\mu_\xi(\phi) \bar{\Psi}_1(\bar{\phi}) \Psi_2(\phi) \tag{48}$$

This construction is thoroughly detailed in [2], where, to relate with the current discussion one must only add the ξ-dependence to J_C.
Notice that we have a different J_C, μ_C, h_C and, lastly, Gaussian measure $D\mu_\xi$ for each $\xi \in \mathcal{B}$. Therefore, through this construction we arrive at a ξ-parametric family of unitarily-inequivalent Hilbert spaces. This result is general, beyond the example used in the construction above, and in the following it will be synthesized in the subindex for the quantum scalar product, $\langle , \rangle_\xi$, either if the domain is given by real (Schrödinger picture) or complex (holomorphic) fields.

geometric quantization procedure is given by the choice of a Lagrangian submanifold of the space of fields over which the quantum states, as wave functionals, will have its domain. This is done by means of a symplectic potential 1-form, θ_C, which defines a polarization. The choice of such 1-form is usually dependent on J_C, which in turn is ξ-dependent. Thus, we have a ξ-parametric family of spaces of states adapted to a ξ-parametric family of polarizations. For details, see [30].

Therefore, notice that not only the quantum sections $\sigma_\Psi \in \Gamma(\mathcal{F}, \mathcal{B})$ will yield a different functional representing the quantum state at each point $\xi \in \mathcal{B}$, but at each point $\xi \in \mathcal{B}$, the probabilistic properties of the state $\sigma_\Psi(\xi) = \Psi \in (\mathcal{N})'$ must be considered with respect to a different Hilbert space structure, given by the ξ-dependence of the scalar product. Besides, the necessity of defining a Poisson bracket and therefore a differentiable calculus on the space of quantum states, forces us to consider a special structure known as Gel'fand triple [3], in fact, a ξ-parametric family of them, given by:

$$(\mathcal{N}) \subset L^2(\mathcal{N}', D\mu_\xi) \sim L^2(\mathcal{N}', D\mu_\xi)' \subset (\mathcal{N})' \, . \tag{49}$$

These structures define a (family of) isomorphism(s) between the space of Hida test functions $(\mathcal{N})$ and a suitable subspace of its dual $(\mathcal{N})'$, which is an essential tool for managing differential tensors on the space of states (see [2, 3] for details). Remarkably, Hida functions conform a nuclear-Frechèt space $(\mathcal{N})$, allowing us to perform Fréchet calculus in a convenient setting ([27]). Being dense in all L^2 spaces considered (and ultimately, in the space of Hida distributions $(\mathcal{N})'$ that includes them all), it justifies the (dense) construction of differential geometry over these infinite dimensional manifolds. This mathematical intricacies will play a pivotal role in the construction of the main kinematical object: the quantum Poisson bracket as a bi-differential operator, or in relation with a quantum symplectic structure. Nonetheless, to focus on the physical aspects, such technical nuances (which are standard in Hida calculus) shall be relegated to the supplementary material for ease of reference.

In conclusion, the choice of ξ-dependent complex structure renders the whole construction leaf dependent and, in the end the quantum states themselves must become leaf dependent to be consistent with this leaf dependence of the Hilbert spaces. Analogously, the self-adjoint operators representing physical magnitudes, for whom the notion of self adjointness is relative to the ξ-dependent scalar product $\langle , \rangle_\xi$, also must acquire a consistent leaf dependence. Inspired by this, we will postulate such section nature of the states and leave their specific dependence on $\xi \in \mathcal{B}$, together with the choice of J_C, as ingredients to be fixed consistently for the quantization to be compatible with the Hamiltonian formulation of the symmetries of spacetime.

3.2. Functional representation of quantum states and leaf dependent quantization. Quantum fibrations

In the usual wave functional picture of Quantum Field Theory, the states Ψ are represented by elements of a functional space endowed with an Hermitian product $\langle , \rangle$, associated to a Gaussian measure over the fields $D\mu$, turning it into a Hilbert space $\mathcal{H} = L^2(\mathcal{N}', D\mu)$. In order to define properly the geometric tools required, such as the integral measure, we will consider the domain $\mathcal{N}'$ as a space of distributions dual to some nuclear-Frechèt space (for example, differentiable functions of compact support, in the case of Σ compact) which represents the classical matter fields ϕ (see [2] for an exhaustive elucidation of these intricacies). For such Hilbert space, we may represent

the dual element to Ψ with $\bar{\Psi}$ under the effect of the measure $D\mu$, by means of the isomorphism of the Hilbert space and its dual $\mathcal{H} \sim \mathcal{H}'$ associated with Riesz theorem. Such Gaussian measure is defined in terms of the Kähler structure of the classical field theory, as introduced above. Different choices of complex structure will ultimately lead to unitarily inequivalent Hilbert spaces, although the Hida functions ($\mathcal{N}$) will be a dense common subset to all of them, and they will all be subsets of the Hida distributions $(\mathcal{N})'$. This inequivalence is also present in the Fock space representation which can be defined from the Hilbert space fixing the measure and a vacuum phase (see [10]).

From the preceding section we must remember that, instead of considering a single one of such structures, in our construction we must consider a ξ-parametric family of inequivalent Hilbert spaces, as the complex structure $J_C(\xi)$ can be ξ-dependent, as in[5], completing the aforementioned Kähler structure differently for each ξ. Thus, the representation of the quantum states (considered from the point of view of probability theory, and then dependent on the Hilbert space structure) must become dependent on the classical (gravitational) degrees of freedom. This classical dependence of the quantum states constitutes the most striking difference with respect to other hybrid physical models where quantum and classical degrees of freedom interact (as in [1]). In those models, one could define the classical and quantum submanifolds separately and construct the hybrid manifold as the Cartesian product. We are going to borrow from those models the main ideas to construct a hybrid dynamics as a Hamiltonian system, but, now, we must define the manifold of quantum states already in an entangled way with the classical (gravitational) variables. Therefore, the quantum states already contain hybrid information, and in the following construction, all quantum structures defined (Poisson bracket, scalar product, relation of operators with physical observables) reproduce the usual construction of Hamiltonian quantum mechanics only fiber-wise for a fibration $\tau_{\mathcal{F}} : \mathcal{F} \to \mathcal{B}$ which is locally trivialized into subsets of

$$\mathcal{B} \times (\mathcal{N})' \quad \text{with base} \quad \mathcal{B} := \mathcal{M}_G \times \mathcal{M}_N \, . \tag{50}$$

Note that the fiber is adapted to the usual functional description of quantum states (in particular, we are choosing the space of Hida distributions [3]), and thus, for a fixed element in the base $\xi := (h, \pi, N, N^i) \in \mathcal{B}$, we would have the ordinary formulation of geometric quantum mechanics [24, 17], particularized to QFT in [2, 3]. In other words, we have all quantum structures defined consistently, but also differently at each point $\xi \in \mathcal{B}$, and we need a way to relate them. To do so, in the following we will reproduce [24], but with a focus on the physical features, relegating most mathematical details, based on a geometric formulation of QFT, to the notes in the supplementary material.

Notice also that $(\mathcal{N})'$ is too big to represent efficiently the physical quantum states, the structures that we present here, such as the hermitian product, are defined on a dense subset $D(\langle , \rangle_\xi) \subset (\mathcal{N})'$, different for each point of the base and representing the Hilbert space of physical quantum states.

Taking this into account, the representation of the quantum state at a certain geometrical point (ξ_0, Ψ_0) is related to other points in $\mathcal{F}$ obtained through a change in ξ. Imagine a curve $\gamma^M(s)$ in $\mathcal{B}$, and let us consider how a given quantum state transform along γ^M. In order to do that, we must introduce a mechanism to lift the curve on the base to the fibration $\mathcal{F}$, in such a way that it projects on γ^M by the projection $\tau_{\mathcal{F}}$. Hence, a connection on $\mathcal{F}$ is required, in such a way that the notion of horizontal direction is defined for the points of the bundle. Associated with this connection, the notion of horizontal lift is well defined and a (locally) unique curve $\gamma^{\mathcal{F}}$ on $\mathcal{F}$ containing the state Ψ_0 exists. Such a curve satisfies that

$$\gamma^M(s=0) = \xi_0; \quad \gamma^{\mathcal{F}}(s=0) = \Psi_0; \quad \tau_{\mathcal{F}}\left(\gamma^{\mathcal{F}}(s)\right) = \gamma^M(s). \tag{51}$$

In a local description, the connection is associated with a one-form $\Gamma \in \Lambda^1(\mathcal{B}) \times \mathrm{Lin}(\mathcal{N})$, which allows us to define the covariant derivative of a section $\sigma : \mathcal{B} \to \mathcal{F}$, using the parallel transport defined through the horizontal lift of base curves:

$$\nabla_X \sigma(\xi) = d\sigma(X) - \hat{\Gamma}(\xi, X)\sigma(\xi), \quad X \in \mathfrak{X}(\mathcal{B})$$

If we consider those sections which are covariant with respect to the connection

$$\nabla_X \sigma(\xi) = 0,$$

we are defining a trajectory describing the change suffered by the quantum state with an initial state $\sigma(\xi_0) = \Psi_0$ due solely to the change on the quantum structures due to a change of $\xi \in \mathcal{B}$, when no quantum evolution is exerted on it. Thus, this would define the evolution of the ξ-dependent representation of a quantum state due to the evolving geometry, but under a vanishing matter Hamiltonian (*i.e.* in the geometrodynamical framework, matter supermagnitudes which are identically null). ‖ If we consider a non-trivial Hamiltonian operator $\hat{H}$ (or, in particular, the Hamiltonian representation of a certain deformation of the hypersurface Σ), the total evolution of the quantum state will be the sum of the image under a covariant section of the geometric transformation (thus, a horizontal change, with respect to the connection) and the effect of Schrödinger functional equation, which is vertical on the fiber of $\mathcal{F}$.

Following this discussion, in order to lift the infinitesimal changes of the geometry (tangent vectors to curves on the base) to the changes induced on the representation of the quantum state (which lives on the fiber) due to the leaf dependence quantization, it becomes relevant to define the subset $\mathcal{M}_{\mathrm{s}}$ of sections on the bundle $\mathcal{F}$ which are covariant for all vector fields on the base of the fibration, $X \in \mathfrak{X}(\mathcal{B})$:

$$\mathcal{M}_{\mathrm{s}} := \{\sigma \in \Gamma(\mathcal{F}) | \nabla_X \sigma = 0 \ \forall X \in \mathfrak{X}(\mathcal{B})\} \tag{52}$$

In turn, in terms of these objects (which are illustrated in Figure 1) we may consider the horizontal distribution on $T\mathcal{F}$ representing the constraints of the transformations

‖ Had we done the same for the classical case on the classical bundle $\mathcal{F}_C$, the classical geometric evolution would define lines where only the gravitational degrees of freedom change. This would correspond to a trivial connection.

of quantum states to be compatible with geometry transformations, given the leaf dependence of the Hilbert space to which they belong. It is defined by the horizontal vector fields on $\mathcal{F}$, or, equivalently, by the directions which are tangent to the former covariant sections taking values at a given point of the fibration $f \in \mathcal{F}$:

$$\mathrm{Hor}^{\nabla}(f) = \left\{ T\sigma_{\tau(f)}(\mathfrak{X}(\mathcal{B})),\ \forall \sigma \in \mathcal{M}_s |\ \sigma(\tau(f)) = f \right\}, \tag{53}$$

where $T\sigma_{\tau(f)}(\mathfrak{X}(\mathcal{B}))$ represents the image of the differential of the mapping $\sigma : \mathcal{B} \to \mathcal{F}$ evaluated at the point on the base given by the vertical projection $\tau(f) \in \mathcal{B}$ acting on all vector fields on the base manifold. Obviously, the tangent space on a point of the fibration can be decomposed as:

$$T_f\mathcal{F} = V_f\mathcal{F} \oplus \mathrm{Hor}^{\nabla}(f); \qquad \forall f \in \mathcal{F}, \tag{54}$$

where $V_f\mathcal{F}$ represents the set of vertical vectors at f.

When the mathematical dust is settled it becomes clear that the definition of $\mathrm{Hor}^{\nabla}(f)$ provides us with a way of defining tangent vectors to curves on $\mathcal{F}$ that are only sensitive to trajectories on the geometrodynamical data, i.e. they are horizontal. This definition encodes the notion of an infinitesimal change of representation of the quantum state without proper quantum evolution, which would be a vector on the vertical subspace.

In fact it is clear that tangent elements to physical states should be represented by a fiber bundle such that $V_f\mathcal{F}$ represent infinitesimal generators of inner transformations to a given Hilbert space associated to the measure $D\mu_{\tau(f)}$ while $\mathrm{Hor}^{\nabla}(f)$ represent generators of isometries between, possibly unitary inequivalent, infinitesimally close Hilbert spaces. In this sense, under the complete evolution, said representation of quantum states will transform to be outside the original Hilbert space, and inside a new Hilbert space. This justifies the chosen construction of the fibration, where the fiber to which the quantum states belong must be a space that contains all the $L^2(\mathcal{N}', D\mu_\xi)$ through which the quantum state will evolve following the curve over $\mathcal{B}$. Such space is chosen to be Hida distributions $(\mathcal{N})'$, although, locally (for a given ξ and thus a given Hilbert space), it is too large to accommodate solely the physical quantum states and one should restrict (locally) the construction to a suitable subspace of it (see Figure 2 for a graphical summary of this construction).

It is important to remark that the construction is, of course, not unique. Every choice of a connection for $\mathcal{F}$, defines a different notion of covariant derivative. Choosing a different connection implies considering equivalent different quantum states for different geometric points (i.e,. different evolutions of the quantum states because of the changing geometry). Nonetheless, as the construction is geometrical, the same connection would define a horizontal lift to the bundle of complex structures, scalar products, linear operators or any other tensor chosen to define a fiber on $\mathcal{B}$. A natural consistency condition is to choose the same connection for all the tensors. When doing that, it makes sense to consider normalized quantum states for all geometrical points, since the

scalar product and the states can be chosen to transform covariantly with respect to the same connection (see below).

Nonetheless, remember that geometrodynamical transformations affect also, in a precise way, to the classical matter fields. Thus, for the whole procedure to be consistent, we must find a connection on $\mathcal{F}$, in such a way that the ξ-dependent quantization procedure that we build lifts the geometrodynamical classical generators on the space of classical fields to a consistent set of geometrodynamical quantum generators. As we will see below, such a construction is possible if the quantization mapping and the covariant scalar product and linear operators are related in a particular way.

The only extra ingredient in relation to [24] is thus that, given the smoothly leaf dependent quantization inherited to all quantum objects from $J_C(\xi)$, the quantum states become related to the quantum sections over the fibration $\tau_{\mathcal{F}}$.

We know already that geometrodynamics consists in adapting the vector fields generating the space-time foliation to the different field-manifolds. In the particular case of the quantum pure states manifold, quantum states and operators must be considered as the evaluation of sections of the fibration over the set of gravitational degrees of freedom. Thus, the geometrodinamical generators on the quantum-state manifold must correspond to horizontally lifted vector fields from the geometrodinamical generators on the space of gravitational fields with respect to the fibration since they must implement the transformation which represents the change of leaf of the space-time foliation at the level of the quantum fields, which depend on the geometric degrees of freedom. Having defined the connection, the quantum states are to be defined as the images of the parallel transported sections with respect to such connection:

$$\mathcal{M}_Q := \{\sigma_\Psi(\xi) \quad \forall \xi \in \mathcal{B}, \ \ \forall \sigma_\Psi \in \mathcal{M}_s\} \tag{55}$$

From Equation (54), we can safely consider that $\mathcal{M}_Q$ is identical to the fiber of $\mathcal{F}$, but we consider that presented in this form, as the image space of the covariant sections with respect to the connection, the meaning of the horizontal directions in $T_\Psi\mathcal{F}$ is more clear. Let us observe that, with an element of the space of covariant sections $\mathcal{M}_s$ and an element of the base $\mathcal{B}$ characterizing geometry, we can obtain the *instantaneous* quantum state just by evaluating the former on the later. This must not be confused with the *history* of the quantum state, *i.e.* the solution curve to the dynamics, as part of the evolution is vertical and, thus, such curve can not be covariant. Nevertheless, following the former isomorphism between $\mathcal{M}_Q$ and $\mathcal{B} \times \mathcal{M}_s$, the history could also be represented as a curve over $\mathcal{M}_s$ (the vertical part of the evolution will change from one covariant section to another) together with a curve over $\mathcal{B}$ (the horizontal part will change the evaluation point for the covariant sections), yielding together the evolution of the quantum state. These properties will be relevant by the end of the following section, and are illustrated in Figure 3.

Once we define a distribution for each one of such variables defining a global direction in the base given by $v_B^x := (\dot{h}_{ij;x}, \dot{\pi}^{ij;x}, \dot{N}^x, \dot{N}^{ix})$, considered with respect the basis $\xi^{i;x} = (h_{ij;x}, \pi^{ij;x}, N^x, N^{ix})$ we can see how the quantum section is parallely

transported as:

$$v_B^{i;x}\partial_{\xi^{i;x}}\sigma_\Psi(\xi) = -(\dot{h}_{ij;x}\hat{\Gamma}_{h_{ij;x}} + \dot{\pi}^{ij;x}\hat{\Gamma}_{\pi^{ij;x}} + \dot{N}^x\hat{\Gamma}_{N^x} + \dot{N}^{ix}\hat{\Gamma}_{N^{ix}})\sigma_\Psi \tag{56}$$

where the ξ-dependence is not showed for compactness of the notation and the contraction of i, j indices implies summation over the elements of the basis, while the contraction of the continuous x-indices implies integration over Σ. Having this in mind, we will frequently work with the notation $\partial_\xi\sigma_\Psi(\xi) = -\hat{\Gamma}(\xi)\sigma_\Psi(\xi)$, to denote the connection associated to any local variable of the base.

Remember, though, that even if the covariant sections are just a tool to define the horizontal distribution Hor^∇ on the bundle $\mathcal{F}$, they represent the transformations of the quantum states under the effect of pure geometrodynamical (and lapse and shift) transformations. Hence, they represent the kinematics of the quantum field theory in the geometrical background where it is defined. Note that, by definition, the each covariant section, as defined above, once evaluated on the point of the base characterizing the geometrodynamical data $\xi_0 \in \mathcal{B}$ on the current Σ_s, yield a certain element of $\mathcal{M}_Q$, isomorphic to an element of the fiber $(\mathcal{N})'$ which is a valid quantum state.

Note that, at the level of QFT in given Curved Spacetime, once the foliation is chosen, the evaluation point ξ_0 is a given time dependent parameter. In the following section we will promote such evaluation point to be part of the kinematics, extending the phase space to contain the quantum sections and the base point over which they must evaluated, as the kinematics of hybrid geometrodynamics considers both elements on the same footing. Summarizing: the necessity of considering the leaf dependence of the quantum theory (complex structure, scalar product, states, operators, etc) to implement geometrodynamical transformations, forces us to introduce a fibration of all those quantum ingredients over the manifold of geometric variables, and quantum objects become the images of sections of that fibration. These section objects are of kinematical nature (required to be consistent with the leaf dependent quantization) and contain more information than just the physical one. True physical objects correspond to the evaluation of those sections on the particular geometric point (gravitational field, momenta, lapse, shift, ...), but the whole section is necessary to encode appropriately the influence of the geometry on them.

Thus, to pose the Cauchy problem we will only need to choose any suitable Hida distribution determining Ψ (plus the geometrodynamical data and in compatibility with the physical constraints introduced later), knowing that the covariant sections of $\mathcal{F}$ allow us to consider, with the former definition of $\mathcal{M}_Q$,

$$\partial_{\xi_0}\Psi = (\partial_\xi\sigma_\Psi(\xi))\,|_{\xi_0} = -\hat{\Gamma}(\xi_0)\Psi \tag{57}$$

This corresponds to the directions at $T_\Psi\mathcal{F}$ which are horizontal with respect to the connection. Obtaining the integral curve from Ψ with that tangent vector, we will define

a series of quantum states which are equivalent from the kinematical point of view, since correspond to changes in the geometry only. The objective of the following construction is to end up determining such connection $\hat{\Gamma}$ in order to have consistent hybrid geometrodynamics, providing compatibility in a certain sense for the ξ-parametric family of quantizations (and resulting quantum structures).

Regarding observables, through quantization they are mapped to be self adjoint operators over the chosen Hilbert space. Given that such quantization procedure Q is J_C dependent, the operators must inherit its leaf dependence. Therefore, it can be considered to define a bundle, with base manifold $\mathcal{B}$ and fiber the space of linear operators on the Hilbert space which defines the fiber of $\mathcal{F}$. For such a bundle, we can again consider the sections which are covariant with respect to connections defined on it, providing the corresponding horizontal directions. Of course, among the connections, we may consider again the connection ∇ on the bundle $\mathcal{F}$ of the space of states. As we are going to see, the choice of the same connection for both bundles will make problems simpler. Furthermore, one must realize that the notion of adjointness is referred to the leaf dependent scalar product $\langle , \rangle_\xi$. More explicitly, let us consider that the adjoint to an operator $\hat{A}$ is given by $\hat{A}^{\dagger_\xi}$ for that particular scalar product, so that:

$$\langle \Psi_1 \mid \hat{A}\Psi_2 \rangle_\xi = \langle \hat{A}^{\dagger_\xi}\Psi_1 \mid \Psi_2 \rangle_\xi \tag{58}$$

then, for a different scalar product $\langle , \rangle_{\xi_2}$ provided by another element of the ξ-parametric family of Gaussian measures, we find that $\hat{A}^{\dagger_\xi}$ no longer defines the adjoint operator:

$$\langle \Psi_1 \mid \hat{A}\Psi_2 \rangle_{\xi_2} \neq \langle \hat{A}^{\dagger_\xi}\Psi_1 \mid \Psi_2 \rangle_{\xi_2} \tag{59}$$

Therefore, the set of self-adjoint operators, *i.e.* those that fulfill $\hat{A} = \hat{A}^\dagger$, must acquire a different representation for each Hilbert space in the ξ-parametric family. In the functional representation, it can easily be apprehended by considering that, in particular, the functional derivatives representing the quantization of the field momenta are chosen to be self-adjoint with respect to a leaf dependent measure $D\mu_\xi$ ¶ (and w.r.t. the vacuum phase, which adds an imaginary multiplicative term, which is also leaf dependent [10]). This leads us to the definition of the algebra of observables $\mathcal{A}_Q$ within this geometrical formulation. As in [24] (and in its hybrid case, [1]), it is precisely given by the set of

¶ As an example one can consider geometric quantization to illustrate this dependence. Given that the symplectic potential θ is chosen relative to J_C and thus it inherits its leaf dependence, the quantization of any element of the classical field Poisson algebra $f \in C^\infty(\mathcal{M}_F \times \mathcal{M}_G \times \mathcal{M}_N)$ given by $Q(f) = (X_f + \theta(\xi)X_f) + f$, with $X_f = \{\cdot, f\}_c$, acquires extra dependences on ξ, in addition to the dependence that f may have already presented on ξ. Note that this dependence is possible even if we only quantize the matter fields (for example, the Hamiltonian in the classical field theory, depended on Lapse, shift and 3-metric h) and, in fact, is the only one that may appear if J_C was chosen ξ-independently, as happens in the more trivial case considered in [1].

functions $f : \mathcal{M}_Q \to \mathbb{R}$, given by expectation values of linear operators over $\mathcal{M}_Q$ which are Hermitian for the scalar product under consideration $\langle , \rangle_\xi$. We denote such space of operators as $H_{\langle,\rangle}(\mathcal{M}_Q)$, and thus we define:

$$\mathcal{A}_Q := \{f_A(\Psi;\xi) := \langle \Psi \mid \hat{A}(\xi) \mid \Psi \rangle_\xi \mid \quad \forall \hat{A} \in H_{\langle,\rangle_\xi}(\mathcal{M}_Q)\} \tag{60}$$

Notice that the elements of such algebra acquire, due to the quantization procedure, a threefold ξ-dependence. The first one arises from the sectional nature of the states, so the simplified notation in (60) means $\Psi = \sigma_\Psi(\xi)$. The second one comes from the scalar product itself, explicitly denoted by $\langle , \rangle_\xi$, associated to the leaf dependent Gaussian measure $D\mu_\xi$ (and ultimately to $J_C(\xi)$, or to the leaf dependent vacuum section). Lastly, the operators are also ξ-dependent (as the notion of self-adjointness is referred to $\langle , \rangle_\xi$), so we must consider $\hat{A} = Q_\xi(A)$ where $Q_\xi(A)$ is a certain ξ-dependent quantization (see [2],[3]) of the classical field function $A \in \mathcal{A}_C$ adapted to the vacuum phase and measure, to make it appropriately self-adjoint. As the whole construction is tensorial, all three dependencies must be consistent with each other, as we will discuss below.

There is a fourth leaf dependence of the elements of the algebra, but this one is natural of the classical field magnitudes before quantization (denoted by $A \in \mathcal{A}_C$ above), as they are assumed to have already been constructed in conjunction with geometrodynamics. For example, the classical field theoretical Hamiltonian in (40) was lapse, shift and 3-metric dependent. Once quantized, it maintains such dependence and acquires the three former ones.

This algebra can be endowed with a Quantum Poisson Bracket (QPB) $\{,\}_Q$ that reproduces the Lie bracket of operators [24, 3, 1], and thus, for any two elements $f_A, f_B \in \mathcal{A}_Q$, defined as $f_A := \langle \Psi \mid \hat{A} \mid \Psi \rangle$ and $f_B := \langle \Psi \mid \hat{B} \mid \Psi \rangle$, its QPB is given by:

$$\{f_A, f_B\}_Q = \frac{-i}{\hbar}\langle \Psi \mid [A, B] \mid \Psi \rangle = -\hbar^{-1} f_{i[A,B]} \, . \tag{61}$$

For future use, we define the algebra resulting under the completion of $\mathcal{A}_Q$ under the ordinary product of functions:

$$\bar{\mathcal{A}}_Q = \{\prod_{i=1}^{n} f_{A_i} | f_{A_i} \in \mathcal{A}_Q \quad \forall i \in [1, n]; \forall n \in \mathbb{N}\} \tag{62}$$

Even though the elements of $\mathcal{A}_Q$ are leaf dependent, we claim that the Poisson bracket itself must be leaf independent, in the sense that:

$$\partial_\xi\{f, g\}_Q = \{\partial_\xi f, g\}_Q + \{f, \partial_\xi g\}_Q \; \forall \xi \in [h, \pi, N, N^i] \tag{63}$$

In the following section, we argue that the main reason for geometric independence of the QPB is to make it compatible with the geometrodynamical Poisson Bracket, $\{,\}_G$, so the sum of both is an appropriate Poisson bracket (fulfilling Jacobi identity)

over the functions on the hybrid manifold that form the Poisson algebra of hybrid observables, allowing us to find hybrid generating functions representing the generators of hypersurface deformations. Nevertheless, two further justifications can already be given for the leaf independence of the quantum Poisson bracket.

The first one goes in regard to the (h, π_h) independence- Given our Hamiltonian formalism, we must claim that hypersurface deformations must be symplectomorphisms (for a symplectic structure, weak inverse of the Poisson tensor under consideration, for further inquiry check the supplementary material). Nevertheless, this deformations also modify the values of the geometric variables, and so, if the Poisson bracket (weak inverse of a quantum symplectic structure) depended on them, we wouldn't be able to construct a symplectomorphic representation.

The second one is in consideration of the dependence on lapse and shift functions. One would argue that the kinematical structure should be leaf independent in order to implement path independence of the theory, reproducing the algebra of generators of symmetries as functions over Cauchy data on each leaf, without additional dependencies on the particular choice of foliation, given by E. If done otherwise, the closing relations of local generators of hypersurface deformations would become lapse and shift dependent, and thus, such functions could not be considered to be Lagrange multipliers for the Hamiltonian and momenta constraints.

In fact, even if regarded as a design choice, in this construction we aim to build the Hamiltonian kinematical relations *before* the choice of dynamics, and the lapse and shift functions are of dynamical nature, as they characterize the evolution vector field E. Therefore, the kinematics must be leaf independent, which is portrayed in (63).

Condition (63) implies a particular relation between the connection chosen for the states and the ξ-dependence for operators and scalar product. For simplicity on this proof we will use the bra-ket notation. As the construction is tensorial, we can consider the covariant derivatives of different types of sections (of different bundles):

- For the quantum states, given by $(1,0)$ tensors (associated with the evaluation on a point $\xi \in \mathcal{B}$ of sections in $\mathcal{M}_s$), their covariant definition implies

$$\partial_\xi \mid \Psi\rangle = -\Gamma_h \mid \Psi\rangle \ . \tag{64}$$

  Where the subindex h is just to state that this connection that depicts the covariant transformation of the vectors is relative to the ξ-dependent hermitian product. Here we are assuming that the connection is adapted in such a way that it does not mix the bra-ket representation.

- For their duals $\langle\Psi \mid$ in the Hilbert space, we may derive its dependence. Now, horizontal directions correspond to tangents to sections of the bundle $\mathcal{F}^*$, the

dual bundle of $\mathcal{F}$. We have introduced around (59) that the notion of adjoint is leaf dependent as it is relative to the leaf dependent scalar product. We define the adjunction C_ξ for a given $\xi \in \mathcal{B}$ as $C_\xi(|\ \Psi\rangle_\xi) := \langle\Psi\ |_\xi$, and analogously, $C_\xi(\hat{A}\mid\Psi\rangle) = \langle\Psi\mid\hat{A}^{\dagger_\xi}$. Notice that C_ξ mixes maximally the bra-ket representation and thus we must proceed with care, as it is a bundle isomorphism $C : \mathcal{F} \to \mathcal{F}^*$. With these considerations:

$$\partial_\xi\langle\Psi\ |_\xi = \partial_\xi C_\xi(|\ \Psi\rangle_\xi) = C_\xi(\partial_\xi\mid\Psi\rangle_\xi) + \langle\Psi\ |_\xi\ (C_\xi^{-1}\partial_\xi C_\xi) \tag{65}$$

where we have defined $\hat{T}(\xi) := (C_\xi^{-1}\partial_\xi C_\xi)$ as the object of adjointness transport, and we make use of eq. (64) to realize that

$$\partial_\xi\langle\Psi\ |_\xi = -\langle\Psi\mid\hat{\Gamma}_h^{\dagger_\xi} + \langle\Psi\ |_\xi\ \hat{T} = -\langle\Psi\mid\hat{\Gamma}_h^T \tag{66}$$

where we have defined $\hat{\Gamma}_h^T := \hat{\Gamma}_h^{\dagger_\xi} - \hat{T}$.

- Finally, linear operators, denoted by $\hat{A}$, are $(1,1)$ tensors whose construction from classical magnitudes via the quantization mapping also depend on ξ. Therefore, we can write the derivative of the expectation values of operators as:

$$\partial_\xi f_A = \langle\Psi\mid\hat{A}'\mid\Psi\rangle \tag{67}$$

where $\hat{A}' := \Big(-\hat{A}\hat{\Gamma}_h - \tilde{\Gamma}_h^T\hat{A} + \partial_\xi(\hat{A})\Big)$.

We will show now that these connections must be almost anti-self adjoint in order to fulfill (63). Thus, with an analogous definition as above for the primed operators, the left hand side of (63) yields:

$$-\hbar^{-1}\partial_\xi f_{i[\hat{A},\hat{B}]} = -\hbar^{-1}\langle\Psi\mid(i[\hat{A},\hat{B}])'\mid\Psi\rangle \tag{68}$$

nevertheless, the right hand side yields:

$$\{\partial_\xi f_A, f_B\}_Q + \{f_A, \partial_\xi f_B\}_Q = -\hbar^{-1}\langle\Psi\mid i([\hat{A}',\hat{B}] + [\hat{A},\hat{B}'])\mid\Psi\rangle \tag{69}$$

and one can easily check that

$$[\hat{A}',\hat{B}] + [\hat{A},\hat{B}'] - ([\hat{A},\hat{B}])' = 0 \Leftrightarrow \tilde{\Gamma}_h^T = -\hat{\Gamma}_h \tag{70}$$

that is, this connection for the bra-ket notation of the sections representing the quantum states must be anti-selfadjoint (with the term T correcting for the leaf dependent notion of adjointness) in order to have a leaf independent Quantum Poisson bracket. In [3] this result is obtained from the construction of the quantum symplectic form in a compatible way with a time dependent quantization.

Note that this constraint for the connection precisely implies the covariant derivative of the operator $\hat{A}$ in eq. (67), as, under $\hat{\Gamma}_h^\dagger - T = -\hat{\Gamma}_h$, we obtain $\hat{A}' := \partial_\xi(\hat{A}) + [\Gamma,\hat{A}] = \nabla_\xi\hat{A}$. This is natural, from the geometrical point of view, since we are considering the covariant derivative of a $(1,1)$–tensor for the fiber of $\mathcal{F}$. Our conclusion is that

the condition holds if all the leaf dependencies inherited from the leaf dependent quantization of the quantum objects correspond to the parallel transport of the same connection ∇.

Let us now exemplify this in the functional notation, where the connection $\hat{\Gamma}$ appears as a linear operator over the quantum states, defined as in (55). In order to do so, we resort to our former example of functions of complex domain, but the construction is analogous in the real case. We proceed to check what does this condition imply in the functional notation for the states and the scalar product:

$$\partial_\xi f_A = \int_{\mathcal{N}'} D\mu_\xi(\phi) \left(\bar{\Psi} \hat{A}(-\hat{\Gamma}\Psi) + \bar{\Psi}\partial_\xi(\hat{A})\Psi + \overline{(-\hat{\Gamma}\Psi)}\hat{A}\Psi + F(\phi,\bar{\phi})\bar{\Psi}\hat{A}\Psi \right) \tag{71}$$

where the last term $F := \dfrac{\partial_\xi(D\mu_\xi)}{D\mu_\xi}$ accounts for the derivative w.r.t. ξ of the leaf dependent Gaussian measure (strictly defined in terms of a Radon-Nikodym derivative [3]). To illustrate the shape of this term, in the particular case of holomorphic quantization of a scalar field considered in [2], for a Gaussian measure with field covariance $\Delta^{xy}(\xi)$ and inverse of the covariance $K_{xy}(\xi)$, one can consider $F(\phi,\bar{\phi}) = (-\phi^x \partial_\xi K_{xy} \bar{\phi}^y - Tr(\partial_\xi \Delta^{xy} K_{yz})$ [+].

On the one hand, through a total derivative, we may find the operator $\hat{\Gamma}^\dagger$ that fulfills

$$\int_{\mathcal{N}} D\mu_\xi(\phi) \overline{\hat{\Gamma}\hat{\Psi}_1}\Psi_2 = \int_{\mathcal{N}} D\mu_\xi(\phi) \bar{\Psi}_1(\hat{\Gamma}^\dagger \Psi_2) \ , \tag{72}$$

which defines the adjointness for such scalar product when considered $\forall \Psi_1, \Psi_2 \in L^2(\mathcal{N}', D\mu_\xi)$.

On the other hand, taking into account the multiplicative nature of F and identifying $T := F(\phi,\bar{\phi})$, we can make use of the former definition $\hat{\Gamma}^T := \hat{\Gamma}^\dagger - T$ to write:

$$\partial_\xi f_A = \int_{\mathcal{N}'} D\mu_\xi(\phi) \left(-\bar{\Psi}\hat{A}\hat{\Gamma}\Psi + \bar{\Psi}\partial_\xi(\hat{A})\Psi - \bar{\Psi}\hat{\Gamma}^T\hat{A}\Psi \right) \ . \tag{73}$$

Following the same procedure in this notation as in eqs. (68),(69) for the bracket notation, we arrive to the conclusion that

$$\hat{\Gamma}^T = -\hat{\Gamma} \ . \tag{74}$$

Expanding on the previous example, for the holomorphic case (for the given F above) it can be shown that this equation is fulfilled (although it is not the only solution) when the connection is given by

$$\hat{\Gamma}\Psi(\phi) := \frac{1}{2}\phi^x \left(\left(\partial_s h_{xy} \partial_{h_{xy}} + \dot{N}^{\mu x} \partial_{N^{\mu x}} \right) K_{xy} \right) \Delta^{yz} \partial_{\phi^z} \Psi(\phi) \tag{75}$$

[+] Although this expression must be taken with care, always together with the measure acting over the functions, given the distributional nature of the derivative of the metric, and regarding its definition through a projective limit through finite dimensional spaces [30].

where $\partial_s h_{xy} = 2N(x)G_{ijkl}(x)\pi^{kl}(x) + 2(D_i N^k(x))h_{kj}(x)$ as in hybrid geometrodynamics and $\dot{N}^\mu$ is just the chosen change for the lapse and shift functions. This is precisely the connection for time dependent quantization reached in [3] following a different argument, not based (solely) on the physical requirement of leaf independence of the kinematics. Beyond the choice of holomorphic picture to exemplify, the procedure is analogous in any other picture, and its relation with the connection for the Schrödinger case (real field polarization) is straightforward taking into account the Segal-Bargman transform relating both pictures, as described in [2].

As a general result we may conclude that, in order to fulfill the leaf independence of the kinematics encoded in (63), any connection defining the quantum states and the ξ-parametric family of Gaussian measures that fulfills the constraint defined in eq. (74) (relating the derivative of the ξ-parametric family of Gaussian measures, the connection and its adjoint) is valid. The existence of such a connection is guaranteed when considering the Gel'fand triple that allows us to embed the current Hilbert space in the space of Hida distributions. The associated Radon-Nikodym derivatives that describe the change of Gaussian measure are distributions, but they exist in this generalized setting $\dfrac{D\mu}{D\nu} \in (\mathcal{N})'$ under mild assumptions.

A more geometric approach, associating the scalar product to a Kähler structure, and the properties of the compatible connection with its relations with the symplectic and complex structures, can be found in the supplementary material.

From this constraint for the connection, together with the condition of not mixing bras and kets (or in the functional example given, the fact that it preserves the holomorphic nature of $\Psi(\phi)$), we obtain a crucial physical implication: the scalar product of two quantum states, both being sections and with the scalar product being also ξ-dependent, does not change along the curves over the base of the bundle, *i.e.*:

$$\partial_\xi \langle \Psi_1 \mid \Psi_2 \rangle = 0 \quad \forall \xi \in [h, \pi, N, N^i]. \tag{76}$$

Although this result is derived from physical claims, under a geometrical perspective this is a natural consequence of our tensorial construction. If we choose the same connection for all the quantum tensors, and we restrict ourselves to considering kinematical transformations, which are tangent to covariant sections of the different bundles involved, scalar magnitudes such as the norm, must be constant.

In particular, this leads to the conservation of norm of the quantum state ($\langle \Psi \mid \Psi \rangle$) under changes of geometric variables, lapse and shift:

$$\partial_\xi \langle \Psi \mid \Psi \rangle = 0 \ \forall \xi \in [h, \pi, N, N^i] \tag{77}$$

which is a novelty of our framework in striking contrast with the usual 3+1 picture of QFT in curved spacetime where norm loss is ubiquitous, making room for the phenom-

ena of *quantum completeness* [18, 4].

As a summary, the main difficulty with a Hamiltonian picture of QFT in generic dynamical spacetimes is that the quantization procedure, or the choice of complex structure J_C over the field manifold, is most generally constructed in a leaf dependent way (this is also the case of the most physically sensible choice of J_C to our knowledge, the restriction to a spatial hypersurface of the one proposed in [5] and also used in [10]).

This implies that, for each $\xi \in \mathcal{M}_G \times \mathcal{M}_N$,

- the states acquire a different functional representation as a Hida distribution $\sigma_\Psi(\xi) = \Psi \in (\mathcal{N})'$,
- the scalar product will be associated to a different Gaussian measure $D\mu_\xi$ over the space of fields and, in turn, the states are bound to be seen belonging to a different Hilbert space, $L^2(\mathcal{N}', D\mu_\xi)$,
- the operators acquire a different representation to be self adjoint for such measure (and vacuum phase).

Thus, the usual notions of Fock spaces, creation and destruction operators, number of particle operators, etc. are constructed in an *a priori* foliation dependent way, which does not come as a surprise to the reader familiar with QFT in curved spacetime. While this may spoil the particle interpretation of the quantum states this is not relevant for our purpose; with the aim of constructing consistent hybrid geometrodynamics compatible with an equivalence principle the object of interest is the Poisson structure of QFT. Following the most sensible physical choice in our judgement, this structure has been made invariant in order to properly reproduce kinematical relations of symmetry generators and the foliation independence principle of geometrodynamics. This postulate is mathematically captured in (63). The consequence is that the quantum states, constructed as sections, or more plainly put, smooth Hida-distribution-valued functions over the geometric manifold, $\sigma : \mathcal{M}_G \times \mathcal{M}_N \to (\mathcal{N})'$, must fulfill eq.(55) for a connection that fulfills (74).

In order to separate clearly the leaf dependent (associated to physical interpretation) and leaf independent (associated to the symplectic) geometric structures, in the supplementary notes we abandon the usual functional picture of Hamiltonian QFT, in order to borrow the Poisson structure for QFT from the more abstract Geometric Formalism of Quantum Mechanics developed in [24] where the symplectic structure is readily available, and the Poisson tensor will be associated to its (weak) inverse. This Kähler formalism was adapted in [3] to QFT for a time dependent quantization, and the resulting connection already fulfilled (74), but instead of claiming (63), an equivalent condition is claimed for the time dependence of geometric structures.

3.3. Physical observables, generating functions of symmetries and supermagnitudes.

Armed with this Poisson algebra $\mathcal{A}_Q$, we are able to represent the infinitesimal generators of symmetries, and in particular of hypersurface deformations, in a Hamiltonian language for QFT.

The association of physical magnitudes to operators is usually elucidated through the quantization procedure $Q(f)$ of the functions representing such magnitudes at the classical level. As we are interested in the quantization of the classical geometrodynamical generators, we consider now the generating functional $A \in \mathcal{A}_F$ of a certain symmetry $a : \mathcal{M}_F \to \mathcal{M}_F$ over classical space of matter fields. This functional is mapped through the quantization Q to a linear operator $\hat{A} := Q(A)$ over the quantum states, and, in turn, it is mapped to a quantum generating function $f_{\hat{A}}(\Psi) = \langle \Psi \mid \hat{A} \mid \Psi \rangle$, in the quantum algebra $\mathcal{A}_Q$. Regarding the Hamiltonian fields, at the quantum level we try to reproduce the usual Hamiltonial dynamics over the classical fields, where the infinitesimal generator of the symmetry acting any other element in the classical algebra B is given by the associated Hamiltonian field $X_A B = \{B, A\}_C$. At the quantum level, the infinitesimal generator of the symmetry is analogously given by the quantum Hamiltonian field X_{f_A}, that acting over any other element of the quantum algebra $f_B \in \mathcal{A}_Q$ is given by:

$$\mathcal{L}_{X_{f_A}} f_B = \omega_Q(X_{f_A}, X_{f_B}) = \{f_B, f_A\}_Q = \frac{-i}{\hbar} f_{[\hat{B},\hat{A}]} \tag{78}$$

Note that this construction does not ensure the preservation of the subalgebra of constraints or generators under quantization, as the generating functions of two symmetries at the classical level and at the quantum level may not have the same closing relations under their respective Poisson brackets. We will return to this issue later.

Let us consider now the generating functions of hypersurface deformations for QFT. Being $N^x \mathcal{H}_x^M(\phi, \pi)$ the generating function over classical fields of a normal deformation characterized by N^x, it is mapped through the quantization to a linear operator over the quantum states, $Q(N^x \mathcal{H}_x^M) = N^x Q(\mathcal{H}_x^M) := N^x \hat{\mathcal{H}}_x$ and thus, the associated element of the quantum Poisson algebra is given by

$$N^x f_{\hat{\mathcal{H}}_x} = N^x \langle \Psi \mid \hat{\mathcal{H}}_x \mid \Psi \rangle \in \mathcal{A}_Q \tag{79}$$

Thus, we define the quantum superhamiltonian as the infinitesimal *local* generator of a normal deformation (still to be contracted with a distribution, N^x) in analogy with the classical case:

$$\mathcal{H}^Q(x) := \langle \Psi \mid \hat{\mathcal{H}}_x \mid \Psi \rangle \tag{80}$$

Analogously, the generating function $N^{ix} \mathcal{H}_{ix}$ at the classical field theory level of a tangential stretching of the hypersurface characterized by the vector distribution N^{ix}, is mapped through the quantization to the quantum generating function:

$$N^{ix} f_{\hat{\mathcal{H}}_{ix}} = N^{ix} \langle \Psi \mid \hat{\mathcal{H}}_{ix} \mid \Psi \rangle \ . \tag{81}$$

Thus, the associated local generators define the quantum supermomenta:

$$\mathcal{H}_i^Q(x) = \langle \Psi \mid \hat{\mathcal{H}}_{ix} \mid \Psi \rangle \tag{82}$$

It is interesting to define at this point the quantum Hamiltonian operator $\hat{H}$, given by the quantization of the classical field matter hamiltonian $N^x\mathcal{H}_x^M + N^{ix}\mathcal{H}_{ix}^M$:

$$\hat{H} := N^x\hat{\mathcal{H}}_x + N^{ix}\hat{\mathcal{H}}_{ix} \tag{83}$$

which of course has acquired further dependences on $\xi \in \mathcal{B}$ in order to be self-adjoint for the given scalar product at each ξ.

On the other hand, if the compatibility of the symmetries is to be preserved under the quantization procedure, it would appear as a desirable property for the quantization Q that the generators of the symmetries of the system commuted the same way they did in the classical field theory before constraints were imposed. In particular, they should commute with the generating function for the dynamics to be a proper (time preserved) physical symmetry.

However, it is well known from Groenewold's no-go theorem[15] that Dirac's quantization relations:

$$Q(\{f, g\}_c) = \frac{-i}{\hbar}[Q(f), Q(g)] \tag{84}$$

do not hold for arbitrary functions $f, g \in \mathcal{A}_c$ over classical phase space and thus the Poisson algebra structure of the functions in classical field theory is not mapped to the algebra of linear operators over quantum states provide with its commutator, $\mathcal{A}_Q$. Nevertheless, a crucial result from Groenewold's no-go theorem is that, if either f or g is a quadratic polynomial, then the equality is satisfied. Besides, if $\{f, g\}_c = 0$, the equality is also trivially fulfilled.

Note that, in particular, the classical field theoretical supermagnitudes are up to quadratic in momenta. As explained in [19], the matter supermomenta $\mathcal{H}_{ix}$ must be linear on matter momenta (quadratic in all field variables) as a consequence of the representation postulate. It ensures that the transformation on the fields is properly associated to an stretching on their domain, which is equivalent to a spatial diffeomorphism intrinsic to the leaf, and thus, if higher powers of the momenta appeared in its generating function, such deformation would acquire an incoherent extrinsic nature.

On the other hand, in [19] the matter superhamiltonian is restricted, as an axiom to be no more than quadratic on momenta (sensibly for the usual Hamiltonian construction, even more so regarding quantization), in order to have the usual canonicity relations between fields and momenta in relation with the generated dynamics.

As a result we know, from Groenewold's no-go theorem, that Dirac's relations for quantization elements, and the former elements in the quantum Poisson algebra reproduce the closing relations of the classical algebra:

$$\{N^{\mu x} f_{\hat{\mathcal{H}}_{\mu x}}, N^{\nu x'} f_{\hat{\mathcal{H}}_{\nu x'}}\}_Q = N^{Ax} N^{Bx'} f_{Q(\{\mathcal{H}_{\mu x}, \mathcal{H}_{\nu x'}\}_c))} \tag{85}$$

where μ, ν represent indices $0, \cdots, 3$, being the non-zero associated to a basis of tangential stretchings and the zeroth, to normal deformations. This result will be crucial to show that the quantum supermagnitudes fulfill the appropriate closing relations for a matter theory.

We must add that being quadratic on field momenta becomes, in this construction, a requisite for the theory to be suitable for quantization in a natural way, to seize this exception of Groenewold's theorem. Otherwise, higher orders in momenta would lead to different closing relations on the quantized generators from the ones fulfilled by the classical theory, which already represented Dirac's generators Lie bracket closing relations, and thus, quantized supermagnitudes would not be representing the closing relations of Dirac's algebra, which is a requisite for consistent matter theories [16].

One must not forget about a fundamental difference of this whole construction in the case of Quantum Geometrodynamics from the case of ordinary QM (even when coupled to classical variables as in [1]): in the current case the quantization procedure Q is leaf dependent. As explained before, the dependence of the operator with the leaf variables will be different from the one of the classical function, $\partial_\xi Q(f) \neq Q(\partial_\xi f)$, as the quantization procedure itself is an additional source of leaf dependence.

We remind that this dependence arises as follows. Once a scalar product defining a Hilbert space and a vacuum state are chosen (or, equivalently, a complex structure over the classical phase space of fields[10]), the representation of the quantized (linear) operators is defined accordingly to be self adjoint and consistent with the vacuum phase. The extension to higher order operators is given by the choice of ordering (either Wick's or Weyl's are both considered in [2, 3] in an adapted language to this formalism). Therefore, all this procedure denoted by the quantization Q ends up being leaf dependent, as so was the scalar product and vacuum phase (or J_C), and while it serves us to map the functions over the classical field phase space to the space of linear operators over quantum states, it is done in a ξ-dependent fashion, properly adapted to be internal operators, at each ξ, to the ξ-dependent Hilbert space defined:

$$Q_\xi : C^\infty(\mathcal{M}_F) \to H_{\langle,\rangle_\xi}(\mathcal{M}_Q) \tag{86}$$

In this line it is relevant to consider that, given the condition (74) for the connection, the elements of $\mathcal{A}_Q$ depend on ξ as:

$$\partial_\xi f_{\hat{A}} = \langle \Psi \mid \left(\partial_\xi Q(A) + [\hat{\Gamma}, Q(A)] \right) \mid \Psi \rangle \tag{87}$$

In the following section it will be shown that when the observable A in (87) is a supermagnitude, such closing relations in the whole hybrid theory will lead to

consistency requirements between the leaf dependence of the quantization and the commutator with the connection. Let us proceed.

4. Hybrid Geometrodynamics.

The ultimate goal of the preceding construction is the definition of a Hybrid Phase Space constructed from Classical Geometrodynamical variables and Quantum Wave Functionals of the quantized matter fields and provided of a Hybrid Poisson Bracket. In the previous section, we have proved that if we consider the bundle $\mathcal{F}$ to represent the classical and the quantum states, the leaf-dependent tensorial structures on the set of quantum states can replace their classical analogues for classical matter fields, building the geometrodynamical generators as Hamiltonian vector fields with respect to the canonical quantum Poisson bracket $\{,\}_Q$. The next and final step is to combine the quantum supermagnitudes with the pure geometrodynamical ones to construct hybrid supermagnitudes with physical meaning that fulfill the total closing relations and fulfill the Momenta and Hamiltonian Constraints on shell, being therefore conserved by the dynamics. Thus, in this section we promote the gravitational degrees of freedom of the former section, from a given background $(h_{ij}(x,s), \pi_h^{ij}(x,s))$ with parametric space-time dependencies, to kinematical variables, being their dynamics no longer externally given, but coupled with quantum matter fields.

Therefore, we proceed now to substitute the classical matter of Section 2 as sources of gravitation in a geometrodynamical framework, by the Quantum Field Theory described as in Section 3.

4.1. Hybrid phase space.

The construction of the hybrid phase space $\mathcal{M}_H$, in [1], is made from the cartesian product of the quantum and classical submanifolds, given that they are constructed independently of one another. In the case of hybrid geometrodynamics this is built analogously, considering the manifold of hybrid states the bundle $\mathcal{F}$ introduced in the previous section.

$$\mathcal{M}_H = \mathcal{F}. \tag{88}$$

Any point in the bundle defines a pair of a classical state (determined by the values of h_{ij}, π^{ij}, N, N^i), and a quantum state Ψ. Nonetheless, the quantum states are dependent on a connection ∇ defined on the bundle, which allows to decompose the tangent space at any point of $\mathcal{F}$ as Equation (54), the horizontal directions being tangent to the covariant sections of the bundle. Physically, these directions represent the set of quantum states which are related by a re-arrangement in the geometry only, without any quantum dynamics.

In contrast with the case in the previous section, now the purely geometrodynamical variables are not associated to a background spacetime, but are promoted to be part of the kinematical variables. Thus, now we are going to consider geometrodynamical transformations acting on both types of states; analogously to what happened in the case of the geometrodynamical construction for classical matter fields analyzed in section 2. We are going to prove that the quantum tools introduced in the previous section will replace their classical analogues and define a consistent implementation of geometrodynamics for the hybrid setting. Thus, the quantum Poisson bracket will be combined with the classical PB to create a well-defined hybrid Poisson bracket on the set of functions of $\mathcal{F}$, which will replace the functions of the classical manifold $\mathcal{M}_G \times \mathcal{M}_F$. Note that the manifold of lapse and shift functions, $\mathcal{M}_N$, is present in the base of the bundle due to the parametric family of quantizations (representation of quantum states, operators and scalar product) which depend on them and need a way to be related (through the horizontal bundle defined above also for such variables), but they will not affect the kinematics (definition of Poisson tensors and closing relations for the local generators of hypersurface deformations) of either $\mathcal{M}_G$ nor $\mathcal{M}_Q$.

Note also that, as happened in the previous section, the dynamics of lapse are shift are not included in the Hamiltonian description, but a result of the choice of foliation of spacetime. Thus, such dynamics are externally given and, in fact, the choice of any particular dynamics for them should not have any physical impact, as they are associated with a symmetry of the formalism, each dynamics defining a *path* among possible hypersurfaces reproducing a certain foliation, which is at the core of the *path independence principle* as stated in [19]. Therefore, armed with a Hybrid state providing the whole information on a Cauchy surface of initial data and with the reconstruction of the evolution field E from the lapse and shift at each foliation label, we can spawn the physical information for the whole spacetime. Consequently, the whole quantum matter and geometrical content of the Universe is equivalent through E to the initial conditions on Σ_0, *i.e.* the intrinsic 3-metric $h_{ij}(0)$ on Σ_0, its conjugate momenta $\pi_h^{ij}(0)$, and the quantum state $\Psi = \sigma(h(0), \pi_h(0), N(0), N^i(0))$ for such initial leaf data that populates the quantum fields all over Σ_0. The connection for the quantum section will allow us to determine the change on the quantum state due to the change of the geometric variables, gluing together the unitarily inequivalent Hilbert spaces defined for infinitesimally neighbouring hypersurfaces.

4.2. Algebra of observables.

As was the case in the hybrid systems studied in [1], The hybrid algebra of observables can be represented by the expectation value of self adjoint linear operators over the quantum manifold $\mathcal{M}_Q$ which had an infinitely differentiable dependence on the classical variables. In this sense, in terms of abstract $C^\star$-algebras one can consider that the hybrid algebra of observables is given by $\mathcal{A}_H := \mathcal{A}_G \otimes \mathcal{A}_Q$ [8]. In such framework, the

operators given by a classical function multiplying the identity, were considered purely classical observables, while the ones independent of the classical degrees of freedom, were thought of as purely quantum. This differentiation was based on the fact that, given that norm of the quantum state was conserved, the expectation value of the identity was a conserved quantity, fixed to the unity.

In this current geometrodynamical case the spirit is the same, but we have already taken one step ahead as $\mathcal{A}_Q$ was defined as the expectation value of leaf dependent operators, for hermitian product and states that were also leaf dependent, so the quantum observables are already dependent on the classical variables, which are now of kinematical nature, no longer an external parameter. Thus, in our framework the hybrid algebra of observables is precisely identified with the quantum one

$$\mathcal{A}_H := \bar{\mathcal{A}}_Q \ , \tag{89}$$

where $\mathcal{A}_Q$ is defined as in Equation (60), noticing that now their dependence on $\xi \in \mathcal{B}$ is not regarded as an external parametric dependence. Notice, nonetheless, that the resulting set is isomorphic to the completion under the product of $\mathcal{A}_G \otimes \mathcal{A}_Q$. We are already considering its completion as defined in (62) for reasons that will become clear later. We will now illustrate a bit how this hybrid observables are constructed and how they represent physical magnitudes, either material or purely geometrical.

Consider first a classical field theoretical magnitude, $A \in C^\infty(\mathcal{M}_F)$ that only depend on field on matter fields, not on geometric fields. It can be expressed as a polynomial on matter field distributions ϕ^x and their associated momenta π^y as:

$$A = \sum_{ij} a_{ij\vec{x},\vec{y}} \phi^{i\vec{x}} \pi^{j\vec{y}} \tag{90}$$

where the coefficient functions $a_{ij\vec{x}\vec{y}}$ are leaf independent. The element of $\mathcal{A}_Q$ given by $\langle \Psi \mid Q(A) \mid \Psi \rangle$ would have been a purely material observable at the classical level, but has acquired a hybrid nature due to the leaf dependence of the quantization, states, and scalar product.

Let us now consider a function B over the classical matter fields whose coefficients already depended on the geometric variables at the classical level (for example, this is the case for the superhamiltonian of a classical scalar field), so:

$$B := \sum_{ij} b_{ij\vec{x},\vec{y}}(h, \pi_h) \phi^{i\vec{x}} \pi^{j\vec{y}}, \tag{91}$$

the element of $\mathcal{A}_Q$ given by $\langle \Psi \mid Q(B) \mid \Psi \rangle$ is a mixed matter-geometrical observable both before and after quantization, but has acquired a different leaf dependence due to the leaf dependence of the quantization, states, and scalar product.

Lastly, if we consider a function g solely of the geometric variables, $g(h,\pi) \in \mathcal{A}_G$, and perform a quantization procedure for the matter fields, given its independence on such fields we get $Q(g) = g\mathbb{I}$. Thus, the hybrid observable representing this purely geometrical observable is given by $f_{g\mathbb{I}} = g(h,\pi)\langle\Psi \mid \mathbb{I} \mid \Psi\rangle \in \mathcal{A}_H$. Given the norm conservation under changes of leaf variables derived from (74), and if the total hybrid dynamics still preserve the norm of the quantum state, under the initial constraint of norm unity, the observable in the geometric algebra of observables and its hybrid counterpart are equal at all times and under all symmetry transformations, $f_{g\mathbb{I}}(h,\pi,\Psi) = g(h,\pi)$ *.

Summarizing, in our framework, the hybrid algebra of observables is constituted by functions (and products of them) defined as the expectation value under the leaf dependent representation of the quantum state $\Psi \in \mathcal{M}_Q$ and leaf dependent scalar product $\langle,\rangle_\xi$ of the Hermitian operator $Q_\xi(f)$ resulting from the quantization procedure (again, leaf dependent) for the matter fields of functions over the space of classical matter fields and geometric variables, $f \in C^\infty(\mathcal{M}_G \times \mathcal{M}_F)$.

Given the construction of the abstract $\mathcal{A}_H$ equivalent to $\mathcal{A}_G \otimes \mathcal{A}_Q$ and the Poisson structures present in the representations as functions over each phase space of $\mathcal{A}_G$ and $\mathcal{A}_Q$, we may endow the representation of $\mathcal{A}_H$ with a bilinear operator given by the sum of both of them:

$$\{,\}_H = \{,\}_G + \{,\}_Q \ , \tag{92}$$

which can be shown to be a Poisson bracket over the set of observables contained in $\mathcal{A}_H$. Leibniz, antisymmetry and bilinearity immediately inherited from the properties of $\{,\}_G$ and $\{,\}_Q$ over their respective algebras. Nevertheless, to fulfill Jacobi identity (and thus, be a proper Poisson bracket) a compatibility condition must be enforced, which is precisely eq. (63), justifying even more so the leaf independence of the quantum PB.

It is trivial to check that $\mathcal{A}_H$ forms a Poisson algebra under $\{,\}_H$, while $\mathcal{A}_Q$ is not a proper subalgebra, given that

$$\{f_A, f_B\}_G = f_{\partial_h A + [\Gamma_h, \hat{A}]} f_{\partial_\pi B + [\Gamma_\pi, \hat{A}]} - (A \leftrightarrow B) \ , \tag{93}$$

where we have made use of (87), compacted in the subindex notation. Hence, the definition of $\mathcal{A}_H$ to be the quantum algebra completed under the ordinary product, $\bar{\mathcal{A}}_Q$.

Over this hybrid Poisson algebra, the infinitesimal generators X_A of any Hamiltonian transformation $a : \mathcal{M}_H \to \mathcal{M}_H$ acquire a Hamiltonian representation over $\mathcal{A}_H$ through its generating function, f_A, such that, for any hybrid observable F:

$$\mathcal{L}_{X_A} F = \{F, f_A\}_H \quad \forall F \in \mathcal{A}_H \tag{94}$$

* If the theory had been constructed to have norm loss for the quantum states, then one would have defined explicitly $\mathcal{A}_H := \mathcal{A}_G \cup \bar{\mathcal{A}}_Q$, to be able to include the purely gravitational observables independently of the norm of the quantum state.

In particular for the generating functions representing the local generators of hypersurface deformations, the hybrid superhamiltonian $\mathcal{H}_H$ and supermomenta $\mathcal{H}_{iH}$ are constructed invoking the equivalence principle as in [19], where the hybrid supermagnitudes must be built as the sum as the pure geometrodynamical (classical) supermagnitude and the matter (quantum) supermagnitude:

$$\mathcal{H}_H := \mathcal{H}(h, \pi; x)\langle\Psi \mid \Psi\rangle + \mathcal{H}_Q(h, \Psi, \bar{\Psi}; x), \tag{95}$$

$$\mathcal{H}_{iH} := \mathcal{H}_i(h, \pi)\langle\Psi \mid \Psi\rangle + \mathcal{H}_{iQ}(h, \Psi, \bar{\Psi}). \tag{96}$$

Note however, that the fact that the gravitational supermagnitude appears multiplied by the norm of the quantum state is just for the supermagnitudes to strictly belong to $\mathcal{A}_H$, but in our framework $\langle\Psi \mid \Psi\rangle$ may just be a constant which can be set to 1.

It is thoroughly argued in [19] that, on the classical field case the matter supermomenta was independent of the gravitational variables, and the matter superhamiltonian was only local on h (*i.e.* independent of the derivatives of the metric or the gravitational momenta). Nevertheless, in this hybrid case the quantization procedure (and states and scalar product) adds non trivial dependences on the geometric variables, lapse and shift, which may even be of derivative nature. For example, the complex structure J_C in [5] adapted to the foliation presents spatial derivatives of the metric and of N, N^i; and so will the quantum connection).

Howbeit, we will restrict to the case where the quantization does not depend on the geometrodynamical momenta and thus the sections representing the states are constant on π_h.

$$\partial_{\pi_h}\sigma_\Psi(\xi) = 0,\ \Gamma_{\pi_h} = 0 \text{ and } \partial_{\pi_h}\langle\Psi \mid Q(f) \mid \Psi\rangle = \langle\Psi \mid Q(\partial_{\pi_h} f) \mid \Psi\rangle \tag{97}$$

where the last equality implies that we allow the observables to depend on π_h as did before the quantization, but do not acquire further dependences on it from the quantization procedure, scalar product or states. The dependence on the 3-metric, lapse and shift remain fully general.

We consider this case for study because, firstly, this includes the case considered in [5], and secondly, we judge it to be simpler, but also the most physical choice, which can be argued as follows.

Given the geometrodynamical principle of equivalence as stated in [19], the classical field geometrical structures and generating functions must be regarded as independent of π_h (they may depend on the intrinsic geometry of the hypersurface, as is h, but not on extrinsic information). If the complex structure J_C over the field manifold used to define the quantization is chosen in reference to the Hamiltonian field over such space (as is the case of [5, 10], following some physical criterium such as, positive energy flux along E), then there is no source of π_h dependence in the quantization procedure. In any case, the discussion for the general case with arbitrary dependence on all geometric

variables is easily (though cumbersomely) generalizable from the following one.

Returning to the hybrid supermagnitudes, we will now see how they fare regarding the closing relations appropriate for Dirac's generators, (24),(25) and (26). Let us make two observations to simplify the problem. Firstly, for the purely geometrodynamical supermagnitudes we know that: i) under the gravitational bracket they already fulfilled all closing relations, and ii) the quantum Poisson bracket of them with any other function in the algebra will be null, as the identity commutes with all operators.

Secondly, the gravitational bracket over any two quantum supermagnitudes is null $\{\mathcal{H}_{\mu Q}(x), \mathcal{H}_{\nu Q}(x')\}_G = 0$ given the restriction to π_h independent quantization and the independence of the classical field supermagnitudes on it, as argued in [19].

Thereby, for $\mu, \nu = 0, \cdots, 3$ representing superhamiltonian if the index is zero, and the corresponding supermomenta if not zero, we may write that the hybrid Poisson bracket of any pair of hybrid supermagnitudes yields:

$$\{\mathcal{H}_{\mu H}(x), \mathcal{H}_{\nu H}(x')\}_H = \{\mathcal{H}_{\mu H}(x), \mathcal{H}_{\nu}(x')\}_G + \{\mathcal{H}_{\mu Q}(x), \mathcal{H}_{\nu Q}(x')\}_Q + \{\mathcal{H}_{\mu}(x), \mathcal{H}_{\nu Q}(x')\}_G \tag{98}$$

On the quantum side, we must remember that the classical field supermagnitudes are up to quadratic in momenta and we have made use of the exception for (up to) quadratic polynomia on Groenewold's no go theorem, obtaining that the quantum Poisson bracket of quantum supermagnitude is the expectation value of the quantization of the classical field Poisson bracket of classical field supermagnitudes, summarized in eq. (85).

At the level of local generators, implies that the quantum supermagnitudes $\mathcal{H}_Q$ and $\mathcal{H}_{iQ}$ already fulfill (24) and (26) for the quantum Poisson bracket, as so did they classical field counterparts.

On the other hand, the supermomenta-superhamiltonian PB is however a bit trickier. For such quantum Poisson bracket, we obtain the expectation value of the quantization of (36):

$$\{\mathcal{H}_{iQ}(x), \mathcal{H}_Q(x')\}_Q = -2h_{i\alpha}(x)D_{x^j}\langle\Psi \mid Q\left(\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)}\right) \mid \Psi\rangle + \mathcal{H}_Q(x)\partial_{x^i}\delta(x,x') \ . \tag{99}$$

However, the crossed gravitational terms yield, as in (35):

$$\{\mathcal{H}_i(x), \mathcal{H}_Q(x')\}_G = 2h_{i\alpha}D_{x^j}\frac{\delta\mathcal{H}_Q(x')}{\delta h_{\alpha j}(x)} \tag{100}$$

and

$$\{\mathcal{H}_{iQ}(x), \mathcal{H}(x')\}_G = G_{ijkl}(x')\pi^{ij}(x')\frac{\delta\mathcal{H}_{iQ}(x)}{\delta h_{\alpha j}(x')} \tag{101}$$

Therefore, in order to fulfill (25) for the total hybrid supermagnitudes, we must have:

$$G_{ijkl}(x')\pi^{ij}(x')\frac{\delta\mathcal{H}_{iQ}(x)}{\delta h_{\alpha j}(x')}+2h_{i\alpha}D_{x^j}\frac{\delta\mathcal{H}_{Q}(x')}{\delta h_{\alpha j}(x)}-2h_{i\alpha}(x)D_{x^j}\langle\Psi\mid Q\left(\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)}\right)\mid\Psi\rangle=0\ . \tag{102}$$

Given that neither the quantization procedure nor the classical field supermagnitudes depend on π_h, from Equations (100) and (101), we obtain that the first term of equation (102) must be null on its own, as the rest of the terms do not depend on π_h:

$$\frac{\delta\mathcal{H}_{iQ}(x)}{\delta h_{\alpha j}(x')}=0\quad\forall\ \Psi,h,N,N^i\Rightarrow\frac{\delta Q(\mathcal{H}_{iM}(x))}{\delta h_{\alpha j}(x')}+[\hat{\Gamma}_h,Q(\mathcal{H}_{iM}(x))]=0, \tag{103}$$

obtaining a new constraint for the quantum connection. In order for the two remaining terms to cancel, we must fulfill:

$$h_{i\alpha}D_{x^j}\frac{\delta\mathcal{H}_{Q}(x')}{\delta h_{\alpha j}(x)}-h_{i\alpha}(x)D_{x^j}\langle\Psi\mid Q\left(\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)}\right)\mid\Psi\rangle=0\ . \tag{104}$$

which, using eq. (87) implies one last constraint on the quantum connection:

$$\frac{\delta Q(\mathcal{H}^M(x))}{\delta h_{\alpha j}(x')}+[\hat{\Gamma}_h,Q(\mathcal{H}^M(x))]=Q\left(\frac{\delta\mathcal{H}^M(x')}{\delta h_{\alpha j}(x)}\right) \tag{105}$$

Moving onto the other two closing relations, given that the two first brackets in the right side of equation (98) already fulfilled (24) and (26) for their respective Poisson structure, the sum of the remaining last two, given by the gravitational bracket crossing gravitational and quantum matter supermagnitudes must be null in order to fulfill such closing relations for the hybrid supermagnitudes:

$$\{\mathcal{H}_\mu(x),\mathcal{H}_{\nu Q}(x')\}_G+\{\mathcal{H}_{\mu Q}(x),\mathcal{H}_\nu(x')\}_G=0 \tag{106}$$

for $\mu=\nu=0$ and $\mu\neq0,\nu\neq0$.

For the supermomenta-supermomenta PB, these terms are null because of equation (103).

In the classical case, these terms for the superhamiltonian-superhamiltonian PB cancel because the matter superhamiltonian depends only ultralocally on h thus it does not depend on π_h, while the purely geometrodynamical superhamiltonian depends locally on π_h and, thus, the antisymmetry of the PB yields the desired cancellation. In the quantum case, making use of eq. (105), one directly inherits such property from classical theory.

At this point we can claim that we can succesfully reproduce the closing relations for the generators of Dirac's group of hypersurface deformations on a hybrid geometrodynamical phase space for QFT and classical geometry, at the cost of a

quantum connection for the quantum states which must fulfill three constraints given by eqs. (74,103,105).

Note that all these conditions is just analogous to claiming that quantum supermagnitudes behave as their classical field counterparts, regarding their dependence on h, π_h, *i.e.*:

$$\langle \Psi \mid Q\left(\frac{\delta \mathcal{H}_{AC}(x')}{\delta h_{\alpha j}(x)}\right)\Psi\rangle = \frac{\delta}{\delta h_{\alpha j}(x)}\mathcal{H}_{AQ}(x') \tag{107}$$

Generalizing this result, it would appear desirable that the quantum connection allows us to extend this property to the generating functions of any symmetry of the system and, ideally, to the whole algebra of operators:

$$\partial_\xi Q(A) + [\hat{\Gamma}, Q(A)] = Q(\partial_\xi A) \tag{108}$$

Notice that this expression represents the compatibility condition of the quantization mapping (which is not tensorial), and the behavior of the quantum connection ∇. To what extent (if any) it can be achieved for arbitrary observables is beyond the scope of this paper and will be subject of future investigation.

Therefore, we can summarize this section by stating that we have found the hybrid generating functions of hypersurface deformations given by (95) and (96), that appropriately reproduce the closing relations of Dirac's group for the hybrid Poisson bracket (92), under the consistency requirement given by (107) which implies constraints on the quantum connection.

4.3. Constraints.

Lastly, we must enforce the path independence criterium, *i.e.* the physical Cauchy data $(h(0), \pi(0), \Psi(0))$ defined on an initial hypersurface Σ_0 should yield under evolution the same Cauchy data $(h(t), \pi(t), \Psi(t))$ on a final hypersurface Σ_t, independently of the path chosen from one leaf to another, *i.e.* of the sheaf of intermediate hypersurfaces $\Sigma_\tau \ \ \forall \tau \in (0, t)$ that conforms the foliation of that region of spacetime.

Given that from one leaf its infinitesimally following leaf in the foliation can be generated through a combination of normal and tangential deformations, path independence implies at the infinitesimal that any two arbitrary deformations should provide the same physical data independently of the order such deformations are applied. This means that, when evaluated on physically relevant matter and metric distributions, *i.e.* a hybrid state (h, π_h, Ψ), the application of the deformations should commute and thus the closing relations should be null *on shell* (*i.e.*, over the submanifold defined by the constraints). Consequently, as in the classical case, the Hamiltonian and momenta

first class constraints must be enforced on Hybrid Geometrodynamics. Thus, one can only consider physical situations (initial data) where the following equations are fulfilled:

$$\mathcal{H}_H(h,\pi,\Psi;x) \simeq 0 \tag{109}$$

and

$$\mathcal{H}_{iH}(h,\pi,\Psi;x) \simeq 0\ . \tag{110}$$

As a technical note, one may consider that the nulity required in these constraints for hybrid supermagnitudes that involve the expectation value of quantum local operators must be seen as the nulity of all expectation values of hybrid operators constructed as contractions of any distribution with the supermagnitudes $f^x\mathcal{H}_{Hx} = 0\ \forall\ f^x \in D'(\Sigma)$.

These constraints, together with the closing relations (which are linear on the supermagnitudes and, thus, null *on shell*) ensure that we have successfully enforced the 3+1 equivalent to the General Covariance of Einstein's gravity in the hybrid theory, representing Dirac's group of hypersurface deformations together with the first class constraints that ensure path independence, and therefore, foliation invariance.

Besides, in relation with the dynamics that we will see in the following section, this implies that, on physical data, the total Hamiltonian function f_H (Geometric and Quantum part, which contains the expected value) is always null for the whole hybrid universe, similarly to the Wheeler-DeWitt equation, but in this case, this nulity applies at each leaf and the 3-metric and its momentum are still classical.

4.4. Dynamics for generic hybrid observables and preservation of first class constraints.

For a generic element of the hybrid algebra of observables $F \in \mathcal{A}_H$ the effect of the hypersurface deformation characterized by the evolution field E_s, characterized by a normal deformation of size N^x and tangential deformations given by N^{ix}, should reproduce (11). The Hamiltonian representation of Dirac's algebra allows us to identify:

$$\mathcal{L}^\star_E F = \{F, f_H\}_H \tag{111}$$

being the Hamiltonian function

$$f_H := N^x\mathcal{H}^H_x + N^{ix}\mathcal{H}^H_{ix}. \tag{112}$$

Let us consider that such F is now an appropriate function over hybrid phase space that is also lapse, shift and s-label dependent, constituting a (N, N^i, s)-parametric family of hybrid observables. This makes up for the most general case of dynamical quantity in the Hamiltonian framework. The dynamics of such functional F will be given by:

$$d_s F = \{F, f_H\}_H + (\dot{N}^x\partial_{N^x} + \dot{N}^{ix}\partial_{N^{ix}} + \partial_s)F \tag{113}$$

where we are taking into account that lapse and shift functions contain their own dynamics, given by $\dot{N}^x = \partial_s N^x$ and $\dot{N}^{ix} = \partial_s N^{ix}$, known beforehand and determining the choice of foliation (or a certain path along possible hypersurfaces).

Let us now examine the case of the Hamiltonian and momenta constraints. If we consider the effect of the Hamiltonian field over the supermagnitudes, given that the closing relations (24,25,26) are linearly proportional to the constraints, and therefore, null on shell, we obtain:

$$\{\mathcal{H}^H_{\mu x}, f_H\}_H \simeq 0 \quad \forall \mu = 0, \cdots, 3 \tag{114}$$

Thus, the only contribution to the dynamics of the supermagnitudes when the constraints are enforced is their lapse and shift dependence. Such dependence was not present in the classical field theoretical case, but is acquired through the quantization procedure and the sectional nature of quantum states. Nevertheless, such dependence must be made null, given that the constraints must be preserved during the dynamics in order to maintain the leaf independent principle. Given that this must be true for all foliations or paths between hypersurfaces, it must be true for any choice of evolution for lapse and shift. Consequently, we must enforce that:

$$\frac{\delta}{\delta N^\mu(x')}\mathcal{H}_\nu(x) = \frac{\delta}{\delta N^\mu(x')}\mathcal{H}^Q_\nu(x) = 0 \ \forall \ \mu, \nu = 0, \cdots, 3 \tag{115}$$

which implies, at the level of the quantum connection,

$$\frac{\delta}{\delta N^\mu(x')}Q(\mathcal{H}^M_\nu(x)) + [\hat{\Gamma}_{N^\mu}(x'), Q(\mathcal{H}^M_\nu(x))] = 0 \tag{116}$$

Note, therefore, that if eq. (115) is not fulfilled, even though the constraints are conserved under the Hamiltonian dynamics given by $\{, f_H\}_H$, they would not be conserved under the curve the lapse and shift functions follow. Therefore, at some step in the evolution the hybrid states would abandon the submanifold of null supermagnitudes and the path independence would be lost from that point onward, falling into the Hamiltonian analogue of losing general covariance.

Note that this is equivalent to extend equation (107) to apply for derivatives not only with respect to purely geometrodynamical variables h, π_h but also for lapse and shift (as the classical field magnitudes did not depend on them). This starts depicting a general trend: symmetry generating functions at the quantum level must present the same kinematical relations and leaf dependence as the classical field theory to properly close with the pure geometrodynamics, and the quantum connection is chosen to provide such compatibility (associated to the leaf-dependent family of vacua invariant under the symmetries).

4.5. Hybrid equations of motion and properties of the dynamics.

Having introduced above the evolution equations for any hybrid observable, we consider illustrative to write down explicitly the equations of motion governing the dynamics of the 3-metric, its associated momenta and the quantum states. For the 3-metric from a hypersurface to a neighbouring one can only be by the extrinsic curvature and the spatial diffeomorphism, its differential equation is as in ordinary geometrodynamics, matter independent:

$$\frac{d}{ds}h_{ij}(x) = \{h_{ij}, f_H\}_G = 2N(x)G_{ijkl}(x)\pi^{kl}(x) + 2(D_iN^k(x))h_{kj}(x) \tag{117}$$

On the other hand, the geometric momenta does couple with matter:

$$\frac{d}{ds}\pi^{ij}(x) = \{\pi^{ij}, f_H\}_G = -\partial_{h_{ij}(x)}H_G - N^{x'}\langle\Psi \mid Q(\partial_{h^{ij;x}}\mathcal{H}^M_{x'}) \mid \Psi\rangle, \tag{118}$$

where the first term is the the usual from pure geometrodynamics and the second one is the coupling with quantum matter, which, by mercy of the constraints on the quantum connection, has no contribution from the quantum supermomenta, given (103), and the derivative w.r.t. h of the quantum superhamiltonian fulfills (105). We identify this last term as the *backreaction of quantum matter into the gravitational dynamics*. Lastly, the quantum state evolves as:

$$\frac{d}{ds}\Psi = \{\Psi, f_H\}_Q + \{\Psi, f_H\}_G + \dot{N}^x\partial_{N^x}\Psi + \dot{N}^{ix}\partial_{N^{ix}}\Psi = \\ \left(\frac{-i}{\hbar}\hat{H} - \{h_{ij;x}, f_H\}_G\hat{\Gamma}_{h_{ij;x}} - \dot{N}^x\hat{\Gamma}_{N^x} - \dot{N}^{ix}\hat{\Gamma}_{N^{ix}}\right)\Psi \tag{119}$$

where we remind that such quantum connections must fulfill eqs. (74,105,103,116), and the notation for continuous indices implies the contraction through integration over Σ of the local connections with the s-derivative of their associated local variables ($\{h_{ij;x}, f_H\}_G\hat{\Gamma}_{h_{ij;x}} = \int_\Sigma d^3x\partial_{\pi^{ij}(x)}f_H\hat{\Gamma}_{h_{ij}}(x)$, and equivalently for lapse and shift $s-$derivatives and local connection). Besides, we remind that the quantum Hamiltonian operator $\hat{H}$ and the connections are (h, N, N^i)-dependent.

This system of equations defines the hybrid dynamics. Note that it cannot be unitary, given the non-linearity arising from the mutual backreaction. Nevertheless, norm conservation is assured by the quantum connection, even if the definition of the scalar product (and thus, of the Hilbert space) is leaf dependent, as already happened in Ehrenfest equations for finite dimensional hybrid systems [1].

Note, on the other hand, that the connections appear acting as operators on Ψ, but they are not self adjoint for the scalar product over such leaf, $\langle,\rangle_\xi$. Thus, for such scalar product associated to a certain $\xi \in \mathcal{B}$ content of the leaf, they would induce also a non-unitarity. In fact, the main property of such connection is that it always maps the

quantum state *out* of the original Hilbert space to which it originally belonged (given by $\langle , \rangle_\xi$), in order to fit it in the infinitesimally neighbouring Hilbert space under the path along the section of scalar products $\langle , \rangle_{\xi+\delta\xi}$, given by the infinitesimal change $\delta\xi$ of (h, π_h, N, N^i). Nevertheless, the quantum connection compensates for the change of the scalar product itself under changes of ξ, as seen in eq. (74), and for such leaf dependent definition of scalar product, we achieve norm conservation. The proof is immediate by applying eq. (113) to the norm:

$$\frac{d}{ds}\langle\Psi \mid \Psi\rangle_\xi = \{\langle\Psi \mid \Psi\rangle_\xi, f_H\}_G + \dot{N}^{\mu x}\partial_{N^{\mu x}}\langle\Psi \mid \Psi\rangle_\xi + \frac{i}{\hbar}\langle\Psi \mid [\hat{H}, \mathbb{I}]\Psi\rangle_\xi = 0 \qquad (120)$$

where the first two terms are null because the image through horizontal sections of the tangent fields on $\mathcal{B}$ conserve the ξ-dependent scalar product, while the quantum Poisson bracket is null because it involves the commutator of the self-adjoint (for the given $\langle , \rangle_\xi$) Hamiltonian operator with the identity. Contrarily to the case of the horizontal lift of the geometric transformation, the term with the quantum Hamiltonian is Hilbert space preserving, not accounting for changes of the base, but only for the vertical evolution on the leaf.

Therefore, one may decompose the hybrid dynamics of the quantum state as the sum of a vertical vector field on the fibration and a horizontal one. We must remember that the quantum state as an element of $\mathcal{M}_Q$ is defined as $\sigma_\Psi|_\xi$, the evaluation of a covariant section $\sigma_\Psi \in \mathcal{M}_s$ on a given point $\xi \in \mathcal{B}$. In this context, the vertical vector, which is given by the quantum Poisson bracket that provides the Schrödinger-like term, provides the change within the space of $\mathcal{M}_s$, the covariant sections, but keeps evaluation point $\xi \in \mathcal{B}$ static. On the other hand, the horizontal one, given by the image through σ_Ψ of the gravitational Poisson bracket and the tangent vector to the curve defining the lapse and shift along the foliation, provides the change of the evaluation point in $\mathcal{B}$, without changing the covariant section σ_Ψ. Therefore, together they yield the total evolution of the quantum state, taking into account both the change of Hilbert space due to the change of ξ and the change of quantum state within the original Hilbert space, as is illustrated in Figure 3.

5. Discussion.

We have constructed a hybrid geometrodynamical framework with classical 3-metric and associated momenta and quantum field theoretical matter. In order to succesfully represent the infinitesimal generators of Dirac's group of hypersurface deformations in a Hamiltonian way over this hybrid manifold, the introduction of the quantum connection has shown to be crucial. Such quantum connection is related to a notion which is widespread in the literature: the time dependence of the vacuum state in quantum field theory in curved spacetime, which leads to time dependent Fock spaces, or analogously, field measures defining a Hilbert space. Depending on the interpretation, this usually lead to a pandemonium of phenomena, from norm loss of quantum states of difficult

physical understanding from the probabilistic point of view, to complicated particle interpretations when Lorentz invariance was missing in the first place. Under this formalism, there is no need of such interpretations, as norm loss is entirely avoided and the variety of Hilbert spaces is clear from the beginning.

In particular, using the mathematical construction of [2, 3], we have introduced the concept of a ξ-parametric family of quantizations (equivalent to the time dependent vacuum), each of them characterized by a measure, a representation of operators and states. Such quantizations are unitarily inequivalent, contrarily to the finite dimensional case. Therefore, we introduce a non-unitary operator to relate them, which does not preserve the Hilbert state structure it acts on, but instead transports the state to the new Hilbert space resulting from the change of ξ. Such operator represents functionally the quantum connection 1-form. From the requirements for consistent hybrid geometrodynamics, we obtain that it must fulfill certain constraints, which in the auxiliary mathematical notes are related to the covariance of Kibble's Kähler structure ([24]). It has remarkable physical implications; it leads to norm conservation throughout evolution, ensures that the quantum supermagnitudes (generating functions of hypersurface deformations) reproduce Dirac's algebra and helps preserving throughout the foliation the hybrid geometrodynamical constraints.

On the other hand, the reader might have notice that the process that has lead to the identification of the quantum supermagnitudes is slightly misaligned with the spirit of geometrodynamics [19]. Instead of invoking the *representation postulate* to find the supermomenta as purely spatial diffeomorphisms on leaf, $\mathcal{L}^{\star}_{N^i}\Psi = \{\Psi, \mathcal{H}^Q_i\}_Q$, we have resorted to the quantization of the appropriate generating functions over the classical field theory to identify such generating function. In the end, the procedure is analogous, for a consistent quantization procedure of the observables yields the appropriate operators (specially if they are no more than quadratic on the fields) representing the transformation for the functions adapted to a certain L^2, taking into acount that momentum operator is represented as a self-adjoint derivative w.r.t. the measure and vacuum phase, in order to be self adjoint.

The geometrodynamical principle of equivalence is a key notion in [19] for the inclusion of of classical matter sources in geometrodynamics. We keep this notion, but apply it only to the classical field theory considered for quantization, and, given that the choice of quantization is made referent to the classical field structures as in [5] , the quantized version does not acquire extra dependencies on the geometric momenta. Nevertheless, we do allow for it to acquire through the quantization procedure new (non-ultralocal) dependencies on the derivative of the 3-metric.

As discussed in the introduction, invoking the geometrodynamical equivalence principle for the classical matter fields as in [19] bans non-minimally coupled theories from this framework, and thus, we have only studied, for the material subsystem, theories

resulting from the quantization of classical supermagnitudes that did not depend on derivatives of h nor on π_h. The extension of hybrid geometrodynamics to non-minimally coupled cases and its implementation regarding the GD equivalence principle, will be explored in future works. On the other hand, one may speculate that, to some extent, some sort of non-minimally coupled field theories could still emerge as effective theories for matter test fields obtained from the current theory were matter fields are sources. The idea would be that the effect of the backreaction of matter on gravity, and its subsequent effect on the propagation of the fields due to the change of metric, makes up for a gravity-mediated self-interaction. Therefore, if the perturbation on the geometry is small, it could be "integrated out", *i.e.* absorbed into the matter theory as a new dynamical pole on the propagator of the fields coupled to a background gravity, considering for this new effective theory the geometry unaffected by matter "test fields".

Furthermore, N, N^i have a dynamical origin, not a kinematical one. Therefore, the fact that the quantization procedure is dependent on them seems rather unnatural, as it renders the quantum kinematical structures (such as the scalar product and the space of states) N, N^i-depdendent, obscuring the difference between kinematics and dynamics. Nevertheless, thanks to eq. (115), at least the generating functions of the symmetries are forced to be independent on them. In any case, a choice of complex structure for quantization that, together with the connection, fulfills all the constraints, but is not lapse and shift dependent, would seem desirable in this sense, although, *a priori*, it would differ from the case considered in [5].

In addition to the former discussion, it is relevant to recognize that the notion of equivalence principle for Quantum Field Theory has been questioned in the literature, although in our construction its enforcing is not required explicitly at the quantum level. However, one of the implications of hybrid geometrodynamics yields some light on this issue and goes as follows. In the same sense that Ehrenfest's theorem *almost* reproduces Newton's equations for the expectation values, we can argue that the expectation values of the operators resulting from quantizing classical matter supermagnitudes *almost* obey this hybrid geometrodynamical equivalence principle. In this way we find an interpretation under the light of the equivalence principle for the particular leaf dependence of hybrid observables,

$$\partial_\xi \langle \Psi \mid Q(A) \mid \Psi \rangle = \langle \Psi \mid Q(\partial_\xi A) \mid \Psi \rangle \tag{121}$$

associated to any classical symmetry generating function A. Note that, in the case of leaf dependent quantization, this is only possible thanks to the inclusion of the quantum connection. Therefore, "purely material" physical observables, at least at the level of expectation values, not of measurement results, have their local laws with the appropriate dependence on the geometry of spacetime, as the classical magnitude A fulfilled the geometrodynamical principle of equivalence.

Another important principle in the construction of geometrodynamics is path in-

dependence, achieved under the hybrid constraints $\mathcal{H}_{\mu H}(x) = 0$ (ensured their preservation through (115) and their first class nature for the Hamiltonian $\{, f_H\}_H$). These constraints might have important phenomenological consequences, as we have hybrid conserved magnitudes for the whole universe. For example, starting from non-divergent initial data for matter and geometry, if at any point of the evolution the pure geometrodynamical part becomes divergent (formation of a singularity, for example in a hybrid dust collapse model), it must be accompanied by a same-sized divergent expected value of the quantum operator, as we know that the Hamiltonian constraint is preserved. To what extent this might prevent the dynamical formation of singularities when matter sources are quantum will be the subject of future work.

In this line, one realizes that, if the phenomenon of quantum completeness as stated in [18],[4] had a backreaction of quantum matter on gravity as in this work, the quantum matter fields would not be able to act as sources of divergent geometry. Such phenomenon is based on the loss of norm for the quantum states while approaching geometric singularities. In that sense, singularity formation starting with non-singular initial data would be to some extent protected in hybrid geometrodynamics if norm loss was allowed, as, in the process of forming the singularity, the material sources would become smaller the nearer to the formation of the singularity.

Nevertheless, in our framework norm loss does not take place, even if the norm is computed inside different Hilbert spaces with different scalar products. The usual argument of time dependent vacuum state is still valid, given by the leaf dependence of such vacuum state, where the leaf variables are dynamical. Precisely, in our work it is the source of the consideration of inequivalent Hilbert spaces, as it provides the associated measure, albeit such measure and the non-vacuum states are always properly normalized. To what extent the phenomenology of quantum completeness could find its way into our formalism, given that norm loss is healed by the quantum connection relating the ξ-parametric family of scalar products, is still a matter of discussion.
Another interesting application of the formalism is the study of the phenomenon of particle creation (for a decomposition of wave functionals into the usual particle interpretation of Fock spaces, see [2, 3]). In particular, if we considered a closed path on the base of the hybrid fibration, starting from an Euclidean measure (and a suitable associated geometromomenta), going through arbitrary Riemannian 3-metrics, back into the Euclidean case, we are reproducing the usual "past Minkowski", intermediate curved spacetime, "future Minkowski" set up. The holonomy of the quantum connection along this curve allows for the precise mathematical characterization of the particle creation phenomenon in our framework, while leaving room for more general phenomena, such as the physical interpretation of a possible torsion for such quantum connection. This will be the subject of study of future works.

We conclude this work by quoting Robert M. Wald who has guided the intertwining of Quantum field theory and curved spacetime for almost half a century. The quote is

an extract from [34] on the consistency of quantum fields in curved spacetime as source for classical gravity:

> *"But if the five axioms* [of QFT in Curved Spacetime] *are inconsistent in a nontrivial manner, then unless one can somehow evade the arguments of Section II* [leading to the five axioms] *one would be forced to conclude that "back reaction" effects cannot be treated within the context of the semiclassical approximation."*

In this context, a natural question that we will need to answer in future investigations is whether or not something has been gained regarding this issue in our depiction of the backreaction in terms of Hamiltonian framework for Dirac's spatial hypersurface deformations.

Acknowledgements.

We express our sincere gratitude to Prof. J.L. Cortés for his insightful comments. We also extend our appreciation to Jan Głowacki for engaging discussions and sharing his extensive knowledge on geometrodynamics. Furthermore, we would like to thank M. Schneider for stimulating conversations that sparked our curiosity in the phenomenology of quantum completeness in relation with our framework.

The authors acknowledge partial finantial support of Grant PID2021-123251NB-I00 funded by MCIN/AEI/10.13039/501100011033 and by the European Union, and of Grant E48-23R funded by Gobierno de Aragón. C.B-M and D.M-C acknowledge financial support by Gobierno de Aragón through the grants defined in ORDEN IIU/1408/2018 and ORDEN CUS/581/2020 respectively.

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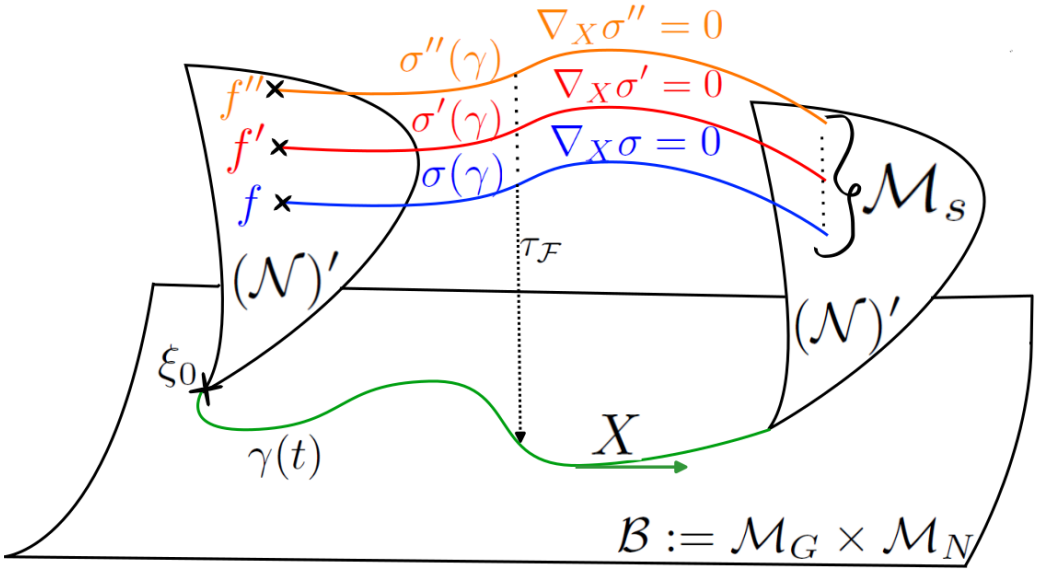

Figure 1. Representation of the fibration with base $\mathcal{B}$ and fiber $(\mathcal{N})'$, and the set of parallel transported sections over it, $\mathcal{M}_s$, associating a Hida distribution to each point of a curve γ along the base. Note that the sections are defined for different points of the fibration $(f,\ f',\ f'',\ \cdots)$ fulfilling $\tau_{\mathcal{F}}(f) = \tau_{\mathcal{F}}(f') = \tau_{\mathcal{F}}(f'') = \xi_0$ and the covariance condition, $\nabla_X\sigma = 0\ \forall X \in \mathfrak{X}(\mathcal{B})$.

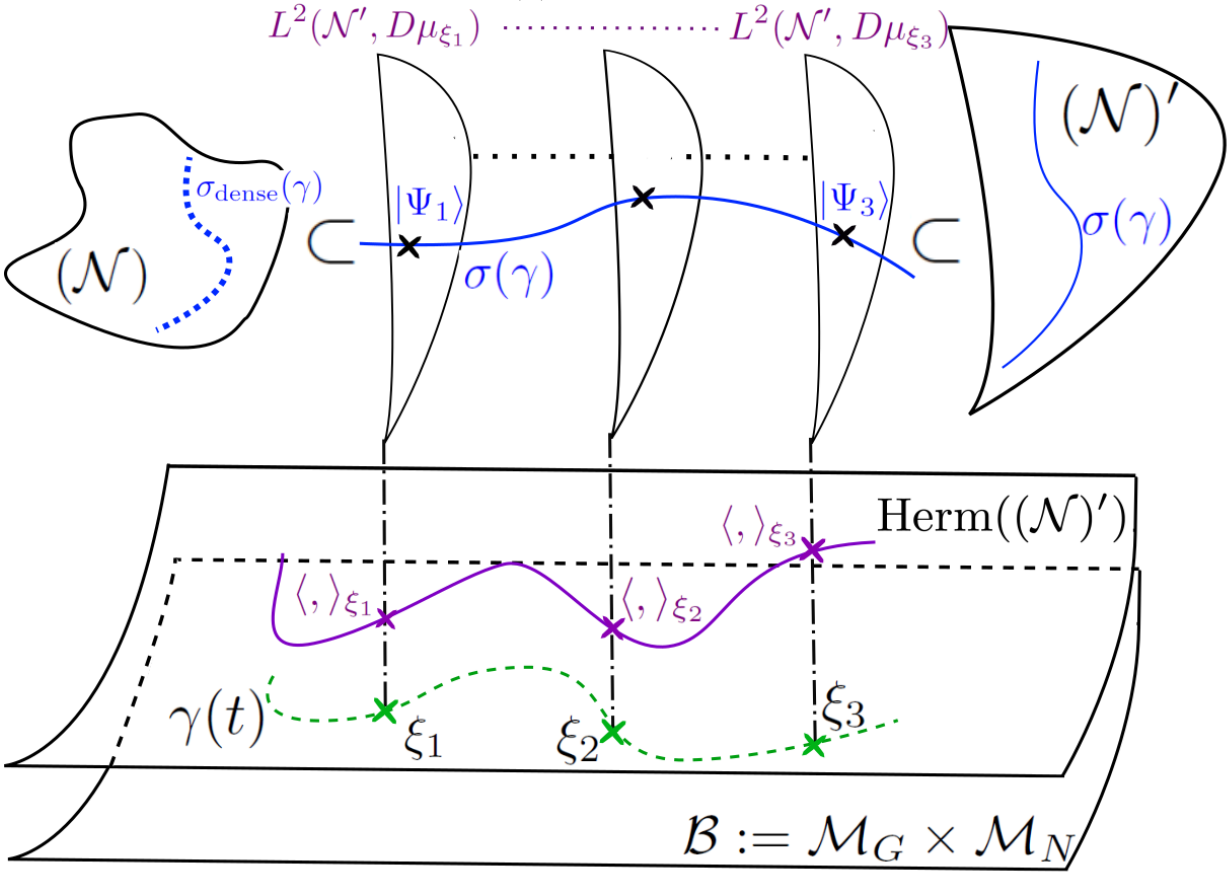

Figure 2. One of the sections of figure 1, seen locally on $\xi_i = \gamma(t_i)$ as $|\ \Psi_i\rangle$, a vector inside a different Hilbert space at each point of the base. Such Hilbert spaces are defined depending on $\xi \in \mathcal{B}$, given the ξ-dependence of the Hermitian product

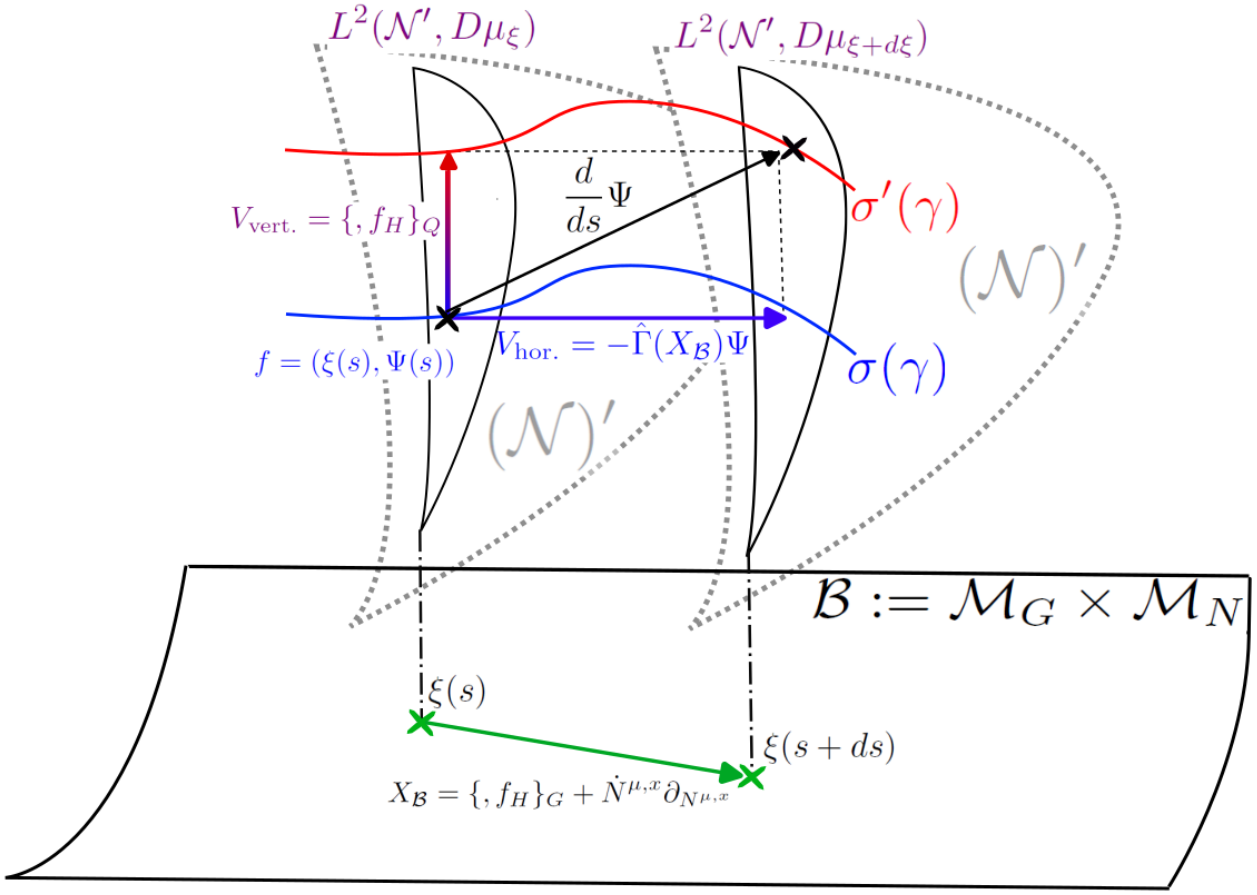

Figure 3. Illustration of the decomposition of a tangent vector to the bundle in its vertical and horizontal decomposition. In particular, we are considering the infinitesimal evolution of the hybrid states, between two infinitesimally close hypersurfaces, $\Sigma_s \to \Sigma_{s+ds}$. Thus the vertical part is given by the "solely quantum" evolution, *i.e.* $V_{\text{vert.}}(\Psi) = \{\Psi, f_H\}_Q = \frac{-i}{\hbar}\hat{H}\Psi$. This part of the dynamics is internal for the original Hilbert space, for the initial $\xi(s) \in \mathcal{B}$, and can be seen as a change between the covariant sections (from black to red) in $\mathcal{M}_s$, without changing the evaluation point. On the other hand, the horizontal one lifts the tangent field on the base through the connection. Therefore, it does not change from one covariant section to another, but it provides the change of Hilbert space due to the change of evaluation point to $\xi(s+ds)$. The sum of both of them conform $\frac{d\Psi}{ds}$, which is a generic change of quantum state, changing both covariant section *and* evaluation point. Remember that the change of Hilbert spaces forces us to see the quantum state inside different (for each ξ) subsets (the L^2 spaces) of $(\mathcal{N})'$, as it engulfs all the L^2 spaces, which is why it is chosen to be the fiber of the given bundle (represented faintly in the background).

Hybrid Geometrodynamics.
Supplementary material.

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Submitted to: *Class. Quantum Grav.*

1. Differential calculus in infinite dimensional manifolds.

The aim of this first section is the definition of the necessary tools from calculus and functional analysis to be able to write the Poisson bracket for the gravitational degrees of freedom and the derivatives with respect to the field-distributions of the quantum states, taken into account the infinite dimensional nature of the associated manifolds. We will start with the gravitational case.

1.1. Gravitational case.

Firstly, we express the metrics in terms of its coordinates $h_{ij}(x_\sigma)$ for the fixed chart on Σ (we assume it constitutes an atlas, but can be extended to several charts with smooth composition) given by x_σ. Now, the derivative with respect to the metric is represented by $\dfrac{\delta}{\delta h_{ij}(x)}\ \forall\ i,j$, and this is the expression we want to make sense for. Originally, for h to be a tensor field, we consider the coordinates as differentiable functions, $h_{ij}(x_\sigma) \in C^\infty(\Sigma)$. In order to have a good notion of derivative, we want to make the space of metric coordinates a Fréchet space, denoted by $\mathcal{N}_h$. We have two options here.

The first one is for Σ to be a compact manifold, thus in order to find a Frechet topology for them we must fix a boundary term for a h_{ij}, for example the euclidean metric η in the whole Σ, and add to it differentiable functions of compact support as a perturbation over η. Then $\mathcal{N}_h = (C_C^\infty(\Sigma))^6 + \eta_{ij} \simeq (C_C^\infty(\Sigma))^6$. Note that in $\mathcal{N}_h$ we are considering 6 copies (one for each independent coordinate given by $i,j = 1,2,3$ substracting the permutations) of the chosen Fréchet space. On the other hand, if Σ is not compact, we must ask for asymptotic properties of the metric h_{ij}, for example match the euclidean metric at infinity, and then perform a one point compactification of the manifold $\bar{\Sigma} = \Sigma \cup \{\infty\}$ and return to the previous case.

Armed with this machinery we identify $\dfrac{\delta}{\delta h_{ij}(x)}$ with its Fréchet derivative, and the directional version, given by Gateaux derivative along f_{ij}, given by $\int\limits_\Sigma dVol_\Sigma(x) f_{ij}(x) \dfrac{\delta}{\delta h_{ij}(x)}$.

Secondly, to extend this notion of derivative to the cotangent bundle, we would like to have the same notion of derivative on the dual space. There is an obstacle that must be overcome: the tangent space is isomorphic to $Riem(\Sigma)$ which in turn can be seen as an element in a Fréchet space, $\mathcal{N}_h$, which yielded the notion of Fréchet derivative. Contrarily, the cotangent space is the dual of the former. If we are to find a natural topology of this space as the dual of $\mathcal{N}_h$ then we would conclude that it must be modelled with distributions, $\pi^{ij} \in D'(\Sigma)^6$, which is the dual to $C_C^\infty(\Sigma)$ The main issue with this approach is that $C_C^\infty(\Sigma) \subset D'(\Sigma)$ is not isomorphic to its dual, but way smaller.

In this case there is a fairly simple solution to this problem, we will restrict the

momenta $\pi^{ij} \in Riem'(\Sigma)$ to be (0,2) symmetric tensor densities of weight 1. This is a dense subspace of the previous choice that has the same topology as $\mathcal{N}_h$ and therefore is a Frechèt manifold.

All these considerations lead to the fact that on $\mathcal{M}_G$, locally trivialized by $Riem(\Sigma) \times Riem'(\Sigma)$, one can define a symplectic form ω_g. Notice that we can only consider a corresponding Poisson tensor as its weak inverse, because the symplectic form is invertible considering the inclusion $C^\infty_C(\Sigma) \subset \mathcal{H}$, where $\mathcal{H}$ must be a Hilbert space. This is achieved with the notion of Gel'fand triple, which we discuss in the next section. In order to focus on the physical applications, we assume that all the necessary considerations of infinite dimensional analysis are made in order to work in the conventional way of differential geometry.

1.2. Matter case.

In the case of classical scalar fields we can proceed analogously. We might model the field variables and their momenta as functions (densities) of compact support $\mathcal{N} = C^\infty_c(\Sigma)$. For tensorial matter fields the construction proceeds as in the gravitational case, with the appropriate vanishing boundary conditions.

For quantum matter the situation is different. It is no longer possible to model the manifold of quantum fields over a nuclear-Frechèt space. The reason is twofold. On the one hand the canonical commutation relations $[\hat{\phi}^x, \hat{\pi}^y] = i\delta^{xy}$, the l.h.s. stands for the Dirac delta, force quantum fields to be considered as operator valued distributions and therefore its eigenvalues, considered as their classical counterparts that belong to a manifold $\phi^x, \pi^x \in \mathcal{M}_F$, must be distributions.

On the other hand, a quantum wave function Ψ must belong to a Hilbert space of square integrable functions $L^2(D\mu)$ where $D\mu$ is a measure over the classical fields $\mathcal{M}_F$. Not such measure exist if $\mathcal{M}_F$ is identified with $\mathcal{N}$, thus we must complete it to a bigger space. It turns out that the natural space to consider integration theory is the dual of a Nuclear-Frechèt space $\mathcal{N}'$, which in our case is the space of distributions $D'(\Sigma)$. For further details on this discussion we refer to [2, 3].

This considered, the definition of a derivative becomes trickier in this setting. For the gravitational case we just reduced the momenta, naturally belonging to $D'(\Sigma)$, to a Frechèt subspace. In this case the situation is reversed, we must extend the fields, naturally belonging to $C^\infty_c(\Sigma)$, to the space of distributions. The tool to perform such an extension is the Rigged Hilbert space or Gel'fand triple. The presence of a riemannian metric h over Σ allows us to "raise" indices of functions $\phi_x \in \mathcal{N}$ to their associated distributions $\phi^x \in \mathcal{N}'$ under the identification

$$\mathcal{N} = C^\infty_c(\Sigma) \subset L^2(d\mathrm{Vol}_h, \Sigma) \subset D'(\Sigma) = \mathcal{N}' \tag{1}$$

Quantum pure states are therefore modelled by wave functions of a space $\Psi \in L^2(D\mu, \mathcal{N}')$ where $D\mu$ is a gaussian measure defined by the characteristic functional, as

in eq. (47) of the main article. The question that arises now is, what notion of derivative is available for matter fields in this context?

To answer this question we will proceed as follows, we introduce the Nuclear-Frechèt of Hida test functions denoted by $(\mathcal{N})$. This space is constructed solely with the structure of $\mathcal{N}$. Frechèt derivatives are well defined objects that we denote $\partial_{\phi^x} : (\mathcal{N}) \to \mathcal{N} \otimes (\mathcal{N})$ and allow for directional derivatives in every direction of $\mathcal{N}'$. Then we introduce the Gel'fand triple

$$(\mathcal{N}) \subset L^2(D\mu, \mathcal{N}') \subset (\mathcal{N})' \tag{2}$$

This allows to extend the derivative ∂_{ϕ^x} to every function in $L^2(D\mu, \mathcal{N}')$ (and even $(\mathcal{N})'$) at the cost of reducing the allowed directional derivatives to those on the Cameron-Martin Hilbert space $\mathcal{H}_\Delta \subset \mathcal{N}'$. This Hilbert space is built upon the covariance of $D\mu$. The new notion of derivative is the (Hida-)Malliavin derivative, an operator

$$\partial_{\phi^x} : L^2(D\mu, \mathcal{N}') \to \mathcal{H}_\Delta \otimes L^2(D\mu, \mathcal{N}') \tag{3}$$

This operator allows us to perform differential calculus over the space of quantum fields for cases of physical interest.

We have thus defined derivatives with respect to the fields acting on the wave functionals. In the following section, we make sense of the quantum Poisson bracket through its associated symplectic form. Its usual biderivative representation can also be defined over the adequate functional spaces, in analogy to the gravitational case, but with a further level of abstraction.

2. Geometry of the Quantum Phase space.

The representation of Hamiltonian QFT we are considering follows the canonical construction in [5] (see also [4] for an equivalent formulation), which begins with the characterization of a phase space for quantum states, appropriately called the manifold of *instantaneous pure states*, $\mathcal{P}$, associated to the projective space of a Nuclear-Frechèt dense subset of a Hilbert space. Such phase space can be made of even dimension (for example, as a realification of a space of complex functions) and is naturally endowed with a symplectic structure ω_Q (at the quantum level, not to be confused with ω_C) from the imaginary part of the hermitian product over such Hilbert space, $\langle \cdot, \cdot \rangle = [\mu_Q(\cdot, \cdot) + i\omega_Q(\cdot, \cdot)]/2$. Of course, we may find the ω_Q-compatible complex structure J_Q completing the Kähler structure, such that $\mu_Q = \omega_Q(J_Q \cdot, \cdot)$. From there, one finds the Poisson bracket $\{,\}_Q$ as the (weak) inverse of ω_Q, identifies a Poisson algebra of observables $\mathcal{A}_Q$ as the expectation value of self-adjoint operators for such Kähler structure and among them one can find the symmetry generators. In particular, for the dynamics generating Hamiltonian function f_H, the integral curves associated to its Hamiltonian field $X_{f_H} := \{, f_H\}_Q$, yield curves among $\mathcal{P}$ called *histories* of the

quantum states, in contrast to the *instantaneous* nature of a single point in $\mathcal{P}$. Thus, the dynamics establishes an isomorphism between initial *the instantaneous pure state* and its *history*, in line with the definition of a Cauchy problem.

The *history* of a state in not granted to exist for any initial state in $\mathcal{P}$. Usually, to state existence and uniqueness theorems for the integral curves of X_{f_H} the dense subset $\mathcal{P}$ is not enough and we must consider the whole Hilbert space, or an even bigger set. Calculus on infinite dimensional spaces outside of the Frechèt category are pledged with ambiguities and problems that turn them into non convenient spaces for geometry[6]. Thus there is a tradeoff between the simplicity of the geometrical presentation of the dynamics and the existence of its resolution.

In our construction of Quantum Geometrodynamics the ultimate goal is constructing a Poisson algebra over a quantum phase space and find within it the generating functions of hypersurface deformations, considered to be symplectomorphisms and check that they fulfil the appropriate closing relations for a matter theory. Nevertheless, Kibble's geometric construction is more convoluted in our case than in ordinary Quantum Mechanics, as we have stated that the Hilbert spaces, the operator representations and even the states are leaf dependent, and, beyond that, there is no explicit notion of time, but of foliation-label, and, furthermore, the solutions to the Cauchy problem should be foliation (and, thus, label) independent, making up for a harder (and, some may argue, intertwined) definition of *instantaneous states* and *histories*, see section 3 of the main article. Thus, the first step to mimic Kibble's geometric formulation is to identify which geometric structures are unavoidably leaf dependent, and which ones can be constructed leaf independently.

Therefore we are facing two kinds of geometrical structures: the leaf independent ones, related to the kinematics, and the ones related to the physical interpretation, leaf dependent. Starting with the leaf independent ingredients, we identify the following kinematical elements:

I The phase space of the quantum theory, Γ_Q. In principle this is a complex space that could be modelled (up to existence and uniqueness problems) over the Frechèt-Nuclear space of Hida test functions $(\mathcal{N})$ which is a complex space. Here we choose to realify this space and represent Γ_Q with two copies of the real Hida test functions $(\mathcal{N})_R \times (\mathcal{N})_R$. This is associated to the space of instantaneous pure states $\mathcal{P}$ in [5], although in this case it is not yet associated to a Hilbert space. Note, nevertheless, that this space of Hida test functions is a common dense subset of all possible Hilbert spaces constructed from Gaussian measures of physiscal interest, therefore, the need to be restricted to a subset of a Hilbert space present in [5], which was necessary to consider only states belonging to the common invariant domain of all operators associated to symmetry generators, will be immediately fulfilled. In addition Γ_Q belongs to the Nuclear-Frechèt category and thus is a convenient space to perform differential geometry with proper definitions of partial (Frechèt) deriva-

tives and tensors.
Another difference with the standard interpretation of $\mathcal{P}$ given in [5] is that the quantum states are not elements of the tangent space to the vacuum but sections of a fiber bundle with base coordinates h, π_h, N, N^i.

Note, lastly, that we are not yet considering a scalar product over Γ_Q, so we have not yet endorsed it with the Gel'fand triple (2) that comes with the leaf-dependent Hermitian product $\langle , \rangle$ constructed from the gaussian measure $D\mu_\xi$ with characteristic functional associated to $\omega_C(J_C\cdot, \cdot)$.

II In the absence of further structure we would like to see the coordinates of Γ_Q as some sort of canonical *Darboux second quantized coordinates* [3]. In this sense we would like to proceed as in classical field theory. We introduce $\Phi^\phi \in (\mathcal{N})_R$ as the first coordinate which is a function, thus the associated canonical coordinate Π_ϕ should be a "density of weight 1". The problem with that approach is that there is not such a notion in infinite dimensions due to the ill defined determinant of a change of coordinates. Fortunately, as is further explained in the supplementary notes, there we noticed that densities of weight 1 were dense in the distributions and distributions are effectively defined with Gel'fand triples, in particular the Riemannian structure of Σ lead to the triple (1).
Consequently we declare that $\Pi_\phi \in (\mathcal{N})'$ is a Hida distribution. Nonetheless this identification poses further problems because $(\mathcal{N})'$ is too large to efficiently describe the conjugate variable to Φ^ϕ. Thus, we introduce a Gel'fand triple that depends only on the Riemanninan struture of Σ and therefore generalizes (1) in the most stightforward way. To do so we introduce the white noise measure $D\beta$ with the characteristic functional

$$\int_{\mathcal{N}'} D\beta(\phi) e^{i(\bar{\rho}_x \phi^x + \rho_x \bar{\phi}^x)} = e^{-\int_\Sigma d\mathrm{Vol}_h \bar{\rho}\rho}. \tag{4}$$

Then we construct the White Noise Gel'fand triple

$$(\mathcal{N}) \subset L^2(D\beta, \mathcal{N}') \subset (\mathcal{N})' \tag{5}$$

not to be confused with (2). We use this Triple to lower the indices of associated coordinates Π^φ that are functions. In other words, the canonical conjugate momenta Π_φ to the functions Φ^φ, that play the roles of densities of weight 1, are the elements of $(\mathcal{N})'$ that can be identified with $(\mathcal{N})$ through the white noise triple.
In summary, each point of Γ_Q will be labelled in canonical *Darboux second quantized coordinates* by $(\Phi^\varphi, \Pi_\varphi)$ where Φ^φ is a function of $(\mathcal{N})$ and Π_φ is a distribution of $(\mathcal{N})'$ that can be identified with a function Π^φ through the white noise triple (5). In this fashion we identify this space with the cotangent bundle $\Gamma_Q = T^\star(\mathcal{N})$

III The third ingredient is a symplectic form ω_Q over Γ_Q. For our particular choice, it

can be constructed as the canonical symplectic form of $T^\star(\mathcal{N})$ *i.e.*

$$\omega_Q = -d\Phi^\varphi \wedge d\Pi_\varphi = \int_{\mathcal{N}'} D\beta(\varphi) d\Phi^\varphi \wedge d\Pi^\varphi \tag{6}$$

As happened in [5], ω_Q must be only weakly defined. This is because we could regard it as the imaginary part of the scalar product of $L^2(D\beta, \mathcal{N}')$, then it is only invertible if we extend the definition to the whole Hilbert space. This weak definition affects mathematical aspects of existence and uniqueness theorems for solutions to differential equations, without ominous implications on the particular physics of the Hamiltonian dynamics we aim to construct.

The essential point of this symplectic form is that, in these coordinates, it is defined in a leaf independent way, $\partial_\xi \omega_Q = 0 \ \forall \ \xi = [h, \pi_h, N, N^i]$ as long as we declare $(\Phi^\varphi, \Pi_\varphi)$ leaf independent. Therefore, with a consistent definition of covariant derivative, its derivative must vanish in every system of coordinates. Notice that for this to be true the function $\tilde{\Pi}^\varphi$ acquire leaf dependence through the dependence of $D\beta$ on h. This is a reflection of the role that it acquires, being $\tilde{\Pi}_\varphi$ analogous to a density of weight 1.
Given the contangent bundle narrative, we have chosen ω_Q to be the canonical one, but, in general, it can be just postulated to exist over Γ_Q. In turn, from a quantization procedure point of view, as is discussed in [3] it can be considered as the generalization of the classical field symplectic form ω_C from 1-particle states (which are isomorphic to classical field solutions) to generic quantum states, and, as it already was leaf independent, such property is inherited through the generalization.

Once this structure is given one may define a weak inverse of the symplectic structure, which is the Poisson tensor Ω_Q.

IV The last kinematical ingredients are the quantum Poisson bracket $\{,\}_Q$ and a set of appropriately differentiable functions over phase space, which form a Poisson algebra $\mathcal{A}_Q$ with it. The Poisson bracket associated to the Poisson bivector, $\Omega_Q(df, dg) = \{f, g\}_Q$, and is a bidiferential operator fulfilling Jacobi, Leibniz, bilinearity and antisymmetry. The definition of $\{,\}_Q$ in the main text is precisely associated to this Poisson tensor, so it inherits all this properties and is a rightful Poisson Bracket. Assuming the symmetries of the system leave the chosen kinematical structure invariant, then they can be casted in a symplectomorph representation, where the closed form $df = \iota_{X_f}\omega_Q$ associates its generators to a Hamiltonian field X_f, constructed in terms of the function $f : \Gamma_Q \to \mathbb{R}$ representing a conserved quantity belonging to the Poisson algebra. This is called the generating function $f \in \mathcal{A}_\Gamma$ and its existence is assured by the triviality of de Rham's cohomology, being the one-form df exact. In this way, the symmetries over the Poisson algebra are implemented *via* the Poisson bracket as $\mathcal{L}_{X_f} g = \{g, f\}_Q$. This

is the most important ingredient for geometrodynamics, and, as long as we have a leaf independent Poisson bracket we can dispense with everything else.
Having a leaf independent quantum Poisson bracket (as ω_Q was leaf independent) implies eq. (63).

Once we have all of these ingredients we are almost able to represent the generators of hypersurface deformations in a Hamiltonian language for QFT. The only ingredient lacking is the association of the elements of the Poisson algebra to physical magnitudes. In other words: what do these functions represent and how do we construct them?

Unluckily, in QM operators are usually related to physical magnitudes through the (not univoquely defined for all observables) quantization procedure of the functions representing such magnitudes at the classical level, and in our case such quantization procedure is leaf dependent.
On the other hand, from [5], [4] (and in the hybrid case, [1]) we know that such Poisson algebra of functions must be given by the expectation value of self-adjoint operators.

To define such objects we will firstly introduce some notation. We will represent the quantum states in this manifold of pure states as vectors $V_\psi = \Psi_1^\phi \partial_{\Phi^\phi} + \Psi_2^\phi \partial_{\Pi^\phi})$ where Ψ_i^ϕ are just its coordinates in the canonical directions (associated, as we will see later, to Ψ as a Hida distribution in the main text). Notice that such coordinates may be ξ-dependent, in order to reproduce the section nature of quantum states. On the other hand, the operators as $(1,1)$-tensors will be denoted by $\check{A}$ (analogously associated to the operator $\hat{A} = Q(A)$ in the main text).

To introduce the scalar product, we introduce a Kähler structure at the quantum level. Given that Γ_Q is already provided with the symplectic structure ω_Q, we must introduce a compatible complex structure J_Q. In complete analogy with the Kähler structure over the classical field manifold, such complex structure is leaf dependent, as it is a suitable generalization of J_C from the 1-particle states (isomorphic to the classical field phase space) to generic states (see [3]). The compatibility condition by the definition of a Riemannian metric μ_Q:

$$\mu_Q(\cdot,\cdot) := \omega_Q(J_Q\ \cdot\ ,\cdot) \tag{7}$$

Armed with this Kähler structure, we may define a Hermitian product:

$$h_Q(V_{\Psi_a}, V_{\Psi_b}) := \left[\mu_Q(V_{\Psi_a}, V_{\Psi_b}) + i\omega_Q(V_{\Psi_a}, V_{\Psi_b})\right]/2\ . \tag{8}$$

Thus, we are able to reproduce the construction of [5] summarized in the first paragraph of these notes, with an interesting difference. The imaginary part of the scalar product is still given by the symplectic structure and it is leaf independent. Nevertheless, the real part is leaf dependent, as μ_Q is constructed from J_Q, that was chosen as a generalization of the leaf dependent J_C. Thus, we have a ξ-parametric family of Hermitian

products which only differ on their real part.

As shown in [3] and summarized at the end of these notes, this Hermitian 2-form reproduces the scalar product of the Hilbert space in the functional picture, as there exists a ξ-parametric family of isometries between the completion $\overline{(\Gamma_Q, h_Q)}^{\xi}$ and $L^2(\mathcal{N}', D\mu_\xi)$. Therefore, the algebra of observables under consideration is constructed from functions like the following:

$$f_A := h_Q(V_\Psi, \check{A}V_\Psi) = \frac{1}{2}\big[\omega_Q(J_Q V_\Psi, \check{A}V_\Psi) + i\omega_Q(V_\Psi, \check{A}V_\Psi)\big] \in \mathcal{A}_Q \ . \tag{9}$$

In this framework, it is straightforward to show that, for the operator $\check{A}$ to be self-adjoint it must fulfil:

$$\omega_Q(V_{\Psi_a}, \check{A}V_{\Psi_b}) = \omega_Q(\check{A}V_{\Psi_a}, V_{\Psi_b}) \quad \text{and} \quad [\check{A}, J_Q] = 0 \ . \tag{10}$$

From this construction, it is inherited from the construction in [5, 3] that the quantum Poisson bracket reproduces the commutator of operators as long as $[\check{A}, J_Q] = 0$ and $[\check{B}, J_Q] = 0$:

$$\{f_A, f_B\}_Q = \frac{-i}{\hbar} f_{[A,B]} \tag{11}$$

This implies that the relevant observables are blind to some parts of Γ_Q or analogusly not all Γ_Q should be considered, it is only necessary to keep the holomorphic part spanned the following vectors $V_h = \frac{1}{2}(1 - iJ_Q)V_\Psi$ that we denote $\Gamma_{Q,Hol}$.

As happened in the main text, the quantum states are covariant sections, where we will denote the connection 1-form by $\check{\Gamma}$:

$$\partial_\xi V_\Psi = -\check{\Gamma} V_\Psi \tag{12}$$

The condition that the connection fulfilled in the main text to achieve leaf independent of the kinematics, eq. (74) of the main text, is given in this language by:

$$\partial_\xi \omega_Q - \omega_Q(\check{\Gamma}\cdot, \cdot) - \omega_Q(\cdot, \check{\Gamma}\cdot) = 0 \tag{13}$$

and the condition that the connection does not mix the braket representation is provided by

$$\partial_\xi J_Q + [\check{\Gamma}, J_Q] = 0 \tag{14}$$

These conditions are, in turn, the preservation of the whole Khäler structure. For the quantum superhamiltonian ($\mu = 0$) and supermomenta ($\mu = 1, 2, 3$) to appropriately fulfil the material closing relations and the associated constraints to hold as in the main text, the must fulfill:

$$\partial_\xi \check{Q}(\mathcal{H}^M_\mu) + [\check{\Gamma}, \check{Q}(\mathcal{H}^M_\mu)] = \check{Q}(\partial_\xi \mathcal{H}^M_\mu) \tag{15}$$

where $\check{Q}$ is the quantization procedure giving operators in this geometric framework.

Relation between the functional and geometric picture and the quantization procedure.

From [3], we learn to construct the usual description of quantum states Ψ belonging to a single Hilbert space $L^2_{Hol}(\mathcal{N}', D\mu_\xi)$ from the second quantized Darboux coordinates (Φ^ϕ, Π^ϕ). The subspace $\Gamma_{Q,hol}$, that depends on the choice of J_Q, can be completed with the hermitian form h_Q. Then there is a unitary isomorphism denoted by $\iota_{J_Q} : \overline{(\Gamma_{Q,hol}, h_Q)} \to L^2_{Hol}(\mathcal{N}', D\mu_\xi)$, such that we may identify $\iota_{J_Q}\begin{pmatrix}\Phi^\varphi \\ \Pi^\varphi\end{pmatrix} = \Psi \in L^2_{Hol}(\mathcal{N}', D\mu_\xi)$. Using this isomorphism, one can define the operators in relation with the ones in the main text as:

$$\check{A} = \iota^{-1}_{J_Q}\hat{A}\iota_{J_Q} \tag{16}$$

and therefore, the quantization procedure defined above as:

$$\check{Q}(A) := \iota^{-1}_{J_Q}Q(A)\iota_{J_Q} \tag{17}$$

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Chapter 4

Discussion

Hybrid theories are powerful frameworks to simulate and understand systems that, usually under the perspective of an effective description, use both quantum and classical degrees of freedom to model the relevant phenomena.

These systems find their historical roots in the Born-Oppenheimer [11] approximation, which exploits the hierarchy between the masses of electrons and nuclei in molecules, allowing for an uncorrelated, though dynamically coupled, description of their motions, by neglecting terms being proportional to powers of $\left(\frac{m_e}{M_N}\right)^{1/2} \leq 0.024$. This approximation formed the basis for the treatment of molecular systems for decades, enabling a simplified representation where electronic degrees of freedom are treated quantum mechanically due to its relatively lower mass, while allowing to approximate classically the nuclear motion.

However, as research advanced and technology evolved, it became apparent that many systems require a more intricate treatment that goes beyond the Born-Oppenheimer-based molecular dynamics. Such approximation usually considered the electronic states to be frozen in an eigenstate of the Hamiltonian which was dependent on the nuclear degrees of freedom. As a consequence, the backreaction of the quantum degrees of freedom on the classical ones was given by the associated eigenvalue, which acted as an effective potential (usually dubbed *energy surface*) for the electronic-nuclear interaction, given its dependence on the nuclear positions. Thus, this picture was *adiabatic* regarding the quantum subsystem, forbidding electronic transitions between different energy levels.

Modern developments showed that *diabatic* dynamics for the quantum subsystem reproduced more accurately the full quantum description and, thus, the real phenomena captured in experimental studies. This led to the emergence of a wide variety of hybrid quantum-classical approaches beyond Born-Oppenheimer approximation. In this context, Ehrenfest dynamics, for example, takes a step ahead. Although it was already commonplace in the literature, its formal derivation was studied by Bornemnann *et al.* [68], who

showed that the bounds on the neglected terms in the approximation depend on the quotient of masses, and also on the quotient of the characteristic widths of the nuclear (σ_N) and electronic (σ_e) marginal probability densities ($\frac{\sigma_N}{\sigma_e} < 5 \cdot 10^{-5}$). The terms that are neglected in the Born-Oppenheimer approximation also depend on the quotient of masses, but in the case of Ehrenfest dynamics the dependence is more restrictive. This dynamics has played a crucial role in the field of hybrid systems, as it fulfils several consistency requirements [63], and can be provided with a Hamiltonian formulation in analogy to classical mechanics [69]. The latter fact, in the context of this thesis, is particularly useful in relation with Liouville's theorem.

While a lot of effort was devoted to the dynamics of hybrid systems, little attention was paid to their statistical and thermodynamic properties. For example, the absence of a precise definition of hybrid entropy was an unnoticed yet relevant hurdle in the literature. Consequently, this deficiency may lead to misconceptions of hybrid thermodynamical ensembles. In particular, a wrong definition of the canonical ensemble may lead to inconsistent thermodynamical properties: its associated extensive magnitudes are non additive, and its thermodynamical limits are consequently ill defined. Furthermore, it does not exhibit a good limit when the classical subsystem becomes trivial – a limit that should yield a proper quantum canonical ensemble. The root cause of this mistake was the foundation of thermodynamical ensembles on the notion of detailed balance for Hamiltonian hybrid dynamics under classical thermostats (see [93] and [60] for reviews on the topic).

To tackle these inconsistencies, in the first article presented in this thesis [1], a different approach is followed: we base the definition of entropy on a probabilistic interpretation of thermodynamics, and therefore it is untainted from any particular dynamical considerations. The key development is the introduction of a well defined notion of exclusive events for the hybrid phase space, which naturally yields a consistent definition of hybrid entropy. The hybrid canonical ensemble can then be derived from the maximum-entropy principle, subject to the constant energy constraint. Instead of basing the definition of the entropy on the intrinsic statistical properties of the hybrid theory, a different avenue could be followed. Departing from a full quantum statistical system and its associated von Neumann entropy, a partial classical limit could be performed for a subsystem, obtaining a top-down derivation of a hybrid entropy. In order to perform that limit for a statistical state, and not count the quantum information of the now-classical subsystem, we need a way to *forget* statistical information. Our preferred way of forgetting quantum details and obtaining a rough, blurred, statistical description is through the process of coarse graining. This is mathematically implemented through a Gaussian convolution, and can be physically interpreted considering finite resolution measurements. This connection with the full quantum entropy through a partial classical limit, together with the relation of entropy and dynamics in the hybrid context, are open problems for future research.

While these results of [1] dissipated the uncertainty around the viability of hybrid thermodynamics, the inconsistency between the dynamical approach and the probabilistic one still remained. In order to recover the applicability of molecular dynamics simulations coupled to classical thermostats, a corrected version of time averages along trajectories was introduced in the following paper of this thesis, [2]. The content of this paper is mostly of interest for practical applications, allowing to reproduce true hybrid thermodynamical ensembles from the dynamics that yielded the wrong (regarding exclusivity of events) detailed balance. Thus, while this paper did not truly solve the inconsistency between dynamics and thermodynamics, it provided with a way to circumvent it. Note that this work is not tied to Ehrenfest dynamics in particular, but it can be used with any molecular dynamics, as long as the trajectory considered visits densely all regions in phase space.

The fundamental problem itself is treated in the third and fourth contributions to this compendium. In [3], a generalization of the formalism of hybrid density matrices to arbitrary moments on quantum projectors of a hybrid probability distribution is shown to be able to capture Liouville's equation for probability density functions over hybrid phase space. There are several lines of work in this context that could be approached in the future. For example, the characterization, in terms of the series of quantum moments, of the thermodynamical ensembles that are invariant under the hybrid dynamics. Likewise, the interpretation of the observability of correlations of quantum observables (and thus, quartic and higher order statistical moments) introduced by the classical subsector. And finally, the application of the truncated expansion to different physical problems, such as Tully's models [83], realistic molecular dynamics and classical measurement aparatus descriptions, test-benching its ability to describe full quantum statistical mechanics, in comparison to other hybrid statistical mechanics.

On the other hand, in [4] a Koopman-von Neumann's formalism for hybrid systems is formulated. It is based on an apparently full quantum density matrix characterizing the hybrid statistical state. We characterized its possible dynamics, and also shown that, in such formalism, for the hybrid Koopman-von Neumann density matrix, the hybrid entropy introduced in [1] is precisely von Neumann's entropy. Further work is being devoted to the characterization of different hybrid dynamics in this framework, beyond the unitary case studied in [4].

These last two works provide with different frameworks able to capture both thermodynamical and dynamical properties of hybrid statistical systems. They may be used for future testing of the thermodynamical consistency of different candidates to hybrid dynamics, while also presenting some interesting applications to current simulations.

The four articles discussed so far are mostly of interest for the community of hybrid statistical systems in the context of molecular dynamics. Nevertheless, it is important to note that the challenges and developments in hybrid quantum-classical systems extend

beyond effective descriptions of molecular dynamics and their statistical mechanics all the way into the foundations of physics, when considering the interplay between fundamental particles described by quantum field theory and the current classical description of gravitation, based on general relativity.

Given the predominant interest devoted to molecular dynamics, there is a notable gap when it comes to extending hybrid systems to the description of field theories, especially within a formalism based on symplectic geometry, as the usual covariant description (without preferred time direction) of field theories obfuscates their Hamiltonian nature. In particular, the characterization of the backreaction of quantum matter on gravity has come to be one of the most sought but slippery concepts at the frontier of theoretical physics.

While quantum field theory in the presence of a fixed curved spacetime treated as a background has been well established, a comprehensive theory that combines in a dynamical way quantum matter fields and classical gravity has proven elusive. Besides the phenomenological motivation, there is also an epistemological difference with molecular dynamics which supposes a paradigm shift and drives the community to explore this kind of hybrid systems. In the realm of molecular dynamics hybrid systems are naturally considered an effective theory, as current experiments are sensible enough to the whole spectra of quantum effects of the more fundamental full quantum theory, which is well established and tested. On the contrary, in the case of quantum fields coupled to classical gravity, the hybrid theory may be of fundamental nature, as argued by Antoine Tilloy in [21, 22], where it is reasoned that there is no scientific motivation to quantize gravity itself. A more conservative statement would be that the effects of any more fundamental theory (occurring at Planck scales) will remain outside of falsifiable reach in any foreseeable future. Therefore, a full quantum description of gravity may be unnecessary and, thus, hybrid gravity arises as a consistent joint description of the fundamental forces of the universe, but not necessarily defined in terms of a partial classical limit of a not-falsifiable full quantum theory. Thus, this hybrid theory is left as the last (from a reductionist perspective) necessary physical theory with falsifiable applications, such as quantum anisotropies in early cosmology, Hawking's radiation in black hole evaporation, particle creation in dynamical space-times such as the Unruh effect, quantum dust collapse and formation of singularities, etc.

In this line, in the fifth and last article of this thesis we have constructed a hybrid geometrodynamical framework for classical gravity (in terms of a spatial 3-metric and its associated momenta) and quantum field theoretical matter. The key development is the proper implementation of the representation the infinitesimal generators of Dirac's group of hypersurface deformations in terms of Hamiltonian generating functions over this hybrid manifold, over a well-defined hybrid Poisson bracket. This group plays a physically equivalent role in this 3+1 picture to the four-dimensional group of diffeomorphisms. In order to have proper invariance one must implement the *path independence principle* in the

form of superhamiltonian and supermomenta constraints for the hybrid supermagnitudes, which are conserved quantities under the dynamics and set to zero. Therefore, only the Cauchy data fulfilling such constraints will be suitable physical content of a hypersurface, which must be taken into account when considering initial data.

In this construction we have also taken into account the usual choice of vacuum state (equivalently, of classical complex structure [121]) which is dependent on the gravitational degrees of freedom, as established by Ashtekar *et al.* in [88]. This makes the measure over the space of fields, and consequently, the Hilbert space for the quantum states, depending on the gravitational variables. As a consequence, the hybrid manifold cannot be considered a trivial Cartesian product of the classical and quantum phase spaces, as was the case of the hybrid systems studied in this thesis in the context of molecular dynamics. Instead, a fibration with base the classical phase space and fiber the quantum one must be defined as hybrid manifold of states, provided with a non trivial connection that allows us to relate the quantum tensors (including states regarded as vectors in a Hilbert space and the Hermitian 2-form associated to the scalar product for the Hilbert spaces) under changes of the gravitational variables, on which they depend. This quantum connection has shown to be crucial for the realization of Dirac's group in a Hamiltonian manner, while preserving the physical interpretation at each spatial leaf. In turn, this provides with a gravitational-wise definition of norm for the quantum state, which is conserved under the evolution, solving one of the most puzzling aspects of QFT in curved spacetime, the norm loss of quantum states and the lack of a satisfactory probabilistic interpretation for it. This contractive property for the evolution on the norm was closely related with the phenomenon quantum completeness, in which the norm loss results in quantum states of null amplitude when reaching a spacetime singularity, forbidding the visitation of regions of divergent geometry for quantum fields. This phenomenon cannot be realized with the current interpretation of norm in our framework. Therefore, the relation between the usual definition of norm for quantum states (with ill-defined probabilistic interpretation) and our gravitational-dependent definition must be further explored in order to elucidate to what extent quantum completeness is a falsifiable and physical property of QFT in curved spacetime.

The theory gives a clear depiction of the backreaction of quantum matter fields onto the gravitational degrees of freedom and did not require full quantum gravity in its construction, just the consistent combination of the differential geometry of both subsystems. The gravitational degrees of freedom have been characterized in terms of a 3-metric h_{ij} and its momenta π_h^{ij}, as it is the Hamiltonian picture of the standard Einstenian approach using a Lorentzian 4-metric $g_{\mu\nu}$ for spacetime. Nevertheless, the formalism constitutes a general framework that can be straightforwardly extended to any other description of gravity, proving a wide range of applications.

In general, for a not metric-based description of gravity, its hybrid geometrodynamics

can be constructed as long as a covariant Lagrangian for the gravitational subsystem can be introduced in its 4-dimensional description. For example, a construction with scalar gravity (such as Nordstrom's gravity) can be regarded as a reduced formalism for sufficiently simple spacetimes. Another possible generalization of this work would be an extension to Palatini formalism (based on tetrads and regarding the connection as an independent variable) with a non-null torsion tensor in the connection can be useful to capture the effects of quantum spins into gravitation, constituting the hybrid geometrodynamical analogue of Einstein's-Cartan theory. On the other hand, instead of considering the canonical variables given by h_{ij} and π_h^{ij}, the classical submanifold can also be written in terms of Ashtekar's canonical variables [133] for 3+1 gravitation, consisting of a SU(2) gauge field and its canonical complementary, which can be useful for computational applications and for comparison with results from loop quantum gravity. Another useful property of the formalism developed in [5] is that the geometric structure and the Hamiltonian nature of the dynamics can be preserved independently of the kind of backreaction implemented. For example, while we have chosen the expectation value of the Hamiltonian to act as effective potential for the gravity, one could choose stochastic outcomes of the measurement of such Hamiltonian, with probabilities associated to the quantum state, in the line of stochastic hybrid systems proposed in [54, 134] and [53]. The rigorous construction of our Hamiltonian system for stochastic variables both for the quantum states and gravitational degrees of freedom would require of the mathematical tools developed in [135].

Some phenomenological problems that can be studied with the current formalism are the following. Firstly, we have recently addressed the quantum backreaction and the consequences of the quantum connection in inflationary spacetimes, which are very relevant in the early universe. Another problem we plan to address is the interplay between black hole shrinking and the hypothesized Hawking's radiation associated to its evaporation. A complete dynamical study with all the quantum and gravitational degrees of freedom for this phenomenon would be the first of its kind and will shed light on singularity remnants after evaporation in this hybrid context, in the line of [136]. The quantum connection will play a key role in the phenomenon of particle creation, and thus, the inclusion of Unruh-de Witt detectors in the theory can be relevant[137]. The description of particle creation as non-unitary maps between Fock spaces characterize in a clean geometrical way in terms of the holonomy of the quantum connection would lay solid theoretical foundations for this elusive phenomenology. Another interesting project is the consideration of quantum dust collapse, which we would expect to form black-holes while dynamically avoiding the formation of central singularities, in the line of Kiefer and Schmitz's work [138]. If, indeed, the dynamical implementation of the backreaction and the gravitation-dependent measure for quantum fields shows that singularities cannot ultimately form in this hybrid context, this result would constitute a strong censorship theorem implying Penrose's cosmic censorship hypothesis [139], a cornerstone of modern gravitation.

Outline

The five works that compose this thesis share as a common ingredient the study of hybrid systems. They do so either in the context of the thermodynamics and statistical mechanics, or for the purpose of studying the fundamental depiction of classical gravity coupled to quantum matter fields. They also share a common mathematical framework, based on differential geometry, for the characterization of the hybrid dynamics. To close this concluding section, we summarize briefly the novel contributions of this thesis:

- Definition of a well-behaved notion of hybrid entropy based on exclusivity of events and derivation of its canonical ensemble through a maximum entropy procedure.
- Correction of time averages over solution curves to hybrid Hamiltonian equations of motion coupled to a classical thermostat in order to reproduce the physical thermodynamical ensembles.
- construction of a new framework for hybrid statistical dynamics in order to capture the non-linearities on quantum projectors of Liouvillian dynamics, in terms of a system of coupled differential equations for the quantum statistical moments of a hybrid probability distribution. Proposal of a truncation procedure of this system of equations for practical applications.
- Development of the Koopman-von Neumann formalism for hybrid statistical states in terms of a new kind of density matrix which is partially classical. Characterization of possible dynamics and entropy in terms of the same mathematical object.
- Proposal of a hybrid theory of classical Einstenian gravitation and quantum field theoretical matter in a common Hamiltonian framework, which is able to capture the *backreaction* of one onto the other and, given its particular geometric structure, allows for norm conservation of quantum states in curved spacetime.

Conclusiones

Los modelos híbridos clásico-cuánticos son potentes marcos teóricos para simular y comprender sistemas que, normalmente bajo la perspectiva de una descripción efectiva, utilizan grados de libertad tanto cuánticos como clásicos para modelar los fenómenos de interés.

Estos sistemas encuentran sus raíces históricas en la aproximación Born-Oppenheimer [11], que explota la jerarquía entre las masas de electrones y núcleos constituyendo moléculas. Esto permite una descripción no entrelazada cuánticamente, pero dinámicamente acoplada, de los movimientos de ambos tipos de partículas al despreciar términos proporcionales a potencias de dicho cociente de masas, $\left(\frac{m_e}{M_N}\right)^{1/2} \leq 0.024$. Esta aproximación constituyó la base para el tratamiento de sistemas moleculares durante décadas, permitiendo una representación simplificada. En ella, los grados de libertad electrónicos se tratan según la mecánica cuántica debido a su masa relativamente menor, al tiempo que permite aproximar clásicamente el movimiento nuclear.

Sin embargo, a medida que avanzaba la investigación y evolucionaba la tecnología, se hizo evidente que muchos sistemas requieren un tratamiento más complejo que va más allá de la dinámica molecular basada en Born-Oppenheimer. Dicha aproximación solía considerar que los estados electrónicos estaban congelados en un autoestado del Hamiltoniano que dependía de los grados de libertad nucleares. Como consecuencia, el efecto de los grados de libertad cuánticos sobre los clásicos venía dado por el autovalor asociado. Dicho autovalor, dada su dependencia de las posiciones nucleares, actuaba como un potencial efectivo para la interacción electrónica-nuclear. Así, esta imagen era adiabática respecto al subsistema cuántico, prohibiendo las transiciones electrónicas entre diferentes niveles de energía.

Dichos desarrollos tecnológicos en dinámica molecular mostraron que la dinámica diabática para el subsistema cuántico reproducía con mayor precisión la descripción cuántica completa y, por tanto, los fenómenos reales captados en los estudios experimentales. Esto condujo a la aparición de una amplia variedad de aproximaciones híbridas clásico-cuánticas más allá de la aproximación de Born-Oppenheimer. En este contexto, la dinámica de Ehrenfest juega un papel prominente. Aunque ya era habitual en la literatura, su derivación formal fue estudiada por Bornemnann *et al.* [68], quienes demostraron que los límites de los términos despreciados en la aproximación dependen del cociente de masas y también

del cociente de las anchuras características de las densidades de probabilidad marginales nuclear (σ_N) y electrónica (σ_e) ($\frac{\sigma_N}{\sigma_e} < 5 \cdot 10^{-5}$). Los términos que se desprecian en la aproximación de Born-Oppenheimer también dependen del cociente de masas, pero en el caso de la dinámica de Ehrenfest dicha dependencia es de orden superior y por lo tanto resulta una mejor aproximación. Esta dinámica ha jugado un papel crucial en el campo de los sistemas híbridos, ya que cumple varios requisitos de consistencia [63] y puede dotarse de una formulación Hamiltoniana en analogía con la mecánica clásica [69]. Esto último, en el contexto de esta tesis, es particularmente útil en relación con el teorema de Liouville.

Aunque históricamente se ha dedicado mucho esfuerzo a la dinámica de los sistemas híbridos, se ha concedido poca atención a sus propiedades estadísticas y termodinámicas. Por ejemplo, la ausencia de una definición precisa de entropía híbrida fue un obstáculo inadvertido, aunque relevante, en la bibliografía. En consecuencia, esta deficiencia condujo a concepciones erróneas de las colectividades estadísticas (en adelante, *ensemble*) híbridas. En particular, una definición errónea del *ensemble* híbrido canónico dio lugar a propiedades termodinámicas inconsistentes: sus magnitudes extensivas asociadas no son aditivas y, en consecuencia, sus límites termodinámicos están mal definidos. Además, no muestra un buen comportamiento cuando el subsistema clásico se vuelve trivial, un límite que debería dar lugar a un conjunto canónico cuántico adecuado. La raíz de este error fue el fundamento de los conjuntos termodinámicos en la noción de *detailed balance* para la dinámica híbrida Hamiltoniana y bajo termostatos clásicos (véase [93] y [60]).

Para hacer frente a estas inconsistencias, en el primer artículo presentado en esta tesis [1], se sigue un enfoque diferente: basamos la definición de entropía en una interpretación probabilística de la termodinámica y, por lo tanto, no está comprometida por ninguna consideración dinámica particular. El desarrollo clave es la introducción de una noción bien definida de sucesos exclusivos para el espacio de fases híbrido, que naturalmente da lugar a una definición coherente de entropía híbrida. El conjunto canónico híbrido puede entonces derivarse del principio de máxima entropía, sujeto a la restricción de energía constante. En lugar de basar la definición de la entropía en las propiedades estadísticas intrínsecas de la teoría híbrida, se podría seguir una vía diferente. Partiendo de un sistema estadístico cuántico completo y su entropía de von Neumann asociada, podría realizarse un límite clásico parcial para un subsistema, obteniendo una derivación como teoría efectiva de una entropía híbrida. Para realizar ese límite sobre un estado estadístico y no contar la información cuántica del subsistema ahora clásico, necesitamos definir la operación matemática de olvidar la información estadística. Nuestra forma preferida de olvidar los detalles cuánticos y obtener una descripción estadística aproximada, borrosa, es mediante el proceso de *coarse graining*. Este proceso puede implementarse matemáticamente a través de una convolución Gaussiana y puede interpretarse físicamente considerando aparatos de medida que presentan una resolución finita, asociada a la desviación estándar del filtro Gaussiano. Esta conexión con la entropía completamente cuántica a través de un límite

clásico parcial, junto con la relación de la entropía y la dinámica en el contexto híbrido, son problemas abiertos para futuras investigaciones.

Aunque estos resultados de [1] disiparon la incertidumbre en torno a la viabilidad de la termodinámica híbrida, la incoherencia entre el enfoque dinámico y el probabilístico seguía existiendo. Para recuperar la aplicabilidad de las simulaciones de dinámica molecular acopladas a termodinámicas clásicas, en el siguiente trabajo de esta tesis, [2], se introdujo una versión corregida de los promedios temporales a lo largo de las trayectorias. El contenido de este trabajo es sobre todo de interés para aplicaciones prácticas, permitiendo reproducir verdaderos *ensembles* termodinámicos híbridos a partir de aquellas dinámicas que proporcionan un *detailed balance* incorrecto respecto a la exclusividad de los eventos. Así, aunque este trabajo no resolvió realmente la incoherencia entre dinámica y termodinámica, proporcionó una forma de eludirla. Nótese que este trabajo no está vinculado a la dinámica de Ehrenfest en particular, sino que puede utilizarse con cualquier dinámica molecular, siempre que la trayectoria considerada visite densamente todas las regiones del espacio de fases.

El problema fundamental en sí se trata en las contribuciones tercera y cuarta a este compendio. En [3], se demuestra que una generalización del formalismo de las matrices de densidad híbridas a momentos estadísticos arbitrarios sobre proyectores cuánticos de una distribución de probabilidad híbrida es capaz de capturar la ecuación de Liouville para funciones de densidad de probabilidad sobre el espacio de fases híbrido. Hay varias líneas de trabajo en este contexto que podrían abordarse en el futuro. Por ejemplo, la caracterización, en términos de la serie de momentos cuánticos, de los conjuntos termodinámicos que son invariantes bajo la dinámica híbrida. Asimismo, se estudiará en el futuro la interpretación física de la observabilidad de las correlaciones de los observables cuánticos (y, por tanto, de los momentos estadísticos cuárticos y de orden superior) introducidas por el subsector clásico. Finalmente, se pretende desarrollar la aplicación de la expansión truncada a diferentes problemas físicos, como los modelos de Tully [83], a sistemas moleculares realistas y a descripciones clásicas de aparatos de medida, poniendo a prueba la capacidad del esquema teórico para describir la mecánica estadística de estos sistemas, en comparación con otros candidatos a dinámica estadística híbrida.

Por otra parte, en [4] se desarrolla un formalismo de Koopman-von Neumann para sistemas híbridos. Este formalismo se basa en una matriz de densidad, en apariencia formal completamente cuántica, que caracteriza el estado estadístico híbrido. Caracterizamos sus posibles dinámicas y también mostramos que, en dicho formalismo y para estas matrices de densidad híbridas Koopman-von Neumann, la entropía híbrida introducida en [1] es precisamente la entropía de von Neumann. Se está trabajando en la caracterización de diferentes dinámicas híbridas en este marco, más allá del caso unitario estudiado en [4].

Estos dos últimos trabajos proporcionan diferentes marcos capaces de captar las propie-

dades tanto termodinámicas como dinámicas de los sistemas estadísticos híbridos. Pueden utilizarse para probar en el futuro la consistencia termodinámica de diferentes candidatos a la dinámica híbrida, al tiempo que presentan algunas aplicaciones interesantes a las simulaciones actuales.

Los cuatro artículos analizados hasta ahora son en su mayoría de interés para la comunidad de sistemas estadísticos híbridos en el contexto de la dinámica molecular. No obstante, es importante señalar que los retos y desarrollos de los sistemas híbridos cuántico-clásicos se extienden más allá de las descripciones efectivas de la dinámica molecular y su mecánica estadística, llegando hasta los fundamentos de la física, al considerar, por ejemplo, la interacción entre las partículas fundamentales descritas por la teoría cuántica de campos y la descripción clásica actual de la gravitación, basada en la relatividad general.

Dado el interés dedicado, sobre todo, a la dinámica molecular, existe una laguna notable cuando se trata de extender los sistemas híbridos a la descripción de las teorías de campos. Esta carencia es especialmente notable si se quiere además un formalismo basado en la geometría simpléctica, ya que la descripción covariante habitual de las teorías relativistas de campos (sin dirección temporal preferente) ofusca su naturaleza Hamiltoniana. En particular, la caracterización de la *backreaction* de la materia cuántica sobre la gravedad ha llegado a ser uno de los conceptos más buscados y escurridizos en la frontera de la física teórica.

Mientras que la teoría cuántica de campos en presencia de un espacio-tiempo curvo fijo, tratado como un fondo dado externamente, ha quedado bien establecida, una teoría que combine consistentemente y de forma dinámica los campos cuánticos de materia y la gravedad clásica ha resultado ser, históricamente, un objetivo elusivo. Además de la motivación fenomenológica, existe también una diferencia epistémica con los modelos híbridos de dinámica molecular que supone un cambio de paradigma e impulsa a la comunidad a explorar este tipo de sistemas híbridos. En el ámbito de la dinámica molecular, los sistemas híbridos se consideran naturalmente una teoría efectiva, ya que los experimentos actuales son suficientemente sensibles a todo el espectro de efectos cuánticos de la teoría completamente cuántica, para núcleos y electrones, que constituye la teoría más fundamental y está bien establecida y probada. Por el contrario, en el caso de los campos cuánticos acoplados a gravedad clásica, la teoría híbrida puede ser de naturaleza fundamental, como argumenta Antoine Tilloy en [21, 22], donde se razona que no hay motivación científica para cuantizar la propia gravedad. Una afirmación más conservadora sería que los efectos de cualquier teoría más fundamental (que se producirían a escalas de Planck) permanecerán fuera del alcance falsable en cualquier futuro previsible. Por lo tanto, una descripción cuántica completa de la gravedad puede ser innecesaria y, así, la gravedad híbrida surge como una descripción conjunta de las fuerzas fundamentales del universo, pero no necesariamente definida en términos de un límite clásico parcial de una teoría cuántica completa

no falsable y, aunque hipotéticamente más fundamental, inaccesible experimentalmente. Así, esta teoría híbrida queda como la última (desde una perspectiva reduccionista) teoría física necesaria con aplicaciones falsables, como las anisotropías cuánticas en la cosmología primitiva, la radiación de Hawking en la evaporación de agujeros negros, la creación de partículas en espacio-tiempo dinámico como el efecto Unruh, el colapso cuántico del polvo y la formación de singularidades asociada, etc.

En esta línea, en el quinto y último artículo presentado en esta tesis hemos construido un marco geometrodinámico híbrido para la gravedad clásica (en términos de una métrica espacial tridimensional y sus momentos canónicos asociados) y la materia descrita mediante una teoría cuántica de campos. El desarrollo clave es la implementación adecuada de la representación de los generadores infinitesimales del grupo de Dirac de deformaciones de hipersuperficies en términos de funciones generadoras Hamiltonianas sobre esta variedad híbrida, mediante un corchete de Poisson híbrido bien definido. Este grupo de simetría desempeña un papel físicamente equivalente en esta imagen 3+1 al grupo de difeomorfismos generales de cuatro dimensiones. Para tener una invariancia adecuada, uno debe implementar el principio de independencia del camino[103] en forma de restricciones superhamiltonianas y de supermomento, para las así llamadas supermagnitudes híbridas, que son cantidades conservadas bajo la dinámica y constreñidas, sobre la variedad de ligaduras, a valor 0. Por lo tanto, sólo los datos de Cauchy que cumplan tales restricciones serán contenido físico adecuado de una hipersuperficie, lo que debe tenerse en cuenta al considerar los datos iniciales.

En esta construcción también hemos tenido en cuenta la elección habitual de estado de vacío (equivalentemente, de estructura compleja clásica [121]) que depende de los grados de libertad gravitatorios, tal y como establecieron Ashtekar *et al.* en [88]. Esto hace que la medida sobre el espacio de campos y, en consecuencia, el espacio de Hilbert para los estados cuánticos, dependa de las variables gravitatorias. Como consecuencia, la variedad híbrida no puede considerarse un producto cartesiano trivial de los espacios de fases clásico y cuántico, como era el caso de los sistemas híbridos estudiados en esta tesis en el contexto de la dinámica molecular. En su lugar, debe definirse una fibración con base el espacio de fases clásico y fibra el cuántico, provista de una conexión no trivial que nos permita relacionar los tensores cuánticos (incluyendo los estados, considerados como vectores en un espacio de Hilbert y la 2-forma Hermítica asociada al producto escalar para los espacios de Hilbert) bajo cambios de las variables gravitatorias, de las que dependen. Esta conexión cuántica ha resultado crucial para la realización del grupo de Dirac de una manera Hamiltoniana, preservando al mismo tiempo la interpretación física en cada hoja espacial, como una generalización cuántica y a foliaciones de espacio-tiempo del principio de equivalencia. A su vez, esto proporciona una definición dependiente de la gravitación del operador norma para el estado cuántico. Esta definición de norma se conserva bajo la evolución, resolviendo así uno de los aspectos más desconcertantes de la QFT en el espacio-tiempo curvo: la pérdida

de norma de los estados cuánticos y la falta de una interpretación probabilística satisfactoria para ello. Esta propiedad contractiva de la evolución sobre la norma estaba estrechamente relacionada con el fenómeno de completitud cuántica, en el que la pérdida de norma da lugar a estados cuánticos de amplitud nula al alcanzar una singularidad del espacio-tiempo, prohibiendo la visita de regiones de geometría divergente para los campos cuánticos. Este fenómeno no puede realizarse con la interpretación actual de norma en nuestro marco. Por lo tanto, la relación entre la definición habitual de norma para estados cuánticos (con una interpretación probabilística no cerrada) y nuestra definición dependiente de la gravitación debe explorarse más a fondo para dilucidar hasta qué punto la completitud cuántica es una propiedad falsable y física de la QFT en el espaciotiempo curvo, o un artefacto propio de una medida de integración no adaptada al espacio funcional.

La teoría presentada ofrece una clara descripción de la reacción de los campos de materia cuántica sobre los grados de libertad gravitatorios y no requiere una gravedad cuántica completa en su construcción, sólo la combinación coherente de la geometría diferencial de ambos subsistemas. En particular, los grados de libertad gravitatorios se han caracterizado en términos de una métrica de 3 dimensiones, h_{ij} y sus momentos, π_h^{ij}, ya que es la imagen Hamiltoniana del enfoque Einsteniano estándar que utiliza una métrica Lorentziana de 4 dimensiones, $g_{\mu\nu}$, para el espaciotiempo. No obstante, el formalismo constituye un marco general que puede extenderse directamente a cualquier otra descripción de la gravedad, demostrando una amplia gama de aplicaciones.

En general, para una descripción de la gravedad no basada en la métrica, puede construirse su geometrodinámica híbrida siempre que pueda introducirse un Lagrangiano covariante para el subsistema gravitatorio en su descripción cuatridimensional. Por ejemplo, una construcción con gravedad escalar (como la gravedad de Nordstrom) puede considerarse un formalismo reducido para espaciostiempos suficientemente sencillos. Otra posible generalización de este trabajo sería una extensión del formalismo de Palatini (basado en tétradas y considerando la conexión como una variable independiente) con un tensor de torsión no nulo en la conexión , lo que puede ser útil para capturar los efectos de los espines cuánticos en la gravitación, constituyendo el análogo geometrodinámico híbrido de la teoría de Einstein-Cartan. Similarmente, en lugar de considerar las variables canónicas dadas por h_{ij} y π_h^{ij}, la subvariedad clásica también puede escribirse en términos de las variables canónicas de Ashtekar [133] para la gravitación 3+1, consistentes en un campo gauge SU(2) y su complementario canónico, lo que puede ser útil para aplicaciones computacionales y para la comparación con resultados de la gravedad cuántica de lazos. Otra propiedad útil del formalismo desarrollado en [5] es que la estructura geométrica y la naturaleza hamiltoniana de la dinámica pueden preservarse independientemente del tipo de *backreaction* implementada. Por ejemplo, mientras que nosotros hemos elegido el valor esperado del Hamiltoniano para que actúe como potencial efectivo para la gravedad, se podría elegir como *backreaction* el resultado estocástico de la medida de dicho Hamiltoniano

con las probabilidades de los distintos resultados dadas por el estado cuántico, en la línea de los sistemas híbridos estocásticos propuestos en las referencias [54, 134] y [53]. La construcción rigurosa de nuestro sistema Hamiltoniano para variables estocásticas tanto para los estados cuánticos como para los grados de libertad gravitatorios requeriría de las herramientas matemáticas desarrolladas en [135].

Algunos problemas fenomenológicos que pueden estudiarse con el formalismo actual son los siguientes. En primer lugar, hemos abordado recientemente la *backreaction* cuántica y las consecuencias de la conexión cuántica en espacio-tiempo inflacionario, muy relevantes en el universo temprano. Otro problema que planeamos abordar es la interacción entre el encogimiento de agujeros negros y la hipotética radiación de Hawking asociada a su evaporación. Un estudio dinámico completo con todos los grados de libertad cuánticos y gravitatorios de este fenómeno sería el primero de su clase y arrojaría, por primera vez, algo de perspectiva sobre la singularidad remanente tras la evaporación, en la línea de la ref. [136]. Por otro lado, la conexión cuántica jugará un papel clave en el fenómeno de la creación de partículas mediada por gravedad y, por ello, la inclusión de detectores Unruh-de Witt en la teoría puede ser relevante [137]. La descripción de la creación de partículas como mapas no unitarios entre espacios de Fock caracterizados de una forma geométrica limpia en términos de la holonomía de la conexión cuántica proporcionará unos cimientos teóricos sólidos para esta esquiva fenomenología. Otro proyecto interesante es el estudio del colapso del polvo cuántico, del que esperamos que forme agujeros negros evitando dinámicamente la formación de singularidades centrales, en la línea del trabajo de Kiefer y Schmitz [138]. Si, en efecto, la implementación dinámica de la *backreaction* y la medida de integración dependiente de la gravitación para campos cuánticos prueba que las singularidades no pueden formarse en este contexto híbrido, este resultado constituiría un teorema de censura fuerte que implicaría la hipótesis de censura cósmica de Penrose [139], piedra angular de la gravitación moderna.

Resumen

Los cinco trabajos que componen esta tesis tienen como ingrediente común el estudio de los sistemas híbridos. Lo hacen bien en el contexto de la termodinámica y la mecánica estadística, bien con el propósito de estudiar la representación fundamental de la gravedad clásica acoplada a campos cuánticos de materia. También comparten un marco matemático común, basado en la geometría diferencial, para la caracterización de las dinámicas híbridas. Para cerrar esta sección de conclusiones, resumimos brevemente las aportaciones novedosas presentadas en esta tesis:

- Definición de una noción de entropía híbrida consistente basada en la exclusividad de eventos estadísticos y derivación de su *ensemble* canónico mediante un procedimiento de máxima entropía.
- Corrección de promedios temporales sobre curvas solución a ecuaciones de movimiento Hamiltonianas híbridas acopladas a termostatos clásicos, con la finalidad de reproducir los *ensembles* termodinámicos consistentes con la anterior definición de entropía.
- Construcción de un nuevo marco para la dinámica estadística híbrida con el fin de capturar las no linealidades en los proyectores cuánticos de la dinámica Liouvilliana, en términos de un sistema de ecuaciones diferenciales acopladas para los momentos estadísticos cuánticos de una distribución de probabilidad híbrida. Se propone también un procedimiento de truncado de este sistema de ecuaciones para aplicaciones prácticas.
- Desarrollo del formalismo Koopman-von Neumann para estados estadísticos híbridos en términos de un nuevo tipo de matriz de densidad que es parcialmente clásica. Esto permite la unificación de la caracterización de las posibles dinámicas de *ensembles* hhíbridos y su entropía en términos del mismo objeto matemático.
- Propuesta de una teoría híbrida de la gravitación clásica Einsteniana y la materia dada por una teoría cuántica de campos en un marco Hamiltoniano común, que es capaz de capturar la *backreaction* de una sobre la otra y, dada su particular estructura geométrica, permite la conservación de la norma de los estados cuánticos en el espacio-tiempo curvo.

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