Geometric formalism for the dynamics of statistical hybrid classical-quantum systems

Bachelor's thesis in Mathematics

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Resumen

La ecuación de Schrödinger formulada para un sistema de núcleos y electrones permite describir teóricamente la mayor parte de los sistemas moleculares. Sin embargo, la naturaleza del espacio de fases cuántico (un espacio producto tensorial de los espacios de estados de cada una de las partículas de la molécula, antisimetrizado para incorporar el tratamiento de partículas idénticas) hace imposible obtener una solución explícita, o incluso numérica, de dicha ecuación. Es por tanto necesario introducir aproximaciones a fin de obtener modelos computacionalmente viables.

Una de estas aproximaciones se basa en un principio básico de la mecánica cuántica: el módulo al cuadrado de la función de onda determina la densidad de probabilidad de la posición de una partícula. En este contexto, la diferencia en escala de masas entre electrones y núcleos se traduce en que estos últimos son modelizados por paquetes de onda comparativamente muy localizados. Parece natural entonces tratar de simplificar el problema aproximando las densidades de probabilidad localizadas por una distribución delta de Dirac centrada en su valor esperado. Además, el teorema de Ehrenfest proporciona la evolución de estos valores, que no es otra que la evolución de un sistema clásico sujeto a fuerzas que dependen de valores esperados de magnitudes de las (otras) partículas cuánticas. En resumen, podemos decir que esta aproximación consiste en tratar las variables nucleares clásicamente, reduciendo el número de grados de libertad cuánticos y con ello la complejidad técnica del problema. No obstante, es preciso notar que estas aproximaciones deben introducirse selectivamente, puesto que un modelo completamente clásico no es predictivo para la mayoría de la fenomenología estudiada en física molecular; por tanto, las variables electrónicas se seguirán tratando cuánticamente. Surgen así los sistemas híbridos clásico-cuánticos: sistemas que incorporan grados de libertad de naturaleza clásica y cuántica que evolucionan de forma acoplada.

Desde el punto de vista técnico, el problema fundamental que debemos abordar al construir modelos híbridos es el de salvar las diferencias formales entre las teorías clásica y cuántica, a fin de lograr una descripción matemática que permita tratar conjuntamente los dos tipos de grados de libertad que posee nuestro sistema. Para ello existen dos alternativas:

- La primera se apoya en el trabajo desarrollado por Koopman y von Neumann [1, 2], en el que se probó que un sistema estadístico clásico cuya dinámica está regida por una ecuación de Liouville puede modelarse mediante una dinámica unitaria en un espacio de Hilbert. Esta es la técnica seguida en [3].

- La segunda, por la que hemos optado en este trabajo, es la descripción geométrica de ambas teorías. Tanto en el caso clásico [4] como en el cuántico [5, 6], es posible codificar la dinámica en términos de campos Hamiltonianos sobre variedades simplécticas. En este marco, el espacio de fases de nuestro sistema híbrido será la variedad producto, sobre la cual se define una nueva forma simpléctica que permite replicar la construcción.

Hasta ahora se han desarrollado herramientas para dotar a los sistemas híbridos de estructura Hamiltoniana y estudiar tanto su microdinámica como física estadística [7, 8, 9, 10]. Sin embargo, por simplicidad matemática se ha escogido $\mathbb{C}^n$ como espacio de fases cuántico, argumentando que se considera una cota superior en los niveles de energía del sistema. El objetivo de este trabajo es eliminar esta aproximación para el caso particular de la dinámica de Ehrenfest y obtener así un modelo geométrico de dimensión infinita en el que la mecánica cuántica esté formulada con total generalidad.

Para ello se ha estructurado el trabajo como sigue:

- En el capítulo 1 se revisan las herramientas de geometría diferencial en dimensión infinita necesarias para construir el espacio de fases, siguiendo el discurso de [11]. Aunque enunciamos la mayor parte de los resultados para variedades modeladas sobre espacios de Banach por consistencia con la referencia escogida, notaremos que se pueden extender a variedades sobre espacios vectoriales topológicos más generales en los siguientes capítulos. Con afán de ilustrar lo anterior, el apéndice B recoge un ejemplo original de la aplicación del concepto de diferenciabilidad en espacios vectoriales generales.

- En el capítulo 2 se presentan los formalismos geométricos de la mecánica clásica y la mecánica cuántica. Para el primero proporcionamos una presentación breve, dado que está ampliamente extendido. Por simplicidad, hemos preferido presentar el formalismo para el caso de un fibrado cotangente, aunque se pueden considerar situaciones más generales (variedades simplécticas, variedades de Poisson). En el segundo, merece la pena destacar algunas de las diferencias formales con su análogo clásico, especialmente las implicaciones de la estructura simpléctica débil debida a la naturaleza infinito-dimensional del espacio modelo de la variedad. También discutimos, por medio de un ejemplo para un Hamiltoniano atómico simple, la posibilidad de dotar al espacio de fases cuántico de una estructura fuertemente simpléctica, situación en la que la analogía con el caso clásico es completa.

- En el capítulo 3, la contribución más relevante del trabajo, se formula el modelo híbrido en dimensión infinita para el sistema dinámico regido por las ecuaciones de Ehrenfest. Dado que el dominio del Hamiltoniano molecular está contenido en la clase de Schwartz, nos vemos obligados a escoger un espacio de fases cuántico que es solamente débilmente simpléctico. Esta propiedad se hereda en el espacio de fases híbrido, pero nos sigue permitiendo definir una estructura Hamiltoniana para las ecuaciones de Ehrenfest.

- Finalmente, en el capítulo 4 se resumen los resultados obtenidos y se proponen líneas de trabajo futuro.

Abstract

The Schrödinger equation formulated for a system of electrons and nuclei allows us to describe theoretically most molecular systems. However, the nature of the quantum phase space (an anti-symmetrised tensor product of each of the state Hilbert spaces of the constituents of the molecule, due to the existence of identical particles within our system) makes it impossible in general to obtain an explicit, or even numerical, solution of said equation, being imperative then to introduce some sort of approximation that leads to computationally viable models.

One of such approximations relies on a basic principle of quantum mechanics: the square module of a wavefunction determines the probability density of a particle's position. In this context, the vast difference in mass scale between electrons and nuclei implies that the latter are modelled by much more localised wave packets. It seems natural then to introduce a simplification to our model by approximating those localised probability densities by a Dirac delta function centred at the position expectation value. Moreover, Ehrenfest's theorem proves that the time evolution of said expectation values is no other than the classical evolution of a system under forces which depend on the expectation values of the (other) quantum particles. To summarise, we have simplified our model by treating some variables classically, which reduces the number of quantum degrees of freedom and, consequently, the technical problems associated with them. Nevertheless, these approximations have to be carefully introduced, as a full-classical molecular model has been proved not to be predictive for most phenomenology of molecular physics; that is, the electronic variables must remain quantum. These facts are the main motivation behind the use of hybrid classical-quantum systems (those which have classical and quantum degrees of freedom with a coupled evolution).

From a technical perspective, the fundamental problem that we must overcome when formulating hybrid systems is the formal difference between classical and quantum theories; in the end, we want to achieve a mathematical description that can jointly handle two sets of variables of different nature. For that purpose, two alternatives exist:

- The first one relies on the work developed by Koopman and von Neumann [1, 2], which proved that a statistical classical system whose dynamics is prescribed by a Liouville equation can be modelled as a unitary dynamics on a Hilbert space. This is the approach followed by [3].

- The second one, which we shall use in the present work, is the geometrical description of both theories. It is possible to encode the dynamics in terms of Hamiltonian vector fields defined on symplectic manifolds in the classical setting [4] as well as in the quantum one [5, 6]. In this framework, the phase space of our hybrid system will be a product manifold, on which a new symplectic form that endows it with Hamiltonian structure is defined.

So far, tools that cast hybrid systems into a Hamiltonian form and allow the study of both microdynamics and statistical physics have been developed [7, 8, 9, 10]. Nonetheless, prioritising mathematical simplicity, $\mathbb{C}^n$ has been frequently chosen as the quantum phase space, arguing the existence of some boundary for the energy levels of the system. The main goal of this work is to free the formalism from that restriction in the particular case of the Ehrenfest dynamics, thus obtaining an infinite-dimensional geometrical model in which the treatment of quantum mechanics does not lose any generality.

The structure of the document is as follows:

- Chapter 1 comprises a revision of the infinite-dimensional differential geometry tools required to construct the (quantum) phase space, closely following [11]. Whereas most results are formulated for Banach manifolds, looking for consistence with our chosen reference, we shall note that they can and will be extended to more general topological vector spaces in the following chapters. Appendix B illustrates this with an original detailed example of the differentiation techniques applied in this generalised setting.

- In chapter 2 we present the geometrical formalisms of classical and quantum mechanics. We provide a brief summary of the first one, as it is currently well established. For the sake of simplicity, we have chosen to present the formalism considering the phase space to be a cotangent bundle, although more general settings (symplectic manifolds, Poisson manifolds) are perfectly admissible. With regards to the second one, some formal differences with its classical analogous are highlighted, specially the implications of the weakly symplectic structure that derives from the infinite-dimensional nature of the quantum manifold's modelling space. We also discuss, by means of a particular example of a simple atomic Hamiltonian, the possibility to endow the quantum phase space with a strongly symplectic structure; in that situation, the analogue with the classical framework is complete.

- In chapter 3, the work's most relevant contribution, an infinite-dimensional geometrical hybrid system is defined to encode the dynamics prescribed by Ehrenfest's equations. As the molecular Hamiltonian's domain is contained in the Schwartz space, we are forced to opt for a quantum phase space which is only weakly-symplectic. Although this structure is inherited by the hybrid phase space, we are still able to prove that Ehrenfest's equations become a Hamiltonian dynamical system on it.

- Finally, chapter 4 provides a summary of the results and some future lines of work.

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Contents

Chapter 1

Geometry on infinite dimensions

The aim of this chapter is to generalise the definition of differentiable manifold by allowing the modelling space, usually $\mathbb{R}^n$, to be an infinite-dimensional topological vector space (namely, a Banach space). For that purpose, we start by introducing the notion of differentiability in a Banach space. After the extension of differential calculus to this setting, we will have the tools to define manifolds and fibre bundles, compulsory ingredients for any geometrical dynamical system. More precisely, the points of this generalised differentiable manifold will represent the physical states of the quantum system whose evolution we want to model. A more in depth discussion on this matter can be found in [11].

1.1 Differential calculus

Let us start by introducing the structure of the modelling space and some related definitions.

Definition 1.1. A **topological vector space** (TVS) E (over the reals $\mathbb{R}$) is a vector space with a topology such that the operations of addition and scalar multiplication

$$+ : E \to E \qquad \cdot : \mathbb{R} \times E \to E$$

are continuous (with respect to the product topology induced by the topology in E and the usual topology of $\mathbb{R}$). We also assume, as part of the definition, that the space is Hausdorff and locally convex (every neighbourhood of 0 contains an open neighbourhood U of 0 such that if $x, y \in U$ and $0 \leq t \leq 1$, then $tx + (1-t)y$ also lies in U)[1].

Definition 1.2. A **toplinear isomorphism** between two topological vector spaces is a linear homeomorphism.

Definition 1.3. A **Banach space** $(E, |\cdot|)$ is a TVS whose topology is induced by a norm and that is also complete with respect to that topology (any Cauchy sequence $(x_n)_{n=1}^{\infty}$ in E has a limit $x \in E$).

Definition 1.4. An **operator** is a continuous linear map between two Banach spaces. If E, F are Banach spaces, the set of operators from E into F is denoted by $L(E, F)$.

Definition 1.5. A **Banach-isomorphism** between two Banach spaces is a toplinear isomorphism which is norm-preserving.

[1] See A for a brief summary of the underlying topological results used in this chapter.

Once we have defined the structure of the modelling space, we are interested in endowing the set of operators with a topology. As in normed vector spaces the continuous linear maps are indeed uniformly continuous and bounded (A.3), a norm can be defined on $L(E,F)$.

Proposition 1.6. *Let E, F be Banach spaces. The set $L(E,F)$ of operators from E into F with the norm*

$$\|A\| \coloneqq \inf\{K \geq 0 \mid |Ax| \leq K|x| \text{ for all } x \in E\}\,, \qquad A \in L(E,F)$$

is a Banach space.

Remark. In a similar way, we define the topology of $L^r(E_1,\dots,E_r;F)$, the set of continuous multilinear maps from the Banach spaces $E_1,\dots,E_r$ into the Banach space F, which is also a Banach space. We define the norm of a continuous multilinear map $A\colon E_1 \times \cdots \times E_r \to F$ by the greatest lower bound of all numbers K such that $|A(x_1,\dots,x_r)| \leq K|x_1|\cdots|x_r|$.

The following result will be needed for defining higher-order derivatives.

Proposition 1.7. *If $E_1,\dots,E_r,F$ are Banach spaces, then the canonical map*

$$L\left(E_1, L\left(E_2,\dots,L\left(E_r,F\right)\cdots\right)\right) \to L^r(E_1,\dots,E_r;F)$$

from the repeated continuous linear maps to the continuous multilinear maps is a Banach-isomorphism.

We are now ready to introduce a generalised notion of differentiability[2]:

Definition 1.8. Let E,F be Banach spaces and U open in E. Let $f\colon U \subset E \to F$ be a continuous map. We shall say that f is **differentiable** at a point $x_0 \in U$ if there exists a continuous linear map λ of E into F such that,

$$\lim_{y\to 0} \frac{|f(x_0+y) - f(x_0) - \lambda y|}{|y|} = 0 \in \mathbb{R}.$$

It then follows trivially that λ is uniquely determined, and we say that it is the **derivative** of f at x_0. We denote the derivative by $Df(x_0)$ or $f'(x_0)$, which by definition is an element of $L(E,F)$. If f is differentiable at every point of U, then we say that f is **differentiable** and f' is a map

$$f'\colon U \to L(E,F)\,.$$

Proposition 1.9 (Chain rule)**.** *Let U,V,W be open subsets of Banach spaces E_1,E_2,E_3 (respectively) and $f\colon U \to V$, $g\colon V \to W$ continuous maps. If $f\colon U \to V$ is differentiable at x_0 and $g\colon V \to W$ is differentiable at $f(x_0)$, then $g\circ f$ is differentiable at x_0, and*

$$(g\circ f)'(x_0) = g'(f(x_0)) \circ f'(x_0).$$

Definition 1.10. Let E,F be Banach spaces and U open in E. Let $f\colon U \subset E \to F$ be a differentiable map. If f' is continuous, then we say that f is of class $\mathcal{C}^1$. We define maps of class $\mathcal{C}^p$ ($p \geq 1$) inductively. The p-th derivative $D^p f$ is defined as $D(D^{p-1}f)$ and is itself a map of U into

$$L\left(E, L\left(E,\dots,L\left(E,F\right)\cdots\right)\right)$$

which can be identified with $L^p(E,F)$ by Proposition 1.7. A map f is said to be of class $\mathcal{C}^p$ if its k-th derivative $D^k f$ exists for $1 \leq k \leq p$, and is continuous. The maps of class $\mathcal{C}^0$ are the continuous maps. We say that f is of class $\mathcal{C}^\infty$ if it is of class $\mathcal{C}^p$ for all integers $p \geq 1$.

[2]The most general notion of derivative (defined on arbitrary TVS) can be found in Appendix B, along with a detailed example.

1.2 Differential geometry

In the previous section we have defined maps of class $\mathcal{C}^p$ ($p \geq 0$) between Banach spaces. Having an analogue of the usual differential calculus on $\mathbb{R}^n$ enables us to seamlessly extend the concept of manifold.

Definition 1.11. Let X be a set. An **atlas** of class $\mathcal{C}^p$ ($p \geq 0$) on X is a collection of pairs (U_i, φ_i) (i ranging in some arbitrary indexing set), satisfying the following conditions:

1. Each U_i is a subset of X and the U_i cover X.
2. Each φ_i is a bijection of U_i onto an open subset $\varphi_i(U_i)$ of some Banach space E_i and for any i, j, $\varphi_i(U_i \cap U_j)$ is open in E_i.
3. The transition map $\Psi_{ij} \coloneqq \varphi_j \circ \varphi_i^{-1} \colon \varphi_i(U_i \cap U_j) \subseteq E_i \longrightarrow \varphi_j(U_i \cap U_j) \subseteq E_j$ is a $\mathcal{C}^p$-isomorphism (a bijection of class $\mathcal{C}^p$ whose inverse is also of class $\mathcal{C}^p$).

There is a unique way to define a topology on X such that the covering is an open one, that is, choosing the collection $\{U_i\}$ as a subbase. This also makes every φ_i an homeomorphism.

Each pair (U_i, φ_i) will be called a **chart** of the atlas. If a point $x \in X$ lies in U_i, then we say that (U_i, φ_i) is a **chart at** x. Note that in condition 2 we have not required all Banach spaces to be the same for all indices i. If they are all equal to some Banach space E we say that we have an E-**atlas**.

Definition 1.12. Let U be an open subset of X and $\varphi(U)$ open in a Banach space E. Let $\varphi \colon U \to \varphi(U)$ be a homeomorphism. We say that (U, φ) is **compatible** with the atlas $\{(U_i, \varphi_i)\}$ if each map $\varphi_i \circ \varphi^{-1}$ (defined on a suitable intersection as in 1.11 3.) is a $\mathcal{C}^p$-isomorphism. Two atlases are said to be **compatible** if each chart of one is compatible with the other atlas. It can easily be verified that the relation of compatibility is an equivalence relation. An equivalence class of atlases of class $\mathcal{C}^p$ on X is said to define a structure of $\mathcal{C}^p$-**manifold** on X. If the elements of the equivalence class are all E-atlases, with E a Banach space, we then say that X is an E-**manifold** or that X is **modelled** on E.

Remark. If $E = \mathbb{R}^n$ for some fixed $n \in \mathbb{N}$, then we say that the manifold is n-**dimensional**. We recover the usual notion, obtaining charts

$$\begin{aligned} \varphi \colon U \subseteq X &\longrightarrow V \subseteq \mathbb{R}^n \\ x &\longmapsto (x_1(x), \ldots, x_n(x)) \,. \end{aligned}$$

The functions $(x_1, \ldots, x_n)$ are called **local coordinates** on the manifold.

Proposition 1.13. *If X, Y are two $\mathcal{C}^p$-manifolds modelled on Banach spaces E, F, with $p \geq 0$, then $X \times Y$ is also a $\mathcal{C}^p$-manifold modelled on $E \times F$.*

Proof. We can give the product set $X \times Y$ a manifold structure straightforwardly: if $\{(U_i, \varphi_i)\}$ and $\{(V_j, \psi_j)\}$ are atlases for X, Y respectively, then

$$\{(U_i \times V_j, \varphi_i \times \psi_j)\}$$

is an atlas of the product (it satisfies 1.11). Now, the product (as defined above) of a pair of compatible atlases of X with a pair of compatible atlases of Y gives rise to two compatible atlases for $X \times Y$, so we get a well-defined manifold structure. □

Remark. From now on we consider $p = \infty$ and therefore the prefix $\mathcal{C}^p$ is omitted.

Definition 1.14. Let X, Y be two manifolds modelled on Banach spaces E, F. Let $f\colon X \to Y$ be a map. We shall say that f is **of class** $\mathcal{C}^p$ $(p \geq 0)$ if, given $x \in X$, there exists a chart (U, φ) at x and a chart (V, ψ) at $f(x)$ such that $f(U) \subset V$, and the map

$$\psi \circ f \circ \varphi^{-1}\colon \varphi(U) \to \psi(V)$$

is of class $\mathcal{C}^p$, in the sense of 1.10. We denote $f_{V,U} \coloneqq \psi f \varphi^{-1}$.

We are now ready to introduce a definition of tangent space.

Definition 1.15. Let X be a manifold modelled on a Banach space E and let x be a point of X. We consider triples (U, φ, v) where (U, φ) is a chart at x and $v \in E$. We say that two such triples (U, φ, v) and (V, ψ, w) are equivalent if the derivative of the transition map at $\varphi x \coloneqq \varphi(x)$, which is an element of $L(E, E)$, maps v on w. The formula reads:

$$\left(\psi\varphi^{-1}\right)'(\varphi x)\, v = w\ .$$

An equivalence class of such triples is called a **tangent vector** of X at x. The set of such tangent vectors is called the **tangent space** of X at x and is denoted by $T_x(X)$.

Proposition 1.16. *Each chart (U, φ) determines a bijection of $T_x(X)$ on E, namely the map $[(U, \varphi, v)] \in T_x(X) \longmapsto v \in E$. By means of this bijection $T_x(X)$ can be endowed with the structure of topological vector space (which is independent of the chosen chart).*

Proposition 1.17. *Let X, Y be two manifolds modelled on Banach spaces E, F. Let $f\colon X \to Y$ be a map of class $\mathcal{C}^\infty$. We call the **differential** of f at a point $x \in X$ to the unique linear map*

$$f_{*,x}\colon T_x(X) \longrightarrow T_{f(x)}(Y)$$

having the following property: if (U, φ) is a chart at x and (V, ψ) is a chart at $f(x)$ such that $f(U) \subset V$, and $\overline{v}$ is a tangent vector at x represented by v in the chart (U, φ), then $f_{*,x}(\overline{v})$ is the tangent vector at $f(x)$ represented by $f'_{V,U}(\varphi x)\, v$ in the chart (V, ψ). That is, the diagram

$$\begin{array}{ccc} T_x(X) & \longrightarrow & E \\ {\scriptstyle f_{*,x}}\downarrow & & \downarrow{\scriptstyle f'_{V,U}(\varphi x)} \\ T_{f(x)}(Y) & \longleftarrow & F \end{array}$$

is commutative. By construction, $f_{*,x}$ is linear and continuous for the structure of topological vector space which we have placed on $T_x(X)$ and $T_{f(x)}(Y)$.

Proof. Let (U_1, φ_1) and (U_2, φ_2) be two charts at $x \in X$, such that $f(U_1), f(U_2) \subset V$. Let v_1 and v_2 be the representations in the charts (U_1, φ_1) and (U_2, φ_2) (respectively) of the tangent vector $\overline{v} \in T_x(X)$. By 1.15, the equation

$$\left(\varphi_2{\varphi_1}^{-1}\right)'(\varphi_1 x)\, v_1 = v_2$$

holds. Now, applying 1.9,

$$\begin{aligned} f'_{V,U_2}(\varphi_2 x)\, v_2 &= \left[f'_{V,U_2}(\varphi_2 x) \circ \left(\varphi_2{\varphi_1}^{-1}\right)'(\varphi_1 x)\right] v_1 = \\ &= \left[\psi f {\varphi_2}^{-1} \circ \varphi_2{\varphi_1}^{-1}\right]'(\varphi_1 x)\, v_1 = f'_{V,U_1}(\varphi_1 x)\, v_1\ , \end{aligned}$$

and $f_{*,x}(\overline{v})$ does not depend on the choice of charts. Therefore, $f_{*,x}$ is well-defined. □

Proposition 1.18. *Let X, Y, Z be manifolds, $f\colon X \to Y$ and $g\colon Y \to Z$ be $\mathcal{C}^\infty$ maps. Then,*

$$(g \circ f)_{*,\,x} = g_{*,\,f(x)} \circ f_{*,\,x}$$
$$\mathrm{id}_{*,\,x} = \mathrm{id}\,.$$

In the modelling of dynamical systems, tangent vectors and their dual objects are essential, as they describe the physical notions of velocity and momenta respectively. We now want to also give a manifold structure to the collection of tangent spaces, cotangent spaces and general tensor spaces; one that adapts the notion of fibre bundle of a manifold modelled on $\mathbb{R}^n$ to the new definitions that have arisen in the infinite-dimensional setting.

Definition 1.19. Let X, A be two manifolds, and let $\pi\colon A \to X$ be a $\mathcal{C}^\infty$ map. Let E be a Banach space. Let $\{U_i\}$ be an open covering of X and $\{\tau_i\}$ a set of mappings such that

$$\tau_i\colon \pi^{-1}(U_i) \longrightarrow U_i \times E\,,$$

satisfying the following conditions:

1. The map τ_i is a $\mathcal{C}^\infty$-isomorphism commuting with the projection on U_i, that is, such that the following diagram is commutative[3]:

$$\begin{array}{ccc} \pi^{-1}(U_i) & \xrightarrow{\quad\tau_i\quad} & U_i \times E \\ & {\scriptstyle\pi}\searrow \quad \swarrow & \\ & U_i & \end{array}\,.$$

   In particular, we obtain an isomorphism on each fibre (the subset $A_x \coloneqq \pi^{-1}(\{x\}) \subset A$, given a point $x \in X$), $\tau_{ix}\colon A_x \longrightarrow \{x\} \times E \cong E$.

2. For each pair of open sets U_i, U_j, the map $\tau_{jx} \circ \tau_{ix}^{-1}\colon E \longrightarrow E$ is a toplinear isomorphism.

3. If U_i and U_j are two members of the covering, then the map of $U_i \cap U_j$ into the set of toplinear isomorphisms from E into E, $L_{\mathrm{aut}}(E) \subset L(E, E)$, given by $x \mapsto \left(\tau_j \tau_i^{-1}\right)_x$ is of class $\mathcal{C}^\infty$.

Then, we shall say that $\{(U_i, \tau_i)\}$ is a **trivialising covering** for A and that $\{\tau_i\}$ are its **trivialising maps**. If $x \in U_i$ we say that (U_i, τ_i) is a trivialisation at x. Two trivialising coverings for A are said to be **equivalent** if taken together they also satisfy the conditions 2 and 3 above. An equivalence class of such trivialising coverings is said to determine a structure of **vector bundle** on A. We say that A is the **total space** of the bundle and that X is the **base space**. We also say that the vector bundle has a fibre E.

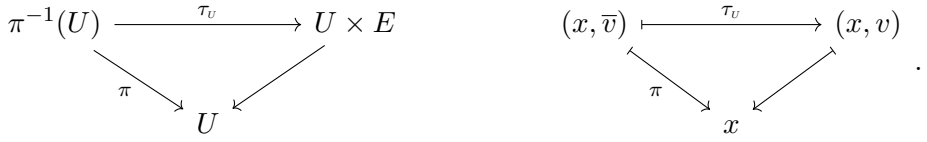
Proposition 1.20. *Let X be a manifold, and let $T(X)$ be the disjoint union of the tangent spaces $T_x(X)$. Then, $T(X)$ has a vector bundle structure and is called the* ***tangent bundle****.*

Proof. We have a natural projection, $\pi\colon T(X) \to X$ mapping $T_x(X)$ on x. If (U, φ) is a chart at $x \in X$ and (U, φ, v) is an element of the equivalence class $\overline{v} \in T_x(X)$, then from 1.16 we get a bijection

$$\tau_U\colon \pi^{-1}(U) = \bigcup_{x \in U} T_x(X) \longrightarrow U \times E$$
$$(x, \overline{v}) \longmapsto (x, v)\,.$$

[3]Here we mean by $\mathcal{C}^\infty$ an infinitely differentiable map in the sense of TVS (see B.3).

It also commutes with the projection on U,



Furthermore, if (U_i, φ_i) and (U_j, φ_j) are two charts of X, and if we denote by φ_{ji} the map $\varphi_j \varphi_i^{-1}$ (defined on $\varphi_i(U_i \cap U_j)$), then we obtain a transition mapping

$$\tau_{ji} = (\varphi_j, \mathrm{id}_E) \circ (\tau_j \tau_i^{-1}) \circ (\varphi_i^{-1}, \mathrm{id}_E) \colon \varphi_i(U_i \cap U_j) \times E \longrightarrow \varphi_j(U_i \cap U_j) \times E$$

by the formula

$$\tau_{ji}(\varphi_i x, v) = (\varphi_j x, \varphi'_{ji}(\varphi_i x) \cdot v)$$

for $x \in U_i \cap U_j$, $v \in E$. Since the derivative φ'_{ji} is of class $\mathcal{C}^\infty$, and is an isomorphism at $\varphi_i x$, it can be proved using a technical lemma ([11], Chapter 1, Proposition 3.10), that $T(X)$ has a vector bundle structure. □

We are now prepared to give a vector bundle structure to the collection of the dual objects of tangent vectors. Let us start by defining them formally.

Definition 1.21. Let X be a manifold, and $x \in X$. By proposition 1.16, the tangent space $T_x(X)$ has a structure of topological vector space. We can then consider its dual (the set of continuous linear maps from $T_x(X)$ into $\mathbb{R}$), $T_x^*(X) \coloneqq L(T_x(X), \mathbb{R})$, which will be called the **cotangent space** of X at x.

Proposition 1.22. *Let X be a manifold, and let $T^*(X)$ be the disjoint union of the cotangent spaces $T_x^*(X)$. Then, $T^*(X)$ has a vector bundle structure and is called the **cotangent bundle**. Similarly, the disjoint union of general tensor spaces at each point can also be endowed with a vector bundle structure. In particular, when we consider the disjoint union of the set of r-multilinear alternated forms $L_a^r(T_x(X), \mathbb{R})$ at each point, the corresponding **bundle of alternating r-multilinear forms** is denoted by $L_a^r(T(X))$.*

Proof. Since it requires concepts from category theory, it is fully detailed in Appendix C. □

Finally, we discuss some concepts of paramount importance for the modelling of dynamical systems, namely the definition of vector field and its dual object, a differential form.

Definition 1.23. Let X be a Hausdorff manifold[4]. Let $\pi \colon T(X) \to X$ be its tangent bundle. A **vector field** on X is a cross section of the tangent bundle, i.e. a $\mathcal{C}^\infty$ map $\xi \colon X \to T(X)$ such that $\xi(x)$ lies in the tangent space $T_x(X)$ for each $x \in X$, or in other words, such that $\pi \circ \xi = \mathrm{id}$. We shall denote the set of vector fields on X as $\mathfrak{X}(X)$.

Definition 1.24. Let X be a manifold, J be an open interval of $\mathbb{R}$. A **curve** in X is a $\mathcal{C}^\infty$ map $\alpha \colon J \to X$. As the tangent bundle of J is the trivial bundle $J \times \mathbb{R}$, let $\imath(t) = (t, 1)$ for all $t \in J$ be the canonical section. Considering the differential of α we have an induced map

$$\begin{array}{ccc} J \times \mathbb{R} & \xrightarrow{\alpha_*} & T(X) \\ \downarrow & & \downarrow \pi \\ J & \xrightarrow[\alpha]{} & X \end{array}$$

and we will denote $\alpha' \coloneqq \alpha_* \circ \imath \colon \mathbb{R} \to T(X)$. Thus, α' is a curve on $T(X)$.

[4]From now on, we assume every manifold to be Hausdorff.

Definition 1.25. Let X be a manifold, ξ a vector field on X and x_0 a point of X. An **integral curve** for the vector field ξ with **initial condition** x_0 is a curve $\alpha\colon J \to X$ mapping an open interval J of $\mathbb{R}$ containing 0 into X, such that

$$\alpha(0) = x_0 \qquad \text{and} \qquad \alpha'(t) = \xi\left(\alpha(t)\right) \quad \text{for all } t \in J\,.$$

On a finite-dimensional manifold, vector fields are usually defined as derivations of functions. We now see that this notion can be also recovered in the infinite-dimensional setting.

Proposition 1.26. *Let X be a manifold and let ξ be a vector field on X. We denote by $\mathcal{C}^\infty(X)$ the ring of functions $\varphi\colon X \to \mathbb{R}$ of class $\mathcal{C}^\infty$ defined on X. Then, ξ defines a derivation ∂_ξ on $\mathcal{C}^\infty(X)$. Moreover, if $\partial_\xi = 0$, then $\xi(x) = 0$ for all $x \in X$.*

Proof. Recall that for every $x \in X$, the differential $\varphi_{*,\,x}\colon T_x(X) \to T_{\varphi(x)}(\mathbb{R}) = \mathbb{R}$ defines a continuous linear map (1.17). With it, we define a new function

$$\begin{aligned} \xi\varphi\colon X &\longrightarrow \mathbb{R} \\ x &\longmapsto \varphi_{*,\,x}\left(\xi(x)\right). \end{aligned}$$

Therefore we can now define an operator, $\partial_\xi\colon \mathcal{C}^\infty(X) \to \mathcal{C}^\infty(X)$ as $\varphi \mapsto \partial_\xi(\varphi) \coloneqq \xi\varphi$ that is linear and satisfies the Leibniz identity. The last assertion can be found in [11], Chapter 5, Proposition 1.2. □

Note that the last statement of proposition 1.26 enables us to univocally define a vector field by its action as a derivation on the ring of functions. Given two vector fields ξ, η on X, we shall now define a new vector field by means of this property.

Definition 1.27. Let ξ, η be two vector fields on X. Then, there exists a unique vector field $[\xi, \eta]$ such that for every function $\varphi \in \mathcal{C}^\infty(X)$ we have

$$[\xi, \eta]\,\varphi = \xi\left(\eta(\varphi)\right) - \eta\left(\xi(\varphi)\right).$$

Definition 1.28. A cross section of the bundle $L^r_a\left(T(X)\right)$ is called a **differential p-form**. It is convenient to agree that a differential form of degree 0 is a function. We shall denote the set of differential p-forms on X as $\Lambda^p(X)$. If $\xi_1, \ldots, \xi_p \in \mathfrak{X}(X)$, $\omega \in \Lambda^p(X)$, we denote by $\langle \omega, \xi_1 \times \cdots \times \xi_p \rangle$ the mapping from X into $\mathbb{R}$ whose value at a point $x \in X$ is $\omega(x)\left(\xi_1(x), \ldots, \xi_p(x)\right)$.

We end this section by defining the exterior derivative of a p-form, the last ingredient that we need for the dynamical description of physical systems. The definition relies on the fact that a differential p-form is univocally determined by its action on vector fields.

Proposition 1.29. *Let $\varphi\colon X \to \mathbb{R}$ be a function, i.e. $\varphi \in \Lambda^0(X)$. Then $d\varphi \in \Lambda^1(X)$ acts on vector fields $\xi \in \mathfrak{X}(X)$ as $\langle d\varphi, \xi \rangle = \xi\varphi$. Now, let $\omega \in \Lambda^p(X)$. Then, there exists a unique $(p+1)$-form $d\omega$ on X such that, for any vector fields $\xi_0, \ldots, \xi_p$ on X we have*

$$\begin{aligned} \langle d\omega, \xi_0 \times \cdots \times \xi_p \rangle = &\sum_{i=0}^{p} (-1)^i \xi_i \left\langle \omega, \xi_0 \times \cdots \times \hat{\xi}_i \times \cdots \times \xi_p \right\rangle \\ &+ \sum_{i<j} (-1)^{i+j} \left\langle \omega, [\xi_i, \xi_j] \times \xi_0 \times \cdots \times \hat{\xi}_i \times \cdots \times \hat{\xi}_j \times \cdots \times \xi_p \right\rangle \end{aligned}$$

where $\hat{\xi}_k$ denotes an omitted vector field for the index k. The operator $d\colon \Lambda^p(X) \to \Lambda^{p+1}(X)$ is called the ***exterior differential****.*

Chapter 2

Geometric mechanics

As discussed in the abstract, hybrid classical-quantum systems are those which have classical and quantum degrees of freedom with a coupled evolution. Since classical and quantum mechanics possess fundamental differences in their respective mathematical formalisms, it is natural to describe the evolution of such hybrid systems geometrically, formulating both theories on the same terms. Geometric classical mechanics was developed in the second half of the 20th century and it is now widely accepted [4]. The development of geometric quantum mechanics began in the 70s and, although it might not be as popular, there exist consolidated references [5, 6]. The purpose of this chapter is to present both geometrical formalisms, paving the ground for later extending the formulation of a particularly relevant hybrid system, the Ehrenfest molecular model, to the infinite-dimensional setting.

2.1 Geometric formalism of classical mechanics

Newton laws, the fundamental postulates of classical mechanics, allow us to describe the evolution of physical systems that fall within a certain range of length, velocity and mass. Since their publication, several reformulations of the theory have been developed using the concept of *phase space*, i.e. the characterisation of the state of a physical system at a precise moment in time by a point of a set. One of them, the Hamiltonian formulation of classical mechanics, is described naturally in terms of symplectic manifolds, allowing us to use the differential geometry tools discussed in 1.2 to tackle mechanical problems. Under the geometric Hamiltonian formalism of classical mechanics, the phase space[1] of a system with $2n$ degrees of freedom is the cotangent bundle $T^*(M)$ of an n-dimensional real manifold M. Taking a local trivialisation, a point of the bundle is mapped onto a $2n$-tuple of real numbers

$$(q, p) \longmapsto \left(q^1, \dots, q^n, p_1, \dots, p_n\right),$$

the generalised positions q (coordinates in the base space) and their associated momenta p (coordinates in the fibre, see below). The aim of this section is to briefly summarise this formalism.

Proposition 2.1. *Let M be a n-dimensional real manifold. A chart (U, φ) of M induces a chart in the bundles $T(U)$ and $T^*(U)$ called the natural chart. Given an atlas $\mathcal{A}$ of M, we call the induced atlas for $T(M)$ and $T^*(M)$ obtained by the union of natural charts, the **natural coordinate system** induced by $\mathcal{A}$.*

[1] As discussed in the abstract, a more general choice of phase space (a symplectic or Poisson manifold) could have been made.

Proof. Let $q \in M$ and (U, φ) a chart at q. The differential of the chart at the point q is a map $\varphi_{*,\,q} \colon T_q(M) \to T_{\varphi q}(\mathbb{R}^n) = \mathbb{R}^n$, which is linear and continuous (1.17). Since φ is a $\mathcal{C}^\infty$-isomorphism, we can apply the chain rule 1.18 to $\varphi^{-1}\varphi = \mathrm{id}_U$ and we have

$$\varphi^{-1}_{*,\,\varphi q} \circ \varphi_{*,\,q} = \left(\varphi^{-1} \circ \varphi\right)_{*,\,q} = \mathrm{id}_{*,\,q} = \mathrm{id}_{\,T_q(M)} \,.$$

Hence, $\varphi_{*,\,q}$ is invertible and its inverse is $\varphi^{-1}_{*,\,\varphi q}$, yielding a toplinear isomorphism from $T_q(M)$ into $\mathbb{R}^n$. That way, we can define a natural basis of $T_q(M)$ mapping the canonical basis $\{e_i\}_{i=1}^n$ of $\mathbb{R}^n$ by $\varphi^{-1}_{*,\,\varphi q}$. Considering the natural basis at every point of U, we can then define the natural basis of vector fields on U,

$$\left.\frac{\partial}{\partial q_i}\right|_q \coloneqq \varphi^{-1}_{*,\,\varphi q}(e_i) \quad q \in U \,.$$

We have then obtained a chart $T(U) \to \mathbb{R}^{2n}$, the natural chart. Considering the open covering of M we have the natural coordinate system induced by the atlas.

Let us consider the set of one-forms on U obtained by applying the exterior differential to the coordinate functions $q_i \colon U \to \mathbb{R}$, $\{dq^i\}_{i=1}^n$. This set of differential forms, at every $q \in U$, is indeed the dual basis of the natural basis of $T_q(M)$, since by definition

$$\left\langle dq^i, \frac{\partial}{\partial q_j} \right\rangle (q) = \left(\frac{\partial}{\partial q_j}\, q_i\right)(q) = q_{i*,\,q}\left(\varphi^{-1}_{*,\,\varphi q}(e_j)\right) = \delta_{ij} \,.$$

We can now proceed analogously for the dual bundle $T^*(U)$. □

We have already set our phase space and a natural chart. Let us see how Hamilton equations (which are equivalent to Newton laws), can be re-written in geometrical terms. In particular, they can be translated into an equation involving a particular type of two-form, called a symplectic form.

Definition 2.2. Let M be an n-dimensional manifold and let $\omega \in \Lambda^2(M)$ be a two-form. We shall say that ω is a **symplectic form** if

1. it is closed, i.e. $d\omega = 0$,
2. and it is non degenerate, i.e. given any vector field $\xi \in \mathfrak{X}(M)$, the relation $\omega(\xi, \eta) = 0$ for every $\eta \in \mathfrak{X}(M)$ implies that $\xi = 0$.

We say that (M, ω) is a **symplectic manifold**.

The next step is to prove that our phase space, the cotangent bundle $T^*(M)$ is indeed a symplectic manifold.

Theorem 2.3. *Let M be a n-dimensional manifold and $T^*(M)$ its cotangent bundle. Then, $T^*(M)$ can be endowed with a structure of symplectic manifold, whose symplectic form ω is exact, i.e. it can be obtained as the exterior differential[2] of a one-form, $\omega = -d\theta$. We call $\theta \in \Lambda^1(T^*(M))$ the Liouville one-form. In the natural coordinate system induced by the atlas of M, ω and θ have the following expressions:*

$$\theta = \sum_{i=1}^n p_i dq^i \qquad \omega = \sum_{i=1}^n dq^i \wedge dp_i \,,$$

where $\wedge$ denotes the antisymmetric tensor product.

[2]The negative sign is introduced by convention.

Proof. Let us take a point $u \in T^*(M)$ whose coordinates in the natural coordinate system are $(q^1, \dots, q^n, p_1, \dots, p_n)$, and let us consider the natural projection of the cotangent bundle, $\pi\colon T^*(M) \to M$. The differential of π at the point u is

$$\pi_{*,\,u}\colon T_u\left(T^*(M)\right) \longrightarrow T_{\pi(u)}(M)\,.$$

Let $\xi(u) \in T_u\left(T^*(M)\right)$, then $\pi_{*,\,u}\left(\xi(u)\right)$ is a tangent vector of M at the point $\pi(u) = q$, whose coordinates are $(q^1, \dots, q^n)$. Now, considering the one-form $p(q) = \sum_{i=1}^n p_i dq^i$, we define

$$\langle \theta(u), \xi(u)\rangle \coloneqq \langle\, p(q), \pi_{*,\,u}\left(\xi(u)\right)\rangle$$

the Liouville one-form. We can extend it over $T^*(M)$ and its coordinate expression in the natural chart is $\theta = \sum_{i=1}^n p_i dq^i$. Applying the exterior differential 1.29 we obtain the coordinate expression of ω, which is a two-form by construction. As the exterior differential is a nilpotent operator ($d^2 = 0$), ω is closed. We only have to check the non-degeneracy. Applying 2.1, the general local expression of a vector field of $T^*(M)$ in natural coordinates is

$$\xi = \sum_{i=1}^{n} \xi^{q^i} \frac{\partial}{\partial q^i} + \xi^{p_i} \frac{\partial}{\partial p_i}$$

and therefore in that same chart, $\langle \omega, \xi \times \cdot\rangle = \sum_i \xi^{q^i} dp_i - \xi^{p_i} dq^i$. The action of that resulting one-form on another vector field η is $\langle \omega, \xi \times \eta\rangle = \sum_i \xi^{q^i}\eta^{p_i} - \xi^{p_i}\eta^{q^i}$, which cannot vanish for every $\eta \in \mathfrak{X}(T^*(M))$ unless $\xi = 0$. □

Definition 2.4. Let M be a n-dimensional manifold, $T^*(M)$ its cotangent bundle and let $H \in \mathcal{C}^\infty\left(T^*(M)\right)$ be a function. We say that a curve $\alpha\colon J \to T^*(M)$, J an open interval of $\mathbb{R}$ containing the origin, is a solution of the Hamiltonian dynamics defined by the function H if α is the integral curve of the **Hamiltonian vector field** ξ_H (with initial condition $\alpha(0)$), which is the unique vector field satisfying

$$\langle \omega, \xi_H \times \cdot\rangle = i_{\xi_H}\omega = dH\,. \tag{2.1}$$

Remark. Note that if we take the natural coordinates, the expression of the vector field ξ_H reads

$$\xi_H = \frac{\partial H}{\partial p_i}\frac{\partial}{\partial q^i} - \frac{\partial H}{\partial q^i}\frac{\partial}{\partial p_i}\,.$$

This implies that the integral curves of the vector field correspond to the solutions of Hamilton equations defined on the chart, that is, if $\alpha'(t) = (\dot q(t), \dot p(t))$ for $t \in J$,

$$\dot q^i = \frac{\partial H}{\partial p_i} \qquad \dot p_i = -\frac{\partial H}{\partial q^i}\,.$$

Once we have obtained a Hamiltonian formalism in terms of a symplectic differential form, it is useful to extend this structure to a more general type of manifolds, called Poisson manifolds. This procedure can always be applied in the finite-dimensional setting; nevertheless, we will later see that in dynamical systems modelled on infinite-dimensional manifolds some problems may arise (due to ω losing its non-degeneracy).

Definition 2.5. Let (X, ω) be a symplectic manifold. The **Poisson tensor** Ω is the unique twice covariant tensor such that

$$\xi_H = \Omega(\cdot, dH)$$

where ξ_H and dH are defined as in 2.4.

Definition 2.6. Let X be a manifold. We denote by $\mathcal{C}^\infty(X)$ the ring of functions $\varphi\colon X \to \mathbb{R}$ of class $\mathcal{C}^\infty$ defined on X. With the pointwise product we can endow $\mathcal{C}^\infty(X)$ with the structure of associative algebra. We define the **Poisson bracket** on $\mathcal{C}^\infty(X)$, as the bilinear operation

$$\{\cdot\,,\cdot\}\colon \mathcal{C}^\infty(X)\times\mathcal{C}^\infty(X) \longrightarrow \mathcal{C}^\infty(X)$$

which

1. is antisymmetric, $\{f,g\} = \{-g,f\}$ for $f,g\in\mathcal{C}^\infty(X)$,
2. satisfies Jacobi identity, $\{f,\{g,h\}\}+\{h,\{f,g\}\}+\{g,\{h,f\}\}=0$ for $f,g,h\in\mathcal{C}^\infty(X)$,
3. and satisfies Leibniz derivation rule, $\{f,g\cdot h\} = \{f,g\}\cdot h + g\cdot\{f,h\}$ for $f,g,h\in\mathcal{C}^\infty(X)$.

Then, $(\mathcal{C}^\infty(X),\cdot,\{\cdot,\cdot\})$ is a **Poisson algebra**, where $\cdot$ denotes the pointwise product.

Proposition 2.7. *Let (X,ω) be a symplectic manifold and Ω its Poisson tensor. Then, the operation $\{\cdot\,,\cdot\}$ defined as*

$$\begin{aligned}\{\cdot\,,\cdot\}\colon \mathcal{C}^\infty(X)\times\mathcal{C}^\infty(X) &\longrightarrow \mathcal{C}^\infty(X)\\ (f,g) &\longmapsto \{f,g\} \coloneqq \Omega(df,dg)\end{aligned}$$

induces a Poisson algebra structure on $\mathcal{C}^\infty(X)$.

Remark. Let M be a n-dimensional manifold. It can be proved that in the natural chart defined on $T^*(M)$ (2.1), we can write the Poisson bracket as

$$\{f,g\} \coloneqq \sum_{i=1}^{n} \frac{\partial f}{\partial q^i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q^i}\,.$$

Therefore, equation (2.1) can be re-written as

$$\xi_H = \{\cdot\,,H\}\,. \tag{2.2}$$

Note that this notion of Hamiltonian vector field can be defined even if the manifold is not symplectic, as it only requires a Poisson bracket. This can be particularly useful when studying systems whose phase space is a manifold of odd dimension, where a symplectic form cannot be defined.

We can now give a brief summary of geometrical classical mechanics:

- The generalised positions q of the physical system lie in a n-dimensional manifold M and determine the phase space, the cotangent bundle, which is a symplectic manifold $(T^*(M),\omega)$ (2.3).
- A function $H\in\mathcal{C}^\infty(T^*(M))$, the Hamiltonian, represents the energy of the system at any given point of the phase space. This function determines the dynamics by equation (2.1), or equivalently, equation (2.2): given an initial condition, the system will follow the corresponding integral curve of the Hamiltonian vector field ξ_H (2.4).
- The set of physical observables corresponds to $\mathcal{C}^\infty(M)$. Their evolution is also prescribed by the Hamiltonian vector field as
$$\dot f = \xi_H f$$
or, in terms of the Poisson bracket,
$$\frac{df}{dt} = \{f,H\} \qquad f\in\mathcal{C}^\infty(M)\,.$$

2.2 Geometric formalism of quantum mechanics

Quantum mechanics in its modern formulation was developed in the 20's of the 20th century to describe physical phenomena at a microscopic scale. In the Schrödinger picture, the states of a system are represented by points of a separable Hilbert space, $\mathscr{H}$ (i.e. $\mathscr{H}$ is the phase space). The physical observables are modelled by continuous self-adjoint operators (densely) defined on $\mathscr{H}$. The evolution is prescribed by the Schrödinger equation,

$$i\hbar\,\partial_t\,|\psi(t)\rangle = H\,|\psi(t)\rangle$$

where $|\psi(t)\rangle$ is a trajectory on $\mathscr{H}$ and $H\colon \mathscr{D}(H) \subset \mathscr{H} \to \mathscr{H}$ is a self-adjoint operator defined on a dense subset $\mathscr{D}(H) \subset \mathscr{H}$, called the Hamiltonian.

The aim of this section is to devise a geometrical interpretation of quantum mechanics, similar to what we achieved in section 2.1. For that purpose, we firstly need to introduce some technical results for the rigorous treatment of self-adjoint operators [12]. Afterwards, we present the construction of geometric quantum mechanics [5]. We will then see that, when considering a general geometric quantum system, some properties have been lost due to the modelling space being infinite-dimensional. However, in the particular case of the atomic Hamiltonian [13] we can recover a treatment in terms of symplectic manifolds, as done in [14], [6].

2.2.1 Summary of operator theory

We summarise briefly some of the concepts of the theory of linear operators in a Hilbert space which are of direct interest for quantum mechanics. We use $\mathscr{H}$ to denote a complex, separable Hilbert space endowed with a scalar product $\langle\cdot\,,\cdot\rangle$. The set of bounded (continuous, A.3) linear operators defined over all of $\mathscr{H}$ will be denoted by $L(\mathscr{H},\mathscr{H})$.

Definition 2.8. Let $A\colon \mathscr{D}(A) \subset \mathscr{H} \to \mathscr{H}$ be a linear operator defined in the subspace $\mathscr{D}(A)$. We say that $\mathscr{D}(A)$ is its **domain** and $\mathscr{R}(A) \coloneqq A\,(\mathscr{D}(A))$ its **range**. The operator A is characterised by its **graph**

$$\Gamma(A) \coloneqq \{(\varphi,\psi) \in \mathscr{H}\oplus\mathscr{H}\colon \varphi \in \mathscr{D}(A), \psi = A\varphi\}\,.$$

Definition 2.9. Let A_1, A_2 be linear operators defined as above. We say that A_2 is an **extension** of A_1, and we will write $A_1 \subset A_2$ if $\Gamma(A_1) \subset \Gamma(A_2)$.

Definition 2.10. Let A be a linear operator. We say that A is **closed** if the subspace $\Gamma(A)$ is closed in $\mathscr{H}\oplus\mathscr{H}$. The operator A is said to be **closable** if $\overline{\Gamma(A)}$, the closure of $\Gamma(A)$, is a graph of another operator $\bar{A}$, that is: $\overline{\Gamma(A)} = \Gamma(\bar{A})$. Then, $\bar{A}$ is called the closure of A and is its minimal closed extension.

Proposition 2.11. *Let $A\colon \mathscr{D}(A) \subset \mathscr{H} \to \mathscr{H}$ be an operator. If $\overline{\mathscr{D}(A)} = \mathscr{H}$, then there exists an operator $A^\dagger$, called the **adjoint operator**, which satisfies*

$$\langle\varphi, A\psi\rangle = \langle A^\dagger\varphi,\psi\rangle \;\; \textit{for all } \psi \in \mathscr{D}(A), \varphi \in \mathscr{D}(A^\dagger)\,.$$

Definition 2.12. An operator $A\colon \mathscr{D}(A) \subset \mathscr{H} \to \mathscr{H}$ is said to be **symmetric** or **Hermitian** if $A \subset A^\dagger$. When $A = A^\dagger$, we say that A is **self-adjoint**. If $\bar{A} = A^\dagger$ we say that it is **essentially self-adjoint**.

2.2.2 Quantum phase space

Following the same structure as in 2.1, the first step is identifying the phase space. Essentially, it is a separable Hilbert space[3] $\mathscr{H}$, but some technical problems arise. Namely, that the Hamiltonian operator and other physical observables under consideration might not be self-adjoint, continuous or even be defined on $\mathscr{H}$. To overcome this problem, we have to choose between two alternative formalisms:

- The first one [14] is to consider $\mathscr{H}$ as the phase space and accept that the Hamiltonian will only be defined on a dense subset.
- The second one [5], which we will present in this section, is to restrict the phase space from the beginning, working with a dense subspace $\mathscr{S}$ of $\mathscr{H}$ which is contained on every self-adjointness domain and which is equipped with a finer topology that makes the observables continuous. Typically, this is the Schwartz space of rapidly decreasing functions. The main drawback of this approach is that because of the lack of a existence and uniqueness theorem for PDEs, vector fields may not have associated integral curves.

Let us begin with the formal definition of the phase space.

Definition 2.13. The **Schwartz space**, or the space of **rapidly decreasing functions** is defined as

$$\mathscr{S}(\mathbb{R}^d) \coloneqq \{\psi\colon \mathbb{R}^d \to \mathbb{C} \mid \psi \in \mathcal{C}^\infty(\mathbb{R}^d) \text{ and } \sup_{x\in\mathbb{R}^d} |x^\alpha D^\beta \psi(x)| < \infty\}$$

where $d \geq 1$ and $\alpha, \beta \in \mathbb{N}_0^d$.

We now study its topology and state without proof some of its most relevant properties [15].

Definition 2.14. Let E be a TVS over $\mathbb{C}$. A **seminorm** is a function $p\colon E \to \mathbb{R}$ such that: (1) $p(x+y) \leq p(x)+p(y)$ for all $x, y \in E$, (2) $p(kx) = |k|p(x)$ for all $k \in \mathbb{C}, x \in E$, (3) $p(x) \geq 0$ for all $x \in E$. We can use a countable family of seminorms $\{p_\alpha\}$ to induce a topology on E: a sequence $\{\phi_k\} \subset E$ converges to 0 if and only if for all α,

$$\lim_{k\to\infty} p_\alpha(\phi_k) = 0.$$

Remark. Equivalently, each seminorm defines an open ball of radius r centred at some $\psi \in E$ by

$$B_{p_\alpha}(\psi, r) \coloneqq \{\phi \in E \mid p_\alpha(\phi - \psi) < r\},$$

inducing a topology τ_α on E. A subset $U \subset E$ is open with respect to the topology induced by the family of seminorms if and only if $U \in \tau_\alpha$ for all α.

Proposition 2.15. *The Schwartz space $\mathscr{S}(\mathbb{R}^d)$ has the following properties:*

1. *The function $p_{\alpha,\beta}\colon \mathscr{S}(\mathbb{R}^d) \to [0,\infty)$ defined as*

$$p_{\alpha,\beta}(\psi) \coloneqq \sup_{x\in\mathbb{R}^d} |x^\alpha D^\beta \psi(x)|$$

is a seminorm over $\mathscr{S}(\mathbb{R}^d)$ for every $\alpha, \beta \in \mathbb{N}_0^d$.

[3] For the sake of simplicity we will disregard for the moment that two points of $\mathscr{H}$ which only differ in a multiplicative complex number characterise the same physical state. To take this into consideration we would have to choose the projective Hilbert space as our phase space.

2. *It is a Fréchet space (metrizable and complete) with respect to the topology induced by the countable family of seminorms* $\{p_{\alpha,\beta}\}_{\alpha,\beta\in\mathbb{N}_0^d}$. *That is, there exists a complete metric whose induced topology is the same as the one induced by the family of seminorms. That metric is defined as*

$$d(\psi,\eta) \coloneqq \sum_{j=1}^{\infty} \frac{1}{2^j} \frac{p_j(\psi-\eta)}{1+p_j(\psi-\eta)} \qquad \psi,\eta\in\mathscr{S}(\mathbb{R}^d)$$

where $\{p_j\}_{j=1}^{\infty}$ *is an enumeration of* $\{p_{\alpha,\beta}\}_{\alpha,\beta\in\mathbb{N}_0^d}$.

3. *It is dense on* $L^p(\mathbb{R}^d)$ *for all* $1\leq p\leq\infty$.

As we will need geometrical objects for our model, we want to endow this phase space with a structure of manifold. In order to adapt definition 1.11 we need to extend the concept of differentiable mapping. In general, the concept of differentiability in a non-Banach TVS is problematic, but in the particular case of the Schwartz space there is a serviceable definition that allows us to calculate functional derivatives explicitly[4]. We can then introduce the following definition:

Definition 2.16. Let Σ be a Hausdorff and paracompact space. An atlas of class $\mathcal{C}^p$ ($p\geq 0$) on Σ is a collection of pairs (U_i,φ_i) (i ranging in some countable indexing set), satisfying the following conditions:

1. Each U_i is a subset of Σ and the U_i cover Σ.
2. Each φ_i is an homeomorphism of U_i onto an open subset $\varphi_i(U_i)$ of some Fréchet space $\mathscr{S}$ and for any i,j, $\varphi_i(U_i\cap U_j)$ is open in $\mathscr{S}$.
3. The transition map $\Psi_{ij}\coloneqq\varphi_j\circ\varphi_i^{-1}\colon \varphi_i(U_i\cap U_j)\subseteq\mathscr{S}\longrightarrow\varphi_j(U_i\cap U_j)\subseteq\mathscr{S}$ is a $\mathcal{C}^p$-isomorphism (a bijection of class $\mathcal{C}^p$ whose inverse is also of class $\mathcal{C}^p$).

An equivalence class of compatible atlases (as in 1.12) defines a **Fréchet manifold** structure on Σ.

Remark. From now on, we will assume that infinite-dimensional differential geometry presented in section 1.2 is conveniently adapted to Fréchet manifolds. This is the approach used in [5]. However, the existence of integral curves for arbitrary vector fields can no longer be guaranteed, due to the loss of the existence and uniqueness theorem for differential equations.

Our phase space $\mathscr{S}(\mathbb{R}^d)$ has now the structure of Fréchet manifold of only one chart. In particular, we consider it to be the natural isomorphism of the real and imaginary parts to a real functional TVS, $\mathscr{S}_r(\mathbb{R}^d)\coloneqq\{\operatorname{Re}\psi\mid\psi\in\mathscr{S}(\mathbb{R}^d)\}$,

$$\mathscr{S}(\mathbb{R}^d)\longrightarrow\mathscr{S}_r(\mathbb{R}^d)\times\mathscr{S}_r(\mathbb{R}^d)\qquad\psi\longmapsto(\operatorname{Re}\psi,\operatorname{Im}\psi)\,.$$

Let us note that the tangent and cotangent bundles will therefore be trivial bundles; we can apply then theorem C.8 (the construction also holds for Fréchet manifolds) to obtain the following isomorphisms:

$$T(\mathscr{S}(\mathbb{R}^d))\cong\mathscr{S}(\mathbb{R}^d)\times\mathscr{S}(\mathbb{R}^d)\qquad T^*(\mathscr{S}(\mathbb{R}^d))\cong\mathscr{S}(\mathbb{R}^d)\times\mathscr{S}'(\mathbb{R}^d)\,, \tag{2.3}$$

where $\mathscr{S}'(\mathbb{R}^d)$ is the space of tempered distributions, the dual of $\mathscr{S}(\mathbb{R}^d)$.

[4] See Appendix B for a complete definition of the general notion of derivative, along with a detailed example of an explicit calculational rule.

2.2.3 Weak symplecticity

In section 2.1 the laws of classical mechanics were formulated in terms of an equation involving a symplectic form (2.2). However, the far more restricted choice of physical observables led us to choose a phase space for which the symplectic structure loses its non-degeneracy. Nonetheless, we can still follow a similar strategy to cast Schrödinger equation into a Hamiltonian form, albeit losing some properties.

Definition 2.17. Let X be a (Fréchet) manifold and let $\omega \in \Lambda^2(X)$ be a two-form. We shall say that ω is a **weakly symplectic form** if

1. it is closed, i.e. $d\omega = 0$,
2. The induced continuous linear map

$$\begin{aligned} \cdot^\flat \colon \mathfrak{X}(X) &\longrightarrow \Lambda^1(X) \\ \xi &\longmapsto \xi^\flat \coloneqq i_\xi\, \omega\,, \end{aligned}$$

   where $\langle i_\xi\, \omega, \eta\rangle = \langle \omega, \xi \times \eta\rangle$ for all $\eta \in \mathfrak{X}(X)$, is injective. If the map is an isomorphism we call the form **strongly symplectic** (or symplectic, as in 2.2).

In the special case of quantum mechanics, ω is defined in terms of the scalar product of $L^2(\mathbb{R}^d)$, which is retained as $\mathscr{S}(\mathbb{R}^d) \subset L^2(\mathbb{R}^d)$.

Proposition 2.18. *The two-form $\omega \in \Lambda^2(\mathscr{S}(\mathbb{R}^d))$ defined as $\langle \omega, \xi \times \eta\rangle = 2\mathrm{Im}\langle \xi, \eta\rangle$ is weakly symplectic*[5].

Let us study more thoroughly why the two-form ω is only weakly symplectic. The structure we are working with consists of the following elements:

- A separable Hilbert space $\mathscr{H}$. In our setting $\mathscr{H} \coloneqq L^2(\mathbb{R}^d)$, the set of square-integrable functions with respect to the Lebesgue measure.
- A dense topological vector subspace $\mathscr{S}$, equipped with a topology that makes the inclusion map continuous. This will be the Schwartz space, $\mathscr{S} \coloneqq \mathscr{S}(\mathbb{R}^d)$.
- A canonical isomorphism $i_c \colon \mathscr{H} \to \mathscr{H}^*$ determined by the inner product, given by the Riesz representation theorem, denoted as $|\psi\rangle \mapsto \langle\psi| \coloneqq i_c\, |\psi\rangle$.
- The inclusion operator $j \colon \mathscr{S} \to \mathscr{H}$ defined as $\psi \mapsto |\psi\rangle$, which is linear, injective and continuous. We can consider its dual, the linear and continuous operator

$$\begin{aligned} j^* \colon \mathscr{H}^* &\longrightarrow \mathscr{S}' \\ \langle\psi| &\longmapsto \langle\psi| \circ j\,. \end{aligned}$$

Definition 2.19. We define a **Gel'fand triple** as the operator sequence

$$\mathscr{S} \xrightarrow{\ j\ } \mathscr{H} \cong \mathscr{H}^* \xrightarrow{\ j^*\ } \mathscr{S}'\,.$$

Remark. Through the Gel'fand triple we have obtained an injection of the Schwartz space in its dual. Moreover, we have proved that $\mathscr{S}$ is not bijective to $\mathscr{S}'$. Given the isomorphisms (2.3), it follows that $T(\mathscr{S})$ is not isomorphic to $T^*(\mathscr{S})$, hence the loss of the strongly symplectic structure that holds in finite dimension (as the map $\cdot^\flat$ of 2.17 cannot be an isomorphism, i.e. there may be one-forms that are not images of any vector field).

[5] In the definition of ω we have used the isomorphisms (2.3). See Appendix E for the proof.

2.2.4 Dynamics on the quantum phase space

Let us now consider dynamics on our phase space $\Sigma \coloneqq (\mathscr{S}, \omega)$, the one-chart Fréchet manifold with the Schwartz space as underlying set endowed with a weakly symplectic structure.

Definition 2.20. A family of diffeomorphisms $\{\tau_t\}_{t\in\mathbb{R}}$, $\tau_t \colon \Sigma \to \Sigma$, such that

1. $\tau_0 = \mathrm{id}_\Sigma$ and
2. $\tau_{t+s} = \tau_t \circ \tau_s$ for all $t, s \in \mathbb{R}$,

is called a **one-parameter subgroup** of diffeomorphisms.

The dynamics on Σ is modelled by one such subgroup of diffeomorphisms which preserves the symplectic structure.

Definition 2.21. Let $\{\tau_t\}_{t\in\mathbb{R}}$ be a one-parameter subgroup of diffeomorphisms on Σ. The **pullback**[6] of the weakly symplectic form ω by τ_t is the two-form $\tau_t^*\omega$ defined as

$$(\tau_t^*\omega)(x)\Big(\xi(x), \eta(x)\Big) \coloneqq \omega\big(\tau_t(x)\big)\Big((\tau_t)_{*,\,x}\,\xi(x), (\tau_t)_{*,\,x}\,\eta(x)\Big)$$

for every $x \in \Sigma$ and $\xi, \eta \in \mathfrak{X}(\Sigma)$.

Definition 2.22. We define a **dynamical system** on Σ by a one-parameter subgroup of diffeomorphisms $\{\tau_t\}_{t\in\mathbb{R}}$ such that

1. the weak symplectic structure is preserved, i.e. $\tau_t^*\omega = \omega$ for all $t \in \mathbb{R}$ and
2. there exists a vector field $\kappa \in \mathfrak{X}(\Sigma)$ such that

$$\tau_t(x) \coloneqq \exp(t\kappa) = \alpha(t)$$

where $\alpha \colon J \to \Sigma$ is an integral curve for the vector field κ with initial condition x, for all $x \in \Sigma$.

We are now ready to prove that the Schrödinger equation can be interpreted in geometrical language.

Theorem 2.23. *The one-form $\kappa^\flat$ is exact, i.e., there exists a function E, unique up to a constant such that*

$$i_\kappa\omega = dE\,. \tag{2.4}$$

Proof. (Sketch, see Appendix D for the definition of Lie derivative, [5] for further details) Since the flow defined on Σ by $\{\tau_t\}$ can be written as the integral curves of a vector field κ, the condition of structure preservation $\tau_t^*\omega = \omega$ for all $t \in \mathbb{R}$ means, by definition, that the Lie derivative $\mathscr{L}_\kappa\,\omega = 0$. Applying the identity $\mathscr{L}_\kappa = i_\kappa d + d i_\kappa$ and definition 2.17 (1.), it follows that $0 = \mathscr{L}_\kappa\omega = i_\kappa d\omega + d i_\kappa\omega = d i_\kappa\omega = d\kappa^\flat = 0$, that is, $\kappa^\flat$ is closed. As Σ is a simply connected paracompact manifold, any closed form is exact. □

It can be verified that equation (2.4) along with the definition of ω and the identification $E(\psi) = \langle\psi \mid H\psi\rangle$ for a self-adjoint operator H, the Hamiltonian, reproduces Schrödinger equation:

$$i\frac{d\psi(t)}{dt} = H\psi(t)\,.$$

[6] Note that the definition of the differential of a mapping still holds in Fréchet manifolds.

We now have discussed every component of the formalism and can thus give a brief summary of geometrical quantum mechanics:

- The states of the physical system are described by points of Σ, an infinite-dimensional Fréchet manifold with the Schwartz space $\mathscr{S}(\mathbb{R}^d)$ as underlying set and a weakly symplectic structure defined by ω (2.18).
- Given a certain dynamics (2.22) on Σ, there exists a function $E \in \mathcal{C}^\infty(\Sigma)$ which represents the energy of the system at any given point of the phase space Σ. The dynamics is determined by equation (2.4), and after identifying E with the expectation value of a self -adjoint operator H called the Hamiltonian, we can recover Schrödinger equation. Thus, on the following we will denote $f_H \coloneqq E$ and $\kappa_{f_H} \coloneqq \kappa$.
- The set of physical observables corresponds to a subset of $\mathcal{C}^\infty(\Sigma)$, the expected values of self-adjoint operators,

$$\mathcal{O} \coloneqq \left\{ f_A \in \mathcal{C}^\infty(\Sigma) \mid f_A(\psi) = \langle \psi \mid A\psi \rangle \text{ with } A^\dagger = A \right\} .$$

  Their evolution is prescribed by the vector field κ_{f_H} that determines the dynamics,

$$\dot{f_A} = \kappa_{f_H} f_A \, .$$

2.2.5 An alternative solution to weak symplecticity: the atomic model

As discussed at the beginning of this chapter, there are two alternative formalisms for geometric quantum mechanics. We have concluded that in order to achieve a geometrical formulation of a general quantum system, the approach of [5] has to be followed. However, we can elude the problem of weak-symplecticity through the introduction of a convenient class of spaces: Sobolev spaces [13]. To illustrate this, in this subsection we are going to work with a system of one atom, whose dynamics is prescribed by the atomic Hamiltonian. More formally:

Definition 2.24. Let us consider a system of N electrons of mass m and charge $-e$, and one nucleus of mass M and charge Ze. The Schrödinger Hamiltonian of this system is

$$H_{at} \coloneqq \sum_{j=1}^{N} \left(-\frac{\hbar^2}{2m} \Delta_{x_j} - \frac{e^2 Z}{|x_j|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|x_i - x_j|} \, ,$$

acting on $L^2(\mathbb{R}^{3N})$. We denote by $x = (x_1, \ldots, x_N)$ the electron coordinates. The first term on the r.h.s. is the kinetic energy of the electrons, the second is the sum of Coulomb interaction potentials between the electrons and the nucleus, which we assume to be at the origin of coordinates, and the third one is the potential energy of interactions between electrons.

Our aim is now to introduce Sobolev spaces as the suitable modelling space for the atomic dynamical system that we are interested in. Let us begin with some technical definitions.

Definition 2.25. We say that a map $u \colon \mathbb{R}^n \to \mathbb{C}$ is **locally integrable** if its restriction to every compact set $K \subset \mathbb{R}^n$ is integrable. We denote the set of locally integrable functions defined on $\mathbb{R}^n$ by ${L^1}_{loc}(\mathbb{R}^n)$.

Definition 2.26. Let $u, w \in {L^1}_{loc}(\mathbb{R}^n)$ and let $\alpha \in \mathbb{N}_0^n$ be a multi-index. We say that w is the α-th **weak partial derivative** of u, and write $\partial^\alpha u = w$ if

$$\int_{\mathbb{R}^n} u \, \frac{\partial^{|\alpha|} \varphi}{\partial x_\alpha} \, \mathrm{d}x = (-1)^{|\alpha|} \int_{\mathbb{R}^n} w \, \varphi \, \mathrm{d}x \quad \text{for all } \varphi \in \mathcal{C}_c^\infty(\mathbb{R}^n).$$

To introduce the concept of Sobolev space, we need the following result:

Lemma 2.27. *The space of integrable functions $L^p(\mathbb{R}^n)$ is a subspace of $L^1{}_{loc}(\mathbb{R}^n)$ for all $1 \leq p \leq \infty$.*

Proof. The case $k = 1$ is trivial. Let us assume $1 < p \leq \infty$. Let $u \in L^p(\mathbb{R}^n)$ and $K \subset \mathbb{R}^n$ a compact subset. Let $1 \leq q < \infty$ be a number such that $1/p + 1/q = 1$. As the characteristic function $\chi_K \in L^q(\mathbb{R}^n)$, we can apply Hölder's inequality, $\int_K |u| \, \mathrm{d}x = \int_{\mathbb{R}^n} |u| \, \chi_K \, \mathrm{d}x \leq \|u\|_p \|\chi_K\|_q < \infty$. □

Definition 2.28. Let $k \in \mathbb{N}$ and $1 \leq p \leq \infty$. Then, the **Sobolev space** of order k, p is defined as

$$W^{k,\,p}(\mathbb{R}^n) \coloneqq \{u \in L^p(\mathbb{R}^n) \mid \partial^\alpha u \text{ exists and } \partial^\alpha u \in L^p(\mathbb{R}^n) \text{ for all } \alpha \in \mathbb{N}_0^n \text{ with } |\alpha| \leq k\} \, .$$

If $p = 2$, we denote $W^{k,\,2}(\mathbb{R}^n) \coloneqq H^k(\mathbb{R}^n)$. We equip $H^k(\mathbb{R}^n)$ with the norm $\|\cdot\|_{H^k}$ defined by

$$\|u\|_{H^k} \coloneqq \left(\sum_{|\alpha| \leq k} \|\partial^\alpha u\|_{L^2} \right)^{1/2} \qquad u \in H^k(\mathbb{R}^n) \, .$$

Lemma 2.29. *In the particular case $k = p = 2$, $H^2(\mathbb{R}^n)$ is a Hilbert space and its norm is equivalent to the norm*

$$\|u\| \coloneqq \left(\|u\|_{L^2}{}^2 + \|\Delta u\|_{L^2}{}^2 \right)^{\frac{1}{2}} \qquad u \in H^2(\mathbb{R}^n) \, .$$

Once we have introduced the definition of Sobolev space, we reach the crucial point of our construction: the self-adjointness domain of H_{at} is one of such spaces.

Lemma 2.30. *Let $x = (x_1, \ldots, x_N) \in \mathbb{R}^{3N}$. The atomic Hamiltonian operator defined in 2.24, $H_{at} \colon H^2(\mathbb{R}^{3N}) \subset L^2(\mathbb{R}^{3N}) \longrightarrow L^2(\mathbb{R}^{3N})$, is self-adjoint.*

Sobolev spaces arise when studying solutions of partial differential equations. The following theorem ensures that we no longer lose the Picard existence-uniqueness theorem for the Schrödinger PDE as we did in the general formalism.

Theorem 2.31. *Let $H \colon \mathscr{D}(H) \subset \mathscr{H} \to \mathscr{H}$ be a self-adjoint operator. Then, for all $u \in \mathscr{D}(H)$, the problem*

$$\begin{cases} i\hbar \, \partial_t \psi(t) = H\psi(t) \\ \psi(0) = u \end{cases}$$

has a unique global solution, $\psi \colon \mathbb{R} \to \mathscr{H}$ satisfying $\psi(t) \in \mathscr{D}(H)$ for every $t \in \mathbb{R}$. Moreover, there exists a unitary group element such that $\varphi(t) = U(t)u$ for all $t \in \mathbb{R}, u \in \mathscr{D}(H)$.

The two-form ω is therefore strongly symplectic when modelling our phase space as a Sobolev manifold [14], and we can understand the evolution prescribed by Schrödinger equation in a geometric framework analogous to the formalism of classical mechanics (2.1). However, the main drawback of this approach is that some observables might not be continuous or even be defined on a Sobolev space. For example, the molecular Hamiltonian with which we work in hybrid mechanics is essentially self-adjoint in a subset of the Schwartz space; therefore, we must choose the approach of [5].

Chapter 3

Hybrid systems

In the previous chapter we have formulated classical and quantum mechanics on geometrical terms; we are now ready to describe the evolution of hybrid classical-quantum systems on the same framework. As we already mentioned, one particularly relevant hybrid system is the molecular model governed by the Ehrenfest equations. This system has already been endowed with a Hamiltonian structure [7], albeit modelling the quantum degrees of freedom on $\mathbb{C}^n$. The aim of this section is to extend this Hamiltonian structure to the more general setting of an infinite-dimensional quantum phase space. The road map is the following: we start by presenting the Ehrenfest model; then, we define a hybrid phase space and find a suitable weakly symplectic form; finally, a dynamical system is implemented in the same way as we did for classical and quantum systems: given an initial condition, the solution to Ehrenfest equations follows the integral curves of a vector field.

3.1 The Ehrenfest model

Definition 3.1. Let us consider a purely quantum **molecular system** of N_e electrons and N_n nuclei of masses m and M_J respectively, and charges $-e$ and $Z_J e$ respectively, for $J = 1, \dots, N_n$. Its state at a particular instant of time is characterised by a wavefunction[1] $\Phi \in L^2\left(\mathbb{R}^{3(N_n+N_e)}\right)$, whose value at a point is denoted as $\Phi(R, r)$, where $R \in \mathbb{R}^{3N_n}$ and $r \in \mathbb{R}^{3N_e}$ are the electronic and nuclear degrees of freedom respectively. The evolution of the system is determined by the full-quantum molecular Hamiltonian,

$$\begin{aligned} H_{mol} \coloneqq & -\sum_J \frac{\hbar^2}{2M_J}\nabla_J^2 - \sum_j \frac{\hbar^2}{2m}\nabla_j^2 + \frac{1}{4\pi\varepsilon_0}\sum_{J<K}\frac{e^2 Z_J Z_K}{|R_J - R_K|} \\ & + \frac{1}{4\pi\varepsilon_0}\sum_{j<k}\frac{e^2}{|r_j - r_k|} - \frac{1}{4\pi\varepsilon_0}\sum_{J,\,j}\frac{e^2 Z_J}{|R_J - r_j|} \\ =: & -\sum_J \frac{\hbar^2}{2M_J}\nabla_J^2 - \sum_j \frac{\hbar^2}{2m}\nabla_j^2 + V_{n-e}(r, R) =: -\hbar^2 \sum_J \frac{1}{2M_J}\nabla_J^2 + H_e(r, R)\ , \end{aligned}$$

where every sum is understood as running over the natural indexing set for electrons and nuclei ($J, K = 1, \dots, N_n$ and $j, k = 1, \dots, N_e$). Note that we have defined two operators, the nuclear -electronic potential operator V_{n-e} and the electronic Hamiltonian H_e.

[1] If we take into consideration that the electrons and some nuclei are identical particles, the wavefunction has to be an element of $L^2_{skew}\left(\mathbb{R}^{3(N_e+N_n)}\right)$, antisymmetric wavefunctions under permutation of two electronic or nuclear coordinates; see [13] for details.

In order to obtain a hybrid classical-quantum model from a full-quantum system, some approximations have to be made. Firstly, the wavefunction can be factorised as

$$\Phi(R,r) = \varphi(R)\psi(r) \quad \text{with} \quad \Phi \in L^2\left(\mathbb{R}^{3(N_n+N_e)}\right),\ \varphi \in L^2\left(\mathbb{R}^{3N_n}\right),\ \psi \in L^2\left(\mathbb{R}^{3N_e}\right),$$

leading to two coupled quantum subsystems (self-consistent-field model). Afterwards, a suitable classical limit is taken on the nuclear variables, leading to the Ehrenfest equations, which prescribe the coupled evolution of classical and quantum degrees of freedom, i.e. a hybrid system [16]. Let us present them without further ado.

Definition 3.2. Let $R_J, P_J \in \mathbb{R}^3$ denote the position and momentum of the J-th nucleus, and let $(R,P) \in \mathbb{R}^{3N_n} \times \mathbb{R}^{3N_n}$ denote the classical positions and momenta of the nuclei collectively. Let $|\psi\rangle \in L^2\left(\mathbb{R}^{3N_e}\right)$ be the wavefunction which encodes the state of the electrons of the system. The **Ehrenfest equations** are

$$\dot{R}_J = \frac{P_J}{M_J} \tag{3.1}$$

$$\dot{P}_J = -\nabla_J \langle\psi|H_e(r,R)|\psi\rangle \tag{3.2}$$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = H_e(r,R)\,|\psi\rangle\ , \tag{3.3}$$

with $J = 1,\dots,N_n$. In equation (3.2), the term $\langle\psi|H_e(r,R)|\psi\rangle$ is called the **effective potential** created by the electronic charge distribution, as it plays that role on the classical subsystem.

Remark. Note that equation (3.3) is the Schrödinger equation depending on a parameter, R, whose evolution is prescribed by equation (3.1); therefore, the evolution of the total system is non-linear and thus, the evolution of the quantum subsystem is not unitary, although the scalar product structure is still preserved.

3.2 Hybrid phase space

Again, we start the construction of our model by identifying the phase space. The central idea is to consider a Cartesian product of two manifolds, each one being the phase space where the classical and quantum degrees of freedom lie.

- Firstly, there are $2n \coloneqq 6N_n$ degrees of freedom associated with the nuclear subsystem, denoted collectively as (R,P) (i.e. N_n three-dimensional positions and their corresponding momenta). As in 2.1, the phase space is the cotangent bundle $T^*(\mathbb{R}^n)$, a real symplectic manifold of dimension $2n$ with symplectic form ω_C (2.3). We denote $\mathcal{M}_C \coloneqq \left(T^*(\mathbb{R}^n), \omega_C\right)$.
- The quantum degrees of freedom associated with the electronic subsystem are modelled on a dense subspace of $L^2\left(\mathbb{R}^{3N_e}\right)$, the Schwartz space $\mathscr{S}(\mathbb{R}^d)$, $d \coloneqq 3N_e$. This set can be endowed with the structure of weakly symplectic Fréchet manifold, with symplectic form ω_Q (2.18). We denote $\mathcal{M}_Q \coloneqq \left(\mathscr{S}(\mathbb{R}^d), \omega_Q\right)$.
- The **hybrid phase space** is defined as

  $$\mathcal{M}_C \times \mathcal{M}_Q$$

  which (for the moment) has the structure of Fréchet manifold modelled on $\mathbb{R}^{2n} \times \mathscr{S}(\mathbb{R}^d)$ (1.13 also holds for Fréchet manifolds).

3.3 Weak symplecticity

Let us define now a weakly symplectic structure on our phase space.

Theorem 3.3. *Let $\mathcal{M}_C \times \mathcal{M}_Q$ be the hybrid phase space and let ω_C and ω_Q the symplectic forms defined on $\mathcal{M}_C$ and $\mathcal{M}_Q$ respectively (section 3.2). Let*

$$\pi_C \colon \mathcal{M}_C \times \mathcal{M}_Q \longrightarrow \mathcal{M}_C \qquad \text{and} \qquad \pi_Q \colon \mathcal{M}_C \times \mathcal{M}_Q \longrightarrow \mathcal{M}_Q$$

be the canonical projections. The two-form defined on $\mathcal{M}_C \times \mathcal{M}_Q$ as (see 2.21)

$$\omega_H \coloneqq \pi_C^* \, \omega_C + \pi_Q^* \, \omega_Q$$

is weakly symplectic.

Proof. Firstly, let us check that the two-form is well-defined. The pullbacks of the symplectic forms ω_C and ω_Q by the canonical projections π_C and π_Q are two-forms defined on $\mathcal{M}_C \times \mathcal{M}_Q$ as

$$\begin{aligned}
(\pi_C^* \, \omega_C)(x)\Big(\xi(x), \eta(x)\Big) &\coloneqq \omega_C(R,P)\Big((\pi_C)_{*,\,x} \, \xi(x), (\pi_C)_{*,\,x} \, \eta(x)\Big) \\
(\pi_Q^* \, \omega_Q)(x)\Big(\xi(x), \eta(x)\Big) &\coloneqq \omega_Q(\psi)\Big((\pi_Q)_{*,\,x} \, \xi(x), (\pi_Q)_{*,\,x} \, \eta(x)\Big)
\end{aligned}$$

for every $x = \Big((R,P),\psi\Big) \in \mathcal{M}_C \times \mathcal{M}_Q$, $\xi, \eta \in \mathfrak{X}\,(\mathcal{M}_C \times \mathcal{M}_Q)$. Their sum is clearly bilinear and antisymmetric, thus a two-form. We have to prove that ω_H is closed and non-degenerate 2.17.

1. Since the exterior derivative commutes with the pullback operation ([11] Chapter 3, p. 135, Property 2) and the two-forms ω_C and ω_Q are weakly symplectic (thus closed),

   $$d\omega_H = d\omega_C + d\omega_Q = d(\pi_C^* \, \omega_C) + d(\pi_Q^* \, \omega_Q) = \pi_C^*(d\omega_C) + \pi_Q^*(d\omega_Q) = 0 \, ,$$

   and therefore ω_H is closed.

2. To prove that the induced continuous linear map

   $$\begin{aligned}
   \cdot^\flat \colon \mathfrak{X}\,(\mathcal{M}_C \times \mathcal{M}_Q) &\longrightarrow \Lambda^1\,(\mathcal{M}_C \times \mathcal{M}_Q) \\
   \xi &\longmapsto \xi^\flat \coloneqq i_\xi \, \omega_H \, ,
   \end{aligned}$$

   is injective, we are going to check that its kernel is zero, that is,

   $$i_\xi \, \omega_H(\eta) = 0 \quad \text{for all } \eta \in \mathfrak{X}\,(\mathcal{M}_C \times \mathcal{M}_Q) \implies \xi = 0 \, .$$

   Firstly, let us calculate the explicit form of the differential map $(\pi_C)_{*,\,x}$. Let us take a chart (φ, U) of $\mathcal{M}_C$ at (R,P). Clearly, $\Phi \coloneqq (\varphi, \mathrm{id}_{\mathscr{S}}) \colon \mathcal{U} \coloneqq U \times \mathscr{S}(\mathbb{R}^d) \longrightarrow \mathbb{R}^{2n} \times \mathscr{S}(\mathbb{R}^d)$ is a chart of $\mathcal{M}_C \times \mathcal{M}_Q$ at x. Then, according to 1.17, the diagram

   $$\begin{array}{ccc}
   T_x(\mathcal{M}_C \times \mathcal{M}_Q) & \longrightarrow & \mathbb{R}^{2n} \times \mathscr{S}(\mathbb{R}^d) \\
   {\scriptstyle (\pi_C)_{*,\,x}}\downarrow & & \downarrow{\scriptstyle (\pi_C)'_{\mathcal{U},\mathcal{U}}(\Phi x)} \\
   T_{(R,\,P)}(\mathcal{M}_C) & \longleftarrow & \mathbb{R}^{2n}
   \end{array}$$

   is commutative. Moreover, $(\pi_C)'_{\mathcal{U},\mathcal{U}}(\Phi x)$ is the canonical projection $\mathbb{R}^{2n} \times \mathscr{S}(\mathbb{R}^d) \to \mathbb{R}^{2n}$ since $(\pi_C)_{\mathcal{U},\mathcal{U}}$ is linear (B.5). We have therefore proved that the differential map $(\pi_C)_{*,\,x}$ is nothing else than the canonical projection on the tangent spaces, $T_x(\mathcal{M}_C \times \mathcal{M}_Q) \cong T_{(R,\,P)}(\mathcal{M}_C) \oplus T_\psi(\mathcal{M}_Q) \longrightarrow T_{(R,\,P)}(\mathcal{M}_C)$. Analogously, $(\pi_Q)_{*,\,x}$ is the other projection.

Let us consider a vector field $\xi \in \mathfrak{X}(\mathcal{M}_C \times \mathcal{M}_Q)$ such that $i_\xi\, \omega_H(\eta) = 0$ for every $\eta \in \mathfrak{X}\,(\mathcal{M}_C \times \mathcal{M}_Q)$. In particular, the above expression will vanish for the vector fields whose projection onto every tangent space $T_\psi(\mathcal{M}_Q)$ is constantly zero for every $\psi \in \mathcal{M}_Q$. We have that, at each $x \in \mathcal{M}_C \times \mathcal{M}_Q$,

$$\begin{aligned}
&\omega_H(x)\Big(\xi(x), \eta(x)\Big) = \\
&= \omega_C(R,P)\Big((\pi_C)_{*,\,x}\,\xi(x), (\pi_C)_{*,\,x}\,\eta(x)\Big) + \omega_Q(\psi)\Big((\pi_Q)_{*,\,x}\,\xi(x), (\pi_Q)_{*,\,x}\,\eta(x)\Big) \\
&= \omega_C(R,P)\Big((\pi_C)_{*,\,x}\,\xi(x), (\pi_C)_{*,\,x}\,\eta(x)\Big) + \underbrace{\omega_Q(\psi)\Big((\pi_Q)_{*,\,x}\,\xi(x), 0\Big)}_{=\,0} = 0\,,
\end{aligned}$$

and the projection of ξ onto every tangent space $T_{(R,\,P)}(\mathcal{M}_C)$ must vanish, since ω_C is weakly symplectic. We can follow an analogous procedure for the projection onto $T_\psi(\mathcal{M}_Q)$ and conclude that ξ must be zero, completing the proof.

□

3.4 Dynamics on the hybrid phase space

We can finally proceed to our goal: the geometrical description of the Ehrenfest equations on infinite-dimensional manifolds. The dynamics is implemented as follows:

- The states of the molecular hybrid classical-quantum system are encoded by points of $\mathcal{M}_C \times \mathcal{M}_Q$, a Fréchet manifold endowed with a symplectic form, ω_H (3.3). Note that a more general classical phase space could be considered, namely a generic symplectic manifold (M, ω_C). Indeed, the most relevant feature is that both spaces, classical and quantum, can be endowed with a symplectic structure.

- The dynamics is then determined by the hybrid energy function, $f_{CQ} \in \mathcal{C}^\infty\,(\mathcal{M}_C \times \mathcal{M}_Q)$, defined as

$$f_{CQ}(R,P,\psi) = \sum_J \frac{P_J^2}{2M_J} + \langle\psi|\, H_e(R,P)\,|\psi\rangle\ ,$$

  where $R_J, P_J \in \mathbb{R}^3, J = 1,\ldots,N_n$ denote the nuclear positions and momenta, $\psi \in \mathcal{M}_Q$ denotes the electronic wavefunction and H_e is the electronic Hamiltonian defined in (3.1). Assuming the existence of a vector field Ξ which satisfies the equation

$$i_\Xi\, \omega_H = df_{CQ}\ ,$$

  it can be verified that the integral curves of Ξ are the solutions to Ehrenfest equations (3.1) - (3.3).

- Similarly to the classical and quantum geometrical formalisms, the observables' evolution is prescribed by the vector field Ξ that encodes the dynamics,

$$\dot{f} = \Xi f \quad f \in \mathcal{C}^\infty\,(\mathcal{M}_C \times \mathcal{M}_Q)\ .$$

Chapter 4

Conclusions

The main objective of this work was the generalisation of the Hamiltonian structure with which the Ehrenfest dynamical system was equipped in [7] to the infinite-dimensional setting. As we proved in chapter 3, we have been successful in our purpose, obtaining an almost identical formalism to the finite-dimensional case. However, the main drawback of this construction is the lack of a strongly symplectic structure due to the nature of the modelling space. Indeed, the fact that the induced continuous linear map

$$\begin{aligned} \cdot^\flat \colon \mathfrak{X}(\mathcal{M}_C \times \mathcal{M}_Q) &\longrightarrow \Lambda^1(\mathcal{M}_C \times \mathcal{M}_Q) \\ \Xi &\longmapsto \Xi^\flat \coloneqq i_\Xi\, \omega_H \end{aligned}$$

is not bijective has some implications:

- Given any Hamiltonian function f, we cannot guarantee that there exists a vector field Ξ such that

  $$i_\Xi\, \omega_H = df\ .$$

  Instead, we have to either assume that df belongs to the subset $\cdot^\flat(\mathfrak{X}(\mathcal{M}_C \times \mathcal{M}_Q)) \subset \Lambda^1(\mathcal{M}_C \times \mathcal{M}_Q)$ or start by defining a vector field Ξ and then obtain its associated function, which is the approach of [5].

- It is no longer possible to relate the symplectic form with Poisson brackets, as the Poisson tensor (2.5) requires the map $\cdot^\flat$ to be invertible. Thus, we have opted for a description in terms of symplectic forms to make the combination of classical and quantum structures easier.

We finally discuss some possible lines of future work:

- Whereas we have proved that the Ehrenfest model can be cast into an infinite-dimensional Hamiltonian structure, we could possibly consider more general dynamics, such as the one defined in [17].

- We could also consider now the extension of the formalism to statistical mechanics; for that purpose, the main requirement would be the definition of a probability measure over the infinite-dimensional phase space which remains invariant under the defined dynamics.

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