TESIS DE LA UNIVERSIDAD
DE ZARAGOZA
2016
8

Carlos Benavides Riveros

Disentangling the marginal problem in quantum chemistry

Departamento
Física Teórica

Director/es
Gracia Bondía, José Mariano

ISSN 2254-7606

Prensas de la Universidad
Universidad Zaragoza

Servicio de Publicaciones

ISSN 2254-7606

Tesis Doctoral

DISENTANGLING THE MARGINAL PROBLEM IN QUANTUM CHEMISTRY

Autor

Carlos Benavides Riveros

Director/es

Gracia Bondía, José Mariano

UNIVERSIDAD DE ZARAGOZA
Física Teórica

2015

Universidad de Zaragoza

Disentangling the marginal problem in quantum chemistry

Carlos L. Benavides Riveros

A thesis submitted in fulfillment of the requirements
for the degree of Doctor en Física

in the

Facultad de Ciencias
Departamento de Física Teórica

September 24, 2015

Antes de nós nos mesmos arvoredos
Passou o vento, quando havia vento,
E as folhas não falavam
De outro modo do que hoje.

Ricardo Reis

He escrito un viento, un soplo vivo
del viento entre fragancias, entre hierbas
mágicas; he narrado
el viento; sólo un poco de viento.

Aurelio Arturo

Universidad de Zaragoza
Facultad de Ciencias
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Disentangling the marginal problem in quantum chemistry

by Carlos L. Benavides Riveros

Abstract

It is well known that determining the energy of molecules and other quantum many-body systems reduces in the standard approximation to optimizing a simple linear functional of a 12-variable object, the two-electron reduced density matrix (2-RDM). The difficulty is that the variation ensemble for that functional has never been satisfactorily determined. This is known as the N-representability problem of quantum chemistry (which to a large extent is a problem of quantum information theory). The situation has given rise to competing research programs, typically trading more complicated functionals for simpler representability conditions. Chief among them is density functional theory, based on a three-variable object for which the N-representability is trivial, whereas the exact functional is very strange indeed, and probably forever unknowable. An intermediate position is occupied by 1-RDM functional theory. Postulated by Pauli to explain the electronic structure of atoms and molecules, the exclusion principle establishes an upper bound of 1 for the fermionic natural occupation numbers ($n_i \leq 1$), accordingly allowing no more than one electron in each quantum state. This is a necessary and sufficient condition for a 1-RDM to be the contraction of an *ensemble* N-body density matrix, provided that $\sum_i n_i = N$. The fermionic one-body quantum marginal problem asks whether given natural occupation numbers can arise from an antisymmetric (*ensemble* or *pure*) N-particle state.

The configuration interaction method affords optimal descriptions of quantum states of atoms and molecules by expanding the wave function in terms of orbital-based configurations of Slater determinants. For these systems, the dimension of the Hilbert space grows binomially with m, the number of spin-orbitals in the basis of the one-particle Hilbert space, and N, the number of electrons of the system. It has been observed that for the rank-six approximation of a *pure-state* $N = 3$ system, belonging to the Hilbert space $\wedge^3\mathcal{H}_6$, the occupation numbers satisfy some additional constraints: $n_r + n_{7-r} \leq 1$, for $r \in \{1, 2, 3\}$ and $n_1 + n_2 + n_4 \leq 2$. The first set of inequalities (which become equalities on imposing the sum rule $\sum_i n_i = 3$) allows exactly *one* electron in the natural orbitals r and $7 - r$. It is worth noting that the second inequality is stronger than the Pauli principle, which only states that $n_1 + n_2 \leq 2$. The recent analysis by Alexander Klyachko and coworkers of the one-body marginal problem of the *pure* N-fermion state establishes a systematic approach to this type of constraints. In fact, for a pure quantum system of N electrons arranged in m spin-orbitals the occupation numbers satisfy a set of linear inequalities, known as *generalized Pauli constraints* (GPC)

$$D^{\mu}_{N,m}(\boldsymbol{n}) = \kappa^{\mu}_0 + \kappa^{\mu}_1 n_1 + \cdots + \kappa^{\mu}_m n_m \geq 0, \tag{1}$$

with $\boldsymbol{n} := (n_1, \ldots, n_m)$, the coefficients $\kappa_j^\mu \in \mathbb{Z}$ and $\mu = 1, 2, \ldots, r_{N,m}$. These inequalities define a convex polytope of allowed states in $\mathbb{R}^m$. They are conditions for a 1-RDM to be the contraction of a *pure* N-body state.

When one of the GPC is completely saturated, the system is said to be *pinned*, and it lies on one of the facets of the polytope. The nature of those conditions has been explored till now only in a few systems: a model of three spinless fermions confined to a one-dimensional harmonic potential, the lithium isoelectronic series and ground and excited states of some three- and four-electron molecules for the rank being at least twice the number of electrons. For all these systems the inequalities are (quite often) *nearly saturated*, that is, in equations like (1) the equality almost holds. This is the so-called *quasipinning* phenomenon.

In this PhD thesis we have taken up the challenge of using numerical and analytical methods to examine pinned and quasipinned states, for atoms and molecules, starting from scratch with configuration-interaction and multiconfiguration self-consistent methods. This procedure serves to study the occurrence of quasipinning in realistic systems. A second goal is to show how the subsets of pinned states defined by GPC give rise to the most efficient approach from a computational viewpoint, yielding the leading order of the electron-electron correlations. As a consequence, we underline in this thesis the theoretical and practical importance of Klyachko's approach to the quantum marginal problem and its impact on the competing research programs to determine feasible electronic densities, 1-RDM, 2-RDM, intracular distributions or Wigner density quasiprobabilities.

In relation with the above, our research provides a new variational optimization method for few-fermion ground states. We quantitatively confirm its high accuracy for quasipinned systems and derive an upper bound on the error of the correlation energy given by the ratio of the numerical value of the Klyachko inequality and the distance to the Hartree-Fock point. Depending on the details of the algorithm, we are able to reach $97\% - 99\%$ of the correlation energy for such systems.

Keywords: *Quantum chemistry*, *Quantum marginal problem*, *N-representability problem*, *Generalized Pauli exclusion principle*.

To the memory of my father

Acknowledgements / Agradecimientos

There are many people that I would like to thank when looking back to my years at Zaragoza, Bielefeld and Saarbrücken. First and foremost, I am deeply indebted to my thesis advisor José Gracia-Bondía who was always there whenever I needed him. Pepe's constant support of my research all these years, as well as his patience, enthusiasm and immense knowledge were essential for this work. I simply could not ask for a better advisor, and this is why I would like to express my deepest gratitude with my former master's advisor Andrés Reyes-Lega, who not only introduced me to Pepe but also encouraged me to come back to physics after three years in the world of financial risks.

This thesis would not be possible without the outstanding researchers with whom I had the opportunity to collaborate and discuss: Joseph Várilly, Michael Springborg, Jesús Sánchez-Dehesa Moreno-Cid and Christian Schilling. I would also like to express my heartfelt gratitude to them for their persistent support and encouragement. I bothered several people with silly and tedious questions and what I got in return was their desire to share with me their knowledge with great patience and kindness: José Luís Alonso Buj, Philippe Blanchard, Jürg Fröhlich, Alonso Botero, Pablo Echenique, David Gross, Heinz Siedentop, Michael Walter, Ángel Plastino, Miguel Marques, Antonio Acín, David Mazziotti, Filiberto Ares and Amílcar de Queiroz.

Ich möchte auch allen meine Kollegen in Saarbrücken meinen tiefsten Dank aussprechen: Jorge Vargas, Stephen Kohaut, Nathalie Kunkel, Mohammad Molayem, Yi Dong, Max Ramírez und Nicolas Louis. Besonderen Dank möchte ich Claudia Iannetti-Myres widmen: vielen Dank für deine Zuneigung und das aufgebrachte Verständnis während meiner Zeit in Deutschland.

Mi sincera gratitud a mis compañeros de despacho en la Universidad de Zaragoza: Arián Abrahantes (su querida esposa Ismara y la pequeña que viene en camino) y Beatriz Romeo quienes muchas veces me sacaron de algunos puntos oscuros. A Pedro Justes, quien me enseñó y animó a correr, y a Esther Gimeno, que me tuvo paciencia con tantas preguntas. A la pequeña comunidad colombiana en Zaragoza (ahora repartida por todo el mundo): Adriana Figueroa, Roberto Boada, Diana Carolina Herrera, Lorena Marín y Luís Alfredo Rodriguez. Mi más sincero agradecimiento a Silvia Castro, por su cariñoso consejo y apoyo permanente.

Esta tesis está dedicada a la memoria de mi padre pero también a todas las personas que con su cariño, comprensión y sincera amistad me acompañaron durante los años de esta investigación. En primerísimo lugar a mi familia: mi amorosa madre y mis hermanos Juan Manuel y Diana Carolina. Quiero mencionar también a Andrea Matiz (por aquellos buenos y felices años juntos en Europa), Rebeca Herrero-Hahn y Carolina Sánchez. A los compañeros cuya amistad vine a recobrar en Europa: Grenfieth Sierra, Felipe Carrillo, Paola Castaño, Carolina Medina y Mariana Herrera. Finally, I'd like to acknowledge also Katarzyna Iwańska and Abhishek Prabhu: Dziękuje bardzo za wspaniały czas który spedzilismy razem w Zaragoza! My last words go to Anna Koudelková. Díky, malá Anno. Tato práce ti vděčí za hodně - víc, než si mysííš. Děkuji, že jsi mi dala inspiraci k dokončení.

Financial acknowledgements

The author would like to acknowledge the financial support of:

- Departamento Administrativo de Ciencia, Tecnología e Innovación (Colciencias).
- Banco Santander Universidades.
- Ministerio de Economía y Competitividad de España, under grant FPA2013-35453.

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FIGURE 2: Alexander Klyachko, a drawing by Juan Manuel Benavides.

Chapter 1

Introduction

1.1 The Pauli principle and its generalization

In January 1925 Wolfgang Pauli announced the famous principle which takes his name. The content of this principle is a rule that excludes the possibility of any two electrons in a quantum system occupying the same state. Hence the original name: *Ausschliessungsregel*: exclusion rule. It is difficult to underestimate the importance of this principle. Since high-school days, every civilized person is familiar with the very basic idea: in an atom there cannot be two identical fermions for which the value of all quantum numbers coincide. Among other things, it explains the classification of atoms in the periodic table, the electronic structure of atoms and molecules and in the end the stability of matter. The entire principle, as well as its counterpart for bosons, can be understood as a constitutively *a priori* element of quantum mechanics [Mas05, RLBR10].

Originally Pauli introduced the exclusion principle as a phenomenological rule to explain some known spectroscopic anomalies [Mas05]. However, a revolution was accomplished when Dirac transplanted the Pauli principle from its phenomenological domain onto the framework of the new quantum mechanics. The exclusion rule became thus the manifestation of a mathematical fact: the antisymmetric character of the wave function of an assembly of indistinguishable fermions. In fact, as Dirac pointed out in 1926 in a celebrated paper, an antisymmetrical wave function vanishes identically when two of the particles occupy the same spin-orbit, which implies the Pauli principle [Dir26].

In quantum chemistry, due to its very involved structure, one is keen to avoid the use of wave functions and replace them for n-body reduced density matrices (n-RDM), the contractions of *pure* or *ensemble* N-body density matrices [Dav76]. In this context, the Pauli exclusion principle is formulated otherwise as stating that the natural occupation numbers (the eigenvalues of the 1-RDM) can be no larger than 1 and no smaller than 0. This upper bound for the spin-orbital occupancies allows no more than one electron in each quantum state. This simple condition, formulated by Coleman in 1963 [Col63], is necessary and sufficient for a 1-RDM to be the contraction of an *ensemble* N-body density matrix, provided the trace condition holds: the sum of all occupation numbers must be equal to N [LS10]. In practice, these numbers are either very close to 0 or very close to 1. Assuming that some states are occupied or empty lessens the configuration space to which the wave function belongs. For instance, the celebrated Hartree-Fock approximation is based on the assumption that each orbital is completely filled from the lowest one up to the highest (the first N occupation numbers are pinned to the upper bound of 1 and the remaining ones pinned to the lower bound). Accordingly, a lone Slater determinant is employed in the optimization Hartree-Fock process.

Given that the Pauli principle, beyond its fundamental nature, allows strong structural implications on the wave function, researches have been looking for ways to generalize it. In the 1970s it was observed that further linear constraints for the natural occupation numbers emerge as a consequence of the global antisymmetry; they are called *generalized Pauli constraints*. One particular example is the so-called Borland-Dennis setting $\wedge^3\mathcal{H}_6$: a pure system of three fermions arranged in a 6-dimensional one-particle Hilbert space [BD72]. For the aforementioned system the natural occupation numbers (arranged in the customary decreasing order $n_i \geq n_{i+1}$) satisfy four additional linear inequalities, stronger than the Pauli principle, namely:

$$n_1 + n_6 \leq 1, \quad n_2 + n_5 \leq 1, \quad n_3 + n_4 \leq 1 \quad \text{and} \quad n_1 + n_2 + n_4 \leq 2. \tag{1.1}$$

Two important observations arise: all these inequalities (the first three actually become equalities on imposing the trace condition) are much stronger than the Pauli principle, which only states that $n_i \leq 1$ and consequently $n_1 + n_2 \leq 2$. More important, there is also a geometric representation of generalized Pauli constraints of the sort (1.1), for the natural occupation numbers lie in a hyperdimensional object with flat sides called a convex polytope.

In a groundbreaking work, Alexander Klyachko (see Fig. 2) and coworkers exhibited an algorithm for computing all such generalized Pauli constraints and provided dozens of them for some systems with tree, four and five fermions [Kly06, AK08]. What they actually did was to solve the *pure* N-representability problem for the 1-RDM, establishing a systematic approach for concrete systems. The bulk of Klyachko's work is connected to a more general effort in quantum information theory, addressing the so-called quantum marginal problem:

> *Consider a system of N identical fermions, whose corresponding Hilbert space of antisymmetric states is $\wedge^N\mathcal{H}_m$. For a given $n \in \{1, 2, \ldots, N-1\}$, the problem of determining the set of admissible n-RDM γ_n that arises via partial integrations from a corresponding* ***pure/ensemble*** *N-density operator γ_N is the quantum marginal problem, or, in the jargon of quantum chemistry, the N-representability problem.*

The starting point is thus a pure fermionic state subject to the total antisymmetry under particle exchange. Klyachko showed that for fixed particle number N arranged in m spin-orbitals, the generalized Pauli constraints amount to affine inequalities of the form

$$D_{N,m}(\vec{n}) = \kappa_0 + \kappa_1 n_1 + \cdots + \kappa_m n_m \geq 0, \tag{1.2}$$

with the coefficients $\kappa_j \in \mathbb{Z}$. These conditions define a convex polytope of allowed states in $\mathbb{R}^m$. When one of the generalized Pauli constraints is completely saturated [i.e., equality holds in Eq. (1.2)], the system is said to be *pinned*, and it lies on one of the facets of the polytope, with remarkable structural simplifications of the wave function [Kly09, SGC13]. This scenario allows us to ask if these additional constraints are physically relevant, meaning: are they close to saturation for realistic systems? It seems that the answer is yes [SGC13, BRGBS13, BRS15b]: although in general the occupation numbers do not lie exactly on a facet of the allowed convex polytope, for some weakly correlated ground states they are significantly closer to the facet than to the Hartree-Fock point (that is, the extreme vertex where Slater determinants lie).

To explain the connection between ground states and quasipinning phenomena, Klyachko postulates that the generalized Pauli constraints might be the mechanism responsible for restricting the ground-state energy [Kly09]. This constitutes an unexpected and intriguing connection because the Pauli principle is purely kinematic (it only talks about allowed states), whereas the ground-state energy is a dynamical quantity which depends on a given Hamiltonian. A broad research program has started in the last three years to study the link between ground-state energy, quasipinning and correlation energy [SGC13, BRGBS13, CM14, BRGBS14, Sch15, BRS15b, CM15b, TLMH15, BRS15a]. A readable review on the subject has been recently written by Chakraborty and Mazziotti [CM15a].

Many years before he faced the firing squad, his father took Colonel Aureliano Buendía to discover ice. “An enormous, transparent block in which the light of the sunset was broken up into colored stars”, that is what he would remember as a prodigious experience, even when he was facing death. The Generalized Pauli principle has been ruling the spectra of pure states from the beginning of quantum mechanics, but it was not until now that Alexander Klyachko opened the pirate chest that contained it, allowing us to see inside. It is not perhaps the greatest invention of our time, but doubtless it is a prodigious experience that we should long remember.

1.2 Statement of results

There are several technical issues that hamper progress towards a more accurate description of quantum chemical systems. Some computational problems are almost intractable, meaning that for a large number of particle modes the solution of the worst case demands a quantity of operations that grows exponentially with that number. Moreover, some problems in quantum chemistry belong to the QMA-complete complexity class, which means that they are at least NP-hard [LCV07]. The ultimate dream of quantum chemistry is to find useful tools to calculate correlation energies at a computational cost as low as possible. We discuss in this thesis how certain proposals (1-RDM and 2-RDM functional theory, intracular distributions, Wigner density quasiprobabilities and quasipinning theory) latch onto it.

New theoretical frameworks need room to fittingly grow, since the application of the full force of methodological criteria could defeat them prematurely. To explain the early stages of a (Kuhnian) scientific change, Imre Lakatos postulated the existence of a temporary suspension of methodological judgment in the sense that some requirements of empirical adequacy are weakened during the birth of nascent theories [Lak78]. We are not advocating a suspension of scientific criteria for some of the proposals contained in this dissertation, but we are justifying our propensity to use sometimes (but not always) ‘toy’ models, in order to gain insight for further developments, as is the case of the pinning-MCSCF optimization procedure we propose in Chapter 8.

For the sake of clarity we would like to summarize some of the main results of this thesis:

- In Wigner density functional theory a legitimate question is whether a Wigner function corresponds to a wave function symmetric or antisymmetric under permutations of its variables. A simple criterion for spinless Wigner quasidistributions is provided. For bodies possessing spin, we endow the spin Wigner functions with ostensible physical meaning, by arranging their entries into tensors under the rotation group.
- We exhaustively study the lowest excited (spin triplet) state of the Moshinsky atom, with the main purpose of revisiting the relation between entanglement measures and correlation energy for this quite different species. The task is performed in the framework of the Wigner density functional theory.
- With the help of the phase-space formulation of density functional theory, we perform a test of some of the most popular density matrix functionals on a completely solvable model. For the ground-state of the Moshinsky atom, the Müller functional, evaluated on the exact 1-RDM, yields the correct value of the energy; we prove this surprising fact.
- A numerical analysis of the nature of generalized Pauli constraints is effected in real atoms and molecules (the lithium atom and the molecule He_2^+). The inequalities are nearly saturated, or quasipinned. For not very strongly correlated systems, the spin-compensated open-shell system $\wedge^3\mathcal{H}_6$ is always pinned to the boundary of the polytope described by the Borland-Dennis conditions.
- The robustness of the quasipinning of a particular type of constraint conspires to explain why double excitations govern configuration interaction calculations of electron correlation, when using natural orbitals. Moreover, our investigations suggest that the constraint $n_1 + n_2 = 1 + n_3$ is stable for three-electron systems.
- We provide upper and lower bounds for the projection of a general wave function $\wedge^3\mathcal{H}_7$ onto the set of configurations pinned to the facet $D^2_{3,7} = 0$.
- An algorithm for simulation problems in quantum chemistry based on the structural simplifications due to quasipinning is provided and tested on a simple system of three valence fermions.

1.3 Outline of the thesis

The outline of this thesis is as follows.

- Chapter 1 is this introduction.
- Chapter 2 is a monographic one whose goal is to situate the quantum-chemistry scenario in which the generalized Pauli principle has been developed.
- Chapter 3 discusses the recently postulated Wigner density functional theory whose main intention is to exploit the one-to-one correspondence between the ground-state N-body density matrix of a nondegenerate many-body system and the corresponding Wigner 1-RDM, defined on phase space. We screen the role of the spin in this theory and propose a novel way to deal with it. We study in depth the lowest excited state of the Moshinsky atom in the light of this new theory. This is mainly based on three papers [BRGBV12, BR13, BRGB13].

- Chapter 4 is dedicated to testing the accuracy of some 1-RDM functionals, currently in use in the literature. We catalogue the predictions for the ground state of the Moshinsky atom by several proposed two-body functionals, measured against the exact model. The work presented is mainly based on [BRV12, BRN14].

- Chapter 5 is a monograph dedicated to discussing the formulation of the generalized Pauli principle as conceived by Klyachko. We based our discussion on [AK08].

- Chapter 6 is based on [BRGBS13, BRS15b]. It reports our effort along two years in taking up the challenge of studying pinning and quasipinning by use of numerical and theoretical methods for the ground state of some elementary three-electron atomic and molecular systems. We provide a proof that the spin-compensated open-shell system $\wedge^3\mathcal{H}_6$ is always pinned to the boundary of the polytope described by the Borland-Dennis conditions.

- Chapter 7 is based on [BRS15b, BRGBS14] and is devoted to explaining that, when using natural orbitals to study (dynamical and nondynamical) electron correlation, determinants with an odd number of excitations play a negligible role. Instead, doubly excited determinants rule the rostrum in this kind of configuration interaction calculations. This phenomenon is explained by use of a quasipinning mechanism.

- Chapter 8 is based on [BRS15a]. The goal is to elaborate variational ground-state Ansätze based on the simplified pinning structure and analyze their numerical quality. We develop a complete MCSCF algorithm for states of pinned natural occupation numbers.

- Chapter 9 contains our conclusions.

- Chapter 10 contains an introduction as well as a discussion of the main conclusions of this work in Spanish for the interested reader.

- This thesis contains three appendices. Appendix A is based on [BRTD14]. The ground-state entropy of entanglement of the N-harmonium system (i.e., a completely integrable model of N particles where both the confinement and the two-particle interaction are harmonic) is shown to be analytically determined. Appendix B discusses the Carlson-Keller duality; and Appendix C presentes the Newton-Raphson method, used in MCSCF optimization.

Chapter 2

The quantum chemistry holy grail

2.1 The electronic Schrödinger equation

In quantum chemistry, we are often interested in the ground state of a nonrelativistic quantum system of electrons and nuclei. The physical description is effected by solving the stationary (or time-independent) Schrödinger equation, namely,

$$H|\Phi_k\rangle = \epsilon_k|\Phi_k\rangle. \tag{2.1}$$

The entire information of the system is contained in the wave vector $|\Phi_k\rangle$, an eigenfunction of the hermitian operator H, called the Hamiltonian. The eigenvalue $\epsilon_k \in \mathbb{R}$ is the corresponding energy of the system. Usually there are infinitely many eigenvalues for which Eq. (2.1) has a solution [LS10]. For our ultimate goals, one of the most important quantities is the lowest eigenvalue $\epsilon_0 \leq \epsilon_1 \leq \cdots$, that is, the ground-state energy of the system. For nondegenerate ground-state systems, the dimension of the eigenspace corresponding to the lowest eigenvalue is equal to 1.

The interaction between electrons and nuclei is a dynamical problem of great complexity. All electric forces involved are of the same order of magnitude and therefore the change in the corresponding momenta due to these forces must also be of the same order. Nuclei are much more massive than electrons (by a factor of the order of 10^4 or 10^5) and thereby, roughly speaking, in the time-scale of the nuclear motion, the electrons relax to its ground-state configuration well-nigh instantly. Based on these facts, the *Born-Oppenheimer approximation* assumes that the nuclei are nearly stationary with respect to the motion of the electrons; and effectively the electrons can be seen as moving in a field of fixed nuclei whose degrees of freedom can be treated as classical [Wei13].

A system of N electrons and K spinless nuclei (whose coordinates, charges counted in terms of electronic charge and masses are given by $\{\boldsymbol{R}_\mu, Z_\mu, m_\mu\}$) is governed by the following Hamiltonian (we do not consider relativistic or spin-orbital effects):

$$H = -\sum_{\mu=1}^{K} \frac{1}{2m_\mu}\Delta_{\boldsymbol{R}_\mu} + \sum_{\mu<\nu}^{K} \frac{Z_\mu Z_\nu}{|\boldsymbol{R}_\mu - \boldsymbol{R}_\nu|} + H_{\mathrm{e}},$$

where the so-called electronic Hamiltonian is given by

$$H_{\mathrm{e}} = \widehat{T} + \widehat{V}_{\mathrm{ext}} + \widehat{W} := -\sum_{i=1}^{N} \frac{1}{2}\Delta_{\boldsymbol{r}_i} + \sum_{i=1}^{N} V_{\mathrm{ext}}(\boldsymbol{r}_i) + \sum_{i<j}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\,. \tag{2.2}$$

The external potential depends on the position of the nuclei and their charges:

$$V_{\mathrm{ext}}(\boldsymbol{r}) = -\sum_{\mu=1}^{K} \frac{Z_\mu}{|\boldsymbol{r} - \boldsymbol{R}_\mu|}\,.$$

We employ here the standard notation in quantum chemistry for the electron coordinates: $\boldsymbol{x}_i := (\boldsymbol{r}_i, \varsigma_i)$, where $\varsigma_i \in \{\uparrow, \downarrow\}$ is the spin coordinate and $\boldsymbol{r}_i \in \mathbb{R}^d$ (say $d = 3$, for ordinary space). For any function depending on space and spin coordinates, we write

$$\int f(\boldsymbol{x})\, d\boldsymbol{x} = \sum_{\varsigma \in \{\uparrow,\downarrow\}} \int_{\mathbb{R}^d} f(\boldsymbol{r}, \varsigma)\, d\boldsymbol{r},$$

that is, $\int d\boldsymbol{x} := \sum_{\varsigma\in\{\uparrow,\downarrow\}} \int_{\mathbb{R}^d} d\boldsymbol{r}$ indicates integration over the complete space and summation over spin indices.

To derive the Born-Oppenheimer approximation, let us assume the following form for an eigenfunction of the Hamiltonian (2.1):

$$\Phi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) = \Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}})\tilde{\Phi}(\vec{\boldsymbol{R}}), \tag{2.3}$$

where for the sake of brevity we denote $\vec{\boldsymbol{x}} := (\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ and $\vec{\boldsymbol{R}} := (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_K)$. The electronic wave function satisfies the time-independent Schrödinger equation:

$$H_{\mathrm{e}}\Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) = E(\vec{\boldsymbol{R}})\Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}),$$

and the eigenvalues of this Hamiltonian are functions of the nuclear positions.

Applying the full Hamiltonian to the wave function (2.3) gives:

$$\begin{aligned} H\Phi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) &= \left[-\sum_{\mu=1}^{K} \frac{1}{2m_\mu}\Delta_{\boldsymbol{R}_\mu} + \sum_{\mu<\nu}^{K} \frac{Z_\mu Z_\nu}{|\boldsymbol{R}_\mu - \boldsymbol{R}_\nu|} + H_{\mathrm{e}} \right] \Phi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) \\ &= \Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) \left[-\sum_{\mu=1}^{K} \frac{1}{2m_\mu}\Delta_{\boldsymbol{R}_\mu} + \sum_{\mu<\nu}^{K} \frac{Z_\mu Z_\nu}{|\boldsymbol{R}_\mu - \boldsymbol{R}_\nu|} + E(\vec{\boldsymbol{R}}) \right] \tilde{\Phi}(\vec{\boldsymbol{R}}) \\ &\quad - \sum_{\mu=1}^{K} \frac{1}{2m_\mu} \left[2\nabla_{\boldsymbol{R}_\mu}\tilde{\Phi}(\vec{\boldsymbol{R}})\nabla_{\boldsymbol{R}_\mu}\Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) + \tilde{\Phi}(\vec{\boldsymbol{R}})\Delta_{\boldsymbol{R}_\mu}\Psi(\vec{\boldsymbol{x}}, \vec{\boldsymbol{R}}) \right]. \end{aligned}$$

The energy $E(\vec{\boldsymbol{R}})$ of the electrons as a function of the nuclear positions is called the *adiabatic* contribution to the energy of the lattice of nuclei [Zim72]. The remaining *non-adiabatic* terms can be neglected for the following reasons:

(i) the expected value of the first non-adiabatic contribution vanishes:

$$\begin{aligned}\int d\vec{\boldsymbol{R}}\, d\vec{\boldsymbol{x}}\, \Phi^*(\nabla_{\boldsymbol{R}_\mu}\tilde{\Phi})(\nabla_{\boldsymbol{R}_\mu}\Psi) &= \int d\vec{\boldsymbol{R}}\, \tilde{\Phi}^*(\nabla_{\boldsymbol{R}_\mu}\tilde{\Phi}) \int d\vec{\boldsymbol{x}}\, \Psi^*(\nabla_{\boldsymbol{R}_\mu}\Psi) \\ &= \frac{1}{2}\int d\vec{\boldsymbol{R}}\, \tilde{\Phi}^*(\nabla_{\boldsymbol{R}_\mu}\tilde{\Phi})\nabla_{\boldsymbol{R}_\mu} \int d\vec{\boldsymbol{x}}\, \Psi^*\Psi = 0,\end{aligned}$$

since the normalization of the electronic wave function does not depend on the position of the nuclei, and

(ii) the second non-adiabatic term is of the order of the electronic kinetic energy times the ratio of the electron to the nuclear masses and therefore is negligible.

The whole argument is actually incomplete. It only says that in perturbation theory the first-order non-adiabatic corrections vanish. For our purposes, however, the moral of this reasoning is that the term $\tilde{\Phi}(\vec{\boldsymbol{R}})$ obeys a Schrödinger equation:

$$\left[-\sum_{\mu=1}^{K}\frac{1}{2m_\mu}\Delta_{\boldsymbol{R}_\mu} + \sum_{\mu<\nu}^{K}\frac{Z_\mu Z_\nu}{|\boldsymbol{R}_\mu - \boldsymbol{R}_\nu|} + E(\vec{\boldsymbol{R}})\right]\tilde{\Phi}(\vec{\boldsymbol{R}}) = \epsilon\,\tilde{\Phi}(\vec{\boldsymbol{R}}),$$

and we can separate the nuclear and electronic dynamics into two different differential equations. From now on, we focus on the electronic Hamiltonian $H_{\mathrm{e}}\Psi(\vec{\boldsymbol{x}}) = E\Psi(\vec{\boldsymbol{x}})$; the electrons are under the influence of a system of frozen nuclei and the electronic energy $E(\vec{\boldsymbol{R}}) := E$ is merely a constant.

As half-integer-spin particles, electrons obey Fermi statistics and hence the allowed electronic states are elements of the set of skewsymmetric functions of N particles, namely, $\mathcal{V}_N$. The ground-state electronic energy and the corresponding wave function satisfy the Rayleigh-Ritz variational principle:

$$E_0 = \min\big\{\langle\Psi|H_{\mathrm{e}}|\Psi\rangle : \langle\Psi|\Psi\rangle = 1,\ |\Psi\rangle \in \mathcal{V}_N\big\}. \tag{2.4}$$

Despite its rather simple formulation, the solution of Eq. (2.4) is a formidable computational task, even ignoring the motion of the nuclei.[1] Part of the reason for this complexity is the rapid growth of the computational cost with the number of electrons and with the size of the one-particle Hilbert space. The electronic quantum states we consider are given by elements of a finite N-fermion Hilbert space [BRRL10, Sch15]

$$\mathcal{V}_N := \wedge^N \mathcal{H}_m,$$

of antisymmetric N-particle states. We assume the one-particle Hilbert space $\mathcal{H}_m$ to be finite dimensional and $m \geq N$. Notice that m in $\mathcal{H}_m$ describes spin as well as orbital degrees of freedom. The well-known Hartree-Fock energy is found by solving Eq. (2.4), running the minimization over a one-dimensional Hilbert space $\wedge^N \mathcal{H}_N$.

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[1] Even the question whether quantum mechanics exhibits finite lower bounds for Eq. (2.4) is by itself a field of research in mathematical physics [LS10].

2.2 On Coulson's program

In 1959, at the Colorado conference on Molecular Quantum Mechanics, Charles Coulson pointed out that, for systems described by the electronic Hamiltonian (2.2), the 2-RDM

$$\gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}_1', \boldsymbol{x}_2') := \binom{N}{2} \int \gamma_N(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \dots, \boldsymbol{x}_N; \boldsymbol{x}_1', \boldsymbol{x}_2', \boldsymbol{x}_3, \dots, \boldsymbol{x}_N)\, d\boldsymbol{x}_3 \cdots d\boldsymbol{x}_N$$

carries all necessary information required for calculating the quantum properties of atoms and molecules, "banishing" the wave function [Cou60]. Because electrons are indistinguishable and interact pairwise in the Hamiltonian, the main idea consists in systematically replacing the quantum wave function by the 2-RDM (a function of four spatial and spin variables), which may be obtained by integration of the original N-body density matrix. By definition, $\gamma_N(\vec{\boldsymbol{x}}; \vec{\boldsymbol{x}}') = \Psi(\vec{\boldsymbol{x}})\Psi^*(\vec{\boldsymbol{x}}')$, *for pure states*, and

$$\gamma_N(\vec{\boldsymbol{x}}; \vec{\boldsymbol{x}}') = \sum_i \alpha_i \Psi_i(\vec{\boldsymbol{x}})\Psi_i^*(\vec{\boldsymbol{x}}') \quad \text{provided that} \quad \sum_i |\alpha_i|^2 = 1, \quad \textit{for ensemble states.}$$

The Coulson proposal can be justified as follows. Since the electronic Hamiltonian (2.2) contains at most two-particle interactions, it is expressible in the second quantization formalism as

$$\widehat{H}_{\text{elec}} = \sum_{ijkl} H_{ijlk} a_i^\dagger a_j^\dagger a_k a_l,$$

where $a_i^\dagger$ and a_i are the creation and annihilation fermionic operators for the state i. Therefore

$$\langle \Psi | \widehat{H}_{\text{elec}} | \Psi \rangle = \sum_{ijkl} H_{ijlk} \langle \Psi | a_i^\dagger a_j^\dagger a_k a_l | \Psi \rangle.$$

Hence, the energy is completely expressible in terms of the coefficients of the Hamiltonian and the 2-RDM as well. The Coulson program consists in expressing the energy of any atom or molecule as a helium-like energy functional, linearly dependent on the 2-RDM, to wit,

$$\mathcal{E}[\gamma_2] = \operatorname{Tr}(K\gamma_2),$$

where

$$K := \frac{1}{N-1}\big[h(1) + h(2)\big] + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}, \quad \text{with} \quad h(i) := -\frac{\Delta_{\boldsymbol{r}_i}}{2} + V_{\text{ext}}(\boldsymbol{r}_i).$$

The ground-state energy [see Eq. (2.4)] minimizes $\mathcal{E}(\gamma_2)$:

$$E_0 = \min\{\mathcal{E}[\gamma_2] : \gamma_2 \in \mathcal{B}_N^2\}; \tag{2.5}$$

here

$$\gamma_n \in \mathcal{B}_N^n \quad \text{iff} \quad \exists\, \gamma_N \in \text{DM}_N \quad \text{such that} \quad \gamma_n = \binom{N}{n} \int \gamma_N \, d\boldsymbol{x}_{n+1} \dots d\boldsymbol{x}_N.$$

We denote by DM_N the set of N-fermion density matrices.

It is remarkable that the entire quantum problem has been recast in the form of the much simpler linear functional (2.5). The conservation of difficulty however appears here in a more subtle form. In fact, finding necessary and sufficient conditions for the set of physically admissible 2-RDM (namely, $\mathcal{B}_N^2$) has proved to be a major challenge for theoretical quantum chemistry. Of course, some necessary conditions are already known for γ_2. By definition, it must be hermitian,

$$\gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2) = \gamma_2^*(\boldsymbol{x}'_1, \boldsymbol{x}'_2; \boldsymbol{x}_1, \boldsymbol{x}_2),$$

and antisymmetric in each pair of subindices since it comes from a fermionic wave function:

$$\gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2) = -\gamma_2(\boldsymbol{x}_2, \boldsymbol{x}_1; \boldsymbol{x}'_1, \boldsymbol{x}'_2) = -\gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_2, \boldsymbol{x}'_1).$$

The normalization condition reads $\operatorname{Tr}\gamma_2 = \binom{N}{2}$. In the fifties, John Coleman noted that these are not sufficient, because when he tried to find the ground-state energy of Lithium imposing only these three conditions, he obtained a value 10% below the correct one. That means that the minimization space contains unphysical states, more than allowed. Coleman himself coined the term *N-representable* for the set of physically admisible 2-RDM [Col07].

To a great extent, the so-called (***pure/ensemble***) *N-representability* problem consists thus in finding necessary and sufficient conditions for a n-RDM to be the contraction of a (***pure/ensemble***) N-body density matrix. In the worst case, the computational problem is almost intractable. In complexity theory, *intractability* means that for large N (the number of particle modes) the solution of the worst case demands a number of operations that grows exponentially with N. Since 2006 we know that the representability problem for the set of 2-RDM belongs to the QMA-complete complexity class, which means —among other things— that the problem is at least NP-hard [LCV07]. However, certain formal solutions are already known. Paul Ayers' version of the problem assures necessary and sufficient conditions for a γ_n to come from a N-fermion density matrix. For instance, γ_2 is representable if and only if for any two-body Hamiltonian $\hat{h}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ the expected value

$$\int \delta(\boldsymbol{x}_1 - \boldsymbol{x}'_1)\delta(\boldsymbol{x}_2 - \boldsymbol{x}'_2)\hat{h}_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2)\, d\boldsymbol{x}_1\, d\boldsymbol{x}'_1\, d\boldsymbol{x}_2\, d\boldsymbol{x}'_2$$

is never less than the ground state energy of N fermions interacting by the same Hamiltonian [Aye06]. Hence, for a given 2-RDM the representability problem is solved if one is able to test it with the complete universe of two-body Hamiltonians and needless to say that this criterion is not feasible.

Some other conditions are known to be necessary for a 2-RDM to be representable. Consider an operator $\widehat{C}_{ij}$ to be the product of any pair of second-quantized operators. From the ground-state wave function, a new set of functions can be derived,

$$\langle\phi_{ij}| = \langle\Psi|\widehat{C}_{ij}.$$

The overlap matrix M with elements

$$M^{ij}_{kl} := \langle\phi_{ij} \mid \phi_{kl}\rangle = \langle\Psi|\widehat{C}_{ij}\widehat{C}^\dagger_{kl}|\Psi\rangle$$

must be positive semidefinite (its eigenvalues are all non negative). The standard notation for such a matrix is $M \geq 0$. The crucial point is that for a representable 2-RDM, this condition is always satisfied [ME01]. The operator $\widehat{C}_{ij}$ can be chosen in three different ways: (i) the product of two creation operators $a_i^\dagger a_j^\dagger$ (ii) the product of two annihilation operators $a_i a_j$ (creation of two holes) and (iii) the product of one annihilation and one creation operator, say $a_i a_j^\dagger$ (creation of one particle and one hole). These different choices of $\widehat{C}_{ij}$ give rise to three different metric matrices, namely,

$$\begin{aligned} \Gamma^{ij}_{lk} &= \langle \Psi | a_i^\dagger a_j^\dagger a_k a_l | \Psi \rangle, \\ Q^{ij}_{lk} &= \langle \Psi | a_i a_j a_k^\dagger a_l^\dagger | \Psi \rangle, \\ G^{ij}_{lk} &= \langle \Psi | a_i^\dagger a_j a_k^\dagger a_l | \Psi \rangle. \end{aligned}$$

The important result is that if the 2-RDM is representable then Γ (two particle RDM), Q (two-hole RDM) and G (hole-particle RDM) must be positive semidefinite [GP64]. Using the anticommutation relations of the fermionic operators

$$\{a_i, a_j^\dagger\} = \delta_{ij} \quad \text{and} \quad \{a_i^\dagger, a_j^\dagger\} = \{a_i, a_j\} = 0,$$

it is possible to show that all these matrices are related. For example,

$$G^{ij}_{lk} = \delta_{jk}\, {}^1\Gamma^i_l - \Gamma^{ik}_{lj}, \quad \text{where} \quad {}^1\Gamma^i_j := \langle \Psi | a_i^\dagger a_j | \Psi \rangle.$$

We note that, while the *pure* N-representability problem for the 2-RDM remains to date unsolved, the *ensemble* N-representability problem for this matrix has been solved, although its computational implementation is still very difficult [Maz12].

2.3 Nobel prize in chemistry 1998

In 1998, the Nobel prize in chemistry was divided between Walter Kohn “for his development of the density-functional theory” and John Pople “for his development of computational methods in quantum chemistry”.[2] Like Janus —the Roman god of beginnings and transitions— it was a double-faced Nobel prize. In fact, Kohn’s and Pople’s contributions represent to a great extent two different approaches to electronic theory. The original contribution of Kohn (joint with Pierre Hohenberg and Lu Jeu Sham) is based on replacing the wave function with the electronic density

$$\rho(\boldsymbol{r}) = \sum_{\varsigma \in \{\uparrow,\downarrow\}} \gamma_1(\boldsymbol{r}, \varsigma; \boldsymbol{r}, \varsigma),$$

which is the only quantity needed for computing the ground-state energy of a given electronic system, based on the knowledge of a nonetheless unknown universal functional [HK64]. In contrast, Pople developed an extensive body of methods to capture the correlation energy and other quantities based on clever approximations to the chemical wave function, such as the Configuration Interaction (CI) picture [Pop99].

Ab initio **electronic structure theory**

For practical and historical reasons, it is useful to distinguish between some components of the exact wave function, namely: the solution of the Hartree-Fock equations and the

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[2] Press release of the Royal Swedish Academy of Sciences (13 October 1998).

others corresponding to excited configurations of the latter. The total wave function is then written as the following linear superposition:

$$|\Psi\rangle = c_0|\psi_{\mathrm{HF}}\rangle + \sum_i c_i|\psi_i\rangle, \tag{2.6}$$

where the first term $|\psi_{\mathrm{HF}}\rangle$ is the solution of the optimization problem of a single determinant and higher configurations are built by exciting the Hartree-Fock term. The whole problem is tackled by means of optimizing the coefficients of the electronic configurations, provided that $\sum_i |c_i|^2 = 1$. In the fifties, Löwdin coined the term *correlation energy* for the difference between the energy in the Hartree-Fock limit and the exact nonrelativistic energy of the quantum system:

$$E_{\mathrm{corr}} = E_0 - E_{\mathrm{HF}},$$

where the Hartree-Fock energy is found by minimizing the Hartree-Fock functional: $\mathcal{E}^{\mathrm{HF}}[\gamma_1]$, where

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}[\gamma_1] = -\frac{1}{2}\int \delta(\boldsymbol{x}-\boldsymbol{x}')\,\Delta_{\boldsymbol{r}}\gamma_1(\boldsymbol{x};\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}' + \int V_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} \\ + \underbrace{\frac{1}{2}\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2}_{\text{Coulomb term}} - \underbrace{\frac{1}{2}\int \frac{\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_2)\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_1)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_1 d\boldsymbol{x}_2}_{\text{exchange term}},\end{aligned} \tag{2.7}$$

over the set of Slater-determinantal wave functions. In other words,

$$E_{\mathrm{HF}} = \min\{\mathcal{E}^{\mathrm{HF}}[\gamma_1] : \gamma_1 = \gamma_1^2 = \gamma_1^*,\ \mathrm{Tr}\,\gamma_1 = N\}.$$

The idempotent expression $\gamma_1^2 = \gamma_1$ means $\int \gamma_1(\boldsymbol{x};\boldsymbol{y})\gamma_1(\boldsymbol{y};\boldsymbol{x})\,d\boldsymbol{y} = \gamma_1(\boldsymbol{x};\boldsymbol{x}')$, which implies that this matrix is a projector on some subspace of the 1-particle Hilbert space. By definition, the correlation energy will always be negative because the Hartree-Fock energy is an upper bound to the exact electronic energy. In principle, the exact value for E_0 could be calculated by performing the energy computation associated to the expression (2.6). Since the Coulomb potential $\frac{1}{|r_i - r_j|}$ is repulsive, it attempts to keep the electrons apart. A slight fraction of this correlation is nevertheless neglected by the single-determinant Hartree-Fock approximation, and the energy this method predicts is affected by an error which is precisely the correlation energy [Löw55].

The so-called *multiconfiguration self-consistent field* (MCSCF) description of atoms and molecules is nowadays one of the most powerful tools available in quantum-chemistry applications. Unlike the CI theory, in which the wave function is expanded in terms of the Hartree-Fock orbitals, the multiconfiguration problem carries out a full variational computation in which the orbitals and the coefficients of the electronic configurations are optimized simultaneously. To date, routine optimization of MCSCF wave functions is a realistic application with millions of configurations involved in the computations [JÅO91]. To see how the MCSCF is effectively implemented, consider a set of spin-orbitals $\{\tilde{\phi}_p(\boldsymbol{x})\}$ obtained from a set $\{\phi_p(\boldsymbol{x})\}$ by an orthogonal transformation:

$$\tilde{\phi}_p = \sum_q \phi_q Q_{qp}.$$

Recall that the real orthogonal matrices satisfy the relation: $\boldsymbol{Q}^t\boldsymbol{Q} = \boldsymbol{Q}\boldsymbol{Q}^t = \boldsymbol{1}$, and can be expressed in exponential form $\boldsymbol{Q} = e^{-\boldsymbol{\kappa}}$, where $\boldsymbol{\kappa} = -\boldsymbol{\kappa}^t$ is a real antisymmetric matrix. The Slater determinants transforms in the following way:

$$|\tilde{\phi}_{p_1}\tilde{\phi}_{p_2}\cdots\tilde{\phi}_{p_N}\rangle = \sum_{q_1\cdots q_N} Q_{q_1p_1}\cdots Q_{q_Np_N}|\phi_{q_1}\phi_{q_2}\cdots\phi_{q_N}\rangle.$$

Within the second quantization method this latter expression can be written as $|\tilde{\boldsymbol{k}}\rangle = \sum_{q_1\cdots q_N} Q_{q_1p_1}\cdots Q_{q_Np_N} a^\dagger_{q_1}\cdots a^\dagger_{q_N}|\text{vac}\rangle$. The one-to-one mapping between Slater determinants in the first quantization formulation and the occupation-number vectors used in second quantization is preserved if the creation operators transform in the same way as the spin orbitals, that is, $\tilde{a}^\dagger_p = \sum_q a^\dagger_q Q_{qp} = \sum_q a^\dagger_q [e^{-\boldsymbol{\kappa}}]_{qp}$. Now, the anti-Hermitian operator

$$\hat{\kappa} := \sum_{pq} [\boldsymbol{\kappa}]_{pq} a^\dagger_p a_q,$$

satisfies the following nice property: $\tilde{a}^\dagger_p = e^{-\hat{\kappa}} a^\dagger_p e^{\hat{\kappa}}$, which can be easily proved. Hence,

$$|\tilde{\boldsymbol{k}}\rangle = \prod_{p=1}^{M} (\tilde{a}^\dagger_p)^{k_p}|\text{vac}\rangle = \prod_{p=1}^{M} (e^{-\hat{\kappa}} a^\dagger_p e^{\hat{\kappa}})^{k_p}|\text{vac}\rangle = e^{-\hat{\kappa}}\left[\prod_{p=1}^{M} (a^\dagger_p)^{k_p}\right] e^{\hat{\kappa}}|\text{vac}\rangle = e^{-\hat{\kappa}}|\boldsymbol{k}\rangle,$$

since $\hat{\kappa}|\text{vac}\rangle = 0$ and consequently $e^{\hat{\kappa}}|\text{vac}\rangle = |\text{vac}\rangle$. The MCSCF wave function then reads

$$|\boldsymbol{\kappa}, \boldsymbol{c}\rangle := e^{-\hat{\kappa}} \sum_i c_i |\boldsymbol{i}\rangle,$$

which is in turn constructed by means of a variational optimization of the expected value of the energy

$$E_{\text{MCSCF}} = \min_{\boldsymbol{\kappa},\boldsymbol{c}} \frac{\langle \boldsymbol{\kappa}, \boldsymbol{c}|H_{\text{e}}|\boldsymbol{\kappa}, \boldsymbol{c}\rangle}{\langle \boldsymbol{\kappa}, \boldsymbol{c}|\boldsymbol{\kappa}, \boldsymbol{c}\rangle},$$

with respect to the parameters of the antihermitian operator $\hat{\kappa}$ as well as the CI coefficients $\boldsymbol{c}$. In practice, this simultaneous optimization is a very demanding nonlinear problem. It is standard in quantum chemistry that these self-consistent field equations can be appropriately solved by expanding the exponential operator to the second-order Taylor series $e^{-\hat{\kappa}} \approx 1 - \hat{\kappa} + \frac{1}{2}\hat{\kappa}^2$ and then by using the well-known Newton-Raphson optimization method [JÅO91, BRS15a].

The original intention of Pople's research was "to use full *ab initio* results to test various integral approximations that were less severe than the use of zero differential overlap", using a systematic procedure to lift Slater-type basis functions by a contraction of a certain number of Gaussians [Pop99]. For atoms and molecules with a small number of active electrons, wave-function methods give in general excellent results since nowadays computers can perform operations with millions of Slater determinants. Nevertheless, these methods are limited to such small active spaces. An *exponential wall* appears for atoms and molecules with many electrons: the configuration space grows exponentially with the number of electrons and effectively for systems with thousands of electrons other methods are employed. *Density functional theory* (DFT) is one of these theories whose main attempt is to replace the wave function with other reliable physical quantities.

Hohenberg-Kohn theorems

The famous Hohenberg-Kohn theorems are milestone results in quantum chemistry. The main statement is based on the observation that for nondegenerate systems there is a one-to-one correspondence between the external potential $V_{\text{ext}}(\boldsymbol{r})$ in the electronic Hamiltonian (2.2), the (nondegenerate) ground state $|\Psi_{\text{gs}}\rangle$ corresponding to the ground-state energy E_0 and the associated ground state electronic density $\rho_0(\boldsymbol{r})$:

$$V_{\text{ext}}(\boldsymbol{r}) \Longleftrightarrow |\Psi_{\text{gs}}\rangle \Longleftrightarrow \rho_{\text{gs}}(\boldsymbol{r}), \tag{2.8}$$

such that these three quantities determine each other uniquely (up to some constant in V_{ext}). In other words, the ground-state wave function can be written as a functional of the ground-state electronic density, denoted as $|\Psi[\rho]\rangle$. This functional is *universal* in the sense that it applies to atoms, molecules or solids. Given a ground-state electronic density, the corresponding wave function satisfies:

$$|\Psi_{\text{gs}}\rangle = |\Psi[\rho_{\text{gs}}]\rangle.$$

The existence of the one-to-one correspondence (2.8) allows us to posit that the ground state energy can be found by means of a density functional, namely:

$$\begin{aligned} E[\rho] = \langle\Psi[\rho]|H_{\text{e}}|\Psi[\rho]\rangle &= F[\rho] + \int V_{\text{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r}, \\ \text{where} \quad F[\rho] &:= \langle\Psi[\rho]|\widehat{T} + \widehat{W}|\Psi[\rho]\rangle, \end{aligned}$$

with $\widehat{T} + \widehat{W}$ as defined in Eq. (2.2). In the same way that $|\Psi[\rho]\rangle$, the functional $F[\rho]$ is universal, since it has the same functional form for all kinds of many-electron systems. The Ritz variational principle says that the energy must be a minimum for the ground state electronic density. Therefore,

$$E_0 = \min_{\rho\in\mathcal{V}_\rho} E[\rho],$$

where $\mathcal{V}_\rho$ is the set of representable electronic densities. The main complication here is that the functional $F[\rho]$ is completely unknown, so some approximations are needed.

The Nobel prize in chemistry 1998 recognized the success of DFT in describing highly correlated many-electron systems. Since then, DFT has enjoyed a spectacular rise in computational chemistry as well as in atomic and molecular physics. It is worth mentioning that Pople himself helped the growth of DFT's reputation. In fact, in 1992 he incorporated it into the GAUSSIAN program and the computations performed by his group showed good agreement with experiments, using even small basis sets. With this endorsement, the popularity of DFT began to grow exponentially, too [Zan14].

2.4 The Löwdin-Shull functionals

Two-electron systems are special in the sense that γ_2 can be reconstructed "almost exactly" in terms of γ_1. In other words, it can be written, up to a sign indetermination, as $\gamma_2[\gamma_1]$. This is the so-called Löwdin-Shull (LS) functional [LS56]. In this section we describe the derivation of this functional for the singlet and the triplet spin states.

Singlet: Consider the spin singlet configuration of a two-electron system, and let us expand the corresponding wave function $\Psi_{\text{singlet}}(\boldsymbol{x}_1, \boldsymbol{x}_2)$ in a suitable orthonormal basis set:

$$\Psi_{\text{singlet}}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2}{\sqrt{2}} \sum_{ij}^{K} c_{ij}\, f_i(\boldsymbol{r}_1) f_j(\boldsymbol{r}_2) \quad \text{where} \quad c_{ij} = c_{ji}. \tag{2.9}$$

The normalization condition reads $\sum_{ij} |c_{ij}|^2 = 1$. To this rank of approximation there are in all $K(K+1)/2$ possible configurations. The corresponding 1-RDM reads

$$\begin{aligned}\gamma_1(\boldsymbol{x}_1; \boldsymbol{x}_1') &= 2\int \Psi_{\text{singlet}}(\boldsymbol{x}_1, \boldsymbol{x}_2)\Psi^*_{\text{singlet}}(\boldsymbol{x}_1', \boldsymbol{x}_2) d\boldsymbol{x}_2 \\ &= (\uparrow_1\uparrow_1' + \downarrow_1\downarrow_1') \sum_{ij} \gamma_{ij}\, f_i(\boldsymbol{r}_1) f_j^*(\boldsymbol{r}_1') \quad \text{with} \quad \gamma = cc^\dagger,\end{aligned}$$

Note that $\operatorname{Tr}\gamma_1 = 2$, the number of particles. If the wave function Ψ_{singlet} is chosen to be real, the matrix c of coefficients is hermitian. Suppose the eigenvalue problem for this matrix has been solved. There is then an orthogonal matrix $\mathcal{O}$ such that

$$\mathcal{O}^t c\, \mathcal{O} = \operatorname{diag}(\nu_1, \dots, \nu_K) \quad \text{and} \quad \mathcal{O}^t \gamma\, \mathcal{O} = \operatorname{diag}(n_1, \dots, n_K).$$

The eigenvalues of the matrix γ are the so-called *natural occupation numbers* (NON). The relation between the eigenvalues of γ and c is $\nu_i^2 = n_i$, $\forall i$. The set of *natural orbitals* (NO), which are the eigenfunctions of the 1-RDM, is defined in the following way:

$$\phi_i = \sum_j \mathcal{O}_{ij} f_j \quad \text{and therefore} \quad f_i = \sum_j \mathcal{O}_{ji}\phi_j.$$

Hence, the 1-RDM reads

$$\begin{aligned}\gamma_1(\boldsymbol{x}_1; \boldsymbol{x}_1') &= (\uparrow_1\uparrow_1' + \downarrow_2\downarrow_2') \sum_{ij}^{K} \gamma_{ij}\, \mathcal{O}_{mi} f_m(\boldsymbol{r}_1) \mathcal{O}_{nj} f_j(\boldsymbol{r}_1') \\ &= (\uparrow_1\uparrow_1' + \downarrow_1\downarrow_1') \sum_{i}^{K} n_i\, \phi_i(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_1').\end{aligned}$$

Except for a sign indetermination that cannot be removed [LS56], the wave function can be written in terms of the NO and NON:

$$\Psi_{\text{singlet}}[\{\phi_i\}, \{n_i\}] = \frac{\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2}{\sqrt{2}} \sum_{i}^{K} (\pm)\sqrt{n_i}\, \phi_i(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_2). \tag{2.10}$$

This is the so-called Löwdin-Shull functional for singlets of two-electron systems; written in terms of the NO, the wave function only needs K configurations and only contains (a subset of the) *double* excitations of the initial state. The exact expression for the wave function can be obtained in the asymptotic limit $K \to \infty$. In general, it is remarkable that just using the NO basis the number of configurations present in the CI wave function drops dramatically [MvMGB14, BRGBS14]. Moreover, since this is nothing more than the well-known Schmidt decomposition, the best finite-rank approximation (in the sense of any orthogonally invariant norm) to the wave function is precisely given by the set of its NO.

The LS functional $\gamma_2^{\mathrm{LS}} := \Psi_{\mathrm{singlet}}(\boldsymbol{x}_1, \boldsymbol{x}_2)\Psi_{\mathrm{singlet}}(\boldsymbol{x}'_1, \boldsymbol{x}'_2)$ then reads:

$$\gamma_2^{\mathrm{LS}} = \frac{(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)(\uparrow'_1\downarrow'_2 - \downarrow'_1\uparrow'_2)}{2} \sum_i \nu_i\nu_j \,\phi_i(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}'_1)\phi_j(\boldsymbol{r}'_2), \tag{2.11}$$

explicitly written in terms of the NO and the NON, up to a sign indetermination, namely $\nu_i = \pm\sqrt{n_i}$. Due to this ambiguity, in order to find the exact functional one needs to determine an infinite number of signs. For some systems this herculean task has already been accomplished. Within the context of a phase-space density functional theory (or Wigner DFT), the alternating choice of signs $\nu_i = (-)^i\sqrt{n_i}$ has been shown to be the correct one for the ground state of the Moshinsky atom or 2-Harmonium: a system of two fermions interacting with an external harmonic potential and repelling each other by a Hooke-type force [BGBV12, GBV10]. For weakly correlated electronic systems, if by convention ν_0 is taken equal to $+\sqrt{n_0}$, then (most of) the other signs are negative, because otherwise there would not be a negative gradient in the energy minimization process [GU00, BGBV12].

Triplet: While the spatial function for the singlet (which can be viewed as a ground-state) is symmetric, and consequently its spin part antisymmetric, for the triplet (which can be understood as a first excited state) the situation is exactly the opposite: the spatial function is antisymmetric and its spin part is symmetric. In fact, the wave function of a two-electron system in a triplet spin state possesses one among three different spin factors, say:

$$\uparrow_1\uparrow_2, \quad \tfrac{1}{2}\big(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2\big) \quad \text{and} \quad \downarrow_1\downarrow_2,$$

and therefore general triplet states can be taken of the form [LS56, Dav76]:

$$\Psi_{\mathrm{triplet}}(\boldsymbol{x}_1, \boldsymbol{x}_2) = (\text{spin part}) \times \sum_{ij} \frac{1}{2} c^{\mathcal{T}}_{ij}\, [f_i(\boldsymbol{r}_1)f_j(\boldsymbol{r}_2) - f_j(\boldsymbol{r}_1)f_i(\boldsymbol{r}_2)], \tag{2.12}$$

where $c^{\mathcal{T}}_{ij} = -c^{\mathcal{T}}_{ji}$. Here $\{f_i\}$ is a complete orthonormal set. In the absence of magnetic fields, the wave functions can be taken real. We thus assume that the matrix $c^{\mathcal{T}}$ is real, as well as the functions f_i. Wave function normalization gives rise to the condition $\sum_{ij}(c^{\mathcal{T}}_{ij})^2 = 1$.

For the spin part, a less conventional and more cogent description is found in terms of polarization vectors and the correlation tensor [Blu12]; however, it is hardly worthwhile to introduce it here. So we shall be content with presenting the 2-RDM for triplet states under the matrix form:

$$\gamma_2^{\mathcal{T}1} = \uparrow_1\uparrow_2\uparrow_{1'}\uparrow_{2'}\rho_2, \quad \gamma_2^{\mathcal{T}0} = \tfrac{1}{2}\big(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2\big)\big(\uparrow_{1'}\downarrow_{2'} + \downarrow_{1'}\uparrow_{2'}\big)\rho_2, \quad \gamma_2^{\mathcal{T},-1} = \downarrow_1\downarrow_2\downarrow_{1'}\downarrow_{2'}\rho_2;$$

where ρ_2 is the spinless 2-RDM given by the expression

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}'_1, \boldsymbol{r}'_2) = \frac{1}{4}\sum_{ij,kl} c^{\mathcal{T}}_{ij}\, c^{\mathcal{T}}_{kl} \begin{vmatrix} f_i(\boldsymbol{r}_1) & f_j(\boldsymbol{r}_1) \\ f_i(\boldsymbol{r}_2) & f_j(\boldsymbol{r}_2) \end{vmatrix} \begin{vmatrix} f_k(\boldsymbol{r}'_1) & f_l(\boldsymbol{r}'_1) \\ f_k(\boldsymbol{r}'_2) & f_l(\boldsymbol{r}'_2) \end{vmatrix}, \tag{2.13}$$

where $|\cdot|$ denotes determinant. By integrating out one set of coordinates, we obtain the corresponding 1-RDM: $\gamma_1^{\tau} = (\text{spin part}) \times \rho_1$. Here ρ_1 is the spinless 1-RDM corresponding to the triplet:

$$\rho_1(\boldsymbol{r};\boldsymbol{r}') = 2\int \rho_2(\boldsymbol{r},\boldsymbol{r}_2;\boldsymbol{r}',\boldsymbol{r}_2)\,d\boldsymbol{r}_2 = 2\sum_{ij} d_{ij} f_i(\boldsymbol{r}) f_j(\boldsymbol{r}'),$$

where $d = c^{\tau}(c^{\tau})^{\dagger} = -(c^{\tau})^2$ is a positive definite matrix.

Now, let c^{τ} be any real antisymmetric square matrix. Then there exists a real orthogonal matrix Q such that $A = Q^t c^{\tau} Q$, with A a real block-diagonal matrix of the sort [HJ12]:

$$A = \operatorname{diag}[A_0, A_1, \dots], \qquad A_0 = 0, \qquad A_i = \begin{pmatrix} 0 & a_i \\ -a_i & 0 \end{pmatrix}.$$

By convention, here $a_i \geq 0$. Therefore

$$c_{ij}^{\tau} c_{kl}^{\tau} = \sum_{vw} a_v a_w \left[q_{i,2v} q_{j,2v+1} - q_{i,2v+1} q_{j,2v}\right]\left[q_{k,2w} q_{l,2w+1} - q_{k,2w+1} q_{l,2w}\right].$$

Let us now make the definition $\phi_r := \sum_m q_{rm} f_m$, so that $f_r = \sum_m q_{mr}\phi_m$. This is the set of NO for the triplet and has the following nice property: $\int \phi_r(\boldsymbol{r})\phi_p(\boldsymbol{r})\,d\boldsymbol{r} = \delta_p^r$. Hence, from (2.13) the spinless 2-RDM can be written in the following way:

$$\rho_2^{\mathrm{LS}}(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2') = \sum_{vw} a_v a_w \begin{vmatrix} \phi_{2v}(\boldsymbol{r}_1) & \phi_{2v+1}(\boldsymbol{r}_1) \\ \phi_{2v}(\boldsymbol{r}_2) & \phi_{2v+1}(\boldsymbol{r}_2) \end{vmatrix} \begin{vmatrix} \phi_{2v}(\boldsymbol{r}_1') & \phi_{2v+1}(\boldsymbol{r}_1') \\ \phi_{2v}(\boldsymbol{r}_2') & \phi_{2v+1}(\boldsymbol{r}_2') \end{vmatrix}. \tag{2.14}$$

The 1-RDM for the triplet is obtained, as before,

$$\rho_1^{\mathrm{LS}}(\boldsymbol{r};\boldsymbol{r}') = 2\sum_{w} a_w^2 \left[\phi_{2w}(\boldsymbol{r})\phi_{2w}(\boldsymbol{r}') + \phi_{2w+1}(\boldsymbol{r})\phi_{2w+1}(\boldsymbol{r}')\right]. \tag{2.15}$$

Notice that in the previous equation each occupation number $n_i := 2a_i^2$ appears twice. This is a consequence of the Pauli exclusion principle. Unlike the singlet case, there is no sign rule to be deciphered here. Instead there are the ambiguities [BRGBV12]:

$$\begin{aligned}
\chi_{2w,2w} &= \chi'_{2w,2w}\cos^2\theta_w - (\chi'_{2w,2w+1} + \chi'_{2w+1,2w})\sin\theta_w\cos\theta_w + \chi'_{2w+1,2w+1}\sin^2\theta_w, \\
\chi_{2w+1,2w+1} &= \chi'_{2w,2w}\sin^2\theta_w + (\chi'_{2w,2w+1} + \chi'_{2w+1,2w})\sin\theta_w\cos\theta_w + \chi'_{2w+1,2w+1}\cos^2\theta_w,
\end{aligned}$$

where $\chi_{i,j}(\boldsymbol{r};\boldsymbol{r}') := \phi_i(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')$. They clearly leave the form (2.15) untouched. We see here the action of $SO(2)$ on each invariant block. One may choose the angles so as to maximize their overlap with the leading natural orbitals for the ground state, as done in the seminal paper by Löwdin and Shull [LS56].

2.5 Reduced density matrix functional theory

As a solution of the Schrödinger equation, the wave function $|\Psi\rangle$ describes a quantum system completely. Hohenberg and Kohn theorem implies the existence of a universal functional of the external potential and the electronic density which reaches a minimum when evaluated on the ground state electronic density. In 1975 Gilbert proved an extension of the Hohenberg-Kohn theorem which shows that there is a one-to-one correspondence between the ground-state wave function of a nondegenerate many-body system and the corresponding 1-RDM [Gil75]:

$$|\Psi_{\mathrm{gs}}\rangle \Longleftrightarrow \gamma_{1\mathrm{gs}}(\boldsymbol{x};\boldsymbol{x}'). \tag{2.16}$$

The main advantage of this theorem is that any observable of the system in its ground state can be written as a functional of the 1-RDM. More importantly, the functional of the kinetic energy, which is unknown in DFT, here is known exactly in terms of the 1-RDM. In fact, notice that the energy functional reads:

$$E[\gamma_1] = -\frac{1}{2}\int \delta(\boldsymbol{x}-\boldsymbol{x}')\,\Delta_{\boldsymbol{r}}\gamma_1(\boldsymbol{x};\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}' + \int V_{\mathrm{ext}}(\boldsymbol{r})\gamma_1(\boldsymbol{x};\boldsymbol{x})d\boldsymbol{x} + E_{\mathrm{ee}}[\gamma_1],$$
$$\text{where}\quad E_{\mathrm{ee}}[\gamma_1] := \langle\Psi[\gamma_1]|\widehat{W}|\Psi[\gamma_1]\rangle,$$

with the operator $\widehat{W}$ as defined in Eq. (2.2). Hence, in comparison with DFT, in reduced density matrix functional theory (RDMFT) it “only” remains to find out the functional dependence of γ_2 in terms of γ_1 and the complete problem would be solved. The second advantage of Gilbert’s theorem is that one can consider nonlocal potentials $V_{\mathrm{ext}}(\boldsymbol{r},\boldsymbol{r}')$, which arise when the quantum problem is formulated in terms of many valence electrons, subject to an external potential of fixed nuclei and core electrons [Gil75]. The main difference is that the relation between nonlocal potentials and ground-state wave functions is no longer one-to-one.

Necessary and sufficient conditions for the *ensemble* N-representability of the 1-RDM have long been stated [Col63]; such admissibility conditions are established by the following theorem.

Theorem 1. Let γ_1 be a self-adjoint, positive semidefinite operator on $L^2(\mathbb{R}^3)\otimes\{\uparrow,\downarrow\}$ with finite trace $\int\gamma_1(\boldsymbol{x};\boldsymbol{x})d\boldsymbol{x} = N$, for some integer $N \geq 1$. Then there exists γ_N, a N-RDM, such that γ_1 is the contraction of that matrix:

$$\gamma_1 = N\int \gamma_N\, d\boldsymbol{x}_2\cdots d\boldsymbol{x}_N,$$

if and only if $\gamma_1 \leq \mathbb{1}$. These conditions do not distinguish between pure and ensemble states at the level of γ_N.

Proof. See [LS10, pp. 46–48]. □

As a corollary of Theorem 1, in the basis of NO, the 1-RDM (which in turn can be interpreted as an integral kernel) reads:

$$\gamma_1(\boldsymbol{x};\boldsymbol{x}') = \sum_i n_i\,\phi_i(\boldsymbol{x})\phi_i^*(\boldsymbol{x}'),\quad\text{where}\quad \sum_i n_i = N \quad\text{and}\quad 0\leq n_i\leq 1,\ \forall i.$$

The NO satisfy $\phi_i \in L^2(\mathbb{R}^3)\otimes\{\uparrow,\downarrow\}$.

For some systems the explicit relation between γ_2 and γ_1 is known. For example, the singlet spin configuration of two-electron systems (2.11), the triplet spin configuration of such systems (2.14) and the well-known Hartree-Fock functional, whose energy is given by the functional (2.7). The reader should remember that $\rho(\boldsymbol{r}) = \sum_\varsigma \gamma_1(\boldsymbol{x};\boldsymbol{x})$.

Volker Bach proved a beautiful theorem (the so-called Lieb variational principle), which states that minimizing the functional $\mathcal{E}^{\mathrm{HF}}[\gamma_1]$ over the complete set of admisible γ_1 (with $0 \leq \gamma_1 \leq \mathbb{1}$ and $\operatorname{Tr}\gamma_1 = N$) does not yield a lower numerical value than the Hartree-Fock energy, so that the following relation holds [Bac92]:

$$\min\{\mathcal{E}^{\mathrm{HF}}[\gamma_1] : 0 \leq \gamma_1 \leq \mathbb{1},\, \operatorname{Tr}\gamma_1 = N\} = \min\{\mathcal{E}^{\mathrm{HF}}[\gamma_1] : \gamma_1 = \gamma_1^2 = \gamma_1^*,\, \operatorname{Tr}\gamma_1 = N\}.$$

His constructive proof actually says that given any representable 1-RDM ($\gamma_1 \in \mathcal{B}_N^1$), then there exists a projector $\tilde{\gamma}_1 = \tilde{\gamma}_1^2 = \tilde{\gamma}_1^*$ with $\operatorname{Tr}\tilde{\gamma}_1 = N$, such that $\mathcal{E}^{\mathrm{HF}}[\gamma_1] \geq \mathcal{E}^{\mathrm{HF}}[\tilde{\gamma}_1]$. Another disadvantage of taking the Hartree-Fock *Ansatz* is that the corresponding 2-RDM functional, namely,

$$\gamma_2^{\mathrm{HF}} := \tfrac{1}{2}[\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1)\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_2) - \gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_2)\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_1)],$$

violates the sum rules for this matrix:

$$\int \gamma_2^{\mathrm{HF}}\, d\boldsymbol{x}_2 \geq \frac{N-1}{2}\gamma_1 \quad \text{and} \quad \int \gamma_2^{\mathrm{HF}}\, d\boldsymbol{x}_2\, d\boldsymbol{x}_1 = \tfrac{1}{2}N^2 - \tfrac{1}{2}\sum_i n_i^2 \geq \frac{N(N-1)}{2}. \tag{2.17}$$

These inequalities are strict except when γ_1 is a projector, which only happens whenever it comes from a determinantal wave function. This latter consideration led people to propose a wide variety of alternative functionals currently used in RDMFT which can be traced back to the Müller functional [Mül84]. The basic idea consists in redefining the exchange term in Eq. (2.7) in order to recover the correct sum rule. The Müller functional reads:

$$\gamma_2^{\mathrm{M}} := \tfrac{1}{2}[\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1)\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_2) - \gamma_1^{1/2}(\boldsymbol{x}_1;\boldsymbol{x}_2)\gamma_1^{1/2}(\boldsymbol{x}_2;\boldsymbol{x}_1)], \tag{2.18}$$

where $\gamma_1^{1/2}$ denotes the positive square root of the operator γ_1 and satisfies

$$\gamma_1(\boldsymbol{x};\boldsymbol{x}') = \int \gamma_1^{1/2}(\boldsymbol{x};\boldsymbol{y})\gamma_1^{1/2}(\boldsymbol{y};\boldsymbol{x})d\boldsymbol{y},$$

which in the basis of the NO is given by the expression:

$$\gamma_1^{1/2}(\boldsymbol{x};\boldsymbol{x}') = \sum_i \sqrt{n_i}\,\phi_i(\boldsymbol{x})\phi_i^*(\boldsymbol{x}').$$

It is clear that when γ_1 is a projector, $\gamma_1 = \gamma_1^{1/2}$. The main advantage of the Müller functional is that it satisfies adequately the sum rules. However, the functional $\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - |\gamma^{1/2}(\boldsymbol{x},\boldsymbol{x}')|^2$ could take negative values and is not skewsymmetric under interchange of particles.

For the case of two-electron systems it happens that the Müller energy functional:

$$\mathcal{E}^{\mathrm{M}}[\gamma_1] = -\frac{1}{2}\int \delta(\boldsymbol{x}-\boldsymbol{x}')\,\Delta_{\boldsymbol{r}}\gamma_1(\boldsymbol{x};\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}' + \int V_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + \int \frac{\gamma_2^{\mathrm{M}}(\boldsymbol{x}_1;\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{x}_1 d\boldsymbol{x}_2$$

gives a lower bound for the ground-state energy [FLSS07, BGBV12]. Although it has not been proved for larger systems, it is believed that the following condition holds in general:

$$\min\{\mathcal{E}^{\mathrm{HF}}[\gamma_1] : \gamma_1 \in \mathcal{B}_N^1\} = E_{\mathrm{HF}} \geq E_0 \geq \min\{\mathcal{E}^{\mathrm{M}}[\gamma_1] : \gamma_1 \in \mathcal{B}_N^1\}.$$

For the Moshinsky atom, three years ago Joseph Várilly and I computed the energy predicted by the Müller functional when evaluated on the correct ground-state 1-RDM. Astonishingly, for such a simple system the Müller energy is equal to the correct one, that is, $\mathcal{E}^{\mathrm{M}}[\gamma_{1\mathrm{gs}}] = E_0$, for any value of the coupling constant [BRV12, BR13, NP10].

In the last twenty years there has been a considerable amount of work on continuing this tradition of *Ansätze* γ_2 in terms of γ_1, expressed through its NO and its NON [Hel06]. Starting with the pioneering work by Müller [Mül84], which was rediscovered in [BB02], several competing functionals have been designed, partly out of theoretical prejudice, partly with the aim of improving predictions for particular systems: among others, the total energy of molecular dissociation [GU98], the correlation energy of the homogeneous electron gas [CGA02] and the band gap behavior of some semiconductors [SDLG08]. Jointly with István Nagy, I recently proposed a variational isospectral deformation of the Müller functional [BRN14]. In order to test the accuracy of some of these 1-RDM functionals, Várilly and I evaluated six of them (Hartree-Fock, Müller, Goedecker–Umrigar, Csányi–Goedecker–Arias, Buijse–Baerends and Corrected Buijse–Baerends) in a completely solvable model (the Moshinsky atom, already discussed), for which the value of the ground-state energy is completely known [BRV12].

2.6 Generalized Pauli constraints

The representability condition for the 1-RDM says that NON (arranged in the customary decreasing order $n_i \geq n_{i+1}$) fulfil the constraint $n_i \leq 1$, allowing no more than one electron in each quantum state. This is necessary and sufficient for a 1-RDM to be the contraction of an *ensemble* N-body density matrix, provided of course that $\sum_i n_i = N$. In a seminal work, Borland and Dennis [BD72] observed that for the rank-six approximation of a *pure-state* $N = 3$ system —belonging thus to the Hilbert space $\wedge^3\mathcal{H}_6$— the NON satisfy the following additional conditions:

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1 \quad \text{and} \quad n_4 \leq n_5 + n_6.$$

Notice that the set of equalities allows exactly *one* electron in the natural orbitals r and $7 - r$.

The analysis by Klyachko and coworkers [Kly06, AK08] of the *pure* N-representability problem for the 1-RDM establishes a systematic approach to the problem, generalizing this type of constraints. In fact, for a pure quantum system of N electrons arranged in m spin orbitals, the occupation numbers satisfy a set of linear inequalities, known as *generalized Pauli constraints* (GPC):

$$D^{\mu}_{N,m}(\vec{n}) = \kappa^{\mu}_0 + \kappa^{\mu}_1 n_1 + \cdots + \kappa^{\mu}_m n_m \geq 0, \tag{2.19}$$

with $\vec{n} := (n_1, \ldots, n_m)$, the coefficients $\kappa^{\mu}_j \in \mathbb{Z}$ and $\mu = 1, 2, \ldots, r_{N,m}$. These conditions define a convex polytope of allowed states in $\mathbb{R}^m$. When one of the GPC is completely saturated [i.e., equality holds in Eq. (2.19)], the system is said to be *pinned*, and it lies on one of the facets of the polytope.

The nature of those conditions has been explored up to now in a few systems: the 3-harmonium, that is, a model of three spinless fermions confined to a one-dimensional harmonic potential [SGC13], the lithium isoelectronic series [BRGBS13, BRS15b], and ground and excited states of some three- and four-electron molecules whose rank equals twice the number of electrons [CM14]. For reasons that remain mysterious, for all these systems some inequalities are (quite often) *nearly saturated*, that is, in equations like (2.19) equality almost holds [BRS15a]. This is the so-called *quasipinning* phenomenon, originally proposed by Christian Schilling, David Gross and Matthias Christandl [SGC13].

Consider one of the conditions of Eq. (2.19), say μ, for which pinning

$$D^{\mu}_{N,m}(\vec{n}) = 0 \tag{2.20}$$

holds. For such systems, the corresponding wave function belongs to the 0-eigenspace of the following operator:

$$\mathbf{D}^{\mu}_{N,m} = \kappa^{\mu}_{0}\mathbb{1} + \kappa^{\mu}_{1}a^{\dagger}_{1}a_{1} + \cdots + \kappa^{\mu}_{m}a^{\dagger}_{m}a_{m},$$

where $a^{\dagger}_{i}$ and a_i are the fermionic creation and annihilation operators of the state i. This condition can be recast as a *superselection rule* for the Slater determinants that appear in the CI decomposition of the wave function:

$$|\Psi\rangle = \sum_{K} c_K|\mathbf{K}\rangle, \tag{2.21}$$

with $|\mathbf{K}\rangle$ denoting a Slater determinant. In fact, given a pinned system that satisfies equality (2.20), each Slater determinant appearing in the expansion (2.21) must be an eigenfunction of $\mathbf{D}^{\mu}_{N,m}$ with a zero eigenvalue. The superfluous or ineffective configurations are thus identified by means of the criterion [Kly09]:

$$\text{if } \mathbf{D}^{\mu}_{N,m}|\boldsymbol{K}\rangle \neq 0, \text{ then } c_K = 0.$$

It immediately demonstrates that the (quasi)pinning phenomenon allows one to drastically reduce the number of Slater determinants in CI expansions. Moreover, the GPC force a promising rethinking of RDMFT, correcting the zoo of functionals by making them GPC-honest, with potentially revolutionary consequences [TLMH15]. Also, violation of the GPC has recently been identified as an encoder of the openness of a quantum system [CM15b]. It is worth saying that we have examined the relation of pinned and quasipinned systems with related aspects of entanglement in atoms and molecules and quantum information theory [BRGBS13]. For a comprehensive and documented review of these rather new ideas see the recent review [CM15a] as well as Chapters ... of this dissertation.

2.7 New wine in old (and new) wineskins

This monographic chapter has been devoted to providing an overview of the history of some of the quantum chemistry holy grails. As could not be otherwise, it is incomplete. We did not mention other famous vessels in which the lineage of quantum-chemistry intelectual dreams is stored. For example, the search for a functional theory based on a family of *intracular* distributions, carried out mainly by Peter Gill and his group of co-workers in Sydney [GCOB06]. Their ideas drink from the living waters of the Coulson program, for the truth is that the 2-RDM —the key issue in the aforementioned program— still possesses much more information than is needed in quantum chemistry. Indeed, the interelectronic integral can be studied in a much simpler way, namely,

$$\int \frac{\gamma_2(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1,\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,d\boldsymbol{x}_1\,d\boldsymbol{x}_2 = \int \frac{\mathcal{I}(r)}{r}\,dr,$$

where the intracular distribution is defined as a contraction of the 2-RDM:

$$\mathcal{I}(r) := \int \gamma_2(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1,\boldsymbol{x}_2)\delta(|\boldsymbol{r}_1-\boldsymbol{r}_2|-r)\,d\boldsymbol{x}_1\,d\boldsymbol{x}_2.$$

As a matter of fact, an intracular functional theory purports to become a theory based on 7 variables instead of 12, which to some extent alleviates the computational cost. Nevertheless the representability problems of such a distribution are much more involved.

More recently, an equivalent theory to RDMFT was formulated in phase space (it is called Wigner DFT) by Philippe Blanchard, José Gracia-Bondía and Joseph Várilly [BGBV12]. Although Wigner phase space quasiprobabilities are equivalent to RDM of any order, this approach highlights the importance of the momenta in the description of the energy of a quantum mechanical system. Moreover, although this phase-space formulation contains no more information than the customary wave-function formulation, it allows a direct comparison with classical descriptions and therefore quantum effects are more directly identified [SD87, BRGBV12]. To a more comprehensive discussion of Wigner DFT is devoted Chapter 3.

In the end, the dream of all these proposals is to find useful tools to calculate correlation energies at a low computational cost. Behind them, in avoiding the wave function, lies a unique mathematical problem: the so-called quantum marginal problem. Throughout these first lines we have emphasized the importance of this problem in order to determine feasible electronic densities, 1-RDM, 2-RDM, intracular distributions or Wigner density quasiprobabilities. To "disentangle" or study some theoretical and practical aspects of this problem in quantum chemistry is the goal of this PhD dissertation.

Chapter 3

Wigner density functional theory

3.1 Introduction and history

By definition, a N-body Wigner quasiprobability distribution (or Wigner function, for short) is given in terms of the density matrix in configuration or momentum space, respectively γ_N, $\tilde{\gamma}_N$, by [Wig32]:

$$\begin{aligned} w_N^{\vec{\varsigma};\vec{\varsigma}'}(\vec{\boldsymbol{r}};\vec{\boldsymbol{p}}) &= \frac{1}{\pi^{dn}} \int \gamma_N(\vec{\boldsymbol{r}}-\vec{\boldsymbol{z}},\vec{\varsigma};\vec{\boldsymbol{r}}+\vec{\boldsymbol{z}},\vec{\varsigma}')\, e^{2i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{z}}}\, d\vec{\boldsymbol{z}} \\ &= \frac{1}{\pi^{dn}} \int \tilde{\gamma}_N(\vec{\boldsymbol{p}}-\vec{\boldsymbol{z}},\vec{\varsigma};\vec{\boldsymbol{p}}+\vec{\boldsymbol{z}},\vec{\varsigma}')\, e^{-2i\vec{\boldsymbol{r}}\cdot\vec{\boldsymbol{z}}}\, d\vec{\boldsymbol{z}}, \end{aligned} \tag{3.1}$$

with the notation $\vec{\boldsymbol{r}} = (\vec{\boldsymbol{r}}_1,\dots,\vec{\boldsymbol{r}}_N)$ for N bodies, where $\boldsymbol{r}_i \in \mathbb{R}^d$ (say, $d=3$ for ordinary space), and similarly for $\vec{\boldsymbol{p}}$, $\vec{\boldsymbol{z}}$ and $\vec{\varsigma}$. Note that $w_N^{\varsigma_1,\dots,\varsigma_N;\varsigma_1',\dots,\varsigma_N'}$ may be regarded as a $2N \times 2N$ matrix in spin space. As the reader should remember, for a pure state one has $\gamma_N(\vec{\boldsymbol{x}};\vec{\boldsymbol{x}}') = \Psi(\vec{\boldsymbol{x}})\Psi^*(\vec{\boldsymbol{x}}')$, with Ψ the corresponding wave function. The relation

$$\gamma_N \Longleftrightarrow w_N$$

is one-to-one, being the restriction to the convex set of positive operators of unit trace of a linear isomorphism of functions of two sets of variables, essentially the inverse of the unitary *Wigner transformation*, which is known to be of order 24 [VGB87]. Hence, from the mathematical viewpoint, Wigner functions are equivalent to density matrices.

The spectral theorem of quantum mechanics has a counterpart in its phase-space formulation. The operational structure requires the introduction of the so-called Moyal or twisted product (denoted by $\star$). For spinless Wigner functions, it is defined in the following way

$$(\chi \star \zeta)(\boldsymbol{r};\boldsymbol{p}) := \frac{1}{\pi^{6N}} \int \chi(\boldsymbol{r}';\boldsymbol{p}')\zeta(\boldsymbol{r}'';\boldsymbol{p}'')e^{2i[(\boldsymbol{q}\cdot(\boldsymbol{p}'-\boldsymbol{p}'')-\boldsymbol{q}'\cdot(\boldsymbol{p}-\boldsymbol{p}'')-\boldsymbol{q}''\cdot(\boldsymbol{p}'-\boldsymbol{p})]} d\boldsymbol{q}'\,d\boldsymbol{p}'\,d\boldsymbol{q}''\,d\boldsymbol{p}'',$$

and satisfies the "tracial" property:

$$\int (\chi \star \zeta)(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{q}\, d\boldsymbol{p} = \int \chi(\boldsymbol{r};\boldsymbol{p})\zeta(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{q}\, d\boldsymbol{p} = \int (\zeta \star \chi)(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{q}\, d\boldsymbol{p}.$$

The Moyal representation for spin particles as functions on the sphere is more involved and it was performed in the eighties [VGB89]. The phase-space version of the stationary Schrödinger equation is given by the eigenvalue problem

$$H \star \zeta_{ij} = E_i \zeta_{ij} \quad \text{and} \quad \zeta_{ij} \star H = E_j \zeta_{ij}.$$

The solutions form a (doubly-indexed) orthogonal basis for functions on phase space and the eigenvalues correspond to the spectrum of the Hamiltonian operator. The following relation is encountered for the solutions of the Schrödinger equation: $\zeta_{ij} \star \zeta_{kl} = \delta_{jk}\zeta_{il}$, as well as the normalization $\int \zeta_{ij}\, d\boldsymbol{r} d\boldsymbol{p} = \delta_{ij}$. Finally, the Hamiltonian operator can be written in the phase-space spectral form

$$H(\boldsymbol{r};\boldsymbol{p}) = \sum_i E_i\, \zeta_{ii}(\boldsymbol{r};\boldsymbol{p}).$$

Averages of Wigner functions with classical phase space observables reproduce the expected values predicted by standard quantum mechanics. This is why they have become an important tool, successfully adopted in statistical physics, quantum optics [Leo10] and, more recently, quantum chemistry [SD87, BGBV12, EFGB12, BRV12, BRGBV12]. It is however not easy to characterize them, although necessary and sufficient conditions for a phase space function to be an admissible Wigner function are known [NO86, GBV88, BGBV12]. Moreover, Wigner functions are always symmetric for bosons or fermions. Whether a Wigner function corresponds to a wave function symmetric or antisymmetric under permutations of its variables, which is a natural question in order to classify the statistical nature of the system it describes, has been elucidated also lately [BRGB13]. In the literature there are other phase-space distributions (Berezin's Q or P functions for example), but the Wigner function is the only one which is in general real. For this reason, Wigner functions could be interpreted as true probability distributions in phase space; it is known nevertheless that there is nothing to prevent them from taking negative values.

By use of the equivalence between Wigner functions and RDM, reduced Wigner density matrices (WRDM) are obtained by partial integration, to wit,

$$\begin{aligned} &w_n^{\varsigma_1,\dots,\varsigma_n;\varsigma_1',\dots,\varsigma_n'}(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n;\boldsymbol{p}_1,\dots,\boldsymbol{p}_n) \\ &\quad = \binom{N}{n} \int w_N^{\varsigma_1,\dots,\varsigma_n,\varsigma_{n+1},\dots,\varsigma_N,\varsigma_1',\dots,\varsigma_n',\varsigma_{n+1},\dots,\varsigma_N}(\vec{\boldsymbol{r}};\vec{\boldsymbol{p}}) \prod_{j=n+1}^{N} d\boldsymbol{r}_j\, d\boldsymbol{p}_j\, d\varsigma_j. \end{aligned} \tag{3.2}$$

Notice that $w_n^{\varsigma_1,\dots,\varsigma_n;\varsigma_1',\dots,\varsigma_n'}$ may be regarded as a $2n \times 2n$ matrix in spin space or, as we will discuss later in this chapter for w_2 and w_1, as a direct sum of tensor representations of the rotation group. For instance,

$$w_1^{\varsigma;\varsigma'} = \begin{pmatrix} w^{\uparrow\uparrow'}(\boldsymbol{r};\boldsymbol{p}) & w^{\uparrow\downarrow'}(\boldsymbol{r};\boldsymbol{p}) \\ w^{\downarrow\uparrow'}(\boldsymbol{r};\boldsymbol{p}) & w^{\downarrow\downarrow'}(\boldsymbol{r};\boldsymbol{p}) \end{pmatrix},$$

can be in turn viewed as the direct sum of one scalar component, plus three vectorial ones. As mentioned, at each order w_n and the corresponding γ_n contain the same information and therefore it is possible to recover the latter matrices from the former ones by means of the following inversion formula:

$$\begin{aligned}\gamma_n(\boldsymbol{x}_1, \dots, \boldsymbol{x}_n; \boldsymbol{x}'_1, \dots, \boldsymbol{x}'_n) \\ = \int w_n^{\varsigma_1,\dots,\varsigma_n;\varsigma'_1,\dots,\varsigma'_n}\left(\tfrac{\boldsymbol{r}_1+\boldsymbol{r}'_1}{2}, \dots, \tfrac{\boldsymbol{r}_n+\boldsymbol{r}'_n}{2}; \boldsymbol{p}_1, \dots, \boldsymbol{p}_n\right) e^{i\sum \boldsymbol{p}_j\cdot(\boldsymbol{r}_j-\boldsymbol{r}'_j)} \prod d\boldsymbol{p}_j.\end{aligned}$$

The traces of these matrices are denoted by $w_n := \int w_n^{\varsigma_1,\dots,\varsigma_n;\varsigma_1,\dots,\varsigma_n} d\varsigma_1 \cdots d\varsigma_n$. By partial integration of w_1 one gets the electronic density: $\rho(\boldsymbol{r}) = \int w_1(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{p}$.

3.2 Wigner density functional theory

In the language of Wigner quasiprobabilities, it is possible to reword the Coulson program by expressing the energy of any nonrelativistic quantum system as a linear functional on the 2-WRDM, namely,

$$\tilde{\mathcal{E}}[w_2] = \int \tilde{K}\, w_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) \prod_{i=1}^{2} d\boldsymbol{r}_i\, d\boldsymbol{p}_i,$$

where the helium-like Hamiltonian now reads:

$$\tilde{K} := \frac{2}{N-1}\left[\frac{1}{2}\boldsymbol{p}_1^2 + V_{\mathrm{ext}}(\boldsymbol{r}_1)\right] + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}.$$

Naturally, the ground-state energy is found by minimizing the functional $\tilde{\mathcal{E}}(w_2)$ over the set of representable 2-WRDM. The representability issue is here more involved than for 2-RDM, because in the first place, in carrying out the Wigner transformation (3.1), we have lost the information on the symmetry under permutations of the variables. Jointly with José Gracia-Bondía, I solved this problem, proposing very simple criteria to decide the statistical nature of the bodies described by a n-WRDM [BRGB13].

Wigner density functional theory (WDFT) is a phase-space extension of RDMFT whose main theorem is due to Blanchard, Gracia-Bondía and Várilly, which establishes a one-to-one correspondence between the ground-state N-body Wigner density matrix of a nondegenerate many-body system and the corresponding 1-WRDM:

$$w_{N\mathrm{gs}}(\vec{\boldsymbol{r}}, \vec{\boldsymbol{p}}) \Longleftrightarrow w_{1\mathrm{gs}}(\boldsymbol{r}, \boldsymbol{p}). \tag{3.3}$$

The proof of this statement, like in the Hohenberg-Kohn theorem, goes by contradiction. Existence and some of the properties of the Wigner energy functional were established three years ago in [BGBV12]. The theory has the flavor of an almost exact Thomas–Fermi formalism in phase space, needing “only” to incorporate electron correlation. It is worth noting that the representability problem for the 1-WRDM is solved in the same way as the one for 1-RDM; that is, in the basis of *Wigner natural orbitals* (WNO), we write

$$w_1(\boldsymbol{r};\boldsymbol{p}) = \sum_i n_i\, \chi_{ii}(\boldsymbol{r};\boldsymbol{p}) \quad \text{where} \quad \sum_i n_i = N \quad \text{and} \quad 0 \le n_i \le 1,\ \forall i.$$

The WNO satisfy $\chi_{ii}(\boldsymbol{r};\boldsymbol{p}) = \frac{1}{\pi^{dn}} \int \phi_i(\boldsymbol{r}-\boldsymbol{z})\phi_i^*(\boldsymbol{r}+\boldsymbol{z})\, e^{2i\boldsymbol{p}\cdot\boldsymbol{z}}\, d\boldsymbol{z}$, where $\phi_i(\boldsymbol{r})$ and n_i are the customary NO and NON respectively, as defined in Section 2.4. In this basis the interferences become $\chi_{ij}(\boldsymbol{r};\boldsymbol{p}) = \frac{1}{\pi^{dn}} \int \phi_i(\boldsymbol{r}-\boldsymbol{z})\phi_j^*(\boldsymbol{r}+\boldsymbol{z})\, e^{2i\boldsymbol{p}\cdot\boldsymbol{z}}\, d\boldsymbol{z}$.

For two-electron systems, the representability problem for w_2 is almost completely solved, giving rise to the Löwdin-Shull functionals. Putting together (2.11) and (3.1), one arrives at the phase-space counterpart of the aforementioned functional for the singlet spin configuration [BGBV12]:

$$w_2^{\mathrm{LS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \sum_{ij} \nu_i \nu_j \chi_{ij}(\boldsymbol{r}_1; \boldsymbol{p}_1) \chi_{ij}(\boldsymbol{r}_2; \boldsymbol{p}_2), \quad \text{where} \quad \nu_i^2 = n_i. \tag{3.4}$$

On the other hand, expressing Eq. (2.14) in phase space by means of the Wigner transformation (3.1) gives the Löwdin-Shull functional for triplet 2-WRDM, namely [BRGBV12]:

$$\sum_{v,w} a_v a_w \big[\chi_{2v,2w}(\boldsymbol{r}_1; \boldsymbol{p}_1)\chi_{2v+1,2w+1}(\boldsymbol{r}_2; \boldsymbol{p}_2) - \chi_{2v,2w+1}(\boldsymbol{r}_1; \boldsymbol{p}_1)\chi_{2v+1,2w}(\boldsymbol{r}_2; \boldsymbol{p}_2) \\ - \chi_{2v+1,2w}(\boldsymbol{r}_1; \boldsymbol{p}_1)\chi_{2v,2w+1}(\boldsymbol{r}_2; \boldsymbol{p}_2) + \chi_{2v+1,2w+1}(\boldsymbol{r}_1; \boldsymbol{p}_1)\chi_{2v,2w}(\boldsymbol{r}_2; \boldsymbol{p}_2)\big], \tag{3.5}$$

and therefore

$$w_1^{\mathrm{T}}(\boldsymbol{r}; \boldsymbol{p}) = 2 \sum_w a_w^2 [\chi_{2w,2w}(\boldsymbol{r}; \boldsymbol{p}) + \chi_{2w+1,2w+1}(\boldsymbol{r}; \boldsymbol{p})].$$

Notice again that in the previous equation each occupation number $n_w := 2a_w^2$ appears twice.

Another important feature of WDFT is that there exists a functional $\mathcal{A}$ of the electronic quasiprobability w_1, such that:

$$E_0 \le \int \left[\frac{1}{2}\boldsymbol{p}^2 + V_{\mathrm{ext}}(\boldsymbol{r})\right] w_1(\boldsymbol{r}; \boldsymbol{p})\, d\boldsymbol{r} d\boldsymbol{p} + \mathcal{A}[w_1] =: \mathcal{E}^{\mathrm{WDFT}}[w_1].$$

The equality holds when $\mathcal{E}^{\mathrm{WDFT}}[\cdot]$ is evaluated on $w_{1\mathrm{gs}}$, the ground-state 1-WRDM. As in DFT, this functional obeys a constrained-search formulation, namely,

$$\mathcal{A}[w_1] = \min_{w_N \to w_1} \int W(\vec{\boldsymbol{r}}; \vec{\boldsymbol{p}}) w_N(\vec{\boldsymbol{r}}; \vec{\boldsymbol{p}})\, d\boldsymbol{r}\, d\boldsymbol{p};$$

the minimization runs over the set of N-Wigner density matrices leading the fixed quasidensity w_1. The interelectronic operator has been defined in Eq. (2.2). The minimization is carrying out in two steps. First, a constrained search on the trial quasidensity w_1 is performed. In the second step, $\mathcal{E}^{\mathrm{WDFT}}[w_1]$ is minimized over the set of representable 1-WRDM. Resembling DFT, this functional exhibits some nice properties. First of all, it is universal: it is independent of the external potential. More important is that, unlike the standard DFT, its scaling behavior is also nice. To see that, let us define the scaled Wigner distribution [BGBV12]:

$$w_N^\lambda(\vec{\boldsymbol{r}}; \vec{\boldsymbol{p}}) := w_N(\lambda\vec{\boldsymbol{r}}; \lambda^{-1}\vec{\boldsymbol{p}}) \Longrightarrow w_1^\lambda(\boldsymbol{r}; \boldsymbol{p}) = w_1(\lambda\boldsymbol{r}; \lambda^{-1}\boldsymbol{p}).$$

It is easy to show that $\mathcal{A}[w_1^\lambda] = \lambda\mathcal{A}[w_1]$ and $\frac{\partial}{\partial\lambda}\mathcal{A}[w_1^\lambda]\big|_{\lambda=1} = \mathcal{A}[w_1]$. In contrast, it is known that the DFT functional displays some bad scaling properties. To see that, take

$$\Psi^\lambda(\vec{\boldsymbol{r}}) := \lambda^{3N/2}\Psi(\lambda\vec{\boldsymbol{r}}) \Longrightarrow \rho^\lambda(\boldsymbol{r}) = \lambda^3\rho(\lambda\boldsymbol{r})$$

and therefore the corresponding universal functional amounts to

$$F[\rho] = \langle \Psi[\rho] | \widehat{T} + \widehat{W} | \Psi[\rho] \rangle = \lambda^{-2} \langle \Psi^{\lambda}[\rho^{\lambda}] | \widehat{T} + \lambda \widehat{W} | \Psi^{\lambda}[\rho^{\lambda}] \rangle.$$

What happens here is that a minimizer $\Psi_{\rho}^{\min}$ gives ρ by minimizing $\widehat{T} + \widehat{W}$; however, $\lambda^{3N/2}\Psi_{\rho}^{\min}(\lambda\vec{r})$ gives ρ^{λ} by minimizing $\lambda^{-2}(\widehat{T} + \lambda\widehat{W})$. Therefore,

$$\lambda^{3N/2}\Psi_{\rho}^{\min}(\lambda\vec{r}) \neq \Psi_{\rho_{\lambda}}^{\min}(\vec{r}),$$

where $\Psi_{\rho_{\lambda}}^{\min}(\vec{r})$ is a minimizer for $\widehat{T} + \widehat{W}$. Hence, the kinetic and interelectronic functionals $\langle \Psi[\rho] | \widehat{T} | \Psi[\rho] \rangle$ and $\langle \Psi[\rho] | \widehat{W} | \Psi[\rho] \rangle$ do not scale homogeneously, while in WDFT the functional $\mathcal{A}$ does so.

With the purpose of calibrating correlation energy, Marcos Moshinsky introduced a completely integrable analogue of a two-electron atom, here called the *Moshinsky atom* [Mos68]. It describes two spin-$\frac{1}{2}$ fermions nteracting with an external harmonic potential and repelling each other by a Hooke-type force; thus the Moshinsky-atom Hamiltonian in Hartree-like units is

$$H = \frac{1}{2}\boldsymbol{p}_1^2 + \frac{1}{2}\boldsymbol{p}_2^2 + \frac{k}{2}(\boldsymbol{r}_1^2 + \boldsymbol{r}_2^2) - \frac{\delta}{4}r_{12}^2, \tag{3.6}$$

where $r_{12} := |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, k is the coupling constant of the harmonic well and the constant δ controls the coupling strength of the harmonic interaction between the particles. It is worth mentioning that this model is rooted in the history of quantum mechanics. In the wondrous library of Bielefeld University, I "discovered" by chance that Heisenberg invoked it to approach the spectrum of helium [Hei26] and since then it has long been regarded as an exactly solvable laboratory bench for quantum chemistry.

Several problems related with this model are analytically solvable, and therefore it is tempting to employ it as a testing ground for methods used in other systems, such as the helium series. Indeed, there is considerable recent work on studying and learning from this atom, including correlation [Mos68, MCCA08, Loo10, NP11], approximation of functionals, questions of entanglement [BMP+12, BRTD14] and black hole entropy [Sre93]. For the analysis of the Moshinsky atom the phase space representation of quantum mechanics recommends itself. Subsection 3.5 is devoted to studying in WDFT the first excited state of the Moshinsky atom.

3.3 Helium: a phase space description

To illustrate some of the tools involved in a formulation of quantum chemistry in phase space, we compute here the ground-state energy of helium using a basis of M s-type Gaussians. The general expression of such a Gaussian —centered at the origin— is given by the expression:

$$g_i(\boldsymbol{r}) = \frac{d_i^{3/4}}{\pi^{3/4}} e^{-\frac{1}{2}d_i\boldsymbol{r}^2 - \frac{i}{2}b_i d_i \boldsymbol{r}^2}, \quad \text{with} \quad d_i > 0 \quad \text{and} \quad b_i \in \mathbb{R}. \tag{3.7}$$

To avoid confusions, we use the symbol g for normalized s-Gaussians. Other primitive functions indexed with (n, l, m) are constructed multiplying $g_i(\boldsymbol{r})$ with $r^{n-1}Y_{lm}(\theta, \phi)$, where Y_{lm} stands for the spherical Harmonics [Spr00]. Since the spin and spatial parts of the helium wave function factorize completely, it reads

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2}{\sqrt{2}} \sum_{ij}^{M} c_{ij}\, g_i(\boldsymbol{r}_1) g_j(\boldsymbol{r}_2), \quad \text{provided that} \quad \langle\Psi|\Psi\rangle = 1.$$

The expression is similar to (2.9), except that here the basis set is non-orthogonal. The corresponding Wigner distribution is given by the expression

$$w_2^{\varsigma_1,\varsigma_2;\varsigma_1',\varsigma_2'}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = (\text{spin part}) \times \sum_{ijkl}^{M} c_{kl}^*\, c_{ij}\, g_{ik}(\boldsymbol{r}_1, \boldsymbol{p}_1) g_{jl}(\boldsymbol{r}_2, \boldsymbol{p}_2). \tag{3.8}$$

Here g_{ik} represents an *interference*, namely,

$$\begin{gathered} g_{ik}(\boldsymbol{r}; \boldsymbol{p}) = \frac{(d_i d_k)^{3/4}}{\pi^3 d_{ik}^{3/2}}\, e^{-A_{ik}\boldsymbol{r}^2 - 2B_{ik}\boldsymbol{r}\cdot\boldsymbol{p} - d_{ik}^{-1}\boldsymbol{p}^2}, \quad \text{where} \\ d_{ik} := \tfrac{1}{2}(d_i + d_k) + \tfrac{i}{2}(b_i d_i - b_k d_k), \quad b_{ik} := \tfrac{1}{2}(b_i d_i + b_k d_k) - \tfrac{i}{2}(d_i - d_k), \end{gathered} \tag{3.9}$$

and $A_{ik} := d_{ik} + b_{ik}^2/d_{ik}$, $B_{ik} := b_{ik}/d_{ik}$. The quadratic form in the exponent of the g_{jk} is given by a symmetric, symplectic matrix with positive definite real part [Lit86, BGBV12]. When $i = k$, we have the Gaussian *pure state*:

$$g_{ii}(\boldsymbol{r}; \boldsymbol{p}) = \pi^{-1}\, e^{-\boldsymbol{u}^t A \boldsymbol{u}}, \quad \text{where} \quad \boldsymbol{u} := (\boldsymbol{r}, \boldsymbol{p}) \quad \text{and} \quad A := \begin{pmatrix} d_i + b_i^2 d_i & b_i \\ b_i & d_i^{-1} \end{pmatrix}.$$

The Hamiltonian of the atom we are considering here is given by the expression

$$H = \frac{1}{2}\boldsymbol{p}_1^2 + \frac{1}{2}\boldsymbol{p}_2^2 - \frac{2}{|\boldsymbol{r}_1|} - \frac{2}{|\boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}.$$

From now on we consider real Gaussians such that $b_i = 0$ in Eq. (3.7). We have to deal with the normalization, kinetic, external and interelectronic integrals as they appear in Table 3.1.

	integrals	expressions
normalization Γ_{ik}	$\int g_{ik}(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{p}\, d\boldsymbol{r}$	$\frac{2\sqrt{2}(d_i d_k)^{3/4}}{(d_i+d_k)^{3/2}}$
kinetic energy K_{ik}	$\frac{1}{2}\int g_{ik}(\boldsymbol{r};\boldsymbol{p})\, \boldsymbol{p}^2\, d\boldsymbol{p}\, d\boldsymbol{r}$	$\frac{3\sqrt{2}(d_i d_k)^{7/4}}{(d_i+d_k)^{5/2}}$
external energy V_{ik}	$-\int \frac{1}{\lvert\boldsymbol{r}\rvert} g_{ik}(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{p}\, d\boldsymbol{r}$	$-\frac{4(d_i d_k)^{3/4}}{\sqrt{\pi}(d_i+d_k)}$
e-e energy I_{ikjl}	$\int \frac{g_{ik}(\boldsymbol{r}_1;\boldsymbol{p}_1) g_{jl}(\boldsymbol{r}_2;\boldsymbol{p}_2)}{\lvert\boldsymbol{r}_1-\boldsymbol{r}_2\rvert}\, d\vec{\boldsymbol{p}}\, d\vec{\boldsymbol{r}}$	$\frac{8\sqrt{2}(d_i d_k d_j d_l)^{3/4}}{\sqrt{\pi}(d_i+d_k+d_j+d_l)^{1/2}(d_i+d_k)(d_j+d_l)}$

TABLE 3.1: Normalization, kinetic, external and interelectronic energy integrals for the interferences g_{ik} as defined in Eq. (3.9).

The expected value of the energy $\int H w_2 \, d\boldsymbol{r}_1 \, d\boldsymbol{r}_2 \, d\boldsymbol{p}_1 \, d\boldsymbol{p}_2$ results in the following functional:

$$E(\boldsymbol{c}, \boldsymbol{d}) = \sum_{ijkl=1}^{M} c_{ij} \, c_{kl}^{*} \left[2\Gamma_{jl}(K_{ik} - V_{ik}) + I_{ikjl} \right], \quad \text{with} \quad C(\boldsymbol{c}, \boldsymbol{d}) := \sum_{ijkl=1}^{M} c_{ij} c_{kl}^{*} \Gamma_{ik} \Gamma_{jl} = 1.$$

Therefore, the energy minimization goes in the following way:

$$\frac{\partial}{\partial c_{ij}} \frac{E(\boldsymbol{c}, \boldsymbol{d})}{C(\boldsymbol{c}, \boldsymbol{d})} = 0 \quad \text{and} \quad \frac{\partial}{\partial d_j} \frac{E(\boldsymbol{c}, \boldsymbol{d})}{C(\boldsymbol{c}, \boldsymbol{d})} = 0.$$

With two Gaussians the energy is barely -2.7578 au, but with just three Gaussians the value for the ground state energy notably drops to -2.8512 au. This value is much better than the Hartree-Fock energy for this atom, namely, -2.8356 au, computed using a 3-21G basis set [Joh13]. Employing seven Gaussians the energy improves greatly, reaching -2.8778 au, which represents 66% of the total correlation energy.

Figures 3.1 and 3.2 display the 1-WRDM for helium by optimizing a set of 7 Gaussians, both their exponents and their coefficients as well. In phase space there are three clearly identifiable subregions. There is an inner region in which the function w_1 takes large positive values and where actually it reaches a maximum at $(r, p) = (0.72, 0.94)$. In the dominant middle region, this function mostly takes positive values, but negative ones also appear, due to entanglement between the pair of electrons. A negative minimum is observed at $(r, p) = (1.01, 1.95)$, for which $w_1 = -0.22$. Finally, an oscillatory decay regime is found beyond these two regions.

Of particular interest are the subregions of the phase space in which the Wigner function takes negative values. This is a classically impossible phenomenon and for this reason is a signature of the highly nonclassical character of a quantum state. In particular, it is a signature of entanglement. It has been proved that s-waves —which depend on the radius $\boldsymbol{r}$ only— are entangled if and only if the corresponding Wigner quasidistribution sports negative values [DMWS06]. This is in effect the case of the Wigner function (3.8): the total amount of negative volume

$$\frac{1}{2} \int \left| w_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) \right| d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p}_1 d\boldsymbol{p}_2 - \frac{1}{2} = 5.42 \times 10^{-3}$$

is bigger than zero. In plain language, it means that in the Schmidt decomposition the wave function exhibits more than one singular value.

3.4 Some basic theorems

Since Wigner functions are symmetric both for bosons and fermions, a natural question is that of when does a Wigner function correspond to a wave function which is symmetric or antisymmetric under permutations of its variables. This was posed since the early days, in view of applications: see the references in [OW84]. But only the latter article purported to offer a general answer. We gave a *simple* answer to the question of quantum statistics for Wigner functions [BRGB13]. We dealt mainly with identical fermions, for which the Wigner function is a spin multiplet; hence definition (3.1) is insufficient. Even so, our characterization takes the form of mere preservations or changes of sign under

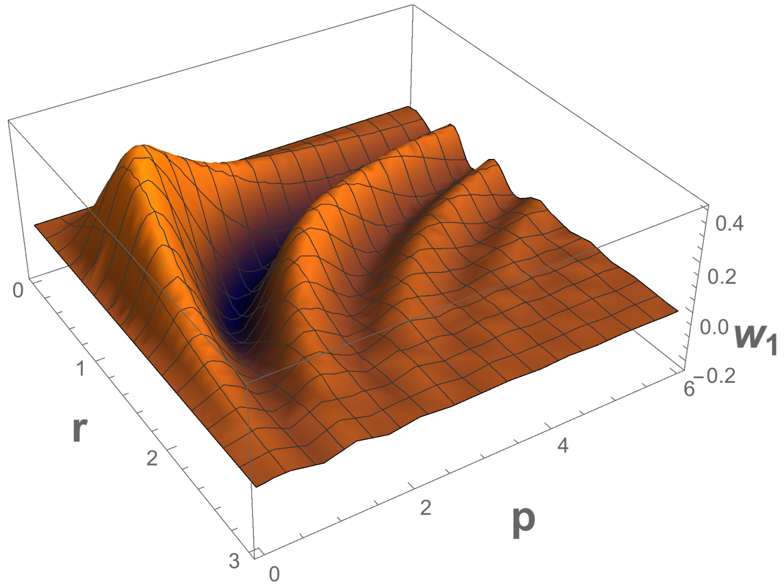

FIGURE 3.1: 1-WRDM for the helium atom using seven Gaussians (in Hartrees).

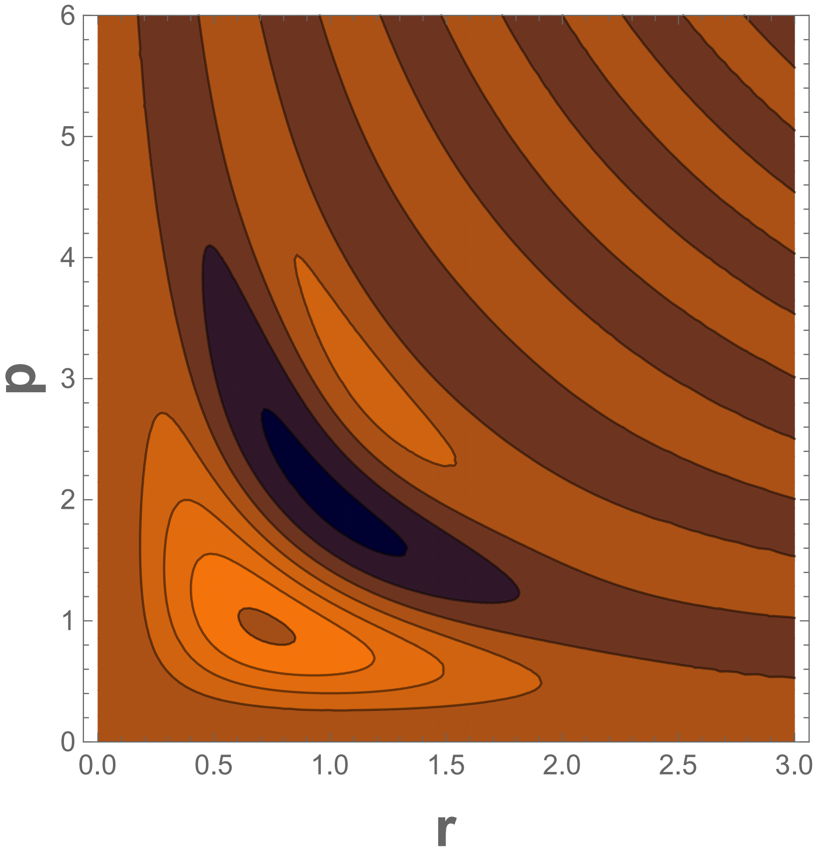

FIGURE 3.2: Contour curves in Hartrees for the 1-WRDM for the helium atom, using seven Gaussians.

exchange of two variables —just like in the ordinary formalism of quantum mechanics. This makes it trivial that the square of a permutation induces the identity, which is not at all obvious in [OW84].

For our purposes, it is enough to consider the two-body problem. Bringing in mean and difference coordinates, or, in chemists' jargon, *extracule* and *intracule* coordinates, respectively given by

$$\boldsymbol{R} = \frac{1}{\sqrt{2}}(\boldsymbol{r}_1 + \boldsymbol{r}_2), \qquad \boldsymbol{r} = \frac{1}{\sqrt{2}}(\boldsymbol{r}_1 - \boldsymbol{r}_2), \tag{3.10}$$

with the customary abuse of notation, the symmetry/antisymmetry conditions (say, on configuration space) for spinless bodies respectively read

$$\gamma_2\big(\boldsymbol{R}, \boldsymbol{r}, \boldsymbol{R}', \boldsymbol{r}'\big) = \pm\gamma_2\big(\boldsymbol{R}, -\boldsymbol{r}, \boldsymbol{R}', \boldsymbol{r}'\big) \quad \text{or} \quad \gamma_2\big(\boldsymbol{R}, \boldsymbol{r}, \boldsymbol{R}', \boldsymbol{r}'\big) = \pm\gamma_2\big(\boldsymbol{R}, \boldsymbol{r}, \boldsymbol{R}', -\boldsymbol{r}'\big).$$

Together they imply

$$\gamma_2\big(\boldsymbol{R}, \boldsymbol{r}, \boldsymbol{R}', \boldsymbol{r}'\big) = \gamma_2\big(\boldsymbol{R}, -\boldsymbol{r}, \boldsymbol{R}', -\boldsymbol{r}'\big); \tag{3.11}$$

and reciprocally, the latter indistinguishability property together with either of the above conditions implies the other.

It is not hard to see that with $\boldsymbol{P} = \frac{1}{\sqrt{2}}(\boldsymbol{p}_1 + \boldsymbol{p}_2)$ and $\boldsymbol{p} = \frac{1}{\sqrt{2}}(\boldsymbol{p}_1 - \boldsymbol{p}_2)$, the meaning of $w_2(\boldsymbol{R}, \boldsymbol{r}; \boldsymbol{P}, \boldsymbol{p})$ is unambiguous. This is due to the linear symplectic invariance of the Wigner function formalism. Then (3.11) is equivalent to

$$w_2(\boldsymbol{R}, \boldsymbol{r}; \boldsymbol{P}, \boldsymbol{p}) = w_2(\boldsymbol{R}, -\boldsymbol{r}; \boldsymbol{P}, -\boldsymbol{p}). \tag{3.12}$$

Since the discussion turns around the intracule variables, it is worth regarding $\boldsymbol{R}, \boldsymbol{P}$ as parameters, introducing the following notation:

$$\omega_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{r}; \boldsymbol{p}) := w_2(\boldsymbol{R}, \boldsymbol{r}; \boldsymbol{P}, \boldsymbol{p}).$$

Let us invoke the following partial Fourier transform on the intracule set of variables:

$$\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{v}; \boldsymbol{p}) := \int \omega_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{r}; \boldsymbol{p})\, e^{2i\boldsymbol{v}\cdot\boldsymbol{r}}\, d\boldsymbol{r} = \tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(-\boldsymbol{v}; -\boldsymbol{p}).$$

The last equality is seen to hold when (3.11) or equivalently (3.12) holds, and reciprocally. Now we have two momentum-like intracular variables, and the following appears natural.

Theorem 2. A scalar Wigner 2-body function comes from a symmetric/antisymmetric density matrix in its first set of variables, respectively in its second set, if and only if, for all $\boldsymbol{v}$ and $\boldsymbol{p}$ [BRGB13]:

$$\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{v}; \boldsymbol{p}) = \pm\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{p}; \boldsymbol{v}); \quad \text{respectively} \quad \tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{v}; \boldsymbol{p}) = \pm\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(-\boldsymbol{p}; -\boldsymbol{v}). \tag{3.13}$$

Proof. Consider the following integral:

$$\begin{aligned}\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{v};\boldsymbol{p}) &= \frac{1}{\pi^{2d}}\int \gamma_2\big(\boldsymbol{R}-\boldsymbol{Z},\boldsymbol{r}-\boldsymbol{z};\boldsymbol{R}+\boldsymbol{Z},\boldsymbol{r}+\boldsymbol{z}\big)\, e^{2i\boldsymbol{P}\cdot\boldsymbol{Z}+2i\boldsymbol{p}\cdot\boldsymbol{z}}\, e^{2i\boldsymbol{v}\cdot\boldsymbol{r}}\, d\boldsymbol{Z}\, d\boldsymbol{r}\, d\boldsymbol{z} \\ &= \frac{\pm 1}{\pi^{2d}}\int \gamma_2\big(\boldsymbol{R}-\boldsymbol{Z},\boldsymbol{z}-\boldsymbol{r};\boldsymbol{R}+\boldsymbol{Z},\boldsymbol{z}+\boldsymbol{r}\big)\, e^{2i\boldsymbol{P}\cdot\boldsymbol{Z}+2i\boldsymbol{v}\cdot\boldsymbol{r}}\, e^{2i\boldsymbol{p}\cdot\boldsymbol{z}}\, d\boldsymbol{Z}\, d\boldsymbol{r}\, d\boldsymbol{z} \\ &= \pm\int \omega_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{z};\boldsymbol{v})\, e^{2i\boldsymbol{p}\cdot\boldsymbol{z}}\, d\boldsymbol{z} =: \pm\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{p};\boldsymbol{v}).\end{aligned}$$

Thus necessity of the first condition is proved. Conversely, given that $\gamma_2 \Longleftrightarrow w_2$ is one-to-one, it is readily seen that (3.13) holds only if γ_2 is respectively symmetric/antisymmetric. The proof of the second condition is similar. Clearly, if we assume $\tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{v};\boldsymbol{p}) = \tilde{\omega}_{\boldsymbol{R},\boldsymbol{P}}(-\boldsymbol{v};-\boldsymbol{p})$, either of the conditions implies the other. Needless to say, one may formulate the conclusion analogously in terms of $\hat{\omega}_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{r},\boldsymbol{s}) := \int \omega_{\boldsymbol{R},\boldsymbol{P}}(\boldsymbol{r};\boldsymbol{p})\, e^{-2i\boldsymbol{s}\cdot\boldsymbol{p}}\, d\boldsymbol{p}$. ☐

This result can be extended to N-particle functions by just considering intracule and extracule coordinates for the first pair of adjacently labeled particles. That is, we require only one condition of the type (3.13), together with the indistinguishability condition (3.12) for all intracules.

Example 1. Take as a boson-type wave function the symmetric product of two general Gaussians centered at the origin:

$$\Psi(r_1,r_2) = C\big[g_1(r_1)g_2(r_2) + g_1(r_2)g_2(r_1)\big], \tag{3.14}$$

where we use the definitions given in (3.7).

The normalization factor C is unimportant here and therefore the corresponding 2-WRDM $w_2(r_1,r_2;p_1,p_2)$ is proportional to

$$g_{11}(r_1;p_1)g_{22}(r_2;p_2) + g_{22}(r_1;p_1)g_{11}(r_2;p_2) + g_{12}(r_1;p_1)g_{21}(r_2;p_2) + g_{21}(r_1;p_1)g_{12}(r_2;p_2).$$

To see that this quasidensity fulfills (3.13), change variables according to (3.10) and let $\lambda_{ijkl}(R,r;P,p) := g_{ij}(r_1;p_1)g_{kl}(r_2;p_2)$. Now, multiplying by e^{2ivr} and integrating with respect to r, we obtain, after a little work,

$$\int \lambda_{jjkk}(R,r;P,p)\, e^{2ivr}\, dr = \int \lambda_{jkkj}(R,r;P,v)\, e^{2ipr}\, dr \quad \text{with} \quad k \neq j,$$

thereby verifying condition (3.13) for this example. *Mutatis mutandis*, Gaussian sets like the ones in (3.14) with a minus instead of a plus sign exemplify the antisymmetric case.

For bodies possessing spin, the 2-WRDM reads:

$$w_2(1,2) = \begin{pmatrix} w^{\uparrow_1\uparrow_2\uparrow'_1\uparrow'_2}(1,2) & w^{\uparrow_1\uparrow_2\uparrow'_1\downarrow'_2}(1,2) & w^{\uparrow_1\uparrow_2\downarrow'_1\uparrow'_2}(1,2) & w^{\uparrow_1\uparrow_2\downarrow'_1\downarrow'_2}(1,2) \\ w^{\uparrow_1\downarrow_2\uparrow'_1\uparrow'_2}(1,2) & w^{\uparrow_1\downarrow_2\uparrow'_1\downarrow'_2}(1,2) & w^{\uparrow_1\downarrow_2\downarrow'_1\uparrow'_2}(1,2) & w^{\uparrow_1\downarrow_2\downarrow'_1\downarrow'_2}(1,2) \\ w^{\downarrow_1\uparrow_2\uparrow'_1\uparrow'_2}(1,2) & w^{\downarrow_1\uparrow_2\uparrow'_1\downarrow'_2}(1,2) & w^{\downarrow_1\uparrow_2\downarrow'_1\uparrow'_2}(1,2) & w^{\downarrow_1\uparrow_2\downarrow'_1\downarrow'_2}(1,2) \\ w^{\downarrow_1\downarrow_2\uparrow'_1\uparrow'_2}(1,2) & w^{\downarrow_1\downarrow_2\uparrow'_1\downarrow'_2}(1,2) & w^{\downarrow_1\downarrow_2\downarrow'_1\uparrow'_2}(1,2) & w^{\downarrow_1\downarrow_2\downarrow'_1\downarrow'_2}(1,2) \end{pmatrix},$$

where $(1,2)$ on the right hand side stands for the orbital phase space variables. Symmetry of γ_2 under interchange of *both* orbital and spin variables entails:

$$w_2(1,2) = A\,w_2(2,1)\,A, \quad \text{where} \quad A = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{3.15}$$

The matrix approach is often redundant in practice and was implicitly criticized by Wigner in his last years [OW84]. He sought instead to endow the spin Wigner functions with ostensible physical meaning, by grouping their entries into tensors under the rotation group. Given the unitary matrix

$$U := \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0 \\ 1 & 0 & 0 & -1 \end{pmatrix}$$

for the 1-WRDM, these are provided by

$$\begin{pmatrix} w^0 \\ w^x \\ w^y \\ w^z \end{pmatrix} = U \begin{pmatrix} w^{\uparrow_1\uparrow_{1'}} \\ w^{\uparrow_1\downarrow_{1'}} \\ w^{\downarrow_1\uparrow_{1'}} \\ w^{\downarrow_1\downarrow_{1'}} \end{pmatrix}.$$

There the entries on the right hand side are not real in general; on the left side they are. Matters turn interesting for the 2-body function, whereupon

$$\begin{pmatrix} w^0 \\ w^x \\ w^y \\ w^z \end{pmatrix} \otimes \begin{pmatrix} w^0 \\ w^x \\ w^y \\ w^z \end{pmatrix} = \big(U \otimes U\big) \left[\begin{pmatrix} w^{\uparrow_1\uparrow_{1'}} \\ w^{\uparrow_1\downarrow_{1'}} \\ w^{\downarrow_1\uparrow_{1'}} \\ w^{\downarrow_1\downarrow_{1'}} \end{pmatrix} \otimes \begin{pmatrix} w^{\uparrow_2\uparrow_{2'}} \\ w^{\uparrow_2\downarrow_{2'}} \\ w^{\downarrow_2\uparrow_{2'}} \\ w^{\downarrow_2\downarrow_{2'}} \end{pmatrix} \right]. \tag{3.16}$$

The central question addressed by O'Connell and Wigner is the transformation of $U \otimes U$ under particle exchange $1 \leftrightarrow 2$; this is better answered in terms of the physical tensor components of w_2. Denoting representations of the rotation group by their dimension, and since the 1-body function is the sum of one rotational scalar and one vector part, the addition rule for angular momentum yields:

$$\big([\mathbf{1}] \oplus [\mathbf{3}]\big)^{\otimes 2} = 2[\mathbf{1}] + 3[\mathbf{3}] + [\mathbf{5}];$$

that is two scalars, three vectors and one quadrupole (symmetric traceless tensor). Let now w^{00} replace $w^0 \otimes w^0$ in the notation, and so on. We reorganize left hand side of (3.16) as a spin multiplet [BRGB13]:

$$\begin{aligned}
w^{sc1} &= w^{00} - w^{xx} - w^{yy} - w^{zz}, \\
w^{sc2} &= \tfrac{1}{3}\big(3w^{00} + w^{xx} + w^{yy} + w^{zz}\big), \\
w^{v1} &= \big(w^{x0} + w^{0x}, w^{y0} + w^{0y}, w^{z0} + w^{0z}\big), \\
w^{v2} &= \big(w_-^{x0} + iw_-^{zy}, w_-^{y0} + iw_-^{xz}, w_-^{0z} + iw_-^{xy}\big), \\
w^{v3} &= \big(w_-^{x0} - iw_-^{zy}, w_-^{y0} - iw_-^{xz}, w_-^{z0} - iw_-^{yx}\big), \\
w^{q} &= \big(-w^{xx} - w^{yy} + 2w^{zz}, w^{xy} + w^{yx}, w^{yz} + w^{zy}, w^{xx} - w^{yy}, w^{xz} + w^{zx}\big),
\end{aligned}$$

with $w_-^{x0} := w^{x0} - w^{0x}$, $w_-^{xy} := w^{xy} - w^{yx}$, and so on. The first two terms of the multiplet are the scalars, then the three vectors, and the quadrupole in a standard presentation.

In summary, collecting $(sc1, sc2, v1, v2, v3, q) \equiv \boldsymbol{f}$, for us an electronic 2-body Wigner function is a multiplet denoted $w(\boldsymbol{r}, \boldsymbol{p}; \boldsymbol{f})$, the extracule labels being suppressed. The Fermi symmetry condition for the exchange of one set of spin coordinates $\varsigma_1 \leftrightarrow \varsigma_2$ *and* of the spatial coordinates, borrowing the notation used in the spin-zero case, reads:

$$\tilde{\omega}(\boldsymbol{v}, \boldsymbol{p}; \boldsymbol{f}) := -\tilde{\omega}\big(\boldsymbol{p}, \boldsymbol{v}, \boldsymbol{f}_{\varsigma_1 \leftrightarrow \varsigma_2}\big).$$

Then the exchange transformation rule for the Wigner function multiplet comes out even simpler, in that there are fewer minus signs than the one for the density matrix:

$$\begin{pmatrix} \tilde{\omega}^{sc1}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{sc2}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v1}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v2}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v3}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{q}(\boldsymbol{v}, \boldsymbol{p}) \end{pmatrix} = \begin{pmatrix} +1 &&&&& \\ & -1 &&&& \\ && -1 &&& \\ &&& -1 && \\ &&&& +1 & \\ &&&&& -1 \end{pmatrix} \begin{pmatrix} \tilde{\omega}^{sc1}(\boldsymbol{p}, \boldsymbol{v}) \\ \tilde{\omega}^{sc2}(\boldsymbol{p}, \boldsymbol{v}) \\ \tilde{\omega}^{v1}(\boldsymbol{p}, \boldsymbol{v}) \\ \tilde{\omega}^{v2}(\boldsymbol{p}, \boldsymbol{v}) \\ \tilde{\omega}^{v3}(\boldsymbol{p}, \boldsymbol{v}) \\ \tilde{\omega}^{q}(\boldsymbol{p}, \boldsymbol{v}) \end{pmatrix}. \tag{3.17}$$

This because $\tilde{\omega}^{sc1}$ is odd under $\varsigma_1 \leftrightarrow \varsigma_2$, while $\tilde{\omega}^{sc2}$ is even, and so on. Of course, one can choose to impose the Fermi condition on the *primed* spin coordinates. Then $\tilde{\omega}^{v2}$, $\tilde{\omega}^{v3}$ are peculiar in that they become respectively odd and even. But the general indistinguishability condition (3.15) now implies

$$\begin{pmatrix} \tilde{\omega}^{sc1}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{sc2}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v1}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v2}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{v3}(\boldsymbol{v}, \boldsymbol{p}) \\ \tilde{\omega}^{q}(\boldsymbol{v}, \boldsymbol{p}) \end{pmatrix} = \begin{pmatrix} +1 &&&&& \\ & +1 &&&& \\ && +1 &&& \\ &&& -1 && \\ &&&& -1 & \\ &&&&& +1 \end{pmatrix} \begin{pmatrix} \tilde{\omega}^{sc1}(-\boldsymbol{v}, -\boldsymbol{p}) \\ \tilde{\omega}^{sc2}(-\boldsymbol{v}, -\boldsymbol{p}) \\ \tilde{\omega}^{v1}(-\boldsymbol{v}, -\boldsymbol{p}) \\ \tilde{\omega}^{v2}(-\boldsymbol{v}, -\boldsymbol{p}) \\ \tilde{\omega}^{v3}(-\boldsymbol{v}, -\boldsymbol{p}) \\ \tilde{\omega}^{q}(-\boldsymbol{v}, -\boldsymbol{p}) \end{pmatrix};$$

and this saves the day.

3.5 Moshinsky atom: its lowest excited configuration

The Hamiltonian of the Moshinsky atom is given by Eq. (8.21). The goal of this Section is to study in WDFT its first excited state; it is mainly based on our papers [BRGBV12, BR13]. Bringing in extracule and intracule coordinates, respectively given by (3.10), the

Moshinsky-atom Hamiltonian is rewritten:

$$H = H_{\boldsymbol{R}} + H_{\boldsymbol{r}} := \frac{1}{2}\boldsymbol{P}^2 + \frac{\omega^2}{2}\boldsymbol{R}^2 + \frac{1}{2}\boldsymbol{p}^2 + \frac{\mu^2}{2}\boldsymbol{r}^2.$$

We have introduced the frequencies $\omega := \sqrt{k}$ and $\mu := \sqrt{k - \delta}$. Let us first note that (a) there is a ground state whenever $\mu^2 > 0$, and (b) the particles are no longer bound if the relative interaction strength $\delta/k \leq 1$. Assume therefore that $\delta < k$, so both "electrons" remain in the potential well. For the Moshinsky-atom ground state the (spinless) Wigner 2-body quasiprobability is readily found [Dah09]:

$$w_{2\mathrm{gs}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \frac{1}{\pi^6} \exp\biggl(-\frac{2H_{\boldsymbol{R}}}{\omega}\biggr) \exp\biggl(-\frac{2H_{\boldsymbol{r}}}{\mu}\biggr). \tag{3.18}$$

For its natural orbital expansion, with i integer ≥ 0 and L_i the corresponding Laguerre polynomial, one finds [BGBV12]:

$$n_i = \frac{4\sqrt{\omega\mu}}{\bigl(\sqrt{\omega} + \sqrt{\mu}\bigr)^2} \biggl(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}}\biggr)^{2i} =: (1 - t^2)\, t^{2i}. \tag{3.19}$$

The WNO reads $\chi_{ii}(\boldsymbol{r}; \boldsymbol{p}) = \chi_{ii}(x; p_x)\chi_{ii}(y; p_y)\chi_{ii}(z; p_z)$, where

$$\chi_{ii}(x; p_x) := \frac{1}{\pi}\, (-1)^i L_i\bigl(2\sqrt{\omega\mu}\, x^2 + 2p_x^2/\sqrt{\omega\mu}\bigr) e^{-\sqrt{\omega\mu}\, x^2 - p_x^2/\sqrt{\omega\mu}}.$$

The functions χ_{ii} determine up to a phase the interferences: for $j \geq k$,

$$\begin{aligned}\chi_{jk}(x; p_x) = \frac{1}{\pi}\, (-1)^k \frac{\sqrt{k!}}{\sqrt{j!}} &\bigl(2\sqrt{\omega\mu}\, x^2 + 2p_x^2/\sqrt{\omega\mu}\bigr)^{(j-k)/2} \\ &\times e^{-i(j-k)\vartheta} L_k^{j-k}\bigl(2\sqrt{\omega\mu}\, x^2 + 2p_x^2/\sqrt{\omega\mu}\bigr) e^{-\sqrt{\omega\mu}\, x^2 - p_x^2/\sqrt{\omega\mu}},\end{aligned}$$

where $\vartheta := \arctan\bigl(p_x/\sqrt{\omega\mu}\, x\bigr)$. The L_k^{j-k} are associated Laguerre polynomials. The χ_{kj} are complex conjugates of the χ_{jk}. Now, with the *alternating choice* (unique up to a global sign):

$$\nu_i = (-)^i \sqrt{n_i} = \sqrt{1 - t^2}\, (-t)^i,$$

and the above χ_{jk}, the Löwdin-Shull formula (3.4) does reproduce (3.18). This was originally proved directly in [BGBV12], and verified by minimization in [EFGB12]; we refer the interested reader to those papers. Trivially, the same sign rule holds for natural orbitals of the garden variety (2.11).

The energy spectrum for this atom is obviously $(\mathbb{N} + \frac{3}{2})\omega + (\mathbb{N} + \frac{3}{2})\mu$. Since $\mu < \omega$, the energy of the first excited state is $E_{\mathrm{fs}} = (3\omega + 5\mu)/2$. For our present purposes, it is enough to choose an intracule excitation state along the z-axis (say). The corresponding 2-quasidensity is given by:

$$\frac{2}{\pi^6} \exp\biggl(-\frac{2H_R}{\omega}\biggr) \exp\biggl(-\frac{2H_r}{\mu}\biggr) \biggl(\frac{(p_{1z} - p_{2z})^2 + \mu^2(z_1^2 - z_2^2)^2}{\mu} - \frac{1}{2}\biggr). \tag{3.20}$$

Since the problem factorizes completely, from now on we work in the chosen nontrivial mode. By integrating out one set of variables, the 1-WRDM is obtained, after some work:

$$w_{1\text{fs}}(r;p) = 2\int w_2(r,r_2;p,p_2)\,dr_2\,dp_2 = \frac{2}{\pi}\left(\frac{2\sqrt{\omega\mu}}{\omega+\mu}\right)^3 e^{-\frac{2\omega\mu}{\omega+\mu}r^2-\frac{2}{\omega+\mu}p^2}\left(\omega r^2+\frac{1}{\omega}p^2\right).$$

Interestingly, w_1 for the first excited state is a non-Gaussian Wigner function taking only positive values. This prompts two remarks. First, in consonance with common wisdom [KZ04, DMWS06], it is confirmed that as of itself w_1 is a nearly classical state. Second, there are mathematical recipes that produce such positive-valued Wigner functions representing mixed states [GBV88]. It would be good to know whether or not w_1 can be obtained as such an output. Of course, the marginals of $w_{1\text{fs}}$ gives the electronic density:

$$\begin{aligned}\rho_{\text{fs}}(r) = \int w_1(r;p)\,dp &= \frac{2}{\pi}\left(\frac{2\sqrt{\omega\mu}}{\omega+\mu}\right)^3 e^{-\frac{2\omega\mu}{\omega+\mu}r^2}\int e^{-\frac{2}{\omega+\mu}p^2}\left(\omega r^2+\frac{1}{\omega}p^2\right)dp\\ &= \frac{2}{\pi}\left(\frac{2\sqrt{\omega\mu}}{\omega+\mu}\right)^3 e^{-\frac{2\omega\mu}{\omega+\mu}r^2}\left(\frac{\pi(\omega+\mu)}{2}\right)^{1/2}\left(\omega r^2+\frac{\omega+\mu}{4\omega}\right),\end{aligned}$$

and as expected we get $\int \rho_{\text{fs}}(r)\,dr = 2$.

From the viewpoint of WDFT, the most interesting part of the energy corresponds to the interelectronic repulsion of this first excited state $E_{2\text{fs}}$. The 1-body Hamiltonian is given by $h(r,p) = p^2/2+\omega^2r^2/2$. It is a simple exercise to obtain the 1-body energy $E_{1\text{fs}}$ by integrating $w_{1\text{fs}}$ with this observable:

$$E_{1\text{fs}} = \frac{\omega}{2}+\frac{3(\mu^2+\omega^2)}{4\mu}.$$

The interelectronic potential in (8.21) is $(\mu^2-\omega^2)r_{12}^2/4$, so to obtain the repulsion energy $E_{2\text{fs}}$, one has just to integrate expression (3.20) with this observable:

$$\begin{aligned}E_{2\text{fs}} &= \int \frac{2}{\pi^2}\exp\left(-\frac{2H_R}{\omega}\right)\exp\left(-\frac{2H_r}{\mu}\right)\left[\frac{2H_r}{\mu}-\frac{1}{2}\right]\frac{\mu^2-\omega^2}{4}\,r_{12}^2\,dR\,dr\,dP\,dp\\ &= \frac{1}{\pi}(\mu^2-\omega^2)\int\exp\left(-\frac{2H_r}{\mu}\right)\left[\frac{r^2p^2}{\mu}+\mu r^4-\frac{r^2}{2}\right]dr\,dp = \frac{3}{4}\,\frac{\mu^2-\omega^2}{\mu},\end{aligned}$$

which is 3 times the interelectronic repulsion energy for the corresponding mode of the singlet [BGBV12]. This is not surprising, since in the triplet configuration the fermions tend to be mutually farther apart than in the singlet.

In order to determine the NON and WNO of this system, first we have to find the appropriate coordinates. Let us perform the symplectic transformation:

$$(Q,P) := \big((\omega\mu)^{1/4}r,(\omega\mu)^{-1/4}p\big); \quad \text{or, in shorthand,} \quad U = Su,$$

where S is a symplectic matrix and $u=(r,p)$. We may also write $\vartheta := \arctan(P/Q)$, so that

$$P = U\sin\vartheta \quad \text{and} \quad Q = U\cos\vartheta.$$

Let us define t as in (3.19); $w_{1\text{fs}}$ takes the simple form

$$w_{1\text{fs}}(U,\vartheta) := w_1(u(U,\vartheta)) = \frac{2(1-t^2)^3}{\pi(1+t^2)^3}\,e^{-(1-t^2)U^2/(1+t^2)}U^2\left(\frac{1+t^2}{1-t^2}+\frac{2t}{1-t^2}\cos 2\vartheta\right).$$

The one-body quasidensity may be expanded in the singlet WNO as follows:

$$w_1(U,\vartheta)=\sum_{rs}\chi_{rs}(U,\vartheta)\,d_{rs}\quad\text{where}\quad w_{rs}=2\pi\int w_1(U,\vartheta)\chi^*_{rs}(U,\vartheta)U\,dU\,d\vartheta.$$

Then, using some well-known properties of the Laguerre polynomials we obtain [BRGBV12]:

$$w_1(U,\vartheta)=(1-t^2)^2\left[\sum_s d_{ss}\chi_{ss}(U,\vartheta)+d_{s+2,s}\chi_{s+2,s}(U,\vartheta)+d_{s,s+2}\chi_{s,s+2}(U,\vartheta)\right],$$

where actually $d_{s+2,s}=d_{s,s+2}$; and by fairly easy manipulations:

$$d_{ss}=s\,t^{2s-2}+(1+s)\,t^{2s}\quad\text{and}\quad d_{s,s+2}=\sqrt{(s+1)(s+2)}\,t^{2s+1}.$$

This means that, to find the occupation numbers, one has to diagonalize a symmetric pentadiagonal matrix:

$$D=(1-t^2)^2\begin{pmatrix}1&0&\alpha_0 t&0&0&\cdots\\0&1+2t^2&0&\alpha_1t^3&0&\cdots\\\alpha_0t&0&2t^2+3t^4&0&\alpha_2t^5&\cdots\\0&\alpha_1t^3&0&3t^4+4t^6&0&\cdots\\0&0&\alpha_2t^5&0&4t^6+5t^8&\cdots\\\vdots&\vdots&\vdots&\vdots&\vdots&\ddots\end{pmatrix},\tag{3.21}$$

where $\alpha_s:=\sqrt{(s+1)(s+2)}\,$.

It is readily checked that the trace of this matrix is 2, as it should be. Its eigenspaces split into two parts: $\ell_2=V_1\oplus V_2$, where $V_1=\{\,\boldsymbol{x}:\ \text{all } x_{2n}=0\,\}$ and $V_2=\{\,\boldsymbol{x}:\ \text{all } x_{2n+1}=0\,\}$. They correspond respectively to two matrices whose sets of eigenvalues are the same, as they should be, since the occupation numbers must appear twice. As was shown in Section 2.4, there is a skewsymmetric matrix C such that $D=C^tC$. This matrix is tridiagonal, and is the sum of two skew-symmetric matrices whose diagonalization is trivial:

$$\begin{aligned}C=(1-t^2)&\begin{pmatrix}0&-1&0&0&0&\cdots\\1&0&0&0&0&\cdots\\0&0&0&-\sqrt{3}t^2&0&\cdots\\0&0&\sqrt{3}t^2&0&0&\cdots\\0&0&0&0&0&\cdots\\\vdots&\vdots&\vdots&\vdots&\vdots&\ddots\end{pmatrix}\\+(1-t^2)&\begin{pmatrix}0&0&0&0&0&\cdots\\0&0&\sqrt{2}t&0&0&\cdots\\0&-\sqrt{2}t&0&0&0&\cdots\\0&0&0&0&\sqrt{4}t^3&\cdots\\0&0&0&-\sqrt{4}t^3&0&\cdots\\\vdots&\vdots&\vdots&\vdots&\vdots&\ddots\end{pmatrix}=:A+B.\end{aligned}$$

Also, D is the sum of two Hermitian matrices, namely A^tA+B^tB, which is diagonal, and A^tB+B^tA. One is reminded here of the Weyl problem: given two $n\times n$ Hermitian matrices A, B whose spectra are known, what could the spectrum of their sum $C:=$

$A + B$ be? Some facts are clear: with an obvious notation for the eigenvalues, these must satisfy

$$c_1 + \cdots + c_n = a_1 + \cdots + a_n + b_1 + \cdots + b_n; \qquad c_1 \leq a_1 + b_1;$$

less clear, but also true, are

$$c_2 \leq a_1 + b_2; \quad c_2 \leq a_2 + b_1;$$

and so on. The conditions written above are already optimal for $n = 2$. The necessary constraints are all linear homogeneous inequalities, bounding convex polyhedra.

To find the NON we fall back on numerical computation in [BRGBV12]. Figure 3.3 compares the behavior of the first two NON for the singlet and triplet states of the Moshinsky atom. For the first system, we mean by $n_{0,\mathrm{gs}}$ and $n_{1,\mathrm{gs}}$ these two numbers, and for the latter $n_{0,\mathrm{fs}}$ and $n_{1,\mathrm{fs}}$, although we know that by degeneracy there are other two pairs of NON with the same numerical values. In both systems, the first NON are very close to 1 in the neighborhood of $t = 0$, while the others are very small. However, beyond $t = 0$, $n_{0,\mathrm{fs}}$ is always bigger than $n_{0,\mathrm{gs}}$. In this sense, the Hartree–Fock approximation works better in the triplet case than for the singlet. Around $t = 0.4$ the second NON for the latter is above 0.13, and for the former is below 0.052. The same behavior was also observed in the toy model studied in [HTR10]. This does not mean, however, that correlation is always weaker in the triplet state —which can be more easily seen by studying entanglement properties of both systems, as we did in [BRGBV12, BR13]; we refer the curious reader to those papers.

To finish this section, note that t is a very nonlinear parameter: although $t \sim \delta/8k$ for small δ, the value $t = 1/2$ means $\mu/\omega = 1/9$ or $\delta/k = 80/81$. In [BRGBV12] we showed that whenever $t \lesssim 0.5$, a good approximation to the first five triplet NON is

$$n_{0,\mathrm{fs}} \approx 1 - 3t^4 + 8t^6, \quad n_{1,\mathrm{fs}} \approx 3t^4 - 8t^6, \quad n_{2,\mathrm{fs}} \approx 5t^8, \quad n_{3,\mathrm{fs}} \approx 7t^{12} \quad \text{and} \quad n_{4,\mathrm{fs}} \approx 9t^{16},$$

so that $n_{0,\mathrm{fs}} + n_{1,\mathrm{fs}} \approx 1$. This shows that, unless δ is pretty close to the dissociation value, the first two NON contain almost all the physical information of this system.

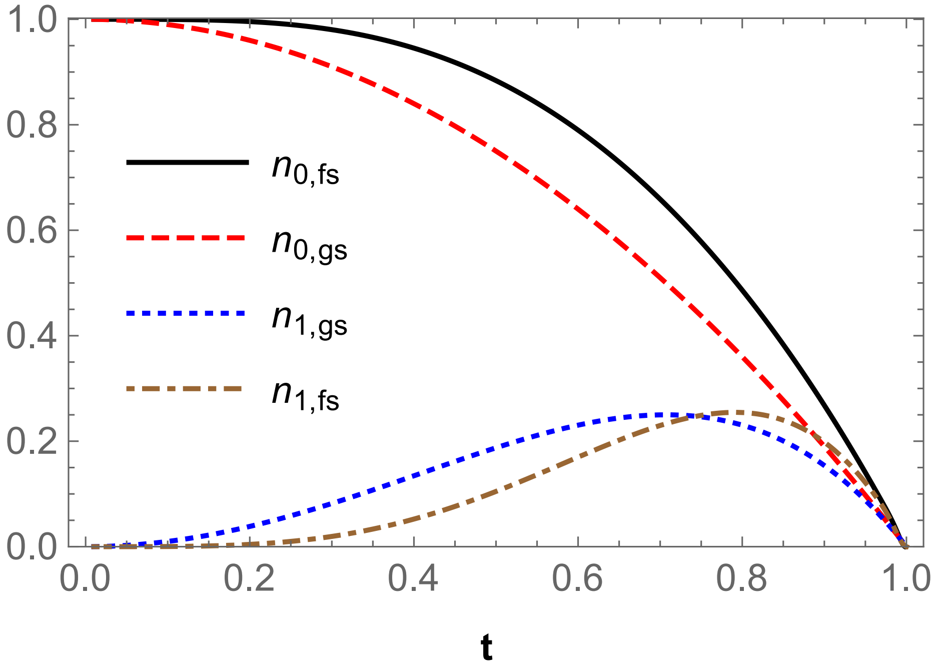

FIGURE 3.3: First and second NON for the ground and first-excited states of the Moshinsky atom as a function of t [BRGBV12].

Chapter 4

Testing 1-RDM functionals

The integrability and solvability of the Moshinsky atom (8.21) enables one to test accurately how some of the 1-RDM functionals behave for this particular system. There are several particularities of the aforementioned atom; for example, for its ground state, the Müller functional (2.18), evaluated on the exact 1-RDM, yields the correct value of the energy [NP10]. We confirm by a different method this surprising coincidence. Thus, for two fermions the Müller functional is also *overbinding* for the harmonic repulsion just as for the Coulombian one [FLSS07, BGBV12], since the minimizing state for that functional will yield a lower value of the energy. In this chapter we catalogue the predictions for the ground state of the Moshinsky atom by several proposed two-body functionals, measured against the exact model. The work presented here is mainly based on [BRV12].

Before beginning our discussion, it is worth summarizing for completeness the highlights of the ground state of the Moshinsky atom, introduced in Sec. 3.5. The Hamiltonian of the system is (8.21) and the corresponding ground-state Wigner quasidensity is given by the Gaussian state (3.18). The NON satisfy the relation $n_i = (1-t^2)t^{2i}$, where

$$t := \frac{\sqrt{\omega}-\sqrt{\mu}}{\sqrt{\omega}+\sqrt{\mu}}.$$

The WNO reads $\chi_{ii}(\boldsymbol{r};\boldsymbol{p}) = \chi_{ii}(x;p_x)\chi_{ii}(y;p_y)\chi_{ii}(z;p_z)$, where

$$\chi_{ii}(x;p_x) := \frac{1}{\pi}\,(-1)^i L_i\big(2\sqrt{\omega\mu}\,x^2 + 2p_x^2/\sqrt{\omega\mu}\big)e^{-\sqrt{\omega\mu}\,x^2 - p_x^2/\sqrt{\omega\mu}},$$

with L_i being the Laguerre polynomials. The interferences χ_{jk} can be determined up to a phase. For $j \geq k$,

$$\begin{aligned}\chi_{jk}(x;p_x) = \frac{1}{\pi}\,(-1)^k \frac{\sqrt{k!}}{\sqrt{j!}}\,\big(2\sqrt{\omega\mu}\,x^2 + 2p_x^2/\sqrt{\omega\mu}\big)^{(j-k)/2} \\ \times e^{-i(j-k)\vartheta} L_k^{j-k}\big(2\sqrt{\omega\mu}\,x^2 + 2p_x^2/\sqrt{\omega\mu}\big)e^{-\sqrt{\omega\mu}\,x^2 - p_x^2/\sqrt{\omega\mu}}.\end{aligned}$$

Since the sign dilemma has been solved for this problem [BGBV12], namely: $\nu_i = (-1)^i\sqrt{n_i}$, the ground state of this atom satisfies exactly the Shull-Löwdin functional (3.4). To alleviate the notation we denotethe diagonal part of the 2-RDM by $\rho(\boldsymbol{r}_1,\boldsymbol{r}_2) := \gamma_1(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1,\boldsymbol{r}_2)$. For simplicity, we put $\chi_{jk}(\boldsymbol{r}) := \int \chi_{jk}(\boldsymbol{r};\boldsymbol{p})\,d\boldsymbol{p}$.

4.1 Hartree–Fock and Müller functionals for harmonium

Recall that in WDFT the total energy of an electronic system is of the form

$$\mathcal{E}[w_1, w_2] = \mathcal{E}_{\mathrm{kin}}[w_1] + \mathcal{E}_{\mathrm{ext}}[w_1] + \mathcal{E}_{\mathrm{ee}}[w_2],$$

where the kinetic $\mathcal{E}_{\mathrm{kin}}$ and potential E_{ext} energies are known functionals of the spinless 1-WRDM. Due to its solvability, it is possible to compute exactly the value of these three quantities for the ground state of the Moshinsky atom:

$$\begin{aligned} E_{\mathrm{kin}}[w_1] &= \int \frac{p^2}{2}\, w_1(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{r}\, d\boldsymbol{p} = \frac{3\omega}{4}\left[1 + \left(\frac{1-t}{1+t}\right)^2\right]; \\ E_{\mathrm{ext}}[w_1] &= \int \frac{\omega^2 r^2}{2}\, w_1(\boldsymbol{r};\boldsymbol{p})\, d\boldsymbol{r}\, d\boldsymbol{p} = \frac{3\omega}{4}\left[1 + \left(\frac{1+t}{1-t}\right)^2\right]. \end{aligned}$$

The interelectronic repulsion energy $\mathcal{E}_{\mathrm{ee}}[w_2]$ is a functional of the 2-WRDM or indeed only of the pairs density:

$$\begin{aligned} \mathcal{E}_{\mathrm{ee}}[w_2] &= -\frac{\delta}{4}\int w_2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{p}_1,\boldsymbol{p}_2) r_{12}^2\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\boldsymbol{p}_1\, d\boldsymbol{p}_2 \\ &= -\frac{\delta}{4}\int \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2) r_{12}^2\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = -\frac{3\omega}{4}\,\frac{8t(1+t^2)}{(1-t^2)^2}. \end{aligned}$$

We note that the kinetic energy of the system stays finite from $\mu = \omega$ $(t = 0)$ to $\mu = 0$ $(t = 1)$. The potential energies diverge as $\mu \downarrow 0$, in the strong repulsion regime; but their sum remains finite and equal to the kinetic energy, as prescribed by the virial theorem.

In the language of Section 2.5 and Chapter 3, DMFT amounts to the search for functionals for w_2 in terms of w_1, expressed through its Wigner natural orbitals and their occupation numbers. We have already pointed out that the wide variety of functionals currently used in DMFT can be traced back to the functional proposed by Müller [Mül84]. Note first that, with an obvious notation, the *exact* phase-space functional for the present system is:

$$\begin{aligned} \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \sum_{j,k\geq 0} (-)^{j+k}\sqrt{n_j n_k}\,\chi_{jk}(\boldsymbol{r}_1)\chi_{jk}(\boldsymbol{r}_2) \\ &= \sum_{j\geq 0} n_j\,\chi_{jj}(\boldsymbol{r}_1)\chi_{jj}(\boldsymbol{r}_2) + \sum_{j\neq k\geq 0} (-)^{j+k}\sqrt{n_j n_k}\,\chi_{jk}(\boldsymbol{r}_1)\chi_{jk}(\boldsymbol{r}_2), \end{aligned} \tag{4.1}$$

This is correctly normalized by $\int \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = \sum_j n_j = 1$, in view of $\int \chi_{jk}(\boldsymbol{r})\, d\boldsymbol{r} = 0$ when $j \neq k$. Translated into our language, the Müller functional for the singlet is of the form

$$\begin{aligned} \rho_2^{\mathrm{M}}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= 2\sum_j n_j\,\chi_j(\boldsymbol{r}_1)\sum_k n_k\,\chi_k(\boldsymbol{r}_2) - \sum_{j,k}\sqrt{n_j n_k}\,\chi_{jk}(\boldsymbol{r}_1)\chi_{kj}(\boldsymbol{r}_2) \qquad (4.2) \\ &= \frac{1}{2}\,\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \sum_j n_j\,\rho_j(\boldsymbol{r}_1)\rho_j(\boldsymbol{r}_2) - \sum_{j\neq k}\sqrt{n_j n_k}\,\chi_{jk}(\boldsymbol{r}_1)\chi_{jk}(\boldsymbol{r}_2). \end{aligned}$$

We have used that $\chi_{jk}(\boldsymbol{r}) = \chi_{kj}(\boldsymbol{r})$ for real orbitals. More generally, Müller considered $n_j^p\, n_k^q$ with $p + q = 1$ instead of $\sqrt{n_j n_k}$. Recently, the case $\frac{1}{2} \leq p = q \leq 1$ has been studied [SDLG08, BRN14]. The Müller functional satisfies some nice properties; among them, the sum rule $2\int \rho_2(\boldsymbol{r},\boldsymbol{r}_2)\,d\boldsymbol{r}_2 = \rho(\boldsymbol{r})$ and hermiticity. For Coulombian systems its energy functional is convex [FLSS07]. Nonetheless, antisymmetry fails. We summarize properties fulfilled or infringed by each functional later on, in Table 4.1.

As suggested by the aforementioned Lieb variational principle, the Hartree–Fock approximation may be regarded as yet another functional of w_1. This is given by

$$\rho_2^{\mathrm{HF}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}\,\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \sum_j n_j^2\,\rho_j(\boldsymbol{r}_1)\rho_j(\boldsymbol{r}_2) - \sum_{j\neq k} n_j n_k\,\chi_{jk}(\boldsymbol{r}_1)\chi_{jk}(\boldsymbol{r}_2). \tag{4.3}$$

Expressions (4.1) and (4.3) coincide only when the occupation numbers are pinned to 0 or 1. The “best” Hartree–Fock state, in the sense of best approximation for the ground state energy with only one $n_j \neq 0$, is a Slater determinant given [EFGB12] by:

$$\frac{1}{\pi^6}\,e^{-(\boldsymbol{r}_1^2+\boldsymbol{r}_2^2)\sqrt{(\omega^2+\mu^2)/2}}\,e^{-(\boldsymbol{p}_1^2+\boldsymbol{p}_2^2)/\sqrt{(\omega^2+\mu^2)/2}}.$$

Use of the energy formulas for this state yields $E_{\mathrm{HF}} = 3\sqrt{(\omega^2+\mu^2)/2}$, and so the *correlation* energy is $E_0 - E_{\mathrm{HF}} = \frac{3}{2}\big(\omega+\mu-\sqrt{2(\omega^2+\mu^2)}\,\big)$. For small values of μ, however, minimization by use of (4.3) gives *lower* values of the energy than E_{HF} [NP11]: the results by Lieb on the Hartree–Fock functional for arbitrary states of *Coulombian* systems do not apply here.

4.2 Exact vs. approximate functionals

Our next goal is simply to evaluate the worth of the functionals by computing their respective values on the *true* ground state. Thus, a feasible procedure is to compute the difference between the values given by the Müller functional and each of the several functionals whose accuracy we want to study. We need only worry about the interelectronic repulsion energy; since all the relevant quantities factorize, for notational simplicity we shall work in dimension one.

The *exactness* of the Müller interelectronic energy

From (4.2) one obtains [BRV12]:

$$\sum_{r,s=0}^{\infty} \sqrt{n_r n_s}\,\chi_{rs}(r_1,p_1)\chi_{sr}(r_2,p_2) = \frac{1}{\pi^2}\,e^{-(U_1^2+U_2^2)(1+t^2)/(1-t^2)}\,e^{4U_1U_2\,t\cos\theta/(1-t^2)},$$

where $\theta = \vartheta_1 - \vartheta_2$; we borrow the notation of Section 3.5; some well-known properties of Laguerre polynomials and modified Bessel functions have been invoked. In all, the spinless phase-space Müller functional for the ground state of the Moshinsky atom is, using the notation $u_s := (r_s,p_s)$,

$$\begin{aligned}\rho_2^{\mathrm{M}}(u_1,u_2) = {}& \frac{2}{\pi^2}\left(\frac{1-t^2}{1+t^2}\right)^2 e^{-(U_1^2+U_2^2)(1-t^2)/(1+t^2)} \\ & - \frac{1}{\pi^2}\,e^{-(U_1^2+U_2^2)(1+t^2)/(1-t^2)}\,e^{4U_1U_2\,t\cos\theta/(1-t^2)}.\end{aligned} \tag{4.4}$$

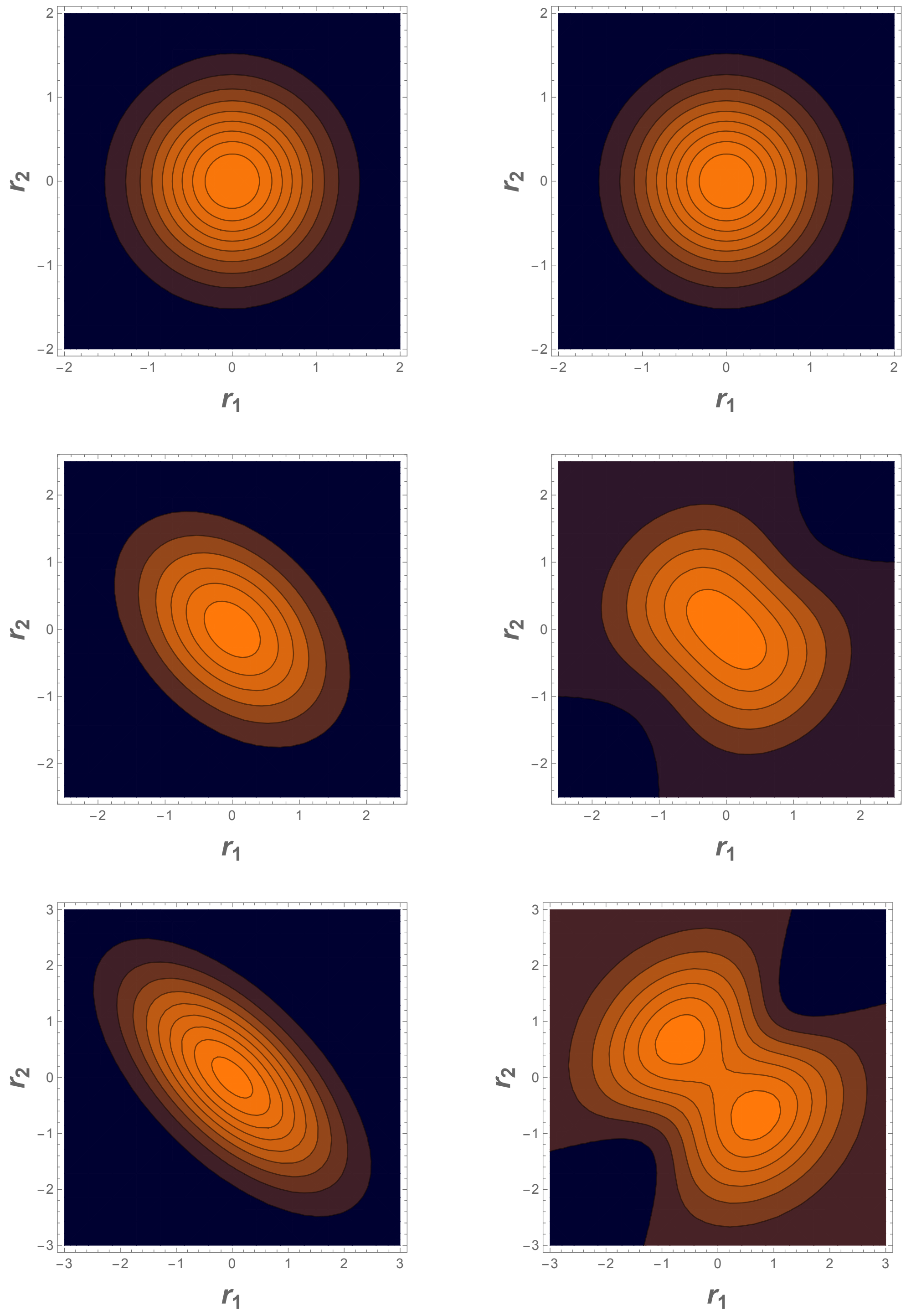

FIGURE 4.1: Contour plots for the exact and Müller pairs density for the ground-state of the Moshinsky atom at $\delta/k = 0$, $\delta/k = 0.8$ and $\delta/k = 0.95$. The graphics show the dimensionless functions $\pi\rho_2/\omega$ (on the left) and $\pi\rho_2^{\mathrm{M}}/\omega$ (on the right) in terms of $\omega^{1/2}\, r_1$ and $\omega^{1/2}\, r_2$.

In order to compute the interelectronic energy, we proceed with the mean value of the electronic separation: $\int r_{12}^2\, \rho_2^{\mathrm{M}}(u_1, u_2)\, du_1 du_2$. For the first term in (4.4), we obtain:

$$\frac{2}{\pi^2}\left(\frac{1-t^2}{1+t^2}\right)^2 \int r_{12}^2\, e^{-(U_1^2+U_2^2)(1-t^2)/(1+t^2)}\, du_1\, du_2 = \frac{\omega+\mu}{\omega\mu}\,.$$

For the second term, we obtain:

$$-\frac{1}{\pi^2}\int e^{-(U_1^2+U_2^2)(1+t^2)/(1-t^2)}\, e^{4U_1U_2\,t\cos\theta/(1-t^2)}\, dp_2\, dp_1 = -\frac{1}{\omega}\,.$$

In the process we have obtained a sort of (spinless) “Müller pairs density” for the true ground state,

$$\rho_2^{\rm M}(r_1,r_2) := \frac{1}{\pi}\,\frac{4\omega\mu}{\omega+\mu}\, e^{-2\omega\mu(r_1^2+r_2^2)/(\omega+\mu)} - \frac{\sqrt{\omega\mu}}{\pi}\, e^{-\frac{1}{2}(\omega+\mu)(r_1^2+r_2^2)} e^{(\omega-\mu)r_1r_2}\,; \tag{4.5}$$

whose predicted mean square value for the distance between the two electrons is

$$\int r_{12}^2\, \rho_2^{\rm M}(u_1,u_2)\, du_1du_2 = \frac{\omega+\mu}{\omega\mu} - \frac{1}{\omega} = \frac{1}{\mu}\,.$$

The *same* mean square value is easily obtained from the *exact* pairs density [BGBV12]:

$$\rho_2(r_1,r_2) = \frac{\sqrt{\omega\mu}}{\pi}\, e^{-\frac{1}{2}(\omega+\mu)(r_1^2+r_2^2)}\, e^{(\mu-\omega)r_1r_2}. \tag{4.6}$$

Thus, the energies $E_{\rm ee} = E_{\rm ee}^{\rm M} = -\delta/4\mu = (\mu^2-\omega^2)/4\mu$ *coincide.* Note that the result is valid for any value of t. This is surprising because the shapes of ρ_2 and $\rho_2^{\rm M}$ grow very distinct as t increases —see Figure 4.1.

In summary, by a somewhat different method, we confirmed the result of [NP10]. The coincidence does not hold for other values $p, q \neq \frac{1}{2}$ in the Müller approach. It may be considered fortuitous, because (4.5) and the exact pairs density (4.6) are rather dissimilar: for $t > 0$, the spinless two-body Müller functional does not have a maximum at the origin in phase space, whereas the exact functional does. More precisely, the Müller functional exhibits two maxima located at the antidiagonal sector of the density [BRV12]. Also, it sports negative values at some points. As pointed out in the original paper [Mül84], this phenomenon is a consequence of the inequality $\sqrt{n_j} \geq n_j$ satisfied by the natural occupation numbers of the system. In [BRV12] we displayed the negativity around the diagonal elements of the density. This indicates that the Müller functional is also unphysical, in a subtler way than the Hartree–Fock functional [Hel06].

2-RDM	Antisymmetry	Hermiticity	Sum Rule
Exact	YES	YES	YES
Müller	NO	YES	YES
Hartree-Fock	YES	YES	NO
GU	NO	YES	NO
BBC	NO	YES	YES
CHF	NO	YES	YES
CGA	NO	YES	YES

TABLE 4.1: Properties fulfilled by the exact two-body functional for two-electron atoms and several two-body reduced density approximations.

Hartree–Fock interelectronic energy

We use the following terms, computed in [EFGB12]:

$$
\begin{aligned}
L_j &:= \frac{\mu^2-\omega^2}{4}\int \chi_j(r_1)\,(r_1-r_2)^2\,\chi_j(r_2)\,dr_1dr_2 = (2j+1)\,\frac{\mu^2-\omega^2}{4\sqrt{\omega\mu}}\,,\\
M_j &:= \frac{\mu^2-\omega^2}{4}\int \chi_{j,j+1}(r_1)\,\chi_{j+1,j}(r_2)(r_1-r_2)^2\,dr_1\,dr_2 = -(j+1)\frac{\mu^2-\omega^2}{4\sqrt{\omega\mu}}\,.
\end{aligned}
$$

The difference between the interelectronic energy predicted by the Hartree–Fock functional (4.3) and that predicted by the Müller functional on the true ground state of the Moshinsky atom is then given by:

$$
\begin{aligned}
E_{\mathrm{ee}}^{\mathrm{HF}}(t)-E_{\mathrm{ee}}^{\mathrm{M}}(t) &= -\sum_{j=0}^{\infty}\big[(n_j^2-n_j)L_j+2(n_jn_{j+1}-\sqrt{n_jn_{j+1}}\,)M_j\big]\\
&= \frac{2\omega t}{(1+t)^2}\left[\frac{1-t^2}{1+t^2}-\frac{1+t^2}{(1+t)^2}\right].
\end{aligned}
$$

At $t=0$ there is of course no difference between these two values of the energy. It is worth noting that there is another point of coincidence, namely $t\sim 0.54$ or $\delta/\kappa\sim 0.99$. Below this value the difference is positive, and above it is negative. At $t=1$, we find $E_{\mathrm{ee}}^{\mathrm{HF}}(1)-E_{\mathrm{ee}}^{\mathrm{M}}(1)=-\omega/4$. Since $\rho_1^{\mathrm{HF}}-\rho_1=2\sum_k(n_k-n_k^2)\chi_k\neq 0$ for $t>0$, this functional does not satisfy the sum rule, except when the Hartree–Fock functional is evaluated on a Hartree–Fock state.

The Goedecker–Umrigar functional

The Goedecker–Umrigar functional [GU98] introduces a small variation of Müller's, attempting to exclude "orbital self-interaction". For our closed-shell situation, it is given by:

$$
\rho_2^{\mathrm{GU}}(r_1,r_2)-\rho_2^{\mathrm{M}}(r_1,r_2)=\sum_j(n_j-n_j^2)\,\chi_j(r_1)\,\chi_j(r_2).
$$

This relation implies that for $t>0$ this functional violates the sum rule: $\rho_1\neq 2\int\rho_2^{\mathrm{GU}}\,dr_2$. The interelectronic part of the energy difference calculation is given by

$$
\sum_r(n_j-n_j^2)L_j=\sum_j\big[(1-t^2)t^{2j}-(1-t^2)^2t^{4j}\big]L_j\,.
$$

Hence, the mean value of the interelectronic repulsion predicted by this functional is

$$
E_{\mathrm{ee}}^{\mathrm{GU}}(t)-E_{\mathrm{ee}}^{\mathrm{M}}(t)=\frac{2\omega t}{(1+t)^2}\left[\frac{1+t^4}{1-t^4}-\left(\frac{1+t^2}{1-t^2}\right)^2\right].
$$

The interelectronic energy calculated by means of the Goedecker–Umrigar functional is higher than the exact value. At $t=1$, the difference diverges. This is unsurprising, given that when the coupling is large enough the self-interacting part is almost half of the total interelectronic energy; for instance, $E_{\mathrm{ee}}^{\mathrm{GU}}(0.8)/E_{\mathrm{ee}}(0.8)\sim 0.44$.

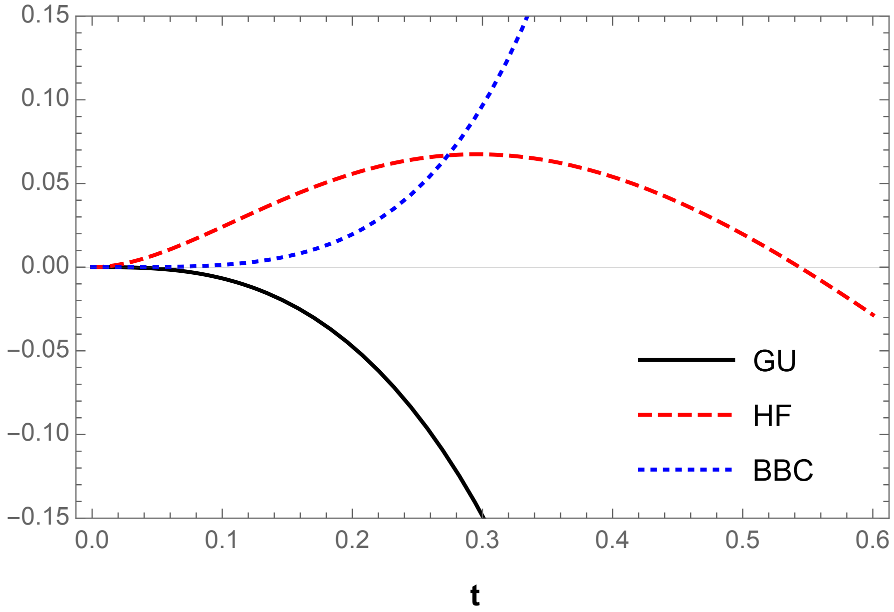

FIGURE 4.2: The error of the energy value calculated for different functionals. The error is defined as the dimensionless $[E_{\mathrm{ee}}^{\mathrm{functional}}(t) - E_{\mathrm{ee}}(t)]/\omega$, evaluated on the exact one-body density matrix for the ground state of the Moshinsky atom. The Müller functional does not appear here since its energy value is exact.

Buijse–Baerends corrected functionals

A few years after the original Buijse and Baerends' paper [BB02], some corrections were introduced, to distinguish between strongly occupied natural orbitals (whose occupation numbers are close to 1) and weakly occupied ones (occupation numbers near 0) [GPB05]. The ground state of the Moshinsky atom possesses only one strongly occupied orbital, namely χ_0, whose occupation number is $n_0 = 1 - t^2$. However, this distinction is lost at high values of the coupling parameter. The first corrected functional (BBC1) is given by $\rho_2^{\mathrm{BBC1}} = \rho_2^{\mathrm{M}} + \rho_2^{\mathrm{C1}}$, where

$$\rho_2^{\mathrm{C1}}(r_1, r_2) = 2 \sum_{\substack{j \neq k \\ j,k>0}} \sqrt{n_j n_k}\, \chi_{jk}(r_1)\, \chi_{kj}(r_2).$$

The second correction (BBC2) modifies BBC1 by adding further terms of the form $(\sqrt{n_j n_k} - n_j n_k)\, \chi_{jk}(r_1)\, \chi_{kj}(r_2)$ for distinct strongly coupled orbitals. For the ground state of the Moshinsky atom, we may ignore it here; thus we write ρ_2^{BBC} for ρ_2^{BBC1}. Since both corrections involve only off-diagonal terms ($j \neq k$), these corrected functionals still fulfil the sum rule.

The functional difference now reads $\rho_2^{\mathrm{BBC}} - \rho_2 = \rho_2^{\mathrm{C1}}$ and the interelectronic energy difference yields

$$E_{\mathrm{ee}}^{\mathrm{BBC}} - E_{\mathrm{ee}}^{\mathrm{M}} = \frac{\mu^2 - \omega^2}{4} \int \rho_2^{\mathrm{C1}} r_{12}^2 \, dr_1 \, dr_2 = \frac{8\omega t^4}{(1+t)^2} \frac{1+t^2}{1-t^2} \left[\frac{1}{1-t^2} + 1 \right].$$

As in the Goedecker–Umrigar functional case, at $t = 1$ the difference has a divergence. Over almost the whole range of t, there is a large error in the energy (see Figure 4.2). Thus, applied to the case of the Moshinsky atom, these functionals do not reproduce the success found for the homogeneous electron gas [LHG07].

CHF and CGA functionals

Corrected Hartree–Fock (CHF) and Csányi–Goedecker–Arias (CGA) functionals introduced in [CGA02] are improvements of the Hartree–Fock functional. They were designed as tensor products to get better predictions for the correlation energy in homogeneous electron gases at high densities. For a closed shell system, they read

$$\rho_2^{\rm CHF}(u_1, u_2) = \frac{1}{2}\,\rho_1(u_1)\,\rho_1(u_2) - \sum_{j,k}\Big(n_j n_k + \sqrt{n_j(1-n_j)n_k(1-n_k)}\,\Big)\chi_{jk}(u_1)\,\chi_{kj}(u_2),$$

$$\rho_2^{\rm CGA}(u_1, u_2) = \frac{1}{2}\,\rho_1(u_1)\,\rho_1(u_2) - \frac{1}{2}\sum_{j,k}\Big(n_j n_k + \sqrt{n_j(2-n_j)n_k(2-n_k)}\,\Big)\chi_{jk}(u_1)\,\chi_{kj}(u_2).$$

First, note that both functionals satisfy the sum rule: $\rho_1^{\rm CHF} = \rho_1^{\rm CGA} = \rho_1$. As regards the interelectronic energy, we find that

$$E_{\rm ee}^{\rm CHF} - E_{\rm ee}^{\rm M} = 2\sum_j \sqrt{n_j\, n_{j+1}}\big(1 - \sqrt{n_j\, n_{j+1}} - \sqrt{(1-n_j)(1-n_{j+1})}\,\big)M_j,$$

$$E_{\rm ee}^{\rm CGA} - E_{\rm ee}^{\rm M} = \sum_j \sqrt{n_j\, n_{j+1}}\big(2 - \sqrt{n_j\, n_{j+1}} - \sqrt{(2-n_j)(2-n_{j+1})}\,\big)M_j.$$

As can be seen in [BRV12, Fig. 4], both functionals show a remarkably good description of the energy. At $t = 0$ and $t = 1$ the energy is exact. For the CHF functional, the worst performance occurs around $t \sim 0.4$ or $\delta/\kappa \sim 0.96$, whose error is $(E_{\rm ee}^{\rm CHF} - E_{\rm ee}^{\rm M})/\omega \sim 0.11$; the CGA functional is worst at $t \sim 0.43$ or $\delta/\kappa \sim 0.97$, with an error of $(E_{\rm ee}^{\rm CHF} - E_{\rm ee}^{\rm M})/\omega \sim 0.03$. The estimates of the energy are lower than the correct one; thus they are both overbinding for the Moshinsky atom.

4.3 Conclusion

In this section I have used the Moshinsky atom as a laboratory to study the performance of some of the 1-RDM functionals proposed to compute the interelectronic repulsion energy in the framework of DMFT. Jointly with Joseph Várilly I have confirmed the exact value of the energy given by the Müller functional when evaluated on the exact ground state. The functionals which exclude self-interacting terms or distinguish between strongly and weakly occupied orbitals display good approximation for the energy at small values of the coupling parameter but very poor values beyond $t \sim 0.3$.

The CHF approximation yields a good description of the interelectronic repulsion, even at high values of the parameter t. The performance of the CGA approximation is remarkably good, taking into account that it was built explicitly for the electron gas case. The reader should keep in mind the violation of some physical constraint or other by each one of the examined functionals [LGH10].

In summary, some of the best-known 1-RDM have been examined in a simple solvable model and, under conditions of relatively strong correlation, have been found wanting. I could hardly avoid the impression that 1-RDM functional theory is still in a very fluid state. With the hope of improving the situation, I decided to turn to a sector of the N-representability problem, which recently looked promising in view of deep results by Klyachko, which I should do in the remaining chapters of this thesis.

Chapter 5

Generalized Pauli constraints

5.1 "Classical" N-representability conditions

A well-known extension of density functional theory is the pair-density functional theory, which is based on the diagonal elements of the 2-RDM [Zie94]. It is known that the corresponding representability constraints are expressed in terms of these latter elements. Consider a system described by a wave function of the sort:

$$|\Psi\rangle = \sum_k \sqrt{w_k}\, e^{-i\theta_k} |\Psi_k\rangle,$$

where θ_k are arbitrary real numbers, the coefficients w_k satisfy

$$w_k \geq 0 \quad \text{and} \quad \sum_k w_k = 1,$$

and Ψ_k are Slater determinants represented in terms of a set of M orthogonal spin-orbitals as

$$|\Psi_k\rangle = \frac{1}{\sqrt{N!}} \det[\phi_{k_1}\, \phi_{k_2}\, \cdots\, \phi_{k_N}],$$

where $k = \{1 \leq k_1 < k_2 < \cdots < k_N \leq M\}$, or in second quantization as

$$\Phi_k = |p_1, p_2, \cdots, p_M\rangle,$$

where $p_i = 1$ if $i \in k$ and 0 otherwise.

Note that all these matrices can be written

$$\gamma_2 = \sum \Gamma_{ijkl}\, \chi_{ij}(1,2)\, \chi^*_{kl}(1',2'),$$

where the 2-RDM orbitals are given by

$$\chi_{ij}(1,2) := \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_i(\boldsymbol{x}_1) & \phi_i(\boldsymbol{x}_2) \\ \phi_j(\boldsymbol{x}_1) & \phi_j(\boldsymbol{x}_2) \end{vmatrix}$$

and the weights can be expressed

$$\Gamma_{ijkl} = \langle\Psi| a^\dagger_k a^\dagger_l a_j a_i |\Psi\rangle.$$

Well, these two guys focused in the diagonal part of this matrix, namely, $\Gamma_{ijij} := \lambda_{ij}$. It is well known that $\sum_{i<j}^{r} \lambda_{ij} = \binom{N}{2}$.

Consider for instance the case $\wedge^3\mathcal{H}_6$, three fermions in six orbitals. The corresponding wave function can be expressed in terms of eight configurations, namely:

$$|\alpha_1\alpha_2\alpha_3\rangle,\ |\alpha_1\alpha_2\alpha_4\rangle,\ |\alpha_1\alpha_3\alpha_5\rangle,\ |\alpha_1\alpha_4\alpha_5\rangle,\ |\alpha_2\alpha_3\alpha_6\rangle,\ |\alpha_2\alpha_4\alpha_6\rangle,\ |\alpha_3\alpha_5\alpha_6\rangle,\ |\alpha_4\alpha_5\alpha_6\rangle.$$

Similarly, the λ_{ij} can also be (lexicographically) ordered, namely by

$$(i,j) = (1,2)\,(1,3)\,(1,4)\,(1,5)\,(2,3)\,(2,4)\,(2,6)\,(3,5)\,(3,6)\,(4,5)\,(4,6)\,(5,6).$$

Hence, the relation between λ_{ij} and w_k is mediated by the matrix

$$\Lambda := \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \end{pmatrix}$$

Then:

$$\Lambda \boldsymbol{w} = \boldsymbol{\lambda}, \tag{5.1}$$

where $\boldsymbol{w} = (w_1, w_2, w_3, w_4, w_5, w_6, w_7, w_8)$ and $\boldsymbol{\lambda} = (\lambda_{12}, \lambda_{13}, \lambda_{14}, \dots)$.

Now, let a set doubly indexed constants λ_{ij} which satisfy

$$\sum_{i<j} \lambda_{ij} = \binom{N}{2}$$

be given. The *diagonal N-representability problem* consists in answering the following question [Yos74]: under what conditions on these λ_{ij} does the system of equations (5.1) have a nonnegative solution[1] for $\boldsymbol{w}$, such that $\sum_k w_k = 1$?

What McRae and Davidson used was a theorem from linear programming which says that equation (5.1) exhibits a nonnegative solution if and only if for every $\boldsymbol{y}$ satisfying

$$\boldsymbol{y}^T \Lambda \geq 0$$

necessarily

$$\boldsymbol{y}^T \boldsymbol{\lambda} \geq 0.$$

---

[1] Here $\boldsymbol{w} \geq 0$ means every $w_k \geq 0$.

What they gave in their paper was an algorithm for such linear inequalities. The problem had been solved for some systems, though. Among them, $\wedge^3\mathcal{H}_6$ by one Kuhn whose paper is impossible to find [Kuh60].

5.2 Davidson inequalities for $\wedge^3\mathcal{H}_6$

For the system $\wedge^3\mathcal{H}_6$:

$$\begin{aligned}|\Psi\rangle_{3,6} = c_{123}|\alpha_1\alpha_2\alpha_3\rangle + c_{124}|\alpha_1\alpha_2\alpha_4\rangle + c_{135}|\alpha_1\alpha_3\alpha_5\rangle + c_{145}|\alpha_1\alpha_4\alpha_5\rangle \\ + c_{236}|\alpha_2\alpha_3\alpha_6\rangle + c_{246}|\alpha_2\alpha_4\alpha_6\rangle + c_{356}|\alpha_3\alpha_5\alpha_6\rangle + c_{346}|\alpha_3\alpha_4\alpha_6\rangle\end{aligned} \tag{5.2}$$

there are in total 70 Slater hull inequalities, grouped in three permutation classes [MD72]. Since the 2-RDM is a positive semidefinite matrix its diagonal elements are never negative. The first class is thus given by 15 inequalities:

$$\langle \hat{n}_i\hat{n}_j\rangle \geq 0, \qquad 1 \leq i < j \leq 6,$$

where $\hat{n}_i := a_i^\dagger a_i$ is the occupation number operator; the second class contains 10 inequalities, namely,

$$\langle(\hat{n}_f + \hat{n}_g + \hat{n}_h)^2 + (\hat{n}_i + \hat{n}_j + \hat{n}_k)^2\rangle \geq 5, \tag{5.3}$$

provided that $1 \leq f, g, h, i, j, k \leq 6$; and the last one is determined by 45 inequalities of the following type:

$$\langle(\hat{n}_f + \hat{n}_g)(\hat{n}_h + \hat{n}_i) + \hat{n}_f\hat{n}_g + \hat{n}_h\hat{n}_i + \hat{n}_j\hat{n}_k\rangle \geq 1. \tag{5.4}$$

For the wave function (5.2), the majority of these inequalities are pinned. Six inequalities of the first class are completely saturated, namely:

$$\langle\hat{n}_i\hat{n}_{7-i}\rangle = 0 \quad \text{and} \quad \langle\hat{n}_3\hat{n}_5\rangle = \langle\hat{n}_3\hat{n}_6\rangle = \langle\hat{n}_5\hat{n}_6\rangle = 0.$$

For the second class [Eq. (5.3)] we have that all are pinned save

$$\begin{aligned}\langle(\hat{n}_1 + \hat{n}_2 + \hat{n}_3)^2 + (\hat{n}_4 + \hat{n}_5 + \hat{n}_6)^2\rangle = 5 + 4n_3 > 5, \\ \langle(\hat{n}_1 + \hat{n}_4 + \hat{n}_5)^2 + (\hat{n}_2 + \hat{n}_3 + \hat{n}_6)^2\rangle = 5 + 4n_5 > 5, \\ \langle(\hat{n}_2 + \hat{n}_4 + \hat{n}_6)^2 + (\hat{n}_1 + \hat{n}_3 + \hat{n}_5)^2\rangle = 5 + 4n_6 > 5.\end{aligned}$$

Since the occupation numbers are arranged in decreasing order, the strongest non-pinned inequality is the first one. The number of linearly independent inequalities belonging to the third class [Eq. (5.4)] drops to only 9. For instance,

$$\langle(\hat{n}_1 + \hat{n}_6)(\hat{n}_2 + \hat{n}_3) + \hat{n}_1\hat{n}_6 + \hat{n}_2\hat{n}_3 + \hat{n}_4\hat{n}_5\rangle = 1 + n_3 > 1.$$

In the end, we deal with 21 inequalities instead of 70, a remarkable reduction.

5.3 Klyachko's representability conditions

This Chapter is devoted to discussing some aspects of relevance to the present work. It is useful to consider the skew Cauchy formula,

$$\wedge^N\left(\mathcal{H}_{\mathrm{s}} \otimes \mathcal{H}_{\mathrm{orb}}\right)=\sum_{|\kappa|=N} \mathcal{H}_{\mathrm{s}}^{\kappa} \otimes \mathcal{H}_{\mathrm{orb}}^{\bar{\kappa}}. \tag{5.5}$$

Here, κ denotes the representation corresponding to the partition or Young tableau κ, and $\bar{\kappa}$ is the dual partition.

In the present work we have exclusively the case $\dim \mathcal{H}_{\mathrm{s}}=2$ and $N=3$, which makes everything relatively simple. The three-electron state space splits into spin-orbital sectors, which one needs to specify in order to check quasi-pinning, as well as gauge entanglement. $\mathcal{H}_{\mathrm{s}}$ corresponds to a spin-$\frac{1}{2}$ particle. Therefore, on the left hand side we may have only representations of $SU(2)$, i.e., either $j=\frac{1}{2}$ or $j=\frac{3}{2}$ for three particles. Since there are no skewsymmetric combinations of three spins-$\frac{1}{2}$, the partition $(1,1,1)$ on the right hand side plays no role; consequently, only tableaux with up to two columns may appear on the left hand side.

Consider for instance the first non-trivial case $\wedge^3(\mathcal{H}_2 \otimes \mathcal{H}_3)$ in the configuration 6^a of Section 6.4.2. There are 20 configurations in all. Clearly there is one with three spins down and one with three spins up, belonging to the representation with $j=\frac{3}{2}$. Of the eighteen remaining states, nine have one spin down in total, and nine have spin up. But only eight of each belong to the $j=\frac{1}{2}$ representation; the other two belong to $j=\frac{3}{2}$; whereby the spatial orbitals enter in the unique completely skewsymmetric combination. This takes care of "spin contamination". Accordingly,

$$\wedge^3\big(\mathcal{H}_{2\,\mathrm{s}} \otimes \mathcal{H}_{3\,\mathrm{orb}}\big)=\downarrow\mathcal{H}_2^{\otimes 3} \oplus \uparrow\mathcal{H}_2^{\otimes 3}+\mathcal{H}_{\mathrm{s}}^{3/2} \otimes \wedge^3 \mathcal{H}_{3\,\mathrm{orb}}.$$

From these simple observations to the generalized Pauli constraints there is still a long haul, demanding generous dollops of Kirillov's theory of orbits of the coadjoint action for compact groups [AK08]; the surprising outcome is that only linear inequalities are found.

Of course, not all of our basis sets conform to the left hand side of (5.5). This causes no problem, however, since any basis set can be considered a special case of a larger one with the "right" structure, with some holes. Iit is important that the Klyachko restrictions are *consistent*, so lower-rank ones can be derived from higher-rank ones. Recall for instance our example $\wedge^3\mathcal{H}_7$, and the four corresponding relations:

$$\begin{aligned} & n_1+n_2+n_4+n_7 \leq 2; \qquad && n_1+n_2+n_5+n_6 \leq 2; \\ & n_2+n_3+n_4+n_5 \leq 2; && n_1+n_3+n_4+n_6 \leq 2. \end{aligned}$$

At first, the original Pauli principle $n_1 \leq 1$ is perhaps not entirely obvious here; it follows from summing the second and the fourth. Also, let us consider the case $n_7=0$. Then summing the second and the third we obtain $n_2+n_5 \leq 1$; the second and fourth yield $n_3+n_4 \leq 1$, and so on: we plainly recover the Borland–Dennis relations for $\wedge^3\mathcal{H}_6$. The reader will have no difficulty in retrieving all the lower-rank relations from those of $\wedge^3\mathcal{H}_8$.

5.4 Selection rules

In the full CI picture, the wave function in a given one-electron basis is expressed as a linear combination of all possible Slater determinants:

$$|\Psi\rangle = \sum_K c_K |\mathbf{K}\rangle, \tag{5.6}$$

with $|\mathbf{K}\rangle$ denoting a determinant. Whenever we write expressions of this type in this thesis, they are eigenfunctions of the spin operator $\mathbf{S}_z$, belonging to the same eigenvalue. In general, they will not be eigenfunctions of $\mathbf{S}^2$, so a spin adaptation is needed [Pau79].

A one-body density matrix is compatible with the pure-state density matrix $|\Psi\rangle\langle\Psi|$ whenever its spectrum satisfies a set of linear inequalities of the type (2.19). For pinned systems, such that the condition (2.20) holds, the corresponding wave function belongs to the 0-eigenspace of the operator

$$\mathbf{D}^{\mu}_{N,m} = \kappa^{\mu}_0 \mathbf{1} + \kappa^{\mu}_1 a^{\dagger}_1 a_1 + \cdots + \kappa^{\mu}_m a^{\dagger}_m a_m,$$

where $a^{\dagger}_i$ and a_i are the fermionic creation and annihilation operators of the state i. By using the expression of the wave function in the full CI picture, this condition can be recast into a *superselection rule* for the Slater determinants that appear in the CI decomposition. Given a pinned system that satisfies equality (2.20), each Slater determinant appearing in the expansion (5.6) must be an eigenfunction of $\mathbf{D}^{\mu}_{N,m}$ with an eigenvalue equal to zero. The superfluous or ineffective configurations are thus identified by means of the criterion [Kly09]

$$\text{if } \mathbf{D}^{\mu}_{N,m}|\boldsymbol{K}\rangle \neq 0, \text{ then } c_K = 0.$$

This latter statement, for nondegenerate occupation numbers, follows from a relatively well known result in symplectic geometry, whose proof can be traced back to the eighties [**?**]. The degenerate case needs a different kind of proof, which is forthcoming [**?**]. It immediately demonstrates that the (quasi)pinning phenomenon allows one to drastically reduce the number of Slater determinants in CI expansions.

The criterion becomes even stricter when more than one pinning constraint is satisfied. Were the corresponding GPC to saturate, for a given set of constraints $\{\mu_1, \mu_2, \ldots, \mu_r\}$, the ineffective configurations would satisfy simultaneously the selection rules:

$$\text{if } \mathbf{D}^{\mu_1}_{N,m}\mathbf{D}^{\mu_2}_{N,m}\cdots\mathbf{D}^{\mu_r}_{N,m}|\mathbf{K}\rangle \neq 0, \text{ then } c_K = 0.$$

Notice that the order of the operators $\mathbf{D}^{\mu}_{N,m}$, $\mathbf{D}^{\nu}_{N,m}$ is irrelevant, since they commute. For such selection rules, the occupation numbers satisfy the following set of simultaneous equations:

$$D^{\mu_1}_{N,m}(\boldsymbol{n}) = D^{\mu_2}_{N,m}(\boldsymbol{n}) = \cdots = D^{\mu_r}_{N,m}(\boldsymbol{n}) = 0.$$

For instance, the Borland-Dennis state $\wedge^3\mathcal{H}_6$ satisfies:

$$\begin{aligned}
(\mathbf{1} - a^{\dagger}_1 a_1 - a^{\dagger}_6 a_6)|\Psi\rangle &= 0,\\
(\mathbf{1} - a^{\dagger}_2 a_2 - a^{\dagger}_5 a_5)|\Psi\rangle &= 0,\\
(\mathbf{1} - a^{\dagger}_3 a_3 - a^{\dagger}_4 a_4)|\Psi\rangle &= 0.
\end{aligned}$$

In general, it is not possible to saturate any arbitrary set of GPC simultaneously, but as we will discuss later on, certain sets are compatible with the rank of approximation when they are pinned.

In the remaining chapters we explore, among other things, (in)effective configurations when a certain number of pinning conditions are imposed. We mainly deal with three-electron systems, with Hilbert space $\wedge^3\mathcal{H}_m$, $m \geq 6$.

Chapter 6

Quasipinning: numerical and theoretical investigations

Two years ago Schilling, Gross and Christandl proposed to give an analytic study of these GPC by means of a toy model, namely: a one-dimensional system of *three spinless* fermions confined to a harmonic well, interacting with each other through Hooke-type forces [SGC13]. They found a series formula for the NON in terms of the coupling. Their tantalizing suggestion is that some GPC are *nearly saturated* for ground states, that is, the equality almost holds. This is the **quasipinning** phenomenon, which points to a deep hold of the GPC in the kinematics of the system. They state "*. . . it is likely extremely challenging to use numerical methods to distinguish between genuinely pinned and mere quasi-pinned states*". In this Chapter we report our effort in taking up this challenge by studying the ground state of some elementary three-electron atomic and molecular systems, starting from scratch with elementary CI and MCSCF methods, up to a rank-eight approximation (here, the rank equals the number of spin orbitals in setting up the expansions). This Chapter is mainly based on [BRGBS13, BRS15b].

6.1 Configuration Interaction

Consider a system of N electrons and M spin orbitals $\{\varphi_i(\boldsymbol{x})\}_{i=1}^{M}$, each being a product of a spatial orbital and a spinor. The number of configurations N_c that can be constructed from M spin orbitals for N electrons and $M - N$ holes is

$$N_c = \binom{M}{N},$$

which grows as a factorial with M. Here, we assume that we have identified a set of *basis functions*, largely under the guidance of physical or chemical intuition [Spr00], that provides an accurate description of the system of our interest. For N-electron systems, we use wave functions made of normalized Slater determinants:

$$|\Psi\rangle = \sum_J C_J |\varphi_{J(1)} \cdots \varphi_{J(N)}\rangle.$$

With the exterior algebra notation, this becomes

$$|\varphi_1\varphi_2\cdots\varphi_N\rangle := \tfrac{1}{\sqrt{N!}}|\varphi_1\rangle\wedge|\varphi_2\rangle\wedge\cdots\wedge|\varphi_N\rangle.$$

In general, we assume that the φ_i have been orthonormalized, although we occasionally relate them to non-orthogonal orbitals by

$$\varphi_i(\boldsymbol{x}) = \sum_{j=1}^{L} R_{ij}\,\psi_j(\boldsymbol{r},\varsigma). \tag{6.1}$$

Now suppose we define in some basis set the following energy integrals:

$$\begin{aligned} h^{\varphi}_{mn} &:= \int \varphi_m(\boldsymbol{x})\big[-\tfrac{1}{2}\nabla^2_{\boldsymbol{r}} + V(\boldsymbol{r})\big]\varphi_n(\boldsymbol{x})\,d\boldsymbol{x},\\ \iota^{\varphi}_{mnop} &:= \int \varphi_m(\boldsymbol{x}_1)\varphi_n(\boldsymbol{x}_1)v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\varphi_o(\boldsymbol{x}_2)\varphi_p(\boldsymbol{x}_2)\,d\boldsymbol{x}_1 d\boldsymbol{x}_2;\\ h^{\psi}_{mn} &:= \int \psi_m(\boldsymbol{x})\big[-\tfrac{1}{2}\nabla^2_{\boldsymbol{r}} + V(\boldsymbol{r})\big]\psi_n(\boldsymbol{x})\,d\boldsymbol{x},\\ \iota^{\psi}_{mnop} &:= \int \psi_m(\boldsymbol{x}_1)\,\psi_n(\boldsymbol{x}_1)v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\psi_o(\boldsymbol{x}_2)\,\psi_p(\boldsymbol{x}_2)\,d\boldsymbol{x}_1 d\boldsymbol{x}_2. \end{aligned} \tag{6.2}$$

From one set of integrals one can construct other sets by means of the relations $h^{\varphi} = (R\otimes R)\,h^{\psi}$ and $\iota^{\varphi} = (R\otimes R\otimes R\otimes R)\,\iota^{\psi}$, where R is the transformation matrix in (6.1).

6.2 Spin (de)contamination

The term *spin contamination* encapsulates the artificial mixing of different electronic spin-states. Such an undesirable phenomenon can occur when an orbital-based wave function is represented in an unrestricted way and therefore the spatial parts of the spin orbitals are permitted to differ [SO96]. Consequently, they are not eigenfunctions of the total spin-squared operator. However, as long as the Hamiltonian commutes with the spin operators, wave functions must be eigenfunctions of both spin operators $\mathbf{S}^2$ and $\mathbf{S}_z$, that is,

$$\mathbf{S}_z|\Psi\rangle = s_z|\Psi\rangle \quad\text{and}\quad \mathbf{S}^2|\Psi\rangle = s(s+1)|\Psi\rangle.$$

The total spin operator reads $\mathbf{S}^2 = \mathbf{S}_-\mathbf{S}_+ + \mathbf{S}_z + \mathbf{S}_z^2$. The spin parts of the wave functions (2.10) and (2.14) are eigenfunctions of both spin operators since

$$\mathbf{S}_z|\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\rangle = \mathbf{S}^2|\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\rangle = 0,$$

$\mathbf{S}_z|\uparrow_1\uparrow_2\rangle = |\uparrow_1\uparrow_2\rangle$, $\mathbf{S}^2|\uparrow_1\uparrow_2\rangle = 2|\uparrow_1\uparrow_2\rangle$, and so on. This section is devoted to present a general scheme to decontaminate any wave function by superposing configurations that belong to the same representation of $SU(2)$.

Let us define a general set of spin-orbitals in the following (spin-restricted) way:

$$\varphi_j(\boldsymbol{x}) = \begin{cases} \phi_{\frac{j+1}{2}}(\boldsymbol{r})\downarrow, & \text{if } j \text{ is odd,}\\ \phi_{\frac{j}{2}}(\boldsymbol{r})\uparrow, & \text{if } j \text{ is even.} \end{cases}$$

Note that $\mathbf{S}_+|\varphi_{2j-1}\rangle = |\varphi_{2j}\rangle$, $\mathbf{S}_-|\varphi_{2j}\rangle = |\varphi_{2j-1}\rangle$ and $\mathbf{S}_-|\varphi_{2j-1}\rangle = \mathbf{S}_+|\varphi_{2j}\rangle = 0$. For three-electron systems, it is easy to check that Slater determinants with two spin-orbitals sharing the same spatial orbital are spin eigenfunctions. To see that, let us choose a number $k \neq 2j$ and $k \neq 2j-1$, then

$$\mathbf{S}_-\mathbf{S}_+|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle = \kappa(k)|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle \quad \text{where} \quad \kappa(k) := \begin{cases} 1 & \text{if } k \text{ is odd} \\ 0 & \text{if } k \text{ is even.} \end{cases}$$

Therefore

$$\mathbf{S}^2|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle = \tfrac{3}{4}|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle \quad \text{and} \quad \mathbf{S}_z|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle = \tfrac{1}{2}(-1)^k|\varphi_{2j-1}\varphi_{2j}\varphi_k\rangle.$$

Since in general Slater determinants are not eigenfunctions of $\mathbf{S}^2$, spin-adapted linear combinations of these determinants are usually imposed. For instance, the linear combination

$$|\varphi_{2j-1}\varphi_{2k}\rangle - |\varphi_{2j}\varphi_{2k-1}\rangle$$

is an eigenfunction of $\mathbf{S}^2$ and $\mathbf{S}_z$ with $s = m = 0$. Consider the Hilbert subspace whose basis is the following ($i \neq j \neq k$):

$$\{|\varphi_{2i-1}\varphi_{2j}\varphi_{2k-1}\rangle, |\varphi_{2i-1}\varphi_{2j-1}\varphi_{2k}\rangle, |\varphi_{2i}\varphi_{2j-1}\varphi_{2k-1}\rangle\}$$

We perform the following basis change [Pau79]:

$$\begin{aligned}
|\widetilde{ijk}\rangle_1 &= \frac{1}{\sqrt{2}}(|\varphi_{2i-1}\varphi_{2j}\varphi_{2k-1}\rangle - |\varphi_{2i-1}\varphi_{2j-1}\varphi_{2k}\rangle) \\
|\widetilde{ijk}\rangle_2 &= \frac{1}{\sqrt{6}}(|\varphi_{2i-1}\varphi_{2j}\varphi_{2k-1}\rangle + |\varphi_{2i-1}\varphi_{2j-1}\varphi_{2k}\rangle - 2|\varphi_{2i}\varphi_{2j-1}\varphi_{2k-1}\rangle) \\
|\widetilde{ijk}\rangle_3 &= \frac{1}{\sqrt{3}}(|\varphi_{2i-1}\varphi_{2j}\varphi_{2k-1}\rangle + |\varphi_{2i-1}\varphi_{2j-1}\varphi_{2k}\rangle + |\varphi_{2i}\varphi_{2j-1}\varphi_{2k-1}\rangle).
\end{aligned}$$

These vectors form orthonormal basis: $\langle\widetilde{ijk}|_\mu|\widetilde{ijk}\rangle_\nu = \delta_{\mu\nu}$ and satisfy

$$\mathbf{S}_-\mathbf{S}_+|\widetilde{ijk}\rangle_1 = |\widetilde{ijk}\rangle_1, \quad \mathbf{S}_-\mathbf{S}_+|\widetilde{ijk}\rangle_2 = |\widetilde{ijk}\rangle_2 \quad \text{and} \quad \mathbf{S}_-\mathbf{S}_+|\widetilde{ijk}\rangle_3 = 4|\widetilde{ijk}\rangle_3.$$

Therefore

$$\mathbf{S}^2|\widetilde{ijk}\rangle_1 = \tfrac{3}{4}|\widetilde{ijk}\rangle_1, \quad \mathbf{S}^2|\widetilde{ijk}\rangle_2 = \tfrac{3}{4}|\widetilde{ijk}\rangle_2 \quad \text{and} \quad \mathbf{S}^2|\widetilde{ijk}\rangle_3 = \tfrac{15}{4}|\widetilde{ijk}\rangle_3$$

while $\mathbf{S}_z|\widetilde{ijk}\rangle_\mu = -\frac{1}{2}|\widetilde{ijk}\rangle_\mu$ for each μ. Therefore, the elements $|\widetilde{ijk}\rangle_1$ and $|\widetilde{ijk}\rangle_2$ belong to the representation $j = \frac{1}{2}$ while the vector $|\widetilde{ijk}\rangle_3$ belongs to the representation $j = \frac{3}{2}$ of $SU(2)$. A quantum state is spin-contaminated when its configurations do not belong to the same representation.

For three-electron systems with $s_z = \pm\frac{1}{2}$, the corresponding wave functions belong to the Hilbert space

$$\wedge^2\mathcal{H}_{m_1} \otimes \mathcal{H}_{m_2} \quad \text{with} \quad m_1 \geq 2 \quad \text{and} \quad m_2 \geq 1.$$

The rank of the approximation is $m_1 + m_2 = m$. The dimension of the corresponding Hilbert space is $\binom{m_1}{2}\binom{m_2}{1}$. Consider for instance the case $m_1 = m_2 = 3$. The dimension

Rank	$s_z = \uparrow$	$j = \frac{3}{2}$	$j = \frac{1}{2}$
6	9	1	8
8	24	4	20
10	50	10	40
12	90	20	70
14	147	35	112
16	224	56	168
18	324	84	240
20	450	120	330

Table 6.1: Dimension of the Hilbert space in the full spin-restricted CI configuration according to the spin representation to which they belong.

of this Hilbert space is 9. The decontaminated states for $j = \frac{1}{2}$ are the following:

$$|\varphi_1\varphi_2\varphi_3\rangle, \quad |\varphi_1\varphi_2\varphi_5\rangle, \quad |\varphi_1\varphi_3\varphi_4\rangle, \quad |\varphi_3\varphi_4\varphi_5\rangle, \quad |\varphi_1\varphi_5\varphi_6\rangle, \quad |\varphi_3\varphi_5\varphi_6\rangle,$$

plus the superpositions

$$\frac{1}{\sqrt{2}}(|\varphi_1\varphi_4\varphi_5\rangle - |\varphi_1\varphi_3\varphi_6\rangle) \quad \text{and} \quad \frac{1}{\sqrt{6}}(2|\varphi_2\varphi_3\varphi_5\rangle - |\varphi_1\varphi_4\varphi_5\rangle - |\varphi_1\varphi_3\varphi_6\rangle),$$

which reduces the dimension of the Hilbert space to 8. Consider the case $m_1 = m_2 = 4$. The dimension of the Hilbert space is 24. The four superpositions: $|\widetilde{123}\rangle_3$, $|\widetilde{124}\rangle_3$, $|\widetilde{234}\rangle_3$, $|\widetilde{134}\rangle_3$, belong to the representation $j = \frac{3}{2}$, so the dimension of the representation $j = \frac{1}{2}$ is 20. In general, the spin-decontaminated basis for the case $m_1 = m_2 = m/2$ contains

$$\binom{m/2}{2}\binom{m/2}{1} - \binom{m/2}{3} = \frac{m}{24}(m^2 - 4)$$

linearly independent elements. Table 6.1 shows the dimension of the Hilbert space as a function of the spin representation for several ranks of approximation. In the asymptotic limit, the $j = \frac{1}{2}$ representation constitutes 2/3 of the elements of the total Hilbert space. Throughout the following chapters, we have used this approach to identify those spin-adapted combinations of Slater determinants that are eigenfunctions to $\mathbf{S}^2$ and, accordingly, are not “spin-contaminated” states.

6.3 Pinning in spin-compensated configurations for $\wedge^3\mathcal{H}_6$

We begin our discussion by exhibiting our first case of pinning. In this Section we are going to prove that spin-compensated configurations for $\wedge^3\mathcal{H}_6$ are always pinned to the boundary of the corresponding polytope. For this rank of approximation for three-electron systems it is known [BD72] that the NON satisfy the following constraints: $n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1$, and

$$n_6 + n_5 - n_4 \geq 0. \tag{6.3}$$

The NON $\{n_i\}$ are arranged in the customary decreasing order $n_i \geq n_{i+1}$ and fulfil the Pauli condition $n_1 \leq 1$. The inequality (6.3) together with the decreasing ordering rule defines a polytope (Fig. 6.1). Clearly, the smallest possible value for the first three NON and largest for the last three is 0.5.

Conditions $n_r + n_{7-r} = 1$ imply that in the NO basis, namely $\{\alpha_i\}_{i=1}^6$, every Slater determinant is composed of three NO $|\alpha_i\alpha_j\alpha_k\rangle$, each belonging to one of three different sets, say

$$\alpha_i \in \{\alpha_1, \alpha_6\}, \quad \alpha_j \in \{\alpha_2, \alpha_5\} \quad \text{and} \quad \alpha_k \in \{\alpha_3, \alpha_4\},$$

that is, $\wedge^3\mathcal{H}_6$ splits with a section equal to $\mathcal{H}_2^{\otimes 3}$ for a system of three fermions with spin. This results in eight possible configurations,

$$\begin{gathered} |\alpha_1\alpha_2\alpha_3\rangle,\ |\alpha_1\alpha_2\alpha_4\rangle,\ |\alpha_1\alpha_3\alpha_5\rangle,\ |\alpha_1\alpha_4\alpha_5\rangle, \\ |\alpha_2\alpha_3\alpha_6\rangle,\ |\alpha_2\alpha_4\alpha_6\rangle,\ |\alpha_3\alpha_5\alpha_6\rangle,\ |\alpha_4\alpha_5\alpha_6\rangle. \end{gathered}$$

A spin-compensated configuration consists of three spin orbitals whose spin points down, and the other three point up. Such a configuration is in general favorable for the energy in comparison with other types of arrangements [BRGBS13]. The 1-RDM (a 6 × 6 matrix) is the direct sum of two (3 × 3) matrices, one related to the spin up and the other related to the spin down:

$$\gamma_1 = \gamma_1^{\uparrow} \oplus \gamma_1^{\downarrow}.$$

The wave function is an eigenstate of the total spin operator $\mathbf{S}_z$ (and of $\mathbf{S}^2$ in the spin-restricted case). Therefore, each acceptable Slater determinant will contain two spin orbitals pointing up (for instance) and one pointing down. It follows that the trace of one of those matrices will be equal to 1, while the sum of the diagonal elements of the other one will be equal to 2. Say, $\operatorname{Tr}\gamma_1^{\uparrow} = 2$ and $\operatorname{Tr}\gamma_1^{\downarrow} = 1$.

For not very strongly correlated systems, two of the first three NON belong to the matrix whose trace is 2. Hence, we have the following two conditions: $n_i + n_j + n_x = 2$ and $n_k + n_y + n_z = 1$, where $i, j, k \in \{1, 2, 3\}$ and $x, y, z \in \{4, 5, 6\}$. For given i and j, there are three possible values of x and therefore there are in principle nine possible solutions,

$$\begin{aligned} n_1 + n_2 + n_x &= 2 \quad \text{and} \quad n_3 + n_y + n_z = 1, \\ n_1 + n_3 + n_x &= 2 \quad \text{and} \quad n_2 + n_y + n_z = 1, \\ n_2 + n_3 + n_x &= 2 \quad \text{and} \quad n_1 + n_y + n_z = 1. \end{aligned}$$

However, we may easily dismiss all but one of them. For instance, the case

$$n_2 + n_3 + n_6 = 2 \quad \text{and} \quad n_1 + n_4 + n_5 = 1$$

is impossible: using $n_1 = 1 - n_6$, one obtains $-n_6 + n_4 + n_5 = 0$. This would imply that $n_4 = n_6 - n_5 \leq 0$, which is out of question. Also, for

$$n_1 + n_3 + n_5 = 2 \quad \text{and} \quad n_2 + n_4 + n_6 = 1,$$

using that $n_2 = 1 - n_5$, one obtains $-n_5 + n_4 + n_6 = 0$, which would imply that $n_4 = n_5 - n_6 < n_5$. Other cases are easily seen to give rise to rank at most four or five for the wave function, except for

$$n_1 + n_2 + n_4 = 2 \quad \text{and} \quad n_3 + n_5 + n_6 = 1,$$

which saturates the representability condition (6.3). Therefore, for not very strongly correlated systems the spin-compensated wave function of $\wedge^3\mathcal{H}_6$ lies on one of the facets of the Borland–Dennis–Klyachko polytope. This is in agreement with the numerical results obtained previously [BRGBS13, CM14].

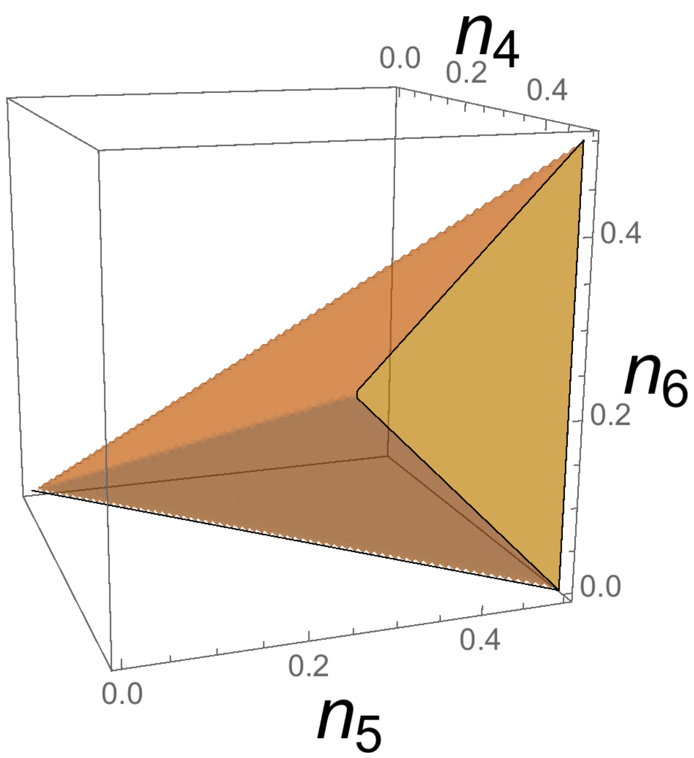

FIGURE 6.1: Polytope defined by the $+n_4 \leq n_5 + n_6$, subject to the condition $0 \leq n_6 \leq n_5 \leq n_4 \leq 0.5$. The saturation condition $n_5 + n_6 = n_4$ is satisfied by the points on one of the faces of the polytope, whereas on the edges $n_5 + n_6 = 0.5$ we have $n_4 = 0.5$ and for $n_4 = n_5$ we have $n_6 = 0$. The single determinant state is placed at the lower left corner $n_i = 0$ of the polytope.

The wave function for this configuration for $\wedge^3\mathcal{H}_6$ in the basis of NO can now be written in terms of the 1-RDM matrix:

$$|\Psi\rangle_{3,6} = c_{123}|\alpha_1\alpha_2\alpha_3\rangle + c_{145}|\alpha_1\alpha_4\alpha_5\rangle + c_{246}|\alpha_2\alpha_4\alpha_6\rangle; \tag{6.4}$$

with the proviso that $|c_{123}| \geq |c_{145}| \geq |c_{246}|$. It is now patent that $|\Psi\rangle$ can be elegantly rewritten as

$$|\Psi(n_i, \alpha_i)\rangle_{3,6} = \sqrt{n_3}\,|\alpha_1\alpha_2\alpha_3\rangle + \sqrt{n_5}\,|\alpha_1\alpha_4\alpha_5\rangle + \sqrt{n_6}\,|\alpha_2\alpha_4\alpha_6\rangle, \tag{6.5}$$

in analogy with the Löwdin–Shull (LS) functional for the two-electron case [LS56]. Note that, just like in the LS functional, only doubly excited configurations are here permitted[1]. (We understand excitations with respect to the "best density" Slater determinant, in the sense of [KS68].)

The pinned configuration $(n_1, n_2, n_3) = \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{2}\right)$ is far from the "Hartree-Fock" $(1, 1, 1)$ state. Now, a little surprise awaits us: for spin-compensated, very strongly correlated systems it is possible to show by the same method as above, the following identity:

$$n_1 + n_2 + n_3 = 2, \quad \text{equivalently} \quad n_4 + n_5 + n_6 = 1. \tag{6.6}$$

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[1] I thank Christian Schilling for pointing out to me that there is no ambiguity of signs in the above display.

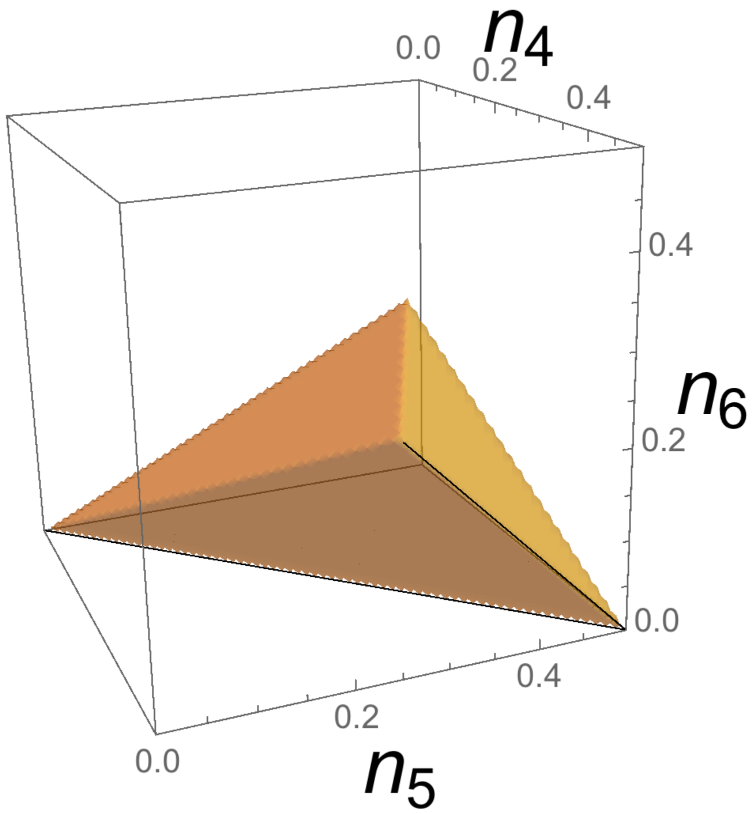

FIGURE 6.2: Polytope defined by the expression $n_4 \leq n_5 + n_6$, subject to the condition $0 \leq n_6 \leq n_5 \leq n_4 \leq 0.5$, plus the condition $n_4 + n_5 + n_6 \leq 1$. The saturation condition $n_4 + n_5 + n_6 = 1$ is satisfied by the points on the face of the polytope whose vertices are $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, $\left(\frac{1}{2}, \frac{1}{4}, \frac{1}{4}\right)$ and $\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$.

In terms of γ_1 the wave function then reads

$$|\Psi\rangle = \sqrt{n_4}|\alpha_1\alpha_2\alpha_4\rangle + \sqrt{n_5}|\alpha_1\alpha_3\alpha_5\rangle + \sqrt{n_6}|\alpha_2\alpha_3\alpha_6\rangle,$$

living in the 0-eigenspace of the operator

$$2\,\mathbb{1} - a_1^\dagger a_1 - a_2^\dagger a_2 - a_3^\dagger a_3.$$

We note that overlap of those wave functions with the $|\alpha_1\alpha_2\alpha_3\rangle$ state is *zero*. For the case $n_4 = n_5 = n_6 = 1/3$ this was already noted by Kutzelnigg and Smith [KS68]. The Borland–Dennis–Klyachko constraint becomes in this case:

$$2\,\mathbb{1} - (n_1 + n_2 + n_4) = n_3 - n_4 \geq 0.$$

Therefore in this regime it is possible to determine $|\Psi\rangle$ from γ_1 even without Klyachko pinning. The border between the two regimes is given by the degeneracy line $n_3 = n_4$. Inequality (6.3) together with the pinning (6.6) cuts out a new facet on the polytope of allowed states: the one whose vertices are $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, $\left(\frac{1}{2}, \frac{1}{4}, \frac{1}{4}\right)$ and $\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$.

In summary, there is still new wine in the old Borland–Dennis bottles: spin-compensated states are restricted to lie in two facets of a smaller polytope, as can be seen in Fig. 6.2.

The Borland–Dennis–Klyachko polytope of states is still too large. In fact, the spin-compensated states lie either on the $n_1 + n_2 + n_4 = 2$ facet of the polytope (when closer to the single-determinant state) or on the plane $n_4 + n_5 + n_6 = 1$ (when farther from the single-determinant state). The edge $n_3 = n_4$ is shared by these two planes. Notice that the exact expressions given above for the spin-compensated formulation of the system $\wedge^3\mathcal{H}_6$ lead to a diagonal 1-RDM, without any restriction on the amplitudes c_{ijk} (provided, of course, that the orbitals are orthonormal). In Chapter 8 we will show that for such a simple system one does not need a previous CI calculation to compute the NO and the value of the ground-state energy.

6.4 Lithium isoelectronic series

In two published papers we obtained rank-six, -seven and -eight approximations for the lithium isoelectronic series by using a set of helium-like one-particle wave functions in addition to one hydrogen-like wave function [BRGBS13, BRS15b]. Guided by the seminal work of Shull and Löwdin [LS56], for the former we employed the following set of orthonormal spatial orbitals:

$$\delta_n(\alpha, \boldsymbol{r}) := D_n \sqrt{\frac{\alpha^3}{\pi}} L^2_{n-1}(2\alpha r) e^{-\alpha r}, \quad n = 1, 2, \dots$$

where $D_n^{-2} = \binom{n-1}{2}$, and we used the standard definition of the associated Laguerre polynomials L_n^ζ [Leb72]. For the hydrogen-like function we used

$$\psi(\beta, \boldsymbol{r}) = \frac{1}{4}\sqrt{\frac{\beta^5}{6\pi}}\, r\, e^{-\beta r/2}.$$

Application of a variational procedure for the state $|\delta_1{\uparrow}\delta_1{\downarrow}\psi{\uparrow}\rangle$ results in $\alpha = 2.68$ and $\beta = 1.27$, and the total energy associated to this Slater determinant becomes -7.4179 au, reasonably close to the Hartree–Fock energy -7.4327 au [Joh13]. See Table 6.2. Notice that the R-matrix mentioned above in (6.1) can be the Gram–Schmidt orthonormalization matrix, i.e.,

$$\begin{pmatrix} \phi_1{\uparrow} \\ \phi_1{\downarrow} \\ \phi_2{\uparrow} \end{pmatrix} = R \begin{pmatrix} \delta_1{\uparrow} \\ \delta_1{\downarrow} \\ \psi{\uparrow} \end{pmatrix}, \quad \text{where} \quad R = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{\langle\delta_1|\psi\rangle}{\sqrt{1-|\langle\delta_1|\psi\rangle|^2}} & 0 & \frac{1}{\sqrt{1-|\langle\delta_1|\psi\rangle|^2}} \end{pmatrix}.$$

To alleviate the discussion, we shall not give below the explicit forms of such matrices.

Now we examine the GPC when the spherical symmetry of the central potential is broken by considering the following Hamiltonian:

$$H(Z, \gamma) = \frac{1}{2}\sum_{i=1}^{3} \boldsymbol{p}_i^2 - \sum_{i=1}^{3} \frac{Z}{|\boldsymbol{r}_i|}\left(1 + \gamma \frac{x_i^2}{|\boldsymbol{r}_i|^2}\right) + \sum_{i<j}^{3} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{6.7}$$

The case $H(3, 0)$ is the Hamiltonian of lithium, whose accurate energy value is -7.478 au. A motivation behind this model is to lift constraints on the possible NON due to the spherical symmetry of the isolated Li atom. Lowering the symmetry makes the model more flexible and allows to envisage more general cases. In addition, the model can serve to describe a Li atom embedded into some environment that does not provide covalent interactions with the Li atom. We have performed the calculations of this section by searching those values of α and β for which the approximation to the ground state leads to the minimum energy with spin-compensated linear combinations of Slater determinants. Analytical expressions for the electron integrals were computed using Mathematica [Wol14] and orthonormalized orbitals were obtained by the Gram–Schmidt procedure. Computations were performed with 36 decimals floating-point precision.

6.4.1 The rank-five computation

A rank-five approximation is obtained by using two helium-like one-particle wave functions and one hydrogen-like [BRGBS13]. We shall adopt the following notation for an orthonormalized basis set of the restricted spin-orbital type:

$$\begin{pmatrix} \phi_1\uparrow \\ \phi_1\downarrow \\ \phi_2\uparrow \\ \phi_3\uparrow \\ \phi_3\downarrow \end{pmatrix} = R \begin{pmatrix} \delta_1\uparrow \\ \delta_1\downarrow \\ \psi\uparrow \\ \delta_2\uparrow \\ \delta_2\downarrow \end{pmatrix}.$$

With rank five, one has in principle $10 = \binom{5}{3}$ Slater determinants. However, since the adopted Hamiltonian is independent of the spin coordinates, only pure spin states are physically meaningful. There are only six determinants which are eigenvectors of the operator $\mathbf{S}_z$, namely,

$$|\phi_1\uparrow\phi_1\downarrow\phi_2\uparrow\rangle,\ |\phi_1\uparrow\phi_1\downarrow\phi_3\uparrow\rangle,\ |\phi_3\uparrow\phi_3\downarrow\phi_1\uparrow\rangle,\ |\phi_3\uparrow\phi_3\downarrow\phi_2\uparrow\rangle,\ |\phi_1\downarrow\phi_2\uparrow\phi_3\uparrow\rangle,\ |\phi_1\uparrow\phi_2\uparrow\phi_3\downarrow\rangle. \tag{6.8}$$

The total spin operator $\mathbf{S}^2$ can be written as $\mathbf{S}_-\mathbf{S}_+ + \mathbf{S}_z + \mathbf{S}_z^2$ (see Sec. 6.2). It is clear that these state are eigenstates of the operator $\mathbf{S}_z$ (and consequently of $\mathbf{S}_z^2$). However, it is less clear whether they are eigenstates of $\mathbf{S}_-\mathbf{S}_+$, too. It is easy to show that the wave function

$$\begin{aligned}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_3) = {} & a|\phi_1\uparrow\phi_1\downarrow\phi_2\uparrow\rangle + b|\phi_1\uparrow\phi_1\downarrow\phi_3\uparrow\rangle + c|\phi_3\uparrow\phi_3\downarrow\phi_1\uparrow\rangle \\ & + d|\phi_3\uparrow\phi_3\downarrow\phi_2\uparrow\rangle + e\big(|\phi_1\downarrow\phi_2\uparrow\phi_3\uparrow\rangle - |\phi_1\uparrow\phi_2\uparrow\phi_3\downarrow\rangle\big),\end{aligned}$$

with $|a|^2+|b|^2+|c|^2+|d|^2+2|e|^2 = 1$, satisfies $\mathbf{S}^2|\Psi\rangle = \frac{3}{4}|\Psi\rangle$, and, accordingly, is a not "spin-contaminated" state.

Conf	Energy (au)	α	β
"exact"	-7.478060	–	–
HF	-7.432727	–	–
$\lvert\phi_1\uparrow\phi_1\downarrow\phi_2\uparrow\rangle$	-7.417919	2.686435	1.274552

TABLE 6.2: The exact, HF and variational energy of Li [$H(3,0)$ in Eq. (6.7)] in the chosen single-determinant configuration [Joh13, BRGBS13].

The corresponding 1-RDM is expressed by the matrix

$$\gamma_1 = \begin{pmatrix} 1-|d|^2-|e|^2 & 0 & cd^*-be^* & ed^*+ae^* & 0 \\ 0 & |a|^2+|b|^2+|e|^2 & 0 & 0 & -bc^*+d^*e+ae^* \\ dc^*-eb^* & 0 & |a|^2+|d|^2+2|e|^2 & ab^*-ec^* & 0 \\ ea^*+de^* & 0 & ba^*-ce^* & 1-|a|^2-|e|^2 & 0 \\ 0 & -cb^*+ea^*+de^* & 0 & 0 & |c|^2+|d|^2+|e|^2 \end{pmatrix}.$$

Note that the $\gamma_1 = \gamma_1^{\uparrow} \oplus \gamma_1^{\downarrow}$ with $\operatorname{Tr}\gamma_1^{\uparrow} = 2$ and $\operatorname{Tr}\gamma_1^{\downarrow} = 1$. By definition, in the basis of NO $\{|\alpha_i\rangle\}$, the 1-RDM is diagonal: $\gamma_1 = \sum_{i=1}^{5} n_i\,|\alpha_i\rangle\langle\alpha_i|$, already assuming that the NON are arranged in decreasing order. Therefore, it is evident that a strong *selection rule* applies [BRGBS13]: we can rewrite the wave function for a three-electron system in rank five in terms of only *two* configurations:

$$|\Psi\rangle_{3,5} = c_{123}|\alpha_1\alpha_2\alpha_3\rangle + c_{145}|\alpha_1\alpha_4\alpha_5\rangle; \quad \text{where} \quad |c_{123}|^2 + |c_{145}|^2 = 1,$$

and the NON satisfy: $n_1 = 1$ and $n_2 + n_4 = n_3 + n_5 = 1$.

6.4.2 Two rank-six approximations

In [BRGBS13] we considered two different approaches for obtaining six-rank approximations for lithium-like ions. One was to work in a scheme of fully restricted spin orbitals. Then, the sixth spin-orbital is chosen as $\psi\!\downarrow$. An alternative is to include $\delta_3\!\uparrow$ instead. For convenience, we use the notation 6^a and 6^b respectively for these two cases:

$$\begin{pmatrix} \phi_1\uparrow \\ \phi_1\downarrow \\ \phi_2\uparrow \\ \phi_2\downarrow \\ \phi_3\uparrow \\ \phi_3\downarrow \end{pmatrix} = R \begin{pmatrix} \delta_1\uparrow \\ \delta_1\downarrow \\ \psi\uparrow \\ \psi\downarrow \\ \delta_2\uparrow \\ \delta_2\downarrow \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \phi_1\uparrow \\ \phi_1\downarrow \\ \phi_2\uparrow \\ \phi_3\uparrow \\ \phi_3\downarrow \\ \phi_4\uparrow \end{pmatrix} = R \begin{pmatrix} \delta_1\uparrow \\ \delta_1\downarrow \\ \psi\uparrow \\ \delta_2\uparrow \\ \delta_2\downarrow \\ \delta_3\uparrow \end{pmatrix}. \tag{6.9}$$

For the first basis set, out of $20 = \binom{6}{3}$ Slater determinants there are nine eigenfunctions of $\mathbf{S}_z$ with eigenvalue $\uparrow$. The six Slater determinants obtained in the rank-five approximation (6.8) plus the following three:

$$|\phi_1\!\uparrow\phi_2\!\uparrow\phi_2\!\downarrow\rangle, \quad |\phi_2\!\uparrow\phi_2\!\downarrow\phi_3\!\uparrow\rangle, \quad |\phi_1\!\uparrow\phi_2\!\downarrow\phi_3\!\uparrow\rangle.$$

For the second basis system in (6.9), among the 20 Slater determinants there are twelve eigenfunctions of the operator $\mathbf{S}_z$ with eigenvalue $\uparrow$. Table 6.3 presents the results for the energy and screening parameters. In the table we have also included the results for higher-rank approximations. Remarkably, the rank-eight approximation for this rather naive model gives for the ground-state energy of lithium -7.4548 au, which represents more than 50% of its correlation energy [BRGBS13].

Table 6.4 gives the results for the litihium NON. The (four) Klyachko inequalities for a three-electron system in a rank-six configuration read

$$n_1 + n_6 \le 1, \quad n_2 + n_5 \le 1, \quad n_3 + n_4 \le 1; \quad 0 \le D_{3,6} := n_5 + n_6 - n_4.$$

However, one must have $\sum_{i=1}^{6} n_i = 3$. As a consequence of this, the first inequalities become saturated (the Borland–Dennis identities), and there is only one inequality left

Rank	Energy	α	β
3	−7.417919	2.686435	1.274552
5	−7.431181	2.711177	1.304903
6^a	−7.431827	2.674424	1.319161
6^b	−7.431639	2.712166	1.323417
7	−7.445443	2.772402	1.336274
8	−7.454889	2.767562	1.331108

Table 6.3: Variational energy of Li in a CI picture for different ranks of approximation.

for further examination. Before analyzing $D_{3,6}$, we emphasize that the Borland–Dennis identities are fulfilled within our numerical accuracy.

Quasipinning is the property of a GPC being "extremely close" to zero (we will provide a more precise definition later). Within our calculation 6^b, we find

$$D_{3,6} = n_5 + n_6 - n_4 = 2.1465 \times 10^{-5}. \tag{6.10}$$

This value of $D_{3,6}$ is slightly smaller than the lowest NON, $D_{3,6}/n_6 \approx 0.97$. $D_{3,6}$ cannot exceed n_6, because otherwise $n_5 > n_4$. As we have already proved in Section 6.3 for the determinant case 6^a, one has the pinning condition $D_{3,6} = 0$.

So far, a number of findings and conclusions can be emphasized [BRGBS13]:

- The energy computed via the restricted basis set 6^a is (marginally) better than that obtained via 6^b.
- As expected, we observe "strict" pinning for 6^a and "lax" quasipinning for 6^b. Indeed, equation (6.10) is still remarkable in absolute terms. But it just means that if the system is close to a vertex, then it is close to a face.
- Both states are truly entangled —neither separable nor biseparable. However, the $\mathcal{T}$-measure of entanglement *vanishes* for 6^a, while $\mathcal{T} \neq 0$ for 6^b [BRGBS13]. This latter is a measure of entanglement proposed in [SL14] on the basis of cubic Jordan algebra theory for a wave function $|\Psi\rangle$ belonging to the abstract twenty-dimensional Hilbert space $\wedge^3\mathcal{H}_6$. Given an ordered basis of $\wedge^3\mathcal{H}_6$ and

$$|\Psi\rangle = \sum_{1\le i<j<k\le 6} c_{ijk}|\varphi_i\varphi_j\varphi_k\rangle, \tag{6.11}$$

Rank	n_1	n_2	n_3	$n_4 \times 10^3$	$n_5 \times 10^3$	$n_6 \times 10^4$	$n_7 \times 10^5$	$n_8 \times 10^6$
5	1	0.998702	0.998702	1.297058	1.297058	–	–	–
6^a	0.999978	0.998677	0.998655	1.344195	1.322335	0.2185	–	–
6^b	0.999977	0.998715	0.998715	1.284753	1.284182	0.2203	–	–
7	0.999868	0.998629	0.998511	1.416148	1.364978	1.2336	8.5241	–
8	0.999839	0.998663	0.998522	1.409339	1.337846	1.3972	8.6559	1.7232

Table 6.4: NON from ranks five to eight for lithium wave functions.

its amount of entanglement is analyzed in terms of the absolute value of the expression

$$\mathcal{T} := 4\big\{[\mathrm{Tr}(M_1M_2) - \mu\nu]^2 - 4\,\mathrm{Tr}(M_1^\# M_2^\#) + 4\mu \det M_1 + 4\nu \det M_2\big\},$$

with $0 \le |\mathcal{T}| \le 1$, where the twenty amplitudes of (6.11) are arranged in two 3×3 matrices and two scalars,

$$M_1 := \begin{pmatrix} c_{156} & -c_{146} & c_{145} \\ c_{256} & -c_{246} & c_{245} \\ c_{356} & -c_{346} & c_{345} \end{pmatrix}, \quad M_2 := \begin{pmatrix} c_{234} & -c_{134} & c_{124} \\ c_{235} & -c_{135} & c_{125} \\ c_{236} & -c_{136} & c_{126} \end{pmatrix},$$

$\mu := c_{123}$ and $\nu := c_{456}$. Here, $M^\#$ denotes the adjugate of a matrix M, such that $MM^\# = M^\# M = (\det M)I$. Under this measure, non-trivial tripartite entanglement can take place in two inequivalent ways: those with $|\mathcal{T}| \neq 0$ and those with $|\mathcal{T}| = 0$ —provided that then a pertinent dual wavefunction $\tilde{\Psi}$ is different from zero. Although both cases exhibit genuine tripartite entanglement, there is no unitary transformation relating the two types of states. The lowest configuration of the energy with the basis set 6^a results in a $\mathcal{T}$-measure of entanglement equal to 0. In contrast, the wave function constructed from 6^b results in $\mathcal{T}$-entanglement equal to 2.57×10^{-6}. Thus, in some sense the latter is “more entangled” than the former [BRGBS13]. It is accordingly natural to conjecture that pinning leads to qualitative differences in multipartite entanglement, and quasipinning correlates *negatively* with entanglement [SL14].

- When employing a restricted basis set, there is no loss of information in working with the wave function (6.4). Even in the general case, at rank six simultaneous variation of orbitals and coefficients is still a tempting proposition for the lithium series, in view of the following. The possible loss of information when projecting the total wave function onto this subspace of pinned states has been computed [SGC13]. Given a wave function $|\Psi\rangle \in \wedge^3\mathcal{H}_6$, and letting P be the projection operator onto the subspace spanned by the Slater determinants $|\alpha_1\alpha_2\alpha_3\rangle$, $|\alpha_1\alpha_4\alpha_5\rangle$ and $|\alpha_2\alpha_4\alpha_6\rangle$, we have the following upper and lower bounds for this projection,

$$1 - \frac{1+2\xi}{1-4\xi} D_{3,6} \le \|P\Phi\|_2^2 \le 1 - \tfrac{1}{2} D_{3,6}, \quad \text{provided} \quad \xi := 3 - n_1 - n_2 - n_3 < \frac{1}{4}.$$

  Within our calculations the lower bound is greater than 99.997%.

6.4.3 A rank-seven approximation

We choose the basis set

$$\begin{pmatrix} \phi_1{\uparrow} \\ \phi_1{\downarrow} \\ \phi_2{\uparrow} \\ \phi_3{\uparrow} \\ \phi_3{\downarrow} \\ \phi_4{\uparrow} \\ \phi_4{\downarrow} \end{pmatrix} = R \begin{pmatrix} \delta_1{\uparrow} \\ \delta_1{\downarrow} \\ \psi{\uparrow} \\ \delta_2{\uparrow} \\ \delta_2{\downarrow} \\ \delta_3{\uparrow} \\ \delta_3{\downarrow} \end{pmatrix}.$$

that is, we include also the spin-up counterpart $\delta_3\uparrow$. In principle we have $35 = \binom{7}{3}$ Slater determinants, of which eighteen have the total $\mathbf{S}_z$ component equal to $\uparrow$ and fifteen are spin-adapted [BRGBS13, BRS15b].

There are four Klyachko inequalities for the lithium isoelectronic series in a rank-seven configuration:

$$\begin{aligned} n_1 + n_2 + n_4 + n_7 &\leq 2; \qquad & n_1 + n_2 + n_5 + n_6 &\leq 2; \\ n_2 + n_3 + n_4 + n_5 &\leq 2; \qquad & n_1 + n_3 + n_4 + n_6 &\leq 2. \end{aligned} \tag{6.12}$$

In our calculations we find

$$\begin{aligned} 0 \leq D^1_{3,7} &= 2 - (n_1 + n_2 + n_4 + n_7) = 0, \\ 0 \leq D^2_{3,7} &= 2 - (n_1 + n_2 + n_5 + n_6) = 1.3045 \times 10^{-5}, \\ 0 \leq D^3_{3,7} &= 2 - (n_2 + n_3 + n_4 + n_5) = 7.7411 \times 10^{-5}, \\ 0 \leq D^4_{3,7} &= 2 - (n_1 + n_3 + n_4 + n_6) = 8.0025 \times 10^{-5}. \end{aligned}$$

There are several interesting issues on the structure of the constraints, which shall now be briefly discussed.

- The pinned system can be factorized,

  $$\wedge^3\mathcal{H}_7 \to \mathcal{H}_3 \otimes \wedge^2\mathcal{H}_4.$$

  That is, the 1-RDM can be split into a direct sum of two matrices,

  $$\gamma_1 = \gamma_1^{\uparrow} \oplus \gamma_1^{\downarrow}.$$

  The first one is a 3×3 square matrix whose trace is equal to 1 and that is associated with the electron with spin pointing $\downarrow$, while the second matrix is a 4×4 square matrix whose trace is equal to two and is associated with the two electrons with spin pointing $\uparrow$.

- For the first time we spy the appearance of two *scales* of quasipinning. The same phenomenon can be seen as a function of the coupling constant: $\gamma \in D^2_{3,7}$ is always below 1.3717×10^{-5}, taking its maximum for $\gamma = 0.01$ (i.e., practically at the "physical point"), as indicated in Fig. 6.3. On the other hand, the remaining two GPC $D^3_{3,7}$ and $D^4_{3,7}$ take values around 7×10^{-5}. As shown in Fig. 6.4, $D^3_{3,7}$ decreases when the value of γ grows, while the last one increases when γ increases. Notice the crossover of two constraints also close by $\gamma \approx 0$.

- If the second constraint were saturated, the selection rule would fix the number of Slater determinants in the decomposition of the wave function to be nine, namely: the "Hartree-Fock" state $|\alpha_1\alpha_2\alpha_3\rangle$, plus

  $|\alpha_1\alpha_4\alpha_5\rangle$, $|\alpha_1\alpha_4\alpha_6\rangle$, $|\alpha_1\alpha_5\alpha_7\rangle$, $|\alpha_1\alpha_6\alpha_7\rangle$, $|\alpha_2\alpha_4\alpha_5\rangle$, $|\alpha_2\alpha_4\alpha_6\rangle$, $|\alpha_2\alpha_5\alpha_7\rangle$, $|\alpha_2\alpha_6\alpha_7\rangle$.

- As for the case of $\wedge^3\mathcal{H}_6$, the loss of information when projecting the total wave function onto this nine-dimensional subspace of twice pinned states can be estimated. In [BRGBS13] we gave a proof of the following theorem: let a wave function

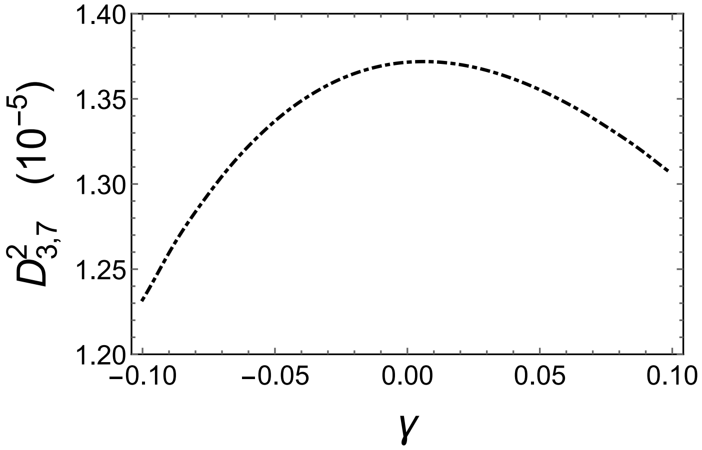

FIGURE 6.3: $D^2_{3,7}$ for the ground-state of the Hamiltonian $H(3,\gamma)$ in a rank-seven approximation as a function of $\gamma \in [-0.1, 0.1]$. For $\gamma = 0.01$, the constraint reaches its maximum value (namely, 1.3717×10^{-5}).

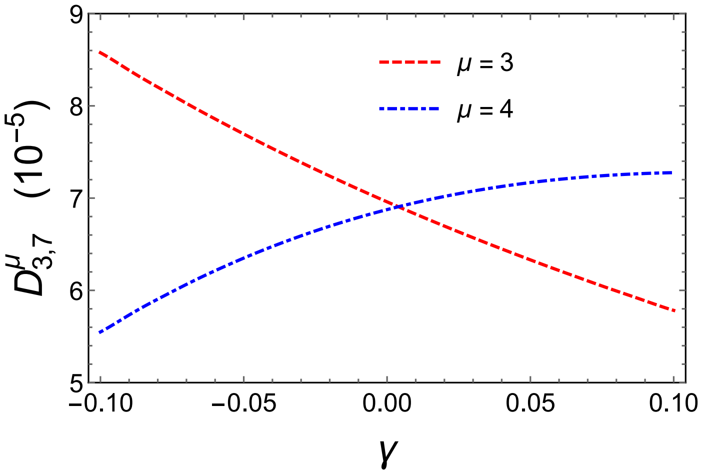

FIGURE 6.4: Third and fourth GPC for the ground-state of the Hamiltonian $H(3,\gamma)$ in a rank-seven approximation as a function of $\gamma \in [-0.1, 0.1]$.

$|\Psi\rangle \in \wedge^3\mathcal{H}_7$ with NO $|\alpha_i\rangle_{i=1}^7$, NON $\{n_i\}_{i=1}^7$, saturating the first GPC $D^1_{3,7}$. Moreover, let P_7 be the projection operator onto the subspace spanned by the Slater determinants above. Then, the upper and lower bounds of this projection are given by

$$1 - \frac{1+9\xi}{1-11\xi} D^2_{3,7} \leq \|P_7\Phi\|_2^2 \leq 1 - \tfrac{1}{2} D^2_{3,7} \quad \text{provided that} \quad \xi < \frac{1}{11}\,.$$

Within our calculations, $1 - \dfrac{1+9\xi}{1-11\xi}\, D^2_{3,7} = 1 - 1.3852 \times 10^{-5} = 99.9986\%$.

- If, in addition, the third or the fourth constraint becomes saturated, the selection rules decreases the number of allowed determinants to just 4. Saturating both simultaneously reduces the case to the saturated rank-six wavefunction.

6.5 The molecular system He_2^+

In this section we study the behavior of the NON of helium's molecular ion He_2^+. The goal is to explore the GPC along the dissociation path of this three-electron system, whose symmetry is lower than spherical, identifying those almost saturated. The Hartree-Fock energy for this system is $-4.9\,\mathrm{au}$ [Joh13], with a 6-31G basis set. The equilibrium bond length is $2.08\,\mathrm{au}$ [Joh13]. The computed value for the ground-state energy is approximately $-4.99\,\mathrm{au}$ [XPG05, Joh13]. Therefore the correlation energy is equal to $90\,\mathrm{mHa}$. We have approximated the atomic orbitals by employing a 6-31G basis set [HDP72]. We here report our results for (rank six, seven and eight) CI approximations for this diatomic ion.

6.5.1 GPC for the He_2^+ ground state

For a dimer with atomic charge Z, the energy is given by the expression

$$-\int \left(\frac{1}{2}\nabla_{\boldsymbol{r}}^2 + \sum_{\mu\in\{A,B\}} \frac{Z}{|\boldsymbol{r}-\boldsymbol{R}_\mu|}\right) \gamma_1(\boldsymbol{x},\boldsymbol{x}')\bigg|_{\boldsymbol{x}=\boldsymbol{x}'} d\boldsymbol{x} + \int \frac{\gamma_2(\boldsymbol{x}_1,\boldsymbol{x}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 + \frac{Z^2}{|\boldsymbol{R}|}.$$

The two atoms are located at $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$ and separated by $\boldsymbol{R} := \boldsymbol{R}_A - \boldsymbol{R}_B$. The molecular orbitals are constructed as linear combinations of the atomic $1s$ and $2s$ orbitals, which are in turn solutions of the Hartree-Fock equations. In the rest of this subsection, standard notation for the bonding (*gerade*) and antibonding (*ungerade*) molecular orbitals is used. The ground-state configuration of He_2^+ is classified as ${}^2\Sigma_u$ and the starting configuration is a single Slater determinant, $|1\sigma_g^\uparrow 1\sigma_g^\downarrow 1\sigma_u^\uparrow\rangle$.

Table 6.5 presents the results for the energy and for the NON from rank-six up to rank-eight approximations for the ground-state of He_2^+. The rank-six approximation is obtained through a spin-compensated configuration,

$$\{1\sigma_g^\uparrow, 1\sigma_g^\downarrow, 1\sigma_u^\uparrow, 1\sigma_u^\downarrow, 2\sigma_g^\uparrow, 2\sigma_g^\downarrow\}.$$

Higher-rank configurations are obtained by successively adding the orbitals $\{2\sigma_u^\uparrow, 2\sigma_u^\downarrow\}$.

A number of findings can now be identified [BRS15b]:

- For rank six, the spin-compensated configuration gives the Borland–Dennis–Klyachko saturation condition $1 + n_3 = n_1 + n_2$.

Rank	Energy	n_1	n_2	n_3	$n_4 \times 10^3$	$n_5 \times 10^3$	$n_6 \times 10^3$	$n_7 \times 10^3$	$n_8 \times 10^4$
6	-4.9125	0.9992	0.9949	0.9941	5.8086	5.0914	0.7172	-	-
7	-4.9194	0.9973	0.9941	0.9915	7.1019	5.8950	2.5530	1.3220	-
8	-4.9239	0.9968	0.9932	0.9901	8.4888	6.8304	3.0819	1.3665	0.1178

Table 6.5: NON and energies for rank-six to rank-eight for He_2^+ in its equilibrium geometry, employing 6-31G basis set.

- For rank seven, we obtain at the equilibrium geometry the following values for the GPC:

$$D^1_{3,7} = 2.42 \times 10^{-5}, \quad D^2_{3,7} = 0,$$
$$D^3_{3,7} = 1.24 \times 10^{-3}, \quad D^4_{3,7} = 1.39 \times 10^{-3}.$$

  The constraint due to spin has “jumped”, with respect to the lithium series!

- For this latter rank, two scales of quasipinning are clearly identified (to the first one belongs $D^1_{3,7}$ and to the second one $D^3_{3,7}$ and $D^4_{3,7}$). Compared with the lithium-like atom, the first level of quasipinning is here more meaningful and probably more useful in order to reduce the number of Slater determinants, since the distance to the “Hartree-Fock” point here is greater, namely, $\xi = 1.06 \times 10^{-2}$.

Unfortunately, it is a fact of life that the number of GPC grows very rapidly with rank. For rank eight there are *31* inequalities [AK08]. They have been listed in a plain-text format in the supplementary material of reference [AK08]. Of those, 19 constraints are given in Table 6.6. The first four are equal to the Klyachko conditions for $\wedge^3\mathcal{H}_7$. Several scales of quasipinning can be identified here, as well. Most important is the ***robustness*** of quasipinning. In particular, the quantity $D^2_{3,8}$, found to be exactly zero in the previous rank, remains in a saturated regime. The first and fifth inequality belong to a strongly quasi-pinned regime, too. For the remaining inequalities we have (listing their magnitudes by size)

$$D^2_{3,8} \le D^5_{3,8} \le D^1_{3,8} \le D^6_{3,8} \le D^3_{3,8} \le D^{12}_{3,8} \le D^8_{3,8} \le D^7_{3,8} \le D^4_{3,8} \le \cdots .$$

GPC for $\wedge^3\mathcal{H}_8$	$\times 10^3$
$0 \le D^1_{3,8} = 2 - (n_1 + n_2 + n_4 + n_7)$	0.0570
$0 \le D^2_{3,8} = 2 - (n_1 + n_2 + n_5 + n_6)$	0
$0 \le D^3_{3,8} = 2 - (n_2 + n_3 + n_4 + n_5)$	1.2712
$0 \le D^4_{3,8} = 2 - (n_1 + n_3 + n_4 + n_6)$	1.4854
$0 \le D^5_{3,8} = 1 - (n_1 + n_2 - n_3)$	0.0452
$0 \le D^6_{3,8} = 1 - (n_2 + n_5 - n_7)$	1.2594
$0 \le D^7_{3,8} = 1 - (n_1 + n_6 - n_7)$	1.4736
$0 \le D^8_{3,8} = 1 - (n_2 + n_4 - n_6)$	1.3164
$0 \le D^9_{3,8} = 1 - (n_1 + n_4 - n_5)$	1.5306
$0 \le D^{10}_{3,8} = 1 - (n_3 + n_4 - n_7)$	2.7449
$0 \le D^{11}_{3,8} = 1 - (n_1 + n_8)$	3.1772
$0 \le D^{12}_{3,8} = -(n_2 - n_3 - n_6 - n_7)$	1.3046
$0 \le D^{13}_{3,8} = -(n_4 - n_5 - n_6 - n_7)$	2.7901
$0 \le D^{14}_{3,8} = -(n_1 - n_3 - n_5 - n_7)$	1.5188
$0 \le D^{15}_{3,8} = 2 - (n_2 + n_3 + 2n_4 - n_5 - n_7 + n_8)$	7.7980
$0 \le D^{16}_{3,8} = 2 - (n_1 + n_3 + 2n_4 - n_5 - n_6 + n_8)$	5.9792
$0 \le D^{17}_{3,8} = 2 - (n_1 + 2n_2 - n_3 + n_4 - n_5 + n_8)$	5.0983
$0 \le D^{18}_{3,8} = 2 - (n_1 + 2n_2 - n_3 + n_5 - n_6 + n_8)$	3.0082
$0 \le D^{19}_{3,8} = -(n_1 + n_2 - 2n_3 - n_4 - n_5)$	5.4973

Table 6.6: First 19 GPC for the system $\wedge^3\mathcal{H}_8$ and numerical values for He_2^+ at its equilibrium geometry.

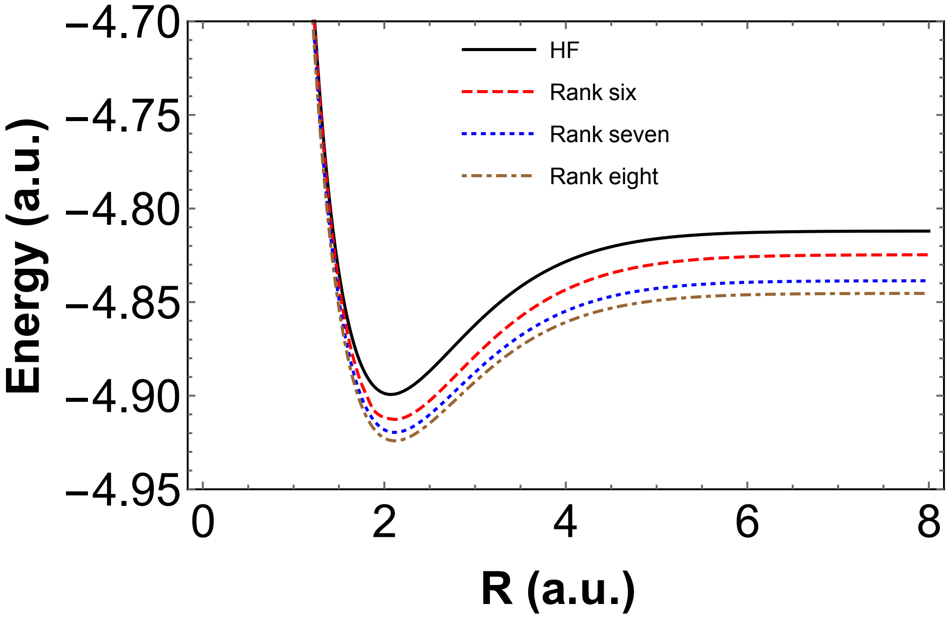

FIGURE 6.5: He_2^+ potential energy curves for the three ranks of CI approximation $\wedge^3\mathcal{H}_m$, $m \in \{3, 6, 7, 8\}$ using 6-31G as a basis set.

6.5.2 NON and potential curves

Potential energy curves for the three different ranks of the CI approximation for He_2^+ are presented in Fig. 6.5. At the equilibrium geometry, as also seen in Table 6.5, a larger rank results in a lower ground-state energy. All approximations behave similarly around the equilibrium distance. At large interatomic distances, the value predicted by the rank-eight configuration is -4.845 au which is to be compared with the total energy of the two separated compounds (He and He^+): -4.903 au [NJK91].

Fig. 6.6 displays rank-seven GPC as functions of the interatomic distance in atomic units. There are again two scales of quasipinning. The first two GPC remain in a strongly pinned regime, since for those $D^\mu_{3,7}$ is very close to 0. For those, we notice a sharp crossover at lengths shorter than that of equilibrium. In fact, one of them is *always* completely saturated: in the region $R < 1.25$ au, i.e., $D^1_{3,7} = 0$ is a very good approximation, whereas for $R > 1.25$ au $D^2_{3,7} = 0$ is also very good. Unfortunately, we do not have yet a good description for this apparent quenching of degrees of freedom, which surely deserves further investigation.

For rank eight, several scales of quasipinning can be observed for He_2^+. Our main result is again the robustness of quasipinning. In particular, we observe that the quantities $D^1_{3,8}$ and $D^2_{3,8}$, found to be exactly zero for some bond-length regime at rank seven, remain in a strongly saturated regime, as shown in Fig. 6.7. The Hilbert space of this system splits then into the direct product of two spin-orbital sectors $\wedge^3\mathcal{H}_8 \to \mathcal{H}_4 \otimes \wedge^2\mathcal{H}_4$. Also $D^5_{3,8}$ is found to be very close to 0.

To a second quasipinning regime belong the quantities

$$D^3_{3,8},\ D^4_{3,8},\ D^6_{3,8},\ D^7_{3,8},\ D^8_{3,8},\ D^9_{3,8},\ D^{12}_{3,8},\ D^{14}_{3,8}.$$

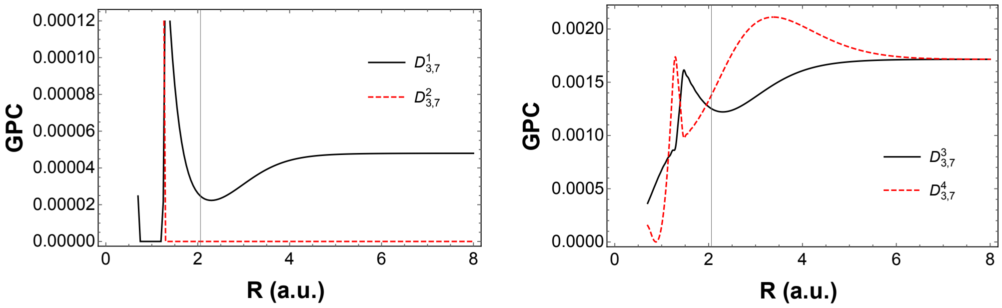

FIGURE 6.6: Rank-seven GPC as functions of the interatomic distance in atomic units. The vertical lines mark the equilibrium bond length.

As seen in Fig. 6.7, these GPC behave roughly in the same way for increasing bond length. Their values tend asymptotically to approximately the same value for large interatomic distances. Finally, as seen in Fig. 6.8, a third quasipinning sector appears to be composed of $D^{10}_{3,8}$, $D^{13}_{3,8}$, $D^{15}_{3,8}$, $D^{18}_{3,8}$ and $D^{19}_{3,8}$.

6.6 What does one mean by quasipinning?

The particular relevance of GPC was suggested by Klyachko in the form of the pinning effect [Kly09], i.e., a given vector $\vec{n}$ saturates one or more GPC, that is, $D^{\mu}_{N,m}(\vec{n}) = 0$. Geometrically, this means that $\vec{n}$ lies on a facet F of the polytope of allowed states, which is given by intersection of the polytope with the hypersurface $D^{\mu}_{N,m}(\vec{n}) = 0$. It is remarkable that pinning as effect in the 1-particle picture allows to reconstruct the structure of the corresponding N-fermion quantum state $|\Psi\rangle|$, which after all is significantly simplified. However, this rigorous structural simplification of the wave function is also the reason why pinning is not expected to show up in realistic physical systems as long as they do not have sufficiently many symmetries [BRS15b]. Indeed, in [SGC13] analytic evidence was found that NON of ground states are very close to but not exactly on the boundary of the polytope. This so-called quasipinning is physically relevant in the sense that several features and implications of pinning hold at least approximately [Sch15]. Since recent investigations [BRGBS13, BRS15b] provide further evidence for the occurrence of quasipinning, or even pinning for the case of model systems with high symmetries and low-dimensional Hilbert spaces, we elaborate in Section 8 variational ground state Ansätze based on the simplified pinning structure and analyze their numerical quality.

In order to consider quasipinning a remarkable phenomenon with useful physical content, the crucial point is that the distance from a given facet must be significantly smaller than the distance to the extreme Hartree-Fock point. Otherwise one would get an obvious quasipinning, for a point in the polytope close to a vertex is therefore close to a facet. In order to quantify the position of a set of NON on the boundary of the polytope, one may define

$$\xi^2 := \sum_{i=1}^{3}(1 - n_i)^2$$

as the Euclidean distance between the spectrum of the state and the extreme point $(1, 1, 1, 0, 0, \dots)$ of the polytope, corresponding to the spectrum of a single determinant.

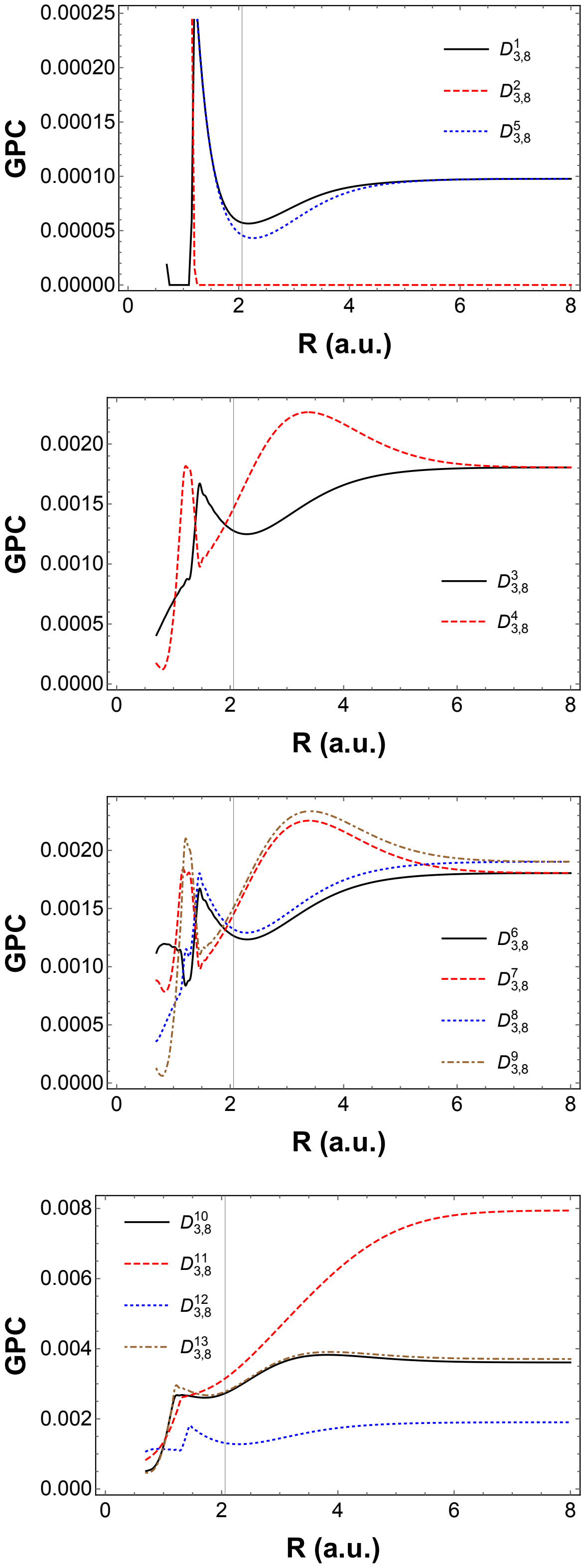

FIGURE 6.7: Rank-eight GPC as functions of the interatomic distance. The vertical lines mark the equilibrium bond length.

Fig. 6.9 shows ξ for small values of γ of the electronic Hamiltonian given in (6.7). For the rank-six approximation, the order of ξ is 10^{-3} while the system is completely pinned to the boundary [BRS15b]. The GPC $D^2_{3,7}$ is of the order 10^{-5} as shown in Fig. 6.3. Compared with the value of ξ, the quasipinning is not due to the proximity of the extreme point.

6.7 Conclusion

By means of numerical and theoretical investigations, we have explored the nature of the (quasi)pinning in real three-electron atoms. In the space $\wedge^3\mathcal{H}_6$, for *compensated* spin-orbitals we find that the Klyachko constraint is saturated. For *uncompensated* configurations, quasi-pinning is bounded by the lowest NON n_6. In approximations of larger rank, the Klyachko constraints split into well differentiated groups of different levels of saturation. A simple geometric probability argument also suggests stability of quasipinning. Moreover, whenever $3 - n_1 - n_2 - n_3$ is not far from zero, projecting the complete wave function of the CI picture into the set of pinned states appears to result in negligible loss of information.

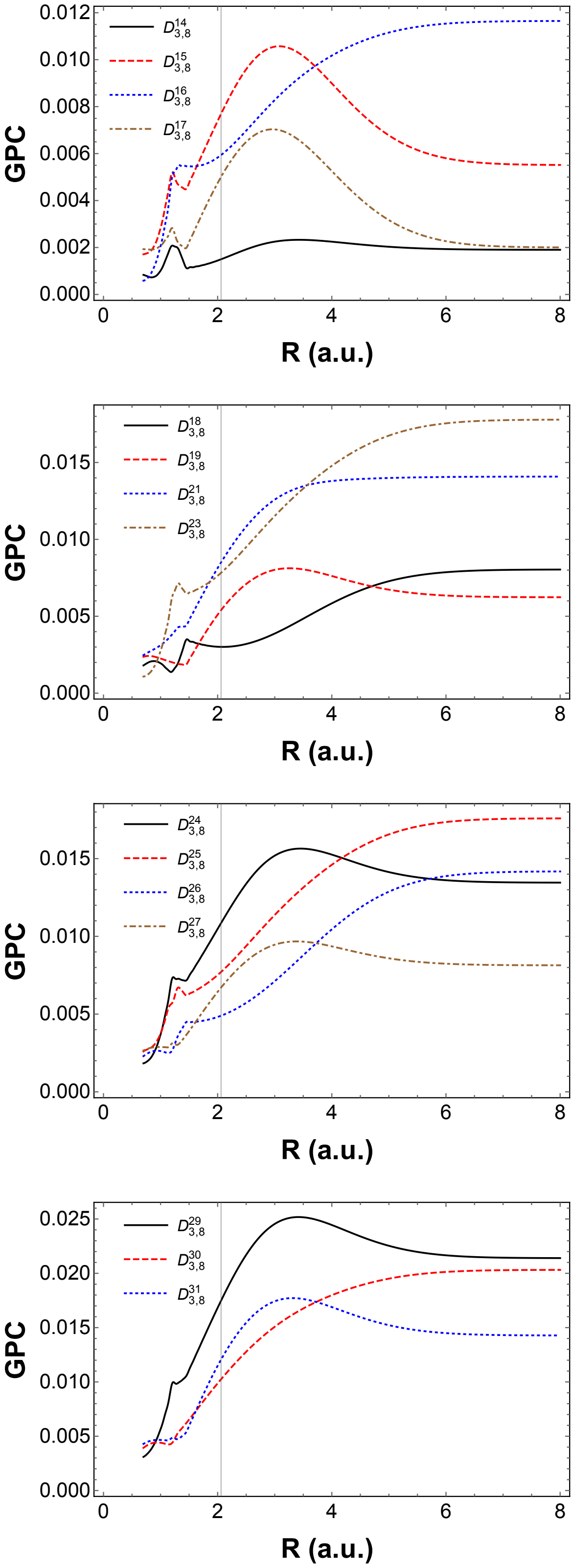

FIGURE 6.8: Rank-eight GPC as functions of the interatomic distance. The vertical lines mark the equilibrium bond length.

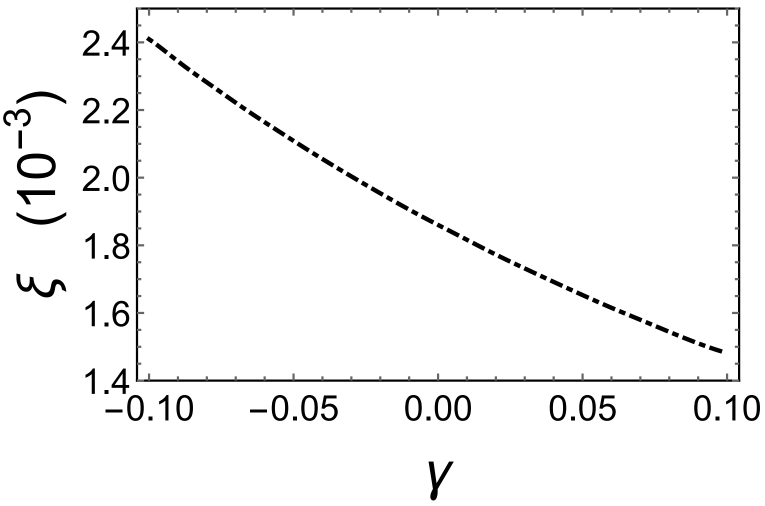

FIGURE 6.9: The distance ξ between the spectrum of the ground state and the extreme point of the polytope as a function of $\gamma \in [-0.1, 0.1]$ for the spin-restricted rank-six approximation to the Hamiltonian $H(3, \gamma)$ given by (6.7).

Chapter 7

Quasipinning, excitations and correlation energy

7.1 Quasipinning and excitations

From the seminal work by Löwdin and Shull it is known that the transformation to NO removes all single (S) excitations of the wave function of two-electron systems [LS56]. For the singlet state the general wave function can be written exactly as

$$|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2)\rangle = \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\sum_{i=1}^{\infty} c_i|\alpha_i(\boldsymbol{r}_1)\alpha_i(\boldsymbol{r}_2)\rangle.$$

Again, we have used $\boldsymbol{x} := (\boldsymbol{r}, \varsigma)$ with ς being the spin coordinates $\{\uparrow, \downarrow\}$. A similar expression can be found for the triplet state in Sec. 2.4. It is also remarkable that the Borland-Dennis wave function (6.4) does not contain S or triple (T) excitations of the best single-determinant state $|0\rangle := |\alpha_1\alpha_2\alpha_3\rangle$. The Slater determinants $|\alpha_1\alpha_4\alpha_5\rangle$ and $|\alpha_2\alpha_4\alpha_6\rangle$ correspond to double (D) excitations of this state.

Single excitations cannot be completely removed from the CI wave function of general many-electron systems when written in terms of NO. However, Mentel and coworkers [MvMGB14] have recently shown that writing the wave function in the basis of NO leads to a sharp drop of the coefficients of Slater determinants containing just S excitations. For the BH molecule, the sum of squares of CI coefficients of singles falls from 1.5×10^{-3} to 5.3×10^{-6} when switching to the NO basis. In this section and the next we argue that this phenomenon is a consequence of the near-saturation of some Klyachko selection rules on the NON. This chapter is mainly based on [BRS15b, BRGBS14].

7.1.1 Selection rule for excitations in $\wedge^3\mathcal{H}_6$

This case has already been discussed. Even if the number of basis spin orbitals pointing up is different from the number of those pointing down, an eventual saturation of condition (6.3) would lead to the situation summarized in Table 7.1. A double excitation is also removed thereby.

Condition	$\vert 0\rangle$	S	D	T	Total
CI	1	3	3	1	8
$\mathbf{D}^1_{3,6}\vert\Psi\rangle = 0$	1	0	2	0	3

TABLE 7.1: Number of Slater determinants in the total and force-pinned CI expansions of the wave function for the system $\wedge^3\mathcal{H}_6$.

7.1.2 Selection rules for excitations in $\wedge^3\mathcal{H}_7$

The four Klyachko inequalities for the three-electron system in a rank-seven approximation $\wedge^3\mathcal{H}_7$ were given in Eq. (6.12). The corresponding operators are

$$\begin{aligned}
\mathbf{D}^1_{3,7} &= 2 - a_1^\dagger a_1 - a_2^\dagger a_2 - a_4^\dagger a_4 - a_7^\dagger a_7,\\
\mathbf{D}^2_{3,7} &= 2 - a_1^\dagger a_1 - a_2^\dagger a_2 - a_5^\dagger a_5 - a_6^\dagger a_6,\\
\mathbf{D}^3_{3,7} &= 2 - a_2^\dagger a_2 - a_3^\dagger a_3 - a_4^\dagger a_4 - a_5^\dagger a_5,\\
\mathbf{D}^4_{3,7} &= 2 - a_1^\dagger a_1 - a_3^\dagger a_3 - a_4^\dagger a_4 - a_6^\dagger a_6.
\end{aligned}$$

As discussed above, for the lithium isoelectronic series [BRGBS13], for the system described by the Hamiltonian of Eq. (6.7) and for the first excited state of beryllium in a rank-ten approximation [Kly09], the first of the four inequalities (6.12) is completely saturated. Accordingly, for all these systems, the exact wave function satisfies the condition

$$\mathbf{D}^1_{3,7}|\Psi\rangle_{3,7} = 0.$$

This implies that in the NO basis, every Slater determinant is composed of three NO, two of them belonging to the set $\{\alpha_1, \alpha_2, \alpha_4, \alpha_7\}$ and one belonging to the set $\{\alpha_3, \alpha_5, \alpha_6\}$. Then, the system $\wedge^3\mathcal{H}_7$ is reduced to $\mathcal{H}_3 \otimes \wedge^2\mathcal{H}_4$, with in total eighteen of those Slater determinants.

Since the second constraint happens to be nearly saturated, it seems fair to conclude that there is a tendency to strong quasipinning of the two first GPC in this approximation. Therefore, imposing as well saturation of the second inequality of (6.12), i.e., $\mathbf{D}^2_{3,7}\mathbf{D}^1_{3,7}|\tilde{\Psi}\rangle_{3,7} = 0$, the singles and the triples are completely removed from the expression, as shown in Table 7.2. The corresponding wave function $|\tilde{\Psi}\rangle_{3,7}$ is written in terms of the initial configuration $|\alpha_1\alpha_2\alpha_3\rangle$, plus the following eight D configurations:

$$\begin{array}{llll}
|\alpha_1\alpha_4\alpha_5\rangle, & |\alpha_2\alpha_4\alpha_6\rangle, & |\alpha_1\alpha_5\alpha_7\rangle, & |\alpha_2\alpha_5\alpha_7\rangle,\\
|\alpha_1\alpha_4\alpha_6\rangle, & |\alpha_2\alpha_4\alpha_5\rangle, & |\alpha_1\alpha_6\alpha_7\rangle, & |\alpha_2\alpha_6\alpha_7\rangle.
\end{array} \tag{7.1}$$

Condition	$\vert 0\rangle$	S	D	T	Total
$\mathbf{D}^1_{3,7}\vert\Psi\rangle_{3,7} = 0$	1	6	9	2	18
$\mathbf{D}^2_{3,7}\mathbf{D}^1_{3,7}\vert\tilde{\Psi}\rangle_{3,7} = 0$	1	0	8	0	9

TABLE 7.2: Number of Slater determinants in the total and force-pinned CI expansions of the wave function for the system $\wedge^3\mathcal{H}_7$.

Condition	$\|0\rangle$	S	D	T	Total
$\mathbf{D}^2_{3,8}\|\Psi\rangle_{3,8} = 0$	1	7	13	3	24
$\mathbf{D}^5_{3,8}\mathbf{D}^2_{3,8}\|\tilde{\Psi}\rangle_{3,8} = 0$	1	0	12	0	13

Table 7.3: Number of Slater determinants in the total and force-pinned CI expansions of the wave function for the system $\wedge^3\mathcal{H}_8$.

Notice moreover that if the two first Klyachko constraints (namely, $D^1_{3,7}$ and $D^2_{3,7}$) were both saturated, then $1 + n_3 = n_1 + n_2$ would follow. Indeed, we would have:

$$2 = n_1 + n_2 + n_4 + n_7 \quad \text{and} \quad 2 = n_1 + n_2 + n_5 + n_6.$$

Summing these two equalities, we see that

$$4 = 2n_1 + 2n_2 + n_4 + n_5 + n_6 + n_7 = 3 - n_3 + n_1 + n_2,$$

where we have used $\sum_i n_i = 3$.

7.1.3 Selection rules for excitations in $\wedge^3\mathcal{H}_8$

The empirical evidence discussed earlier shows that the inequalities for the following GPC are almost or completely saturated:

$$D^1_{3,8}, \quad D^2_{3,8}, \quad D^5_{3,8}.$$

The constraint $D^2_{3,8} \geq 0$ appears to be saturated exactly for the diatomic ion; and the constraints

$$D^1_{3,8} \geq 0, \quad D^5_{3,8} := 1 - n_1 - n_2 + n_3 \geq 0,$$

nearly so. Here, once again, the “unreasonable effectiveness” of the single quasipinning $1 + n_3 \simeq n_1 + n_2$ is enough to suppress the odd excitations, obtaining a reduction to 13 (the strongly occupied one plus 12 doubly excited) configurations. The operator

$$\mathbf{D}^5_{3,8} = \mathbb{1} - a_1^\dagger a_1 - a_2^\dagger a_2 + a_3^\dagger a_3$$

does kill 12 double excitations. Therefore, imposing the saturation of the second and fifth constraints, say, the singles and the triples are removed completely, as shown in Table 7.3. The corresponding wave function $|\tilde{\Psi}\rangle_{3,8}$ is written in terms of the 9 configurations of the pinned rank-seven wave function (7.1), plus the configurations

$$|\alpha_1\alpha_5\alpha_8\rangle, \quad |\alpha_2\alpha_6\alpha_8\rangle, \quad |\alpha_2\alpha_5\alpha_8\rangle, \quad |\alpha_1\alpha_6\alpha_8\rangle.$$

7.1.4 Selection rules for excitations in $\wedge^3\mathcal{H}_m$

We summarize our findings in a quite parsimonious theorem [BRGBS14]:

Theorem 3. The wave function of a three-fermion system, whose NON satisfy the saturated Borland–Dennis–Klyachko condition $1+n_3 = n_1+n_2$, contains no odd excitations.

Proof. Let us write the wave function as follows, with $1 \leq i < j < k \leq m$ always:

$$|\Psi\rangle = \sum_{i<j<k} c_{ijk} \, |\alpha_i \alpha_j \alpha_k\rangle;$$

The condition $1 + n_3 = n_1 + n_2$ implies that the surviving Slater determinants after imposing this pinning condition live in the 0-eigenspace of the operator $\hat{P} := (1 + a_3^\dagger a_3 - a_1^\dagger a_1 - a_2^\dagger a_2)$. It is clear that in order to reach this condition, each Slater determinant must be an eigenfunction of the operator

$$a_3^\dagger a_3 - a_1^\dagger a_1 - a_2^\dagger a_2,$$

with eigenvalue equal to -1. Clearly, the singly excited determinants:

$$|\alpha_1 \alpha_2 \alpha_x\rangle_{x \neq 3}, \quad |\alpha_1 \alpha_x \alpha_3\rangle_{x \neq 2}, \quad |\alpha_x \alpha_2 \alpha_3\rangle_{x \neq 1}$$

are eigenfunctions of $\hat{P}$ with eigenvalue equal to 2. Triply excited determinants are also eigenfunctions of $\hat{P}$ but their eigenvalue is 0. ☐

Therefore, the wave function, subject to the condition $1 + n_3 = n_1 + n_2$, then reads:

$$|\Psi\rangle_{3,m} = c_{123} \, |\alpha_1 \alpha_2 \alpha_3\rangle + \sum_{4 \leq j < k \leq m} [c_{1jk} \, a_j^\dagger a_2 a_k^\dagger a_3 + c_{j2k} \, a_j^\dagger a_1 a_k^\dagger a_3] \, |\alpha_1 \alpha_2 \alpha_3\rangle.$$

Of course in practice we will not have $1 + n_3 = n_1 + n_2$ exactly most of the time; but all the evidence so far available points to very strong quasipinning here.

7.2 He_2^+: electronic energy and pinning truncations

An idea behind quasipinning is to approximate the wave function through a truncated expansion by using the selection rules that emerge after imposing pinning. Therefore, it is a relevant issue to examine how the electronic energy is affected as the number of configurations is reduced in the truncation. Here we explore the ground-state energy for the helium dimer He_2^+ for different pinned wave functions, compared with the energy predicted by the CI expansion *within the same rank*. (It must be said beforehand that, contrarily to the case of lithium-like systems, up to rank eight less than 30% of the absolute correlation energy is recovered. This is due partly to a less than optimal choice of the basis set, partly to the difficulty of capturing some aspects of correlation with such short basis sets.)

Table 7.4 contains the value of the correlation energy for (force-pinned and complete) wave functions for the rank-six up to -eight approximations for the ground state of He_2^+. It is remarkable that the force-pinned wave function $|\tilde{\Psi}\rangle_{3,7}$ reconstructs 99.79% of the rank-seven correlation energy, employing just 9 configurations. The CI rank-eight wave function contains 24 Slater determinants belonging to the Hilbert space $\wedge^2 \mathcal{H}_4 \otimes \mathcal{H}_4$. The correlation energy is 24.64 mHa. The pinned wave function $|\tilde{\Psi}\rangle_{3,8}$ reconstructs 99.51% of this available correlation energy, employing 13 Slater determinants.

Fig. 7.1 shows the absolute value of the correlation energy along the dissociation path for CI rank-six up to rank-eight expansions ($|\Psi\rangle_{3,6}$, $|\Psi\rangle_{3,7}$, $|\Psi\rangle_{3,8}$) and for the pinned wave

Wave function	$\lvert E - E_{\mathrm{HF}}\rvert$
$\lvert\Psi\rangle_{3,6}$	13.22
$\lvert\tilde{\Psi}\rangle_{3,6}$	13.22
$\lvert\tilde{\Psi}\rangle_{3,7}$	20.12
$\lvert\Psi\rangle_{3,7}$	20.17
$\lvert\tilde{\Psi}\rangle_{3,8}$	24.56
$\lvert\Psi\rangle_{3,8}$	24.64

Table 7.4: Ground-state correlation energies predicted for the complete and force-pinned CI wave functions for He_2^+ in the rank-six up to rank-eight approximations. The values are given in mHa.

functions $|\tilde{\Psi}\rangle_{3,7}$ and $|\tilde{\Psi}\rangle_{3,8}$. It is also remarkable that the pinned rank-seven and rank-eight wave functions almost contain the complete correlation energy to the corresponding rank of approximation along the complete path, demonstrating the negligible role of the single and triple excitations. These results suggest that in spite of saturation of one GPC reducing notably the number of Slater determinants, remarkably good values for the correlation energies are obtained.

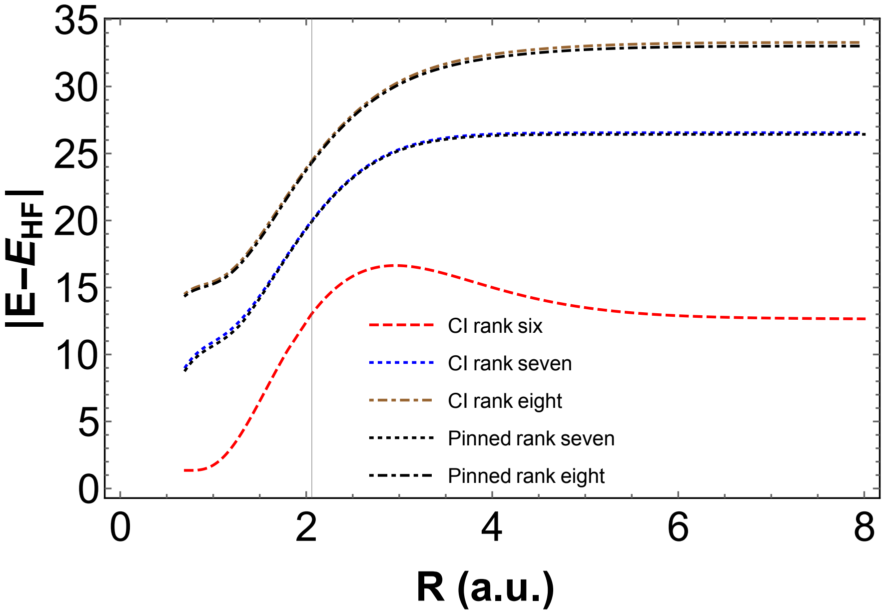

Figure 7.1: Absolute value of the correlation energy $|E - E_{HF}|$ for CI expansion and pinned wave functions for approximations of ranks six up to eight, along the dissociation path for He_2^+. Pinned wave function $|\tilde{\Psi}\rangle_{3,6}$ is equivalent to the CI rank-six expansion, so it is not included. The values are given in mHa [BRS15b].

7.3 On four-electron systems

For the case of a four-electron system with a 8-dimensional one-electron Hilbert space, $\wedge^4\mathcal{H}_8$, there are in total 14 GPC. Derived initially by Klyachko [AK08], they read

$$\begin{aligned} D^{\mu}_{4,8} &:= \sum_{i=1}^{8} \kappa^{\mu}_i n_i \geq 0, \\ D^{7+\mu}_{4,8} &:= 2 - \sum_{i=1}^{8} \kappa^{\mu}_{9-i} n_i \geq 0, \end{aligned} \tag{7.2}$$

for $1 \leq \mu \leq 7$ and provided that $n_1 \leq 1$. The coefficients κ^{μ}_i are given in Table 7.5.

For quantum states with an even number of fermions, vanishing total spin and time-reversal symmetry, Smith proved that a 1-RDM is *pure* N-representable if and only if all its eigenvalues are doubly degenerate [Smi66]. Therefore, for these systems, the NON obey

$$n_{2i-1} = n_{2i} \qquad i = 1, 2, \cdots . \tag{7.3}$$

The double degeneracy of the NON forces the GPC for the system $\wedge^4\mathcal{H}_8$ to reduce to the traditional Pauli exclusion principle [CM14]. Therefore, a state will be pinned only if it is pinned to the traditional Pauli conditions, which only occurs for a single-determinant wave function. For instance,

$$\begin{aligned} D^{1}_{4,8} &:= -n_1 + n_4 + n_6 + n_7 = 2(1 - n_1), \\ D^{8}_{4,8} &:= 2 - n_2 - n_3 - n_5 + n_8 = 2n_8, \\ D^{14}_{4,8} &:= 2 - n_1 - n_2 - n_3 + n_4 = 2(1 - n_1). \end{aligned}$$

Chakraborty and Mazziotti [CM14] computed the NON for the ground state of some four-electron molecules for rank equal to twice the number of electrons, employing a STO-3G basis set. In this range of approximation, the two energetically lowest orbitals of LiH are completely occupied (therefore $D^1_{4,8} = 0$) and the Shull–Löwdin functional guarantees that doubly excited determinants completely govern rank-eight CI calculations for this molecule. However, there are important effects of dynamical electron correlation which involve the core electrons, so the molecule cannot be considered as a two-electron system. In fact, for higher ranks the two largest NON ($n_1 = n_2$) become

μ	κ^{μ}_1	κ^{μ}_2	κ^{μ}_3	κ^{μ}_4	κ^{μ}_5	κ^{μ}_6	κ^{μ}_7	κ^{μ}_8
1	−1	0	0	1	0	1	1	0
2	−1	0	0	1	1	0	0	1
3	−1	0	1	0	0	1	0	1
4	−1	1	0	0	0	0	1	1
5	0	−1	0	1	0	1	0	1
6	0	0	−1	1	0	0	1	1
7	0	0	0	0	−1	1	1	1

TABLE 7.5: Sets of coefficients for the GPC of (7.2) for the system $\wedge^4\mathcal{H}_8$.

Condition	$\lvert 0\rangle$	S	D	T	Total
CI	1	6	9	0	16
$\mathbf{D}^{14}_{4,8}\lvert\Psi\rangle = 0$	1	0	9	0	10

TABLE 7.6: Number of Slater determinants in the full and pinned CI expansions of the wave function for the spin-restricted system $\wedge^4\mathcal{H}_8$ with $\mathbf{S}_z = 1$.

Condition	$\lvert 0\rangle$	S	D	T	Total
CI	1	8	16	5	30
$\mathbf{D}^{14}_{4,8}\lvert\Psi\rangle = 0$	1	0	11	0	12

TABLE 7.7: Number of Slater determinants in the full and pinned CI expansions of the wave function for the spin-unrestricted system $\wedge^4\mathcal{H}_8$ with $\mathbf{S}_z = 1$.

less than 1. The first (and also the second) NON of BH is very close to 1 and accordingly $D^1_{4,8}$ is quasipinned. For LiH and BeH$_2$, the seventh NON is almost 0 and hence for these systems $D^8_{4,8}$ is quasipinned.

In a spin-compensated description, the system $\wedge^4\mathcal{H}_8$ with total spin component $\mathbf{S}_z$ equal to 1 contains 16 configurations, corresponding to $\wedge^3\mathcal{H}_4 \otimes \mathcal{H}_4$. The CI expansion only contains double or single excitations. In a spin-uncompensated description, the system $\wedge^4\mathcal{H}_8$ with total spin component $\mathbf{S}_z$ equal to one would contain 30 configurations, corresponding to $\wedge^3\mathcal{H}_5 \otimes \mathcal{H}_3$. Notice that if the GPC

$$D^{14}_{4,8} = 2 - n_1 - n_2 - n_3 + n_4 \geq 0 \tag{7.4}$$

is completely saturated, the corresponding wave function is a member of the 0-eigenspace of the operator

$$\mathbf{D}^{14}_{4,8} = 2\,\mathbb{1} - a^\dagger_1 a_1 - a^\dagger_2 a_2 - a^\dagger_3 a_3 + a^\dagger_4 a_4. \tag{7.5}$$

and, for both configurations, single and triple excitations are entirely suppressed. This is a non-trivial fact. See Tables 7.6 and 7.7. Besides the initial configuration $\lvert\alpha_1\alpha_2\alpha_3\alpha_4\rangle$, the configurations present in the expansion are just double excitations of this state which, in addition, do not contain the fourth NO α_4.

In general, for the system $\wedge^N\mathcal{H}_m$, the condition

$$(N-2) + n_N = n_1 + \cdots + n_{N-1}$$

has as consequence that only double excitations become the relevant configurations in a CI expansion [BRGBS14]. Moreover, the only configuration containing the orbital α_N is $\lvert\alpha_1\alpha_2\cdots\alpha_N\rangle$.

7.4 Quasipinning and correlation energy

The distance to a facet of the polytope and the error in the energy are related by means of the following theorem.

Theorem 4. Let H be an N-fermion Hamiltonian on $\wedge^N \mathcal{H}_m$ with a unique ground state with NON $\vec{n} = (n_i)_{i=1}^m$. The error ΔE in the energy of the MCSCF Ansatz based on pinning to a given facet of the polytope is bounded from above,

$$\Delta E \leq C D^{\mu}_{N,m}(\vec{n}), \tag{7.6}$$

for some constant C of order one. Moreover,

$$\frac{\Delta E}{E_{\text{corr}}} \leq \frac{D^{\mu}_{N,m}(\vec{n})}{S(\vec{n})} \tag{7.7}$$

where $E_{\text{corr}} = E_{\text{HF}} - E_0$ is the correlation energy, $K \propto C/N$ and

$$S(\vec{n}) = \sum_{i=1}^{N}(1 - n_i) + \sum_{i=N+1}^{m} n_i.$$

Proof. See [BRS15a]. □

Estimate (7.6) confirms our expectation that the MCSCF ansatz based on pinning works very well whenever the exact ground state exhibits quasipinning. Intriguingly, this can be geometrically quantified by referring to the distance of the exact ground state NON from the facet of the polytope. Another important estimate on the numerical quality is provided by estimate (7.7). It states that the fraction of the correlation energy which is not covered by the MCSCF ansatz, is bounded from above by the ratio $D^{\mu}_{N,m}(\vec{n})/S(\vec{n})$. Hence, the overwhelming part of the correlation energy is reconstructed whenever the quasipinning is nontrivial, i.e., $D^{\mu}_{N,m}(\vec{n}) \ll S(\vec{n})$.

Chapter 8

Extended Hartree-Fock method based on GPC

Electronic wave functions often call for more than one configuration to correctly describe quantum systems for which the single-determinantal Hartree-Fock description is not suitable. For such systems, to carry out CI calculations on top of a previous Hartree-Fock computation is problematic, inasmuch as the set of orbitals generated in the field of a single electronic configuration may have little or no pertinence to a system with several configurations [HJJ12]. The standard solution to this problem is to conduct a full optimization calculation where both the orbitals and the coefficients of the electronic configurations are optimized simultaneously. This latter approach is known as the *multiconfigurational self-consistent field* (MCSCF) method. For several reasons, the optimization of a MCSCF wave function is a very demanding computational problem. First of all, the functional of the energy is highly nonlinear with potentially several local solutions, a problem already observed in Hartree-Fock theory but exacerbated here since one confronts more than one configuration.

To successfully ward off the potential problems and carry out a MCSCF computation, it is convenient to choose a parametrization of the wave function which allows an efficient optimization. As suggested in Chapter 7, pinned wave functions undergo remarkable structural simplifications, which suggest a natural extension of the Hartree-Fock ansatz of the form:

$$|\Psi\rangle = \sum_{K\in\mathcal{I}_D} c_K|\mathbf{K}\rangle. \tag{8.1}$$

Here $\mathcal{I}_D$ stands for the family of configurations that may contribute to the wave function in case of pinning to some facet $D^{\mu}_{N,m}(\vec{n}) = 0$ of the Klyachko polytope. Pinned wave functions recognize immediately that the electronic properties are dominated by more than one electronic configuration. The total number of configurations, however, are limited to those that lie on one facet of the polytope. Minimization of the following energy functional:

$$E[\{c_K\}_{K\in\mathcal{I}_D}, \{|\alpha_i\rangle\}] = \langle\Psi|H|\Psi\rangle, \tag{8.2}$$

with $|\Psi\rangle$ as in (8.1), by simultaneously varying the expansion coefficients $\{c_K\}_{K\in\mathcal{I}_D}$ as well as the NON $|\alpha_i\rangle$, defines a pinned-MCSCF optimization.

The minimization of the energy functional (8.2) for the specific pinned ansatz (8.1) is subject both to the constraint that the orbitals be orthogonal and the normalization of the quantum state. At least in principle, this leads to a wide set of Lagrange multipliers. Nevertheless, unlike the Hartree-Fock problem, the MCSCF equations cannot in general be reduced to an eigenvalue problem since the energy functional is not invariant under a unitary transformation of the orbitals. Therefore, it is advantageous to dodge the use of the Lagrange multipliers. If a Hartree-Fock optimization precedes, this could be given by employing the Hartree-Fock molecular orbitals, or in its absence by using the 1-particle eigenstates of the external potential. In any case, by expressing the NON $|\alpha_i\rangle$ for the Ansatz (8.1) according to

$$|\alpha_i\rangle = e^{-\hat{\kappa}}|\tilde{\alpha}_i\rangle, \ \forall i,$$

with an antihermitian operator $\hat{\kappa}$, the orbital optimization is realized in form of an optimization of $\hat{\kappa}$ and the unitarity of $e^{-\hat{\kappa}}$ makes the use of Lagrange multipliers obsolete. Harnessing this fact, the energy functional (8.2) becomes:

$$E[\{c_K\}_{K\in\mathcal{I}_D},\boldsymbol{\kappa}] = \langle\tilde{\Psi}|e^{\hat{\kappa}}He^{-\hat{\kappa}}|\tilde{\Psi}\rangle, \tag{8.3}$$

where

$$|\tilde{\Psi}\rangle = \sum_{K\in\mathcal{I}_D} c_K|\tilde{\mathbf{K}}\rangle,$$

the configurations $|\tilde{\mathbf{K}}\rangle$ are written in terms of the orbitals $|\tilde{\alpha}_i\rangle$ and the second quantization formulation is used for the operator

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q, \qquad \boldsymbol{\kappa} \equiv [\kappa_{pq}].$$

The variational optimization of (8.3) leads to coupled generalized Hartree-Fock equations, which can iteratively be solved, e.g., by using the well-known Newton-Raphson optimization method [JÅO91]. The core of the computation is the construction of a Hessian matrix, as we will show later in this chapter.

This chapter is devoted to implement a MCSCF algorithm for pinned states, and to discuss some topics concerning the relation between quasipinning and correlation energy. We apply this algorithm to a concrete system: the spinless N-harmonium model with three valence fermions (see Appendix A for more information), and discuss its outcomes in the light of standard procedures in quantum chemistry. The chapter is organized as follows: Section 8.1 summarizes the second quantization formulation of quantum mechanics; in particular, it deals with the case of fermionic systems. Section 8.2 shows the implementation of the second quantization formulation on pinned wave functions. The basic fact is that

$$|\alpha_i\rangle = e^{-\hat{\kappa}}|\tilde{\alpha}_i\rangle, \ \forall i, \quad \text{implies} \quad |\Psi\rangle = e^{-\hat{\kappa}}|\tilde{\Psi}\rangle.$$

Section 8.3 describes a new MCSCF algorithm for pinned states. Section 8.4 is devoted to discussing the explicit application of the algorithm for the Borland-Dennis state for the case of the 3-harmonium system. The goal is to discuss the accuracy of the method by measuring the percentage of the correlation energy recovered in comparison with the correlation energy reached in a standard CI scheme and the leading order of the computational cost. Finally, the chapter ends with a conclusion section.

8.1 Second quantization formulation

Let $\{\phi_{p_k}(\boldsymbol{x})\}_{k\in\{1,\ldots,M\}}$ be a basis of M orthonormal spin-orbitals, such that $\langle\phi_p|\phi_{p'}\rangle = \delta_{p,p'}$. A Slater determinant for $N \leq M$ electrons may be written as:

$$|\phi_{p_1}\phi_{p_2}\cdots\phi_{p_N}\rangle := \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{p_1}(\boldsymbol{x}_1) & \phi_{p_2}(\boldsymbol{x}_1) & \cdots & \phi_{p_N}(\boldsymbol{x}_1) \\ \phi_{p_1}(\boldsymbol{x}_2) & \phi_{p_2}(\boldsymbol{x}_2) & \cdots & \phi_{p_N}(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{p_1}(\boldsymbol{x}_N) & \phi_{p_2}(\boldsymbol{x}_N) & \cdots & \phi_{p_N}(\boldsymbol{x}_N) \end{vmatrix}. \tag{8.4}$$

The Fock space is an abstract linear vector space where each Slater determinant of the sort (8.4) is represented by an occupation-number vector, namely,

$$|\boldsymbol{p}\rangle = |p_1, p_2, \ldots, p_M\rangle, \tag{8.5}$$

p_k being 1 or 0 according as ϕ_{p_k} is occupied or unoccupied. The Fock space is equipped with the following inner product between two occupation-number vectors:

$$\langle\boldsymbol{p}|\boldsymbol{p}'\rangle = \delta_{\boldsymbol{p},\boldsymbol{p}'} = \prod_{k=1}^{M}\delta_{p_k,p'_k}.$$

It is easy to note that this latter definition is consistent with the overlap of the corresponding two Slater determinants [HJJ12]. The Fock space allows a comprehensive description of quantum systems with a variable number of fermions. In fact, the occupation-number vectors (8.5) constitute a basis of a 2^M-dimensional Fock space, which may be decomposed as the direct sum

$$F(M) = F(M,0) \oplus F(M,1) \oplus \cdots \oplus F(M,M),$$

where $F(M,N)$ denotes the $\binom{M}{N}$-dimensional space containing all the occupation-number vectors whose sum of occupation numbers gives N. The subspace $F(M,0)$ is a one-dimensional space containing the vacuum state:

$$|\mathrm{vac}\rangle = |0_1, 0_2, \ldots, 0_\mathrm{M}\rangle,$$

which is normalized to unity.

In the language of second quantization, all operators and states can be constructed from a set of creation and annihilation operators defined in the following way. The M creation operators satisfy the relations:

$$\begin{aligned} a_k^\dagger|p_1, p_2, \ldots, 0_k, \ldots, p_M\rangle &= \Gamma_k^{\boldsymbol{p}}|p_1, p_2, \ldots, 1_k, \ldots, p_M\rangle, \\ a_k^\dagger|p_1, p_2, \ldots, 1_k, \ldots, p_M\rangle &= 0. \end{aligned}$$

It is easy to check that the factor $\Gamma_k^{\boldsymbol{p}} := \prod_{i=1}^{k-1}(-1)^{p_i}$ is necessary to obtain a wave functions and operators consistent with the first quantization version of quantum mechanics. More remarkably, the occupation-number vector can be expressed as a string of creation operators arranged in the same order as they appear in the occupation-number vector:

$$|\boldsymbol{p}\rangle = \prod_{k=1}^{M} (a_k^\dagger)^{p_k} |\mathrm{vac}\rangle. \tag{8.6}$$

The annihilation operators satisfy

$$a_k|p_1, p_2, \ldots, p_M\rangle = \delta_{p_k 1} \Gamma_k^{\boldsymbol{p}} |p_1, p_2, \ldots, 0_p, \ldots, p_M\rangle$$

and the operators satisfy the anticommutation relations

$$\{a_k^\dagger, a_l\} = \delta_{kl}, \qquad \{a_k^\dagger, a_l^\dagger\} = 0 \quad \text{and} \quad \{a_k, a_l\} = 0.$$

The creation and annihilation operators change the number of particles when applied to a given state. Some operators conserve the particle number; for instance, the occupation-number operators:

$$\hat{n}_k = a_k^\dagger a_k,$$

which counts the number of fermions in the spin-orbital k:

$$\hat{n}_k|\boldsymbol{p}\rangle = a_k^\dagger a_k|\boldsymbol{p}\rangle = p_k|\boldsymbol{p}\rangle.$$

8.2 Unitary spin-orbital transformation

Consider a set of spin-orbitals $\{\tilde{\phi}_q(\boldsymbol{x})\}$ obtained from the set $\{\phi_p(\boldsymbol{x})\}$ by a unitary transformation:

$$\tilde{\phi}_q = \sum_p \phi_p U_{pq}. \tag{8.7}$$

Unitary matrices satisfy the relation: $\boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{U}\boldsymbol{U}^\dagger = \mathbb{1}$, and can be expressed in exponential form $\boldsymbol{U} = e^{-\boldsymbol{\kappa}}$, where $\boldsymbol{\kappa}^\dagger = -\boldsymbol{\kappa}$ is an anti-Hermitian matrix. By expanding the orbitals according to (8.7), Slater determinants like (8.4) transform in the following way:

$$\begin{aligned} |\tilde{\phi}_{q_1}\tilde{\phi}_{q_2}\cdots\tilde{\phi}_{q_N}\rangle &= \sum_{p_1\cdots p_N} U_{p_1 q_1}\cdots U_{p_N q_N} |\phi_{p_1}\phi_{p_2}\cdots\phi_{p_N}\rangle \\ &= \sum_{q_1\cdots q_N} U_{q_1 p_1}\cdots U_{q_N p_N} \prod_{k=1}^{N} a_k^\dagger |\mathrm{vac}\rangle. \end{aligned} \tag{8.8}$$

In second quantization the preceding transformation reads

$$|\tilde{\boldsymbol{q}}\rangle = \sum_{q_1\cdots q_N} U_{q_1 p_1}\cdots U_{q_N p_N} a_{q_1}^\dagger \cdots a_{q_N}^\dagger |\mathrm{vac}\rangle.$$

The one-to-one mapping between Slater determinants in the first quantization formulation and the occupation-number vectors is preserved if the creation operators transform in the same way as the spin orbitals [HJJ12], that is,

$$\tilde{a}_q^\dagger = \sum_p a_p^\dagger U_{pq} = \sum_p a_p^\dagger [e^{-\boldsymbol{\kappa}}]_{pq}.$$

Now, let us introduce the anti-Hermitian operator

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q, \tag{8.9}$$

where the parameters κ_{pq} are the elements of the anti-Hermitian matrix $\boldsymbol{\kappa}$ and the summation runs over all excitation operators. The operator (8.9) is anti-Hermitian since $\hat{\kappa}^\dagger = -\hat{\kappa}$.

Theorem 5. The creation operators $\tilde{a}_p^\dagger$ and $a_p^\dagger$ are linked by means of the following relation:

$$\tilde{a}_p^\dagger = e^{-\hat{\kappa}} a_p^\dagger e^{\hat{\kappa}}, \tag{8.10}$$

where $\hat{\kappa}$ is the operator given by (8.9).

Proof. Recall the well-known BCH expansion: $e^{-\boldsymbol{A}}\boldsymbol{B}e^{\boldsymbol{A}} = \boldsymbol{B} + [\boldsymbol{B},\boldsymbol{A}] + \frac{1}{2!}[[\boldsymbol{B},\boldsymbol{A}],\boldsymbol{A}] + \frac{1}{3!}[[[\boldsymbol{B},\boldsymbol{A}],\boldsymbol{A}],\boldsymbol{A}] + \cdots$, and note that

$$[a_p^\dagger, \hat{\kappa}] = a_p^\dagger \hat{\kappa} - \hat{\kappa} a_p^\dagger = a_p^\dagger \sum_{rq} \kappa_{rq} a_r^\dagger a_q - \sum_{rq} \kappa_{rq} a_r^\dagger a_q a_p^\dagger = -\sum_{qp} a_q^\dagger \kappa_{qp}.$$

A similar computation gives $[\ldots[[a_p^\dagger,\hat{\kappa}],\hat{\kappa}],\ldots] = (-1)^n \sum_{qp} a_q^\dagger [\boldsymbol{\kappa}^n]_{qp}$. Then,

$$\begin{aligned} e^{-\hat{\kappa}} a_p^\dagger e^{\hat{\kappa}} &= a_p^\dagger + [a_p^\dagger,\hat{\kappa}] + \tfrac{1}{2!}[[a_p^\dagger,\hat{\kappa}],\hat{\kappa}] + \tfrac{1}{3!}[[[a_p^\dagger,\hat{\kappa}],\hat{\kappa}],\hat{\kappa}] + \cdots \\ &= a_p^\dagger + \sum_{qp} a_q^\dagger \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} [\boldsymbol{\kappa}^n]_{qp} = \sum_q a_q^\dagger [e^{-\boldsymbol{\kappa}}]_{qp} \end{aligned}$$

and the assertion holds. A similar reasoning shows that the annihilation operators satisfy the relation $\tilde{a}_p = e^{-\hat{\kappa}} a_p e^{\hat{\kappa}}$. □

The usefulness of the exponential operator $e^{-\hat{\kappa}}$ pointed out by Theorem 5 becomes clear when the occupation-number vector (8.6) is considered. Employing the expression (8.10) for the transformed operators $\tilde{a}_p^\dagger$ we obtain

$$|\tilde{\boldsymbol{k}}\rangle = \prod_{p=1}^{M} (\tilde{a}_p^\dagger)^{k_p} |\mathrm{vac}\rangle = \prod_{p=1}^{M} (e^{-\hat{\kappa}} a_p^\dagger e^{\hat{\kappa}})^{k_p} |\mathrm{vac}\rangle = e^{-\hat{\kappa}} \left[\prod_{p=1}^{M} (a_p^\dagger)^{k_p} \right] e^{\hat{\kappa}} |\mathrm{vac}\rangle = e^{-\hat{\kappa}} |\boldsymbol{k}\rangle,$$

since $\hat{\kappa}|\mathrm{vac}\rangle = 0$ and consequently $e^{\hat{\kappa}}|\mathrm{vac}\rangle = |\mathrm{vac}\rangle$. To sum up, the orthogonal transformation of the occupation-number vector is given by the expression $|\tilde{\boldsymbol{k}}\rangle = e^{-\hat{\kappa}}|\boldsymbol{k}\rangle$. Consequently, a superposition of Slater determinants under unitary transformations of the spin-orbitals is parametrized by a set of expansion coefficients, normalized to unity, the coefficients of the anti-Hermitian matrix and a set of initial configurations $\{|\boldsymbol{k}\rangle\}$:

$$|\boldsymbol{c},\boldsymbol{\kappa}\rangle = e^{-\hat{\kappa}} \sum_k c_k |\boldsymbol{k}\rangle. \tag{8.11}$$

The minimization of the energy functional

$$\min_{\boldsymbol{c},\boldsymbol{\kappa}} \frac{\langle \boldsymbol{c},\boldsymbol{\kappa}|H|\boldsymbol{c},\boldsymbol{\kappa}\rangle}{\langle \boldsymbol{c},\boldsymbol{\kappa}|\boldsymbol{c},\boldsymbol{\kappa}\rangle}$$

with respect to the parameters of the rotation operator $e^{-\hat{\kappa}}$ and the CI coefficients, gives the MCSCF ground-state energy. The presence of this operator is the main difference with a standard CI computation in which the set of spin-orbitals remain fixed along the process and consequently are not optimized [HJJ12]. Therefore, the MCSCF wave function (8.11) is optimal in the sense that the orbitals are variationally found. However, the price to pay for the simultaneous optimization of orbitals and coefficients is the rise of a highly nonlinear problem, whose counterpart is the restriction of the length of the MCSCF expansion.

The crucial part of the MCSCF optimization process is the selection of the configuration space in which the wave function is described. In the early years of quantum chemistry, such configurations were chosen by use of physical intuition, but nowadays there are several techniques based mainly on the subdivision of the space of configurations [Spr00]. The quasipinning theory offers a method to systematically answer this question. For instance, for the space $\wedge^3\mathcal{H}_6$ the quasipinning theory says that a good approximation to the complete MCSCF vector is the Borland-Dennnis state which reads:

$$|\mathrm{BD}\rangle = e^{-\hat{\kappa}}\big(c_{123}\ a_1^\dagger a_2^\dagger a_3^\dagger + c_{145}\ a_1^\dagger a_4^\dagger a_5^\dagger + c_{246}\ a_2^\dagger a_4^\dagger a_6^\dagger\big)|\mathrm{vac}\rangle.$$

In general, the total number of configurations present in the expansion are limited to those that lie on one facet of the polytope of physical states.

$$|\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}\rangle = e^{-\hat{\kappa}} \sum_{k\in\mathcal{I}_D} c_k|\boldsymbol{k}\rangle, \tag{8.12}$$

where $\mathcal{I}_D$ stands for the configurations which may contribute in case of pinning to some facet $D^{\mu}_{N,m}(\vec{n}) = 0$ of the Klyachko polytope. The corresponding expression for the energy functional is then the following:

$$\mathcal{E}(\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}) = \frac{\langle\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}|H|\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}\rangle}{\langle\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}|\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}\rangle}. \tag{8.13}$$

Notice that the denominator is independent of $\boldsymbol{\kappa}$ and depends on the expansion coefficients only:

$$\langle\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}|\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}\rangle = \sum_{k\in\mathcal{I}_D} |c_k|^2.$$

The minimization of (8.13) with respect to the parameters of the operator $\hat{\kappa}$ and the CI coefficients $\boldsymbol{c}$ yields the ground-state energy for pinned states, namely:

$$E_0 = \min_{\{c_k\},\boldsymbol{\kappa}} \mathcal{E}(\boldsymbol{c}, \boldsymbol{\kappa}).$$

In the next section we present a general algorithm for computing the ground-state energy of MCSCF pinned states. The main idea is to perform the minimization of the energy functional subject to the normalization of the wave function by use of a lone Lagrange multiplier:

$$\min_{\{c_k\}_{k\in\mathcal{I}_D},\boldsymbol{\kappa}} \left[\langle\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}|H|\{c_k\}_{k\in\mathcal{I}_D}, \boldsymbol{\kappa}\rangle - \lambda\bigg(\sum_{k\in\mathcal{I}_D} |c_k|^2 - 1\bigg)\right]. \tag{8.14}$$

The advantage of the orbital-rotation operator $e^{-\hat{\kappa}}$ is now patent: we have in fact circumvented the use of Lagrange multipliers and reduced their use to a single one.

8.3 MCSCF energy for pinned states

The optimization of MCSCF wave functions results simply from imposing on the energy functional expression (8.13) the condition that the energy be stable with respect to both orbital and coefficient variations. Therefore, from applying this condition to the energy functional expression, a new orbital basis is found and hence a new reference wave function is obtained [She07]. As explained in Section 6.1, this requires transforming the one- and two-electron integrals from one basis set to another, by means of the unitary operator $e^{-\boldsymbol{\kappa}}$.

Let us consider the electronic energy of the transformed pinned state $e^{-\hat{\kappa}}|\tilde{\Psi}\rangle$, namely:

$$\mathcal{E}(\boldsymbol{c}, \boldsymbol{\kappa}) = \langle\tilde{\Psi}|e^{\hat{\kappa}} H e^{-\hat{\kappa}}|\tilde{\Psi}\rangle \quad \text{provided that} \quad \langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1 \tag{8.15}$$

where $\hat{\kappa} = \sum_{p>q} \kappa_{pq} \hat{E}^{-}_{pq}$. Here we denote the operators in an explicit anti-Hermitian form:

$$\hat{E}^{-}_{pq} = a^{\dagger}_p a_q - a^{\dagger}_q a_p.$$

The functional (8.15) can be expanded in a BCH series, namely:

$$\mathcal{E}(\boldsymbol{c}, \boldsymbol{\kappa}) = \langle\tilde{\Psi}|H|\tilde{\Psi}\rangle + \langle\tilde{\Psi}|[\hat{\kappa}, H]|\tilde{\Psi}\rangle + \tfrac{1}{2}\langle\tilde{\Psi}|[\hat{\kappa}, [\hat{\kappa}, H]]|\tilde{\Psi}\rangle + \cdots \tag{8.16}$$

The terms in the expansion (8.16) can be identified with the terms that occur in the Taylor expansion of the same functional (8.15). The variational optimization of the rotational-operator parameters κ_{pq} leads to generalized Hartree-Fock equations and the optimization of the coefficients $\boldsymbol{c}$ to so-called secular equations [HJJ12]. These self-consistent field equations can be solved iteratively, by using the Newton-Raphson optimization method which we describe in Appendix C.

The parameters κ_{pq} are arranged as a column vector $\boldsymbol{\kappa}$. The electronic gradient at $\boldsymbol{\kappa} = 0$ is given by

$$\mathcal{E}^{(1)}_{pq} := \frac{\partial \mathcal{E}(\boldsymbol{c}, \boldsymbol{\kappa})}{\partial k_{pq}} = \langle\tilde{\Psi}|[\hat{E}^{-}_{pq}, H]|\tilde{\Psi}\rangle \tag{8.17}$$

and the electronic Hessian is

$$\mathcal{E}^{(2)}_{pq,rs} := \frac{\partial^2 \mathcal{E}(\boldsymbol{c}, \boldsymbol{\kappa})}{\partial k_{rs} \partial k_{pq}} = \tfrac{1}{2}\big(\langle\tilde{\Psi}|[\hat{E}^{-}_{pq}, [\hat{E}^{-}_{rs}, H]]|\tilde{\Psi}\rangle + \langle\tilde{\Psi}|[\hat{E}^{-}_{rs}, [\hat{E}^{-}_{pq}, H]]|\tilde{\Psi}\rangle\big). \tag{8.18}$$

Let us define $E_{pq} := a^{\dagger}_p a_q$. Notice that

$$[E_{pq}, H]^{\dagger} = H E^{\dagger}_{pq} - E^{\dagger}_{pq} H = H E_{qp} - E_{qp} H = -[E_{qp}, H]$$

and therefore for real wave functions: $\langle\tilde{\Psi}|[E_{pq}, H]|\tilde{\Psi}\rangle = -\langle\Psi|[E_{qp}, H]|\tilde{\Psi}\rangle$. Moreover, since $[\hat{\kappa}, H]^{\dagger} = [\hat{\kappa}, H]$ then

$$[E_{pq}, [\hat{\kappa}, H]]^{\dagger} = [\hat{\kappa}, H] E_{qp} - E_{qp} [\hat{\kappa}, H] = -[E_{qp}, [\hat{\kappa}, H]].$$

For the same reasons, $[\hat{\kappa}, [E_{pq}, H]]^{\dagger} = [E_{qp}, H]\hat{\kappa} - \hat{\kappa}[E_{qp}, H] = -[\hat{\kappa}, [E_{qp}, H]]^{\dagger}$. Summing up, for real wave functions we can rewrite the electronic gradient (8.17) in the following form:

$$\mathcal{E}^{(1)}_{pq} = 2\langle\tilde{\Psi}|[\hat{E}_{pq}, H]|\tilde{\Psi}\rangle$$

and the electronic Hessian (8.18):

$$\mathcal{E}^{(2)}_{pq,rs} = \langle\tilde{\Psi}|[\hat{E}^{-}_{pq},[\hat{E}_{rs},H]]|\tilde{\Psi}\rangle + \langle\tilde{\Psi}|[\hat{E}^{-}_{rs},[\hat{E}_{pq},H]]|\tilde{\Psi}\rangle.$$

The optimization of the parameters is guided by a single equation:

$$\boldsymbol{\kappa} = -[\mathcal{E}^{(2)}_{pq,rs}]^{-1}\mathcal{E}^{(1)}_{pq}\,. \tag{8.19}$$

Both electronic gradient and Hessian in the Newton-Raphson method may be constructed from the set of one- and two-particle density matrices and transition density matrices. Once the new parameters are found by use of the equation (8.19) a new wave function is obtained:

$$|\Psi\rangle = e^{-\hat{\kappa}}|\tilde{\Psi}\rangle$$

and consequently a new value for the energy. The task is made easier by remembering that one- and two-body integrals (defined in some basis set):

$$\begin{aligned} h^{\alpha}_{mn} &:= \int \alpha_m(\boldsymbol{r})\big[-\tfrac{1}{2}\nabla^2_{\boldsymbol{r}} + V(\boldsymbol{r})\big]\alpha_n(\boldsymbol{r})\,d\boldsymbol{r}, \\ \iota^{\alpha}_{mnop} &:= \int \alpha_m(\boldsymbol{r}_1)\alpha_n(\boldsymbol{r}_1)v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\alpha_o(\boldsymbol{r}_2)\alpha_p(\boldsymbol{r}_2)\,d\boldsymbol{r}_1\,d\boldsymbol{r}_2, \end{aligned} \tag{8.20}$$

change under a unitary rotation of the orbitals in the following way:

$$\begin{aligned} h^{\alpha}_{mn} &\to (e^{-\boldsymbol{\kappa}} \otimes e^{-\boldsymbol{\kappa}})\,h^{\alpha}_{mn} \\ \iota^{\alpha}_{mnop} &\to (e^{-\boldsymbol{\kappa}} \otimes e^{-\boldsymbol{\kappa}} \otimes e^{-\boldsymbol{\kappa}} \otimes e^{-\boldsymbol{\kappa}})\,\iota^{\alpha}_{mnop}. \end{aligned}$$

The CI coefficient optimization in (8.14) is much simpler since it only requires a lone Lagrange multiplier. Let us define the Hamiltonian matrix

$$H_{kl} = \langle k|H|l\rangle$$

for $k, l \in \mathcal{I}_D$. Such a minimization translates into the eigenvalue equation $H\boldsymbol{c} = \lambda_k \boldsymbol{c}$. The lowest eigenvalue λ_0 corresponds to the ground state energy and the corresponding eigenvector to the CI coefficients $\{c_k\}_{k\in\mathcal{I}_D}$.

The electronic gradient (8.17) and Hessian (8.18) are computed in order to find a new set of parameters $\boldsymbol{\kappa}$ until convergence is reached. A flow chart of the algorithm described in this section is shown in the next section.

8.4 Description of the algorithm

In this Section we present a flow diagram of the MCSCF algorithm described previously in Section 8.3. The inputs are a spin-orbital basis set, the facet of the polytope where the wave vector is supposed to lie and a threshold ϵ which will indicate if the convergence is reached and therefore the program must stop. In the next section we will perform a complete implementation of the algorithm.

The output is the MCSCF energy value. In general, there is no guarantee that the procedure will converge to the correct MCSCF solution. The Newton-Raphson procedure

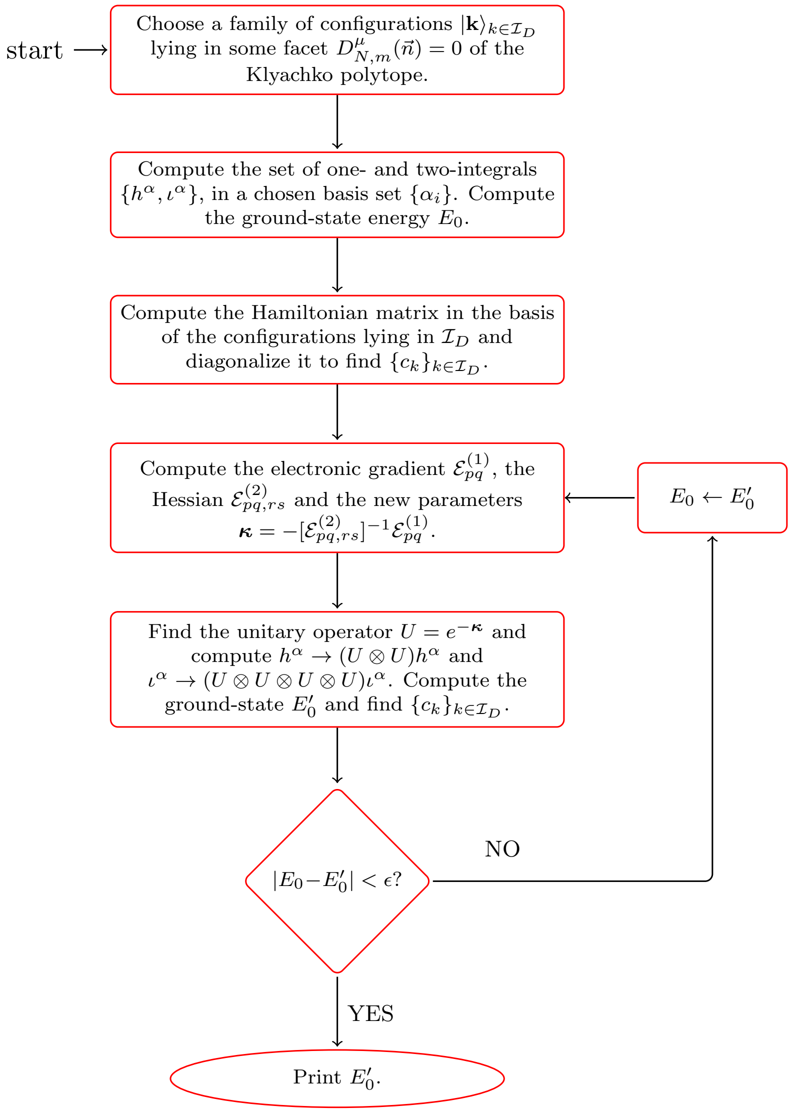

Figure 8.1: Flow diagram of the MCSCF algorithm described in Section 8.3.

only attempts to locate stationary points of the energy, only a small subset of which satisfy the eigenvalue minimization [She07].

8.5 Numerical test of the new Ansatz

In this section we apply our new algorithm to a concrete system and test the predictions of Theorem 3.

The Hamiltonian

$$H=\frac{1}{2}\sum_{i=1}^{N}p_i^2+\frac{\omega^2}{2}\sum_{i=1}^{N}x_i^2+\frac{\delta}{2}\sum_{i<j}^{N}x_{ij}^2, \tag{8.21}$$

where $x_{ij} := x_i - x_j$. The Hartree-Fock equations for this system read:

$$\hat{h}\phi_m(x) + \frac{\delta}{2}\sum_{k=0}^{N-1}\int dy\,(x-y)^2\phi_k(y)\Big[\phi_k(y)\phi_m(x) - \phi_m(y)\phi_k(x)\Big] = \sum_n \epsilon_{mn}\phi_n(x),$$

where $\hat{h} = -\frac{1}{2}\nabla^2 + \frac{\omega^2}{2}x^2$. Since the orbitals are orthonormal:

$$\begin{aligned}\Big[\hat{h} + \frac{\delta}{2}(N-1)x^2\Big]\phi_m(x) + \frac{\delta}{2}\sum_{k=0}^{N-1}\int dy\,y^2\phi_k(y)\Big[\phi_k(y)\phi_m(x) - \phi_m(y)\phi_k(x)\Big]\\ + \delta x\sum_{k=0}^{N-1}\int dy\,y\,\phi_k(y)\phi_m(y)\phi_k(x) = \sum_n \epsilon_{mn}\phi_n(x).\end{aligned} \tag{8.22}$$

The Hermite functions are solution of this equation. To see it, recall that the Hermite functions read:

$$\varphi_i(x) = \frac{\eta^{1/4}}{\pi^{1/4}}\frac{1}{\sqrt{2^n n!}}H_i[\sqrt{\eta}\,x]e^{-\eta x^2/2};$$

One well-known property of the Hemite polynomials $\{H_k\}$ is the following

$$2xH_k[x] = H_{k+1}[x] + 2kH_{k-1}[x],$$

which can be translated into the Hermite functions

$$x\varphi_k(x) = \frac{1}{\sqrt{2\eta}}\Big[\sqrt{k+1}\,\varphi_{k+1}(x) + \sqrt{k}\,\varphi_{k-1}(x)\Big]$$

Then:

$$\begin{aligned}\int dy\,y\,\varphi_k(y)\varphi_m(y) &= \frac{1}{\sqrt{2\eta}}\Big[\sqrt{m}\,\delta_k^{m-1} + \sqrt{m+1}\,\delta_k^{m+1}\Big]\\ \int dy\,y^2\varphi_k(y)\varphi_m(y) &= \frac{1}{2\eta}\Big[(2m+1)\,\delta_k^m + \sqrt{(m-1)m}\,\delta_k^{m-2} + \sqrt{(m+1)(m+2)}\,\delta_k^{m+2}\Big]\end{aligned}$$

and note that

$$\begin{aligned}x\sum_{k=0}^{N-1}\int dy\,y\,\varphi_k(y)\varphi_m(y)\varphi_k(x) &= \frac{x}{\sqrt{2\eta}}\Big[\sqrt{m}\,\varphi_{m-1}(x) + \sqrt{m+1}\,\varphi_{m+1}(x)\Big]\\ &= \frac{1}{2\eta}\Big[(2m+1)\,\varphi_m(x) + \sqrt{(m-1)m}\,\varphi_{m-2}(x) + \sqrt{(m+1)(m+2)}\,\varphi_{m+2}(x)\Big]\end{aligned}$$

8.6 Conclusion

This chapter is devoted to implement a MCSCF algorithm for pinned states, and to discuss some topics concerning the relation between quasipinning and correlation energy. We apply this algorithm to a concrete system: the spinless N-harmonium model with three valence fermions (see Appendix A for more information), and discuss its outcomes in the light of standard procedures in quantum chemistry.

The goal is to elaborate variational ground-state Ansätze based on the simplified pinning structure and analyze their numerical quality. We develop a complete MCSCF algorithm for states of pinned natural occupation numbers.

An algorithm for simulation problems in quantum chemistry based on the structural simplifications due to quasipinning is provided and tested on a simple system of three valence fermions.

Chapter 9

Final comments

The recent solution of the pure N-representability problem, due to Klyachko, promises to generate a wide set of conditions (the GPC) on the natural occupation numbers for fermionic systems. The Klyachko algorithm does indeed produce sets of linear inequalities with integer coefficients for those numbers. The derivation of these inequalities, and of their consequences, is still a work in progress.

For reasons that nobody has yet been quite able to fathom, some of these inequalities appear to be nearly saturated, in a far from random way —this is the quasipinning phenomenon. A research program is born around these facts. By means of both theoretical and numerical results, in this dissertation we have continued to explore the nature of pinning and quasipinning in some atomic and molecular models for several finite-rank approximations whose GPC are known.

We sum up our opinions on the outcomes of that program, so far.

- Saturation of some of the GPC leads to strong selection rules for identifying the most (in)effective configurations in CI expansions. In simple cases, this gives means for reducing the number of Slater determinants in the CI picture and therefore reducing computational requirements [Kly09, SGC13, BRGBS13, BRS15b]. In general, it does provide insights into the structure of the wave function, which brute force methods are unable to do. For instance, the robustness of the almost saturation of a particular type of constraint conspires to "explain" why double excitations govern CI calculations of electron correlation, when using NO [BRGBS14].
- We could question the proposal of CI selection rules based on the GPC as logically flawed, since to reliably apply such rules one has to carry out beforehand a CI calculation of the considered system without these rules in order to get the NO occupations, which feature in GPC. However, some CI methods use initial sets of molecular orbitals which could be found by solving Hartree-Fock equations, being then transformed by on-the-shelf programs to more compact sets of natural orbitals appropriate for electron correlation. A CI method based on GPC —like the one we discuss in Chapters 6 and 7— describes a general procedure in order to select non-superfluous configurations prior to the CI computation. Indeed, knowing the saturation level of the GPC allows us to construct efficient wave functions before carrying out a CI-type calculation. A part of our work is devoted to identifying such GPC which are candidates to be (quasi)saturated for ground states. Just

to mention an example, the spin-adapted version for the $\wedge^3\mathcal{H}_6$ system requires in principle 8 configurations. However, by considering GPC and symmetry properties we proved that only 3 of those 8 are needed, as in (6.4). It is worth mentioning that one does not even need the solution of the Hartree-Fock equation to construct the CI Hilbert space. As shown in Chapter 8, it is possible to establish a general MCSCF variational procedure based on pinned wave functions whose accuracy is high and whose computational cost is notably cheaper than the existing CI routines [BRS15a].

- Unfortunately, it is unlikely that Klyachko paradigm will be relevant for computational quantum chemistry, at least in the short run. The main problem is the dramatic increase of the number of GPC with the rank of the spin-orbital systems introduced in the calculations. However, we note that imposing pinning reduces notably the number of Slater determinants needed in the expansion, while losing less than 1% of the correlation energy. The difficulty in extending our method to larger systems is just a matter of computational resources. The recent solution of the *pure* N-representability problem [AK08] provides an algorithm to produce the complete set of GPC for any system, being nevertheless expensive from the computational viewpoint. To date, we know the set of GPC for the following systems:

  $$\wedge^3\mathcal{H}_6,\ \wedge^3\mathcal{H}_7,\ \wedge^3\mathcal{H}_8, \wedge^3\mathcal{H}_9,\ \wedge^3\mathcal{H}_{10},\ \wedge^4\mathcal{H}_8, \wedge^4\mathcal{H}_9,\ \wedge^4\mathcal{H}_{10},\ \wedge^5\mathcal{H}_{10}.$$

  Currently I am collaborating with the Institute for Biocomputation and Physics of Complex Systems (University of Zaragoza), in order to develop an algorithm to produce further sets of GPC using the *Janus supercomputer*, a modular, massively parallel and reconfigurable FPGA-based computing system for High Performance Scientific Computing.

- A natural question is whether the exact "Löwdin–Shull" formula (6.5) for three-electron systems can be generalized to higher rank. The answer is a qualified, approximate yes, the price to pay being to invoke a second type of constraint less strongly quasi-pinned that the one referred to in the previous point. We exhibited a procedure to impose simultaneous selection rules as an outcome of different scales of quasipinning.

- A very promising avenue of research is to use the GPC to improve on the 1-RDM theory. There are now in the literature quite a few physically motivated density matrix functionals, built from the knowledge of the natural orbitals and occupation numbers, which can be traced back to the one proposed by Müller thirty years ago [Mül84]; they have mostly amounted to figuring out *Ansätze* for reasonable two-body reduced density matrices, failing to date to fulfil some physical requirement or other [BRV12]. The approach discussed in this dissertation suggests to construct 1-RDM by restricting the minimization set to the subset of GPC-honest systems. A promising start in this direction is [TLMH15].

Summing up, our research proves the existence of the quasipinning phenomenon in real systems. The stability of the selection rule has been also recently studied [Sch15]. Moreover, there is a strong and beautiful connection between quasipinning and correlation energy [BRS15a]. Our research also provides a new variational optimization method for few-fermion ground states and its high accuracy for quasipinned systems has been proved. Depending on the details of the algorithm, we are able to reach $97\% - 99\%$ of the correlation energy for such systems. We think that our current research and results are evidence that developing a GPC-based CI algorithm should play an important role in future quantum chemical computations.

Chapter 10

Resumen y conclusiones (spanish)

10.1 Resumen

Sabido es que en la aproximación de Born-Oppenheimer para determinar la energía de átomos, moléculas y otros sistemas cuánticos de muchos cuerpos basta con optimizar un funcional lineal, uno de cuyos argumentos es un objeto de 12 variables, a saber, la matriz de densidad reducida a dos cuerpos (2-RDM, por sus siglas en inglés). Aunque la expresión analítica de dicho funcional es conocida, este procedimiento tiene como principal dificultad que el conjunto de variación no ha sido determinado a la fecha de manera completamente satisfactoria. Encontrar condiciones necesarias y suficientes para que una 2-RDM corresponda a un estado cuántico realizable (ya sea un estado puro o una mezcla estadística) se conoce en química cuántica como el problema de N-representabilidad (el cual, en cierta medida, es también un problema de información cuántica). Esta situación ha dado lugar a un amplio conjunto de programas de investigación orientados bien a encontrar funcionales alternativos, aunque más complicados, o bien a hallar condiciones de representabilidad más simples. El más importante entre ellos es la teoría del funcional de densidad, que se basa en un objeto de 3 variables y para el cual el problema de representabilidad tiene una solución muy sencilla. Para esta teoría el funcional tiene, sin embargo, una estructura desconocida. A medio camino entre la teoría del funcional de densidad y el funcional lineal de la 2-RDM se encuentra la así llamada teoría del funcional de la 1-RDM.

Postulado por Pauli para explicar la estructura electrónica de átomos y moléculas, el principio de exclusión que lleva su nombre establece una cota superior de 1 para los números naturales de ocupación fermiónicos (o sea $n_i \leq 1$), de manera que no es posible encontrar más de un electrón en un mismo estado cuántico. Ésta es una condición necesaria y suficiente para que una 1-RDM sea la contracción de una mezcla estadística de N cuerpos, siempre y cuando se cumpla que $\sum_i n_i = N$ [Col63]. El problema cuántico marginal de un cuerpo busca responder la pregunta de si un conjunto dado de números naturales de ocupación fermiónicos proviene de un estado (puro o estadístico) de N cuerpos.

El método de interacción de configuraciones normalmente aporta descripciones óptimas de estados cuánticos de átomos y moléculas expandiendo la función de onda en términos de una superposición de configuraciones de determinantes de Slater, empleando para ello tantas como sea posible desde el punto de vista computacional. Para estos sistemas la dimensión del espacio de Hilbert crece de manera binomial con m (el número de orbitales en la base del espacio de Hilbert de una partícula) y N (el número de electrones del sistema en consideración). Se sabe que en la aproximación de rango seis ($m = 6$) para un estado puro de tres electrones ($N = 3$) los números de ocupación satisfacen condiciones adicionales a las ya mencionadas condiciones de Pauli:

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1 \quad \text{y} \quad n_1 + n_2 + n_4 \leq 2.$$

El primer conjunto de igualdades da lugar a un solo electrón en los orbitales naturales r y $7-r$. Vale la pena mencionar que la desigualdad es más restrictiva que el principio de exclusión de Pauli, el cual sólo permite establecer que $n_1 + n_2 \leq 2$. El reciente análisis de Alexander Klyachko y sus colaboradores sobre el problema de representabilidad de la 1-RDM constituye una aproximación sistemática a este tipo de ligaduras [AK08]. En general, un sistema cuántico puro de N electrones descrito por un espacio de Hilbert de una partícula cuya dimensión es m satisface un conjunto de desigualdades lineales, conocidas como ligaduras generalizadas de Pauli (GPC, por sus siglas en inglés)

$$D^{\mu}_{N,m}(\boldsymbol{n}) = \kappa^{\mu}_0 + \kappa^{\mu}_1 n_1 + \cdots + \kappa^{\mu}_m n_m \geq 0, \tag{10.1}$$

con $\boldsymbol{n} := (n_1, \ldots, n_m)$, los coeficientes $\kappa^{\mu}_j \in \mathbb{Z}$ y $\mu = 1, 2, \ldots, r_{N,m}$. Estas desigualdades definen un politopo convexo de estados permitidos en $\mathbb{R}^m$, y son condiciones para que una 1-RDM sea la contracción de un estado *puro* de N cuerpos.

Cuando una GPC está completamente saturada se dice que el sistema está fijado (*pinned*, en inglés), además de yacer en una de las caras del correspondiente politopo. A la fecha de escritura de este documento, la naturaleza de estas ligaduras ha sido explorada en algunos sistemas cuánticos de pocos electrones; entre ellos, un sistema de 3 fermiones sin espín confinados a un potencial armónico unidimensional [SGC13], la serie isoelectrónica del litio [BRGBS13] y en estados fundamentales o excitados de sistemas moleculares de 3 y 4 electrones cuyo rango es al menos el doble del número de electrones [CM14, BRS15b, CM15a, BRGBS14, TLMH15]. Para todos estos sistemas algunas desigualdades están a menudo cuasi saturadas, esto es, en ecuaciones como (10.1) la igualdad "casi" se satisface. Este es el fenómeno de cuasifijación (o *quasipinning* en inglés).

La principal motivación de esta tesis doctoral es la de examinar la ocurrencia del fenómeno de fijación o cuasifijación en sistemas atómicos y moleculares por medio de métodos analíticos y numéricos bien establecidos en el campo de la química cuántica. Han sido escogidos de manera preferencial métodos de interacción de configuraciones (CI) así como de multiconfiguraciones (MCSCF). Estos procedimientos permiten identificar qué tipo de GPC se encuentran fijadas o cuasifijadas para sistemas específicos y de allí intentar predecir cuáles lo estarán de manera general. Un segundo objetivo es mostrar de qué manera la saturación de algunas GPC da lugar a aproximaciones de mayor eficiencia computacional para la estimación de propiedades químicas, como por ejemplo la energía del estado fundamental. Más allá de examinar la ocurrencia de fijación o cuasifijación, queremos enfatizar la importancia de la aproximación de Klyachko al problema cuántico marginal y su impacto potencial en los programas de investigación actualmente en curso para determinar densidades electrónicas, funcionales de 1-RDM y 2-RDM, así como densidades intraculares o funciones de cuasiprobabilidad de Wigner.

No quisiéramos concluir estas líneas introductorias sin antes destacar que nuestra investigación provee un nuevo método variacional para calcular estados fundamentales de sistemas de pocos electrones. Confirmamos cuantitativamente el alto nivel de precisión de este método para sistemas cuasifijados y derivamos un límite superior para la energía de correlación dado como la relación entre el valor numérico de la GPC y la distancia desde el punto de Hartree-Fock (esto es, uno de los vértices del politopo). En efecto, nuestro algoritmo es capaz de alcanzar el 99% de la energía de correlación para tales sistemas [BRS15a].

10.2 Principales resultados

Para comodidad del lector, resumiremos aquí los principales resultados de este trabajo:

- En teoría del funcional de densidad de Wigner una pregunta legítima es si una función de Wigner corresponde o no a función simétrica o antisimétrica bajo la permutación de sus variables. Esta es una pregunta pertinente ya que dicha información se pierde al efectuar la transformación de Wigner. Nosotros proveemos un criterio muy simple para el caso de cuasiprobabilidades de partículas sin espín. Para el caso de partículas con espín, damos cuenta de la pregunta dotando a las funciones de Wigner con una estructura de mayor contenido físico por medio de las representaciones irreducibles del grupo de rotaciones.

- Esta disertación contiene un estudio exhaustivo del estado excitado más bajo del átomo de Moshinsky con el propósito de entender la relación entre energía de correlación y medidas de enredamiento para dicho sistema, muy diferente del estado fundamental. La tarea es llevada a cabo en el marco de la teoría del funcional de densidad de Wigner.

- Con la ayuda de la formulación del funcional de densidad en el espacio de fase, ponemos a prueba algunos de los más populares funcionales de la matrix de densidad reducida a un cuerpo, usando para ello un modelo completamente soluble del cual se conoce el valor exacto de la energía. Para el estado fundamental del átomo de Moshinsky, el funcional de Müller, evaluado en la expresión exacta de la matriz reducida a un cuerpo, da lugar al valor correcto de la energía; nosotros probamos este hecho sorprendente.

- Esta disertación contiene un análisis numérico de la naturaleza de GPC realizado en átomos y moléculas reales (en concreto, el átomo de litio y lel catión He_2^+). Para estos sistemas algunas ligaduras estás cuasi saturadas o cuasifijadas. Para sistemas bajamente correlacionados, el sistema espín compensado $\wedge^3\mathcal{H}_6$ está siempre fijado a una de las cara del politopo descrito por las ya conocidas condiciones de Borland-Dennis.

- La robustez de la cuasifijación de un tipo particular de ligaduras permite explicar por qué las excitaciones dobles son las que gobiernan las cómputos de energía de corelación en expansiones de configuración de interacciones cuando es usado el conjunto de orbitales naturales. Nuestro trabajo sugiere que la ligadura $n_1 + n_2 = 1 + n_3$ no sólo está cuasifijada de manera general sino que es estable para sistemas de tres electrones a cualquier rango de aproximación.

- Esta tesis provee cotas superiores e inferiores para la proyección de una función de onda general $\wedge^3\mathcal{H}_7$ en el conjunto de configuraciones fijadas a la cara del politopo definida por $D^2_{3,7} = 0$.

- Un algoritmo para simular problemas de química cuántica basado en la simplificación estructural debida a la cuasifijación de los números de ocupación es provisto al final de esta disertación. Este algoritmo es puesto a prueba en un sistema cuántico de tres electrones de valencia.

- Finalmente, esta disertación contiene por primera vez una solución analítica de todas las matrices reducidas del N-harmonium (un atomo de N fermiones o bosones que interactúan armónicamente entre ellos y están constreñidos a un potencial externo de perfil armónico). El computo es realizado para bosones y para el sistema unidimensional de fermiones. La expresión analítica de la 1-RDM permite calcular expresiones analíticas para la entropía de ambos sistemas.

10.3 Conclusiones

La elegante y celebrada solución del problema puro de N-representabilidad, debida principalmente a Klyachko y Altunbulak, promete generar el conjunto completo de las GPC que satisfacen los números de ocupación de cualquier sistema fermiónico. En principio, su algoritmo es capaz de producir conjuntos de desigualdades lineales para estos números con coeficientes enteros. A no ser que se trate de sistemas sencillos de tres o cuatro electrones con rango bajo, la determinación de estas desigualdades es aún un trabajo en progreso que enfrenta grandes exigencias de tipo computacional.

Por razones que nadie ha dilucidado, algunas GPC aparecen cuasi saturadas de una manera que no parece ser completamente arbitraria. Dicho fenónemo se conoce con el nombre de cuasifijación de los números de ocupación fermiónicos y un programa de investigación (en el cual esta tesis se inscribe) ha sido creado con el fin de estudiarlo. En nuestro caso, por medio de investigaciones numéricas y teóricas hemos explorado no sólo la naturaleza de la fijación y la cuasifijación en algunos sistemas atómicos y moleculares para diferentes rangos de aproximación, sino la forma en que ambos fenónemos son capaces de producir un conjunto de reglas de selección que permiten identificar aquellas configuraciones que son superfluas en la expresión de la función de onda.

En esta parte se ofrece un resumen de las conclusiones de esta disertación doctoral.

- La saturación de algunas GPC da lugar a un conjunto de reglas de selección que permiten, entre otras cosas, identificar las configuraciones menos efectivas en expansiones de configuración de interacciones. De manera general, este procedimiento da lugar a una notable reducción del número de determinantes de Slater presentes en la función de onda, y por lo tanto a una reducción de los requerimientos computacionales para cálculos de química cuántica [Kly09, SGC13, BRGBS13, BRS15b]. Más aún, dichas reglas de selección permiten dar una idea general de la estructura de la función de onda, cosa que los métodos de fuerza bruta no siempre son capaces de hacer. Por ejemplo, el hecho de que la cuasi saturación de algunas GPC sea robusta permite explicar porqué las dobles excitaciones del estado de "Hartree-Fock" son las que gobiernan la correlación en cálculos de multiconfiguraciones cuando se emplean en ellos orbitales naturales [BRGBS14].

- Es posible cuestionar la propuesta de seleccionar las configuraciones más importantes por medio de las reglas de selección que emergen al considerar la fijación o cuasifijación de las GPC. La razón es que para identificar aquellas ligaduras que son fijas o cuasifijas ha de completarse previamente un cálculo de CI que permita conocer la ocupación de los orbitales naturales y calcular a partir de allí el valor numérico de las GPC. Esta objeción puede responderse de dos maneras. Por una parte, algunos métodos de configuraciones emplean como punto de partida los orbitales moleculares que han sido hallados de manera previa por medio de un método alternativo, por ejemplo el método de Hartree-Fock. Algunos programas, ya estándares en química cuántica, permiten reescribir los orbitales de Hartree-Fock como un conjunto de orbitales naturales. Un método de interacción de configuraciones basado en GPC —como los discutidos en los Capítulos 6 y 7— da pie a un procedimiento general que selecciona configuraciones (determinantes de Slater para ser precisos) cuyo aporte a la estructura de la función de onda es más significativo; en consecuencia, si se conoce el nivel de saturación de las GPC es posible construir funciones de onda más eficientes, antes de completar un cálculo de configuración de interacciones. Una parte muy importante de nuestro trabajo está dedicada a identificar las GPC que de manera general están fijas o cuasifijas en estados fundamentales. Para mencionar un ejemplo, la versión adaptada de espín del sistema $\wedge^3\mathcal{H}_6$ requiere en principio de 8 configuraciones. Sin embargo, considerando las condiciones de representabilidad de dicho sistema así como ciertas propiedades de simetría, nosotros probamos que sólo 3 de esas 8 son necesarias. La escritura de dicha función de onda es la siguiente:

$$|\Psi\rangle_{3,6} = c_{123}|\alpha_1\alpha_2\alpha_3\rangle + c_{145}|\alpha_1\alpha_4\alpha_5\rangle + c_{246}|\alpha_2\alpha_4\alpha_6\rangle,$$

donde los α_i describen orbitales naturales y las amplitudes satisfacen la siguiente condición de normalización:

$$|c_{123}|^2 + |c_{145}|^2 + |c_{246}|^2 = 1.$$

Una segunda respuesta, y tal vez más importante que la primera, es que no es necesario resolver las ecuaciones de Hartree-Fock para construir el espacio de Hilbert al que pertenece la función de onda. Hemos mostrado en el Capítulo 8 que es posible establecer un procedimiento variacional basado en funciones de onda fijadas a la cara del politopo de estados físicamente realizables. El nivel de precisión de dicho procedimiento es notablemente alto y su costo computacional es económico si se le compara con rutinas existentes para cálculos multiconfiguracionales [BRS15a].

- Ahora bien, hemos de admitir que es poco probable que el paradigma de Klyachko vaya a ser relevante para el ámbito de la química cuántica, al menos en el corto plazo. Aquí el problema a solucionar es el crecimiento dramático del número de GPC a medida que el número de particulas y el rango de aproximación crecen; así pues, la dificultad de extender nuestro método a sistemas con muchos cuerpos es de naturaleza meramente computacional. Aunque costosa desde el punto de vista computacional, la solución del problema *puro* de N-representabilidad de la 1-RDM en realidad consiste en la formulación de un algoritmo que produce el conjunto completo de GPC para cualquier sistema fermiónico. A la fecha, sólo conocemos el conjunto de GPC para los siguientes sistemas:

$$\wedge^3\mathcal{H}_6,\ \wedge^3\mathcal{H}_7,\ \wedge^3\mathcal{H}_8, \wedge^3\mathcal{H}_9,\ \wedge^3\mathcal{H}_{10},\ \wedge^4\mathcal{H}_8, \wedge^4\mathcal{H}_9,\ \wedge^4\mathcal{H}_{10},\ \wedge^5\mathcal{H}_{10}.$$

En la actualidad, el autor de este trabajo está colaborando con el Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), para desarrollar un algoritmo que produzca un conjunto más amplio de GPC y que posiblemente será implementado en el superordenador *Janus*.

- Siempre ha sido un enigma si la fórmula de "Löwdin–Shull" (6.5), exacta para sistemas de dos fermiones, puede extenderse para sistemas con un mayor número de partículas. Con nuestros métodos es posible dar una respuesta aproximada a la pregunta para sistemas de tres electrones. El precio a pagar es el de imponer un segundo tipo de ligaduras cuyo "grado" de cuasifijación es menor.
- Hay un proyecto de investigación muy prometedor que consiste en emplear las GPC para mejorar la teoría del funcional de la 1-RDM. En la literatura científica hay un conjunto de funcionales de la 1-RDM físicamente motivados y construidos a partir del conocimiento de los orbitales naturales y los números de ocupación. Todos ellos hallan su principal ancestro en el funcional propuesto por Müller hace más de 30 años [Mül84], y de manera general no satisfacen condiciones físicas que deberían cumplir dado que una 1-RDM es la contracción de una 2-RDM [BRV12]. Creemos que nuestros resultados sugieren la construcción de 1-RDM restringiendo el conjunto de minimización al subconjunto de sistemas que cumplen condiciones de representabilidad, es decir, que no violan las GPC. Un inicio prometedor en esa dirección es [TLMH15].

En suma, uno de los principales resultados de esta investigación es probar la existencia del fenómeno de cuasifijación en sistemas reales. La estabilidad de imponer reglas de selección para dichos sistemas ha sido estudiada recientemente [Sch15]. Más interesante, hay una fuerte conexión entre cuasifijación y energía de correlación [BRS15a]. Proveemos también un nuevo método de optimización para estados fundamentales de pocos fermiones cuya precisión probamos como alta. Según los detalles del algoritmo es posible alcanzar entre el 97% y el 99% de la energía de correlación para tales sistemas. Pensamos que nuestra investigación y los resultados que de ella se desprenden son evidencia de que desarrollar un algoritmo de multiconfiguraciones basado en GPC jugará un papel importante en el futuro de la química cuántica computacional.

Appendix A

N-Harmonium: entanglement entropy

In the early years of quantum mechanics, Heisenberg invented an exactly solvable model as a proxy for the spectral problem of two-electron atoms [Hei26]. It exhibits two fermions interacting with an external harmonic potential and repelling each other by a Hooke-type force; its Hamiltonian, in Hartree-like units, is

$$H = \frac{1}{2}\boldsymbol{p}_1^2 + \frac{1}{2}\boldsymbol{p}_2^2 + \frac{k}{2}(\boldsymbol{r}_1^2 + \boldsymbol{r}_2^2) + \frac{\delta}{2}r_{12}^2,$$

with $r_{12} := |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, k and δ as in (8.21). Many years later, Moshinsky [Mos68] came back to it with the purpose of calibrating correlation energy —see also [MCCA08, Loo10, NP11]. Also, Srednicki [Sre93] used this model to study the black-hole entropy, proving its proportionality to the black-hole area. As mentioned in Sec. 2.4, within the context of a phase-space density functional theory [Dah09], the alternating choice of signs in the reconstruction of the coefficients of the 2-RDM has been shown to be the correct one for the ground state of this system [BGBV12, EFGB12].

The N-*harmonium* model is a system of N interacting particles (fermions or bosons) which interact harmonically in a three-dimensional harmonic well. It is characterized by the Hamiltonian

$$H = \frac{1}{2}\sum_{i=1}^{N}\boldsymbol{p}_i^2 + \frac{k}{2}\sum_{i=1}^{N}\boldsymbol{r}_i^2 + \frac{\delta}{2}\sum_{i<j}^{N}r_{ij}^2. \tag{A.1}$$

This system is also integrable and solvable [BRTD14]. The treatment of harmonically interacting bosons by means of this Hamiltonian represents the first exact solution of a N-particle system using just representability conditions on the reduced space of 2-RDM [GM04]. By means of a change of coordinates already suggested by [CM70], the ground-state wave function for the spinless fermionic system has been recently computed [WWYL12]. General results of the theory of antisymmetric functions ensure that the wave function of a system of spinless fermions is equal to the wave function of the corresponding boson system multiplied by the N-variable Vandermonde determinant (see [Pro07, Sec. 2.3.1]).

The N-harmonium system can be expressed in a separable form (i.e., as a system of uncoupled oscillators) using the set of normal coordinates $\{\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_N\}$ given by

$$\boldsymbol{\xi}_N := \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \boldsymbol{r}_i \quad \text{and} \quad \boldsymbol{\xi}_m := \frac{1}{\sqrt{m(m+1)}} \sum_{i=1}^{m} (\boldsymbol{r}_i - \boldsymbol{r}_{m+1}), \tag{A.2}$$

with $m \in \{1, \ldots, N-1\}$. As can be easily checked, this is an orthogonal transformation of the position variables. A similar change of coordinates for momenta results in a canonical transformation, preserving the symplectic form. Let us call the new set of momenta $\{\boldsymbol{\Xi}_m\}$. A direct calculation shows that

$$\sum_{m=1}^{N-1} \boldsymbol{\xi}_m^2 = \frac{1}{N} \sum_{i<j}^{N} r_{ij}^2 = \sum_{m=1}^{N} \boldsymbol{r}_m^2 - \boldsymbol{\xi}_N^2,$$

so that the Hamiltonian (A.1) can be expressed in the following separable form:

$$H = H_N + \sum_{m=1}^{N-1} H_m, \quad \text{where} \quad H_N = \frac{1}{2}\boldsymbol{\Xi}_N^2 + \frac{1}{2}\omega^2 \boldsymbol{\xi}_N^2 \quad \text{and} \quad H_m = \frac{1}{2}\boldsymbol{\Xi}_m^2 + \frac{1}{2}\mu^2 \boldsymbol{\xi}_m^2,$$

where $\omega^2 := k$ and $\mu^2 := k + N\delta$, depending on the number of particles. Therefore, the physical solutions of the associated Schrödinger equation can be readily obtained. Here, let us first note that (a) there is a ground state whenever $\mu^2 > 0$, and (b) the particles are no longer bound if the relative interaction strength satisfies

$$\frac{\delta}{k} \leq -\frac{1}{N}.$$

Jointly with Irene Toranzo and Jesús S. Dehesa, I considered the entanglement entropy of this problem [BRTD14]. For the case of an assembly of bosons we computed the von Neumann entropy of the 1-RDM, finding analytical expressions for the occupation numbers of the system. For fermions we used the 1-RDM to compute an explicit expression for its purity and its linear entropy as well. To do so, in this Appendix we change the sum rule by imposing that the 1-RDM can be decomposed in terms of its NO $\{\phi_i(\boldsymbol{x})\}$ and its eigenvalues $\{n_i\}$: $\gamma_1(\boldsymbol{x};\boldsymbol{y}) = \sum_i n_i \phi_i(\boldsymbol{x})\phi_i(\boldsymbol{y})$, where $\sum_i n_i = 1$, with (for fermions) $0 \leq n_i \leq 1/N$.

A.1 Bosonic case

Taking into account the Gaussian character of the ground-state oscillator wave function, the ground-state distribution on phase space is characterized by the Wigner N-body density function

$$\begin{aligned} w_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N) &= \frac{1}{\pi^{3N}}\, e^{-2H_N/\omega} e^{-2\sum_{m=1}^{N-1} H_m/\mu} \\ &= \frac{1}{\pi^{3N}} \exp\biggl[-(\omega-\mu)\, \boldsymbol{\xi}_N^2 - \mu \sum_{i=1}^{N} \boldsymbol{r}_i^2 + \frac{\omega-\mu}{\omega\mu}\, \boldsymbol{\Xi}_N^2 - \frac{1}{\mu} \sum_{i=1}^{N} \boldsymbol{p}_i^2 \biggr]. \end{aligned} \tag{A.3}$$

The energy of the ground state is the total sum of the contributions of each individual oscillator, i.e. $E_{\text{gs}}^b = \frac{3}{2}\bigl[\omega + (N-1)\mu\bigr]$. On the other hand the 1-WRDM factorizes as a product of two separable quantities, to wit:

$$
\begin{aligned}
w_1(\boldsymbol{r};\boldsymbol{p}) :=& \int w_N(\boldsymbol{r},\boldsymbol{r}_2,\dots,\boldsymbol{r}_N;\boldsymbol{p},\boldsymbol{p}_2,\dots,\boldsymbol{p}_N) \prod_{m=2}^{N} d\boldsymbol{r}_m d\boldsymbol{p}_m \\
=& \, e^{-\mu \boldsymbol{r}^2 - \frac{1}{\mu}\boldsymbol{p}^2} \, \Delta^{\boldsymbol{r}}(\boldsymbol{r},\mu,\omega,N)\, \Delta^{\boldsymbol{p}}(\boldsymbol{p},\mu,\omega,N).
\end{aligned}
\tag{A.4}
$$

It can be shown that the $\Delta^{\boldsymbol{r}}$-function fulfills the following recursion relation:

$$
\begin{aligned}
\Delta^{\boldsymbol{r}}(\boldsymbol{r},\mu,\omega,N) :=& \frac{1}{\pi^{3N/2}} \int \exp\left[-\frac{\omega-\mu}{N}\left(\boldsymbol{r}+\sum_{m=2}^{N}\boldsymbol{r}_m\right)^2 - \mu\sum_{m=2}^{N}\boldsymbol{r}_m^2 \right] \prod_{m=2}^{N} d\boldsymbol{r}_m \\
=& \frac{1}{\mu_1^{3/2}} \frac{1}{\pi^{3(N-1)/2}} \int \exp\left[-\frac{\omega-\mu}{N}\frac{\mu}{\mu_1}\left(\boldsymbol{r}+\sum_{m=2}^{N-1}\boldsymbol{r}_m\right)^2 - \mu\sum_{m=2}^{N-1}\boldsymbol{r}_m^2 \right] \prod_{m=2}^{N-1} d\boldsymbol{r}_m \\
=& \frac{1}{\mu_1^{3/2}} \frac{1}{\pi^{3(N-1)/2}} \int \exp\left[-\frac{\omega-\mu_1}{N-1}\frac{\mu}{\mu_1}\left(\boldsymbol{r}+\sum_{m=2}^{N-1}\boldsymbol{r}_m\right)^2 - \mu\sum_{m=2}^{N-1}\boldsymbol{r}_m^2 \right] \prod_{m=2}^{N-1} d\boldsymbol{r}_m \\
=& \,(\text{const.})\, \Delta^{\boldsymbol{r}}\left(\sqrt{\frac{\mu}{\mu_1}}\boldsymbol{r},\mu_1,\omega,N-1\right),
\end{aligned}
$$

where $\mu_m := \frac{m}{N}\,\omega + \frac{N-m}{N}\mu$. The constant (const.) will be determined by normalization so that it will depend on the number of particles as well as on the frequencies. Therefore,

$$
\begin{aligned}
\Delta^{\boldsymbol{r}}(\boldsymbol{r},\mu,\omega,N) &= (\text{const.})\, \Delta^{\boldsymbol{r}}\left(\sqrt{\frac{\mu}{\mu_1}}\boldsymbol{r},\mu_1,\omega,N-1\right) = (\text{const.})\, \Delta^{\boldsymbol{r}}\left(\sqrt{\frac{\mu}{\mu_2}}\boldsymbol{r},\mu_2,\omega,N-2\right) \\
&= \cdots = (\text{const.})\, \exp\left(-\frac{\omega-\mu}{N}\frac{\mu}{\mu_{N-1}}\boldsymbol{r}^2 \right).
\end{aligned}
$$

Since $\Delta^{\boldsymbol{p}}(\boldsymbol{p},\mu,\omega,N) \equiv \Delta^{\boldsymbol{r}}(\boldsymbol{p},\mu^{-1},\omega^{-1},N)$, we have that the expression (A.4) satisfies:

$$
w_1(\boldsymbol{r};\boldsymbol{p}) = \frac{N^3}{\pi^3}\left(\frac{\omega\mu}{\mathcal{A}_N}\right)^{3/2} \exp\left(-\frac{N\omega\mu}{(N-1)\,\omega+\mu}\boldsymbol{r}^2 - \frac{N}{\omega+(N-1)\,\mu}\boldsymbol{p}^2 \right),
$$

where $\mathcal{A}_N = [(N-1)\,\omega+\mu][\omega+(N-1)\,\mu]$.

Let us now diagonalize this expression by decomposing it into its set of NO as well as into its NON. The task is made easier by noting that the 1-WRDM is a linear combination of Laguerre polynomials (the phase-space counterpart of the Hermite polynomials). To see that, let us define

$$
\eta_N := (\omega\mu)^{1/4}\left[\frac{\omega+(N-1)\,\mu}{(N-1)\,\omega+\mu}\right]^{1/4} \quad \text{and} \quad \lambda_N := \frac{N\sqrt{\omega\mu}}{\sqrt{\mathcal{A}_N}},
$$

as well as the symplectic transformation

$$
S_N := \begin{pmatrix} \eta_N & 0 \\ 0 & \eta_N^{-1} \end{pmatrix} \quad \text{and} \quad U := S_N \boldsymbol{u} \quad \text{where} \quad \boldsymbol{u}^T = (\boldsymbol{r},\boldsymbol{p}).
$$

Then the 1-WRDM can be rewritten in the Gaussian way as follows,

$$
w_1(U) = \frac{\lambda_N^3}{\pi^3} e^{-\lambda_N U^2},
\tag{A.5}
$$

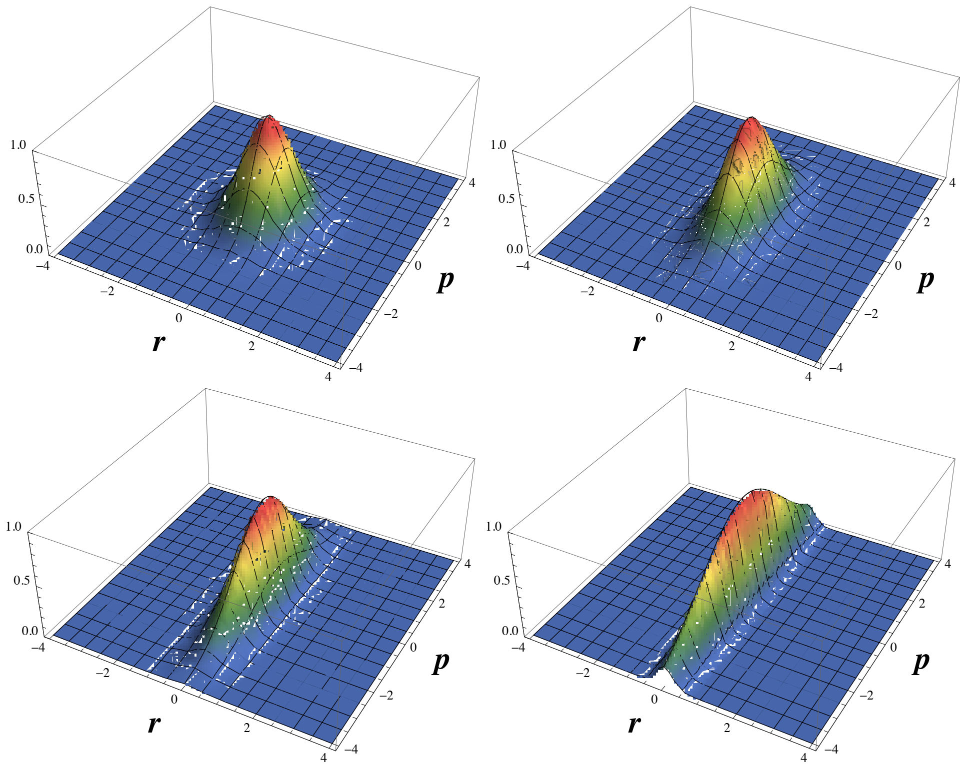

FIGURE A.1: The 1-WRDM (A.5) plotted for $N \in \{2, 6, 20, 50\}$. The strength δ/k is taken to be equal to 1. Note that as the number of bosons grows, the profiles of the position and momentum densities become narrower and wider, respectively.

showing that it is actually a *Gibbs state*. Note that $\lambda_N \leq 1$ for all N, since $\omega + \mu \geq 2\sqrt{\omega\mu}$ and $\mathcal{A}_N \geq N^2\omega\mu$ and that $\lambda_N \to 1$ when $N \to \infty$. In Figure A.1 is plotted the numerical behavior of the 1-WRDM of the N-boson harmonium for different values of the number of bosons. We observe that, as the number of bosons grows, the profiles of the position and momentum densities become narrower and wider, respectively. This clearly indicates that the more precisely the particles are localized in position space, the larger the spread in momentum space, as one should expect according to the position-momentum uncertainty principle. There is no relevant difference for negative values of the coupling constant δ except that in this case it can be plotted only when $\delta/k \geq -1/N$.

It is known that associated to any symplectic transformation (say, S_N), there is a unitary operator acting on the Hilbert space [Lit86]. Let us use this transformation to find the set of ON in the basis of Wigner eigenfunctions of the harmonic oscillator. Since the 1-WRDM factorizes completely, from now on we work in one dimension. From the series formula

$$(1-t)\sum_{r=0}^{\infty} L_r(z)\, e^{-z/2}\, t^r = e^{-\frac{1+t}{1-t}\frac{z}{2}},$$

where $L_r(z)$ is the Laguerre polynomial, it follows that

$$w_1(U) = \sum_{r=0}^{\infty} \frac{(-1)^r}{\pi}\, L_r(2U^2)\, e^{-U^2}\, n_r,$$

where the occupation numbers are equal to

$$n_r = \frac{2\lambda_N}{1+\lambda_N}\left(\frac{1-\lambda_N}{1+\lambda_N}\right)^r =: (1-t_N)\, t_N^r,$$

fulfilling $\sum_r n_r = 1$. Using this analytical expression, it is possible to compute the von Neumann entropy, obtaining the value

$$S(N) := -\sum_{r=0} n_r \log n_r = -\log(1-t_N) - \frac{t_N \log(1-t_N)}{1-t_N}. \tag{A.6}$$

This expression complements and extends a similar formula encountered by other means in a black-hole context [Sre93].

This entanglement entropy (A.6) is examined in Fig. A.2 in terms of the number N of bosons and δ/k. As it is stated, the minimum value of this relative strength is $-1/N$. There is a critical point around $N_c \sim 3.5$, where the entanglement acquires its maximum value [BRTD14]. Below this critical value, for *positive* values of the coupling constant δ/k, the first occupation number decreases as the number of particles increases. Beyond this value the situation is reversed: the value of the first occupation number increases as the number of particles increases. This implies that $n_0 \sim 1$ in the limit when the number of particles tends to infinity, which is a necessary condition for the existence of a Bose-Einstein condensation [PP00].

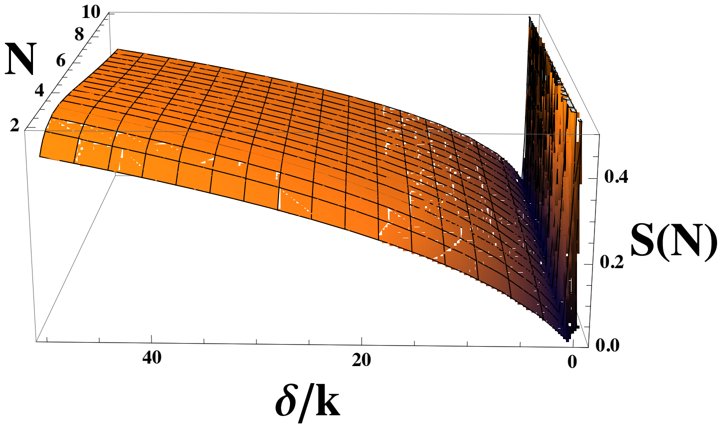

FIGURE A.2: Von Neumann entropy of the 1-WRDM for the N-boson harmonium is plotted as a function of the number of bosons N and the relative interaction strength δ/k. It is apparent that there is a critical point around $N_c \sim 3.5$, where the entanglement acquires its maximum value.

A.2 Fermionic case

The linear entropy is a first order approximation of the von Neumann entropy of the 1-RDM of the system. In [BRTD14] we considered this measure for the case in which the spinless fermions are confined in a one-dimensional well, mainly because the antisymmetric fermion case requires more elaborate computations. Taking into account the Hamiltonian (A.1) for the N-fermion harmonium, one has that the ground-state energy of the system is $E^f_{\text{gs}} = \frac{1}{2}\omega + \sum_{j=1}^{N-1} \mu\big(m + \frac{1}{2}\big) = \frac{1}{2}\omega + \frac{1}{2}\mu(N^2-1)$ and the corresponding eigenfunction can be expressed as

$$\Psi^f(\xi_1,\dots,\xi_N) = \frac{1}{\sqrt{N!}} \sum_{J\in S_N} (-)^J J \left[\phi^{\omega}_{\nu_N}(\xi_N) \prod_{m=1}^{N-1} \phi^{\mu}_{\nu_m}(\xi_m) \right],$$

where $\nu_m \in \{0,\cdots,N-1\}$, so that $\nu_i \neq \nu_j$ whenever $i \neq j$. The symbol J denotes an element of the permutation group S_N of N elements (acting on the r-coordinates), and ϕ^{μ}_{ν} is the single-particle wave function given by an Hermite function of degree ν with frequency μ. The collective mode ξ_N is symmetric under any exchange of the position coordinates. Therefore, one has $\nu_N = 0$; otherwise one would have $\nu_m = 0$ for some $m \neq N$, and the wave function would not be totally antisymmetric. Therefore, the eigenfunction can be rewritten as

$$\Psi^f_{\mathrm{gs}}(\xi_1,\dots,\xi_N) = (\text{const.}) \sum_{J\in S_N} (-)^J J \left[\prod_{m=1}^{N-1} H_{\nu_m}(\sqrt{\mu}\,\xi_m) \right] e^{-\frac{\omega}{2}\xi_N^2 - \frac{\mu}{2}\sum_{m=1}^{N-1}\xi_m^2}, \tag{A.7}$$

where H_ν is the Hermite polynomial of degree ν and now $\nu_m \in \{1,\cdots,N-1\}$. The exponential power of (A.7) is the bosonic wave function, counterpart of the Wigner function in (A.3).

The wave function of a system of spinless fermions is equal to the wave function of the corresponding bosonic system multiplied by the N-variable Vandermonde determinant [Pro07]. Hence, the ground-state wave function of the spinless N-fermion harmonium described by the Hamiltonian (A.1) has the form [Sch13]:

$$\Psi^f(r_1,\cdots,r_N) = (\text{const.}) \prod_{i<j} (r_i - r_j) \, \exp\left[-\frac{\omega-\mu}{2}\,\xi_N^2 - \frac{\mu}{2}\sum_{i=1}^{N} r_i^2 \right], \tag{A.8}$$

where the product-like symbol on the right hand of this expression denotes the Vandermonde determinant:

$$\mathcal{V}_{(r_1,\cdots,r_N)} := \begin{vmatrix} 1 & \cdots & 1 \\ r_1 & \cdots & r_N \\ \vdots & \ddots & \vdots \\ r_1^{N-1} & \cdots & r_N^{N-1} \end{vmatrix} = \prod_{1\le i<j\le N} (r_i - r_j). \tag{A.9}$$

It has been pointed out by several authors that this function is actually a generalization of Laughlin's wave function for the fractional quantum Hall effect [Lau83]. This is not surprising since in the Hall effect the magnetic field can be understood as a harmonic potential acting on the electrons.

So far, we have considered only spinless particles. Our conclusions for the bosonic system also apply to the total entanglement from a qualitative point of view, because the spin part of the ground-state eigenfunction fully factorizes. In [BRTD14] we considered the entanglement entropy of the N-fermion harmonium (i.e., the entanglement of both spatial and spin degrees of freedom) using the linear entropy as a measure of entanglement. For simplicity, we considered one-dimensional models with an even number (say $2N$) of spinned electrons. Therefore, the total spin of the system is zero, and all the spatial orbitals are doubly occupied (restricted configuration).

Let us define the set of spin orbitals in the following way:

$$\varphi_j(x) = \begin{cases} \phi_{\frac{j-1}{2}}(r)\uparrow, & \text{if } j \text{ is odd,} \\ \phi_{\frac{j}{2}}(r)\downarrow, & \text{if } j \text{ is even.} \end{cases}$$

The symbols ↑ and ↓ mean spin up and spin down, respectively, and we denote $x := (r, \varsigma)$, ς being the spin coordinate. To illustrate our strategy, let us begin with the consideration of the simpler non-interacting case; that is, when $\delta = 0$, and hence $\mu = \omega$. The corresponding ground-state eigenfunction is then given by a lone Slater determinant whose expression is

$$\begin{aligned} \Psi^f(x_1, \ldots, x_N) &= \frac{1}{\sqrt{2N!}} \sum_{J \in S_{2N}} (-)^J \left[\prod_{i=1}^{2N} \varphi_{i-1}(x_{J(i)}) \right] \\ &= \frac{1}{\sqrt{2N!}} \sum_{J \in S_{2N}} (-)^J \, J \left[\prod_{i=1}^{N} \uparrow_{2i-1} \downarrow_{2i} \phi^\omega_{i-1}(r_{2i-1}) \, \phi^\omega_{i-1}(r_{2i}) \right]. \end{aligned} \tag{A.10}$$

In the non-interacting case, the basis of the one-particle Hilbert space is the set of Hermite functions whose degree is less than N. Let us now define

$$\begin{aligned} H &= \{ j \in S_{2N} : j \text{ fixes } 1, \ldots, N \} \simeq S_N \\ K &= \{ j \in S_{2N} : j \text{ fixes } N+1, \ldots, 2N \} \simeq S_N \end{aligned}$$

and $\tilde{S}_N = H \times K$ the direct product of these two subgroups. The set $S'_{2N} = S_{2N}/\tilde{S}_N$ is the set of right cosets in S_{2N}, giving the following equivalence relation: $J \sim J'$ if and only if there exists $(j, j') \in \tilde{S}_N$ such that $J' = (j, j')J$.

Therefore we can reorganize the expression (A.10) in the following form:

$$\begin{aligned} \Psi^f(x_1, \ldots, x_N) = \frac{1}{\sqrt{2N!}} & \sum (-)^J \prod_{i=1}^{N} \uparrow_{J(i)} \prod_{i=N+1}^{2N} \downarrow_{J(i)} \\ & \times \begin{vmatrix} \phi^\omega_0(r_{J(1)}) & \cdots & \phi^\omega_0(r_{J(N)}) \\ \vdots & \ddots & \vdots \\ \phi^\omega_N(r_{J(1)}) & \cdots & \phi^\omega_N(r_{J(N)}) \end{vmatrix} \begin{vmatrix} \phi^\omega_0(r_{J(N+1)}) & \cdots & \phi^\omega_0(r_{J(2N)}) \\ \vdots & \ddots & \vdots \\ \phi^\omega_N(r_{J(N+1)}) & \cdots & \phi^\omega_N(r_{J(2N)}), \end{vmatrix}, \end{aligned}$$

where the sum runs over a representative of each coset. The choice of the representative $J \in [J] \in S'_{2N}$ is immaterial. The 1-RDM is diagonal in the spin space and is given by the expression

$$\gamma_1(x, x') = \begin{pmatrix} \gamma_1^{\uparrow\uparrow}(r, r') & 0 \\ 0 & \gamma_1^{\downarrow\downarrow}(r, r') \end{pmatrix}, \tag{A.11}$$

where

$$\begin{aligned}
\gamma_1^{\uparrow\uparrow}(r,r') = \gamma_1^{\downarrow\downarrow}(r,r') &= \int dx_2 \cdots dx_{2N}\, \Psi^f(r,\varsigma_1,x_2,\dots,x_N)\Psi^f(r',\varsigma_1,x_2,\dots,x_N)|_{\varsigma_1=\uparrow} \\
&= \frac{1}{2N}\frac{1}{(N-1)!}\int dr_2\cdots dr_N \begin{vmatrix} \varphi_0(r) & \cdots & \varphi_0(r_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(r) & \cdots & \varphi_N(r_N) \end{vmatrix} \begin{vmatrix} \varphi_0(r') & \cdots & \varphi_0(r_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(r') & \cdots & \varphi_N(r_N) \end{vmatrix} \\
&= \frac{1}{2N}\sum_{i=0}^{N-1} \varphi_i(r)\varphi_i(r').
\end{aligned}$$

The occupation numbers appear twice.

Let us now return to the general interacting case, for which $\delta \neq 0$, and hence $\mu \neq \omega$. The ground-state eigenfunction for the Hamiltonian (A.1) is similar to the spinless case, except that each spatial orbital is doubly occupied. For the same reasons as in the spinless case, the collective mode ξ_{2N} occupies the Hermite function of degree zero. The other coordinates $\{\xi_m\}_{m=1}^{2N-1}$ occupy the other spatial orbitals in such a way that the total wave function is totally antisymmetric under interchange the coordinates $\{x_m\}_{m=1}^{2N}$. The ground-state eigenfunction schematically reads

$$\Psi^f(x_1,\dots,x_{2N}) = \frac{1}{\sqrt{2N!}}\sum_{J\in S_{2N}} (-)^J \left[\prod_{i=1}^{N} \uparrow_{J(i)} \prod_{i=N+1}^{2N} \downarrow_{J(i)}\right] J\left[\phi_0^\omega(\xi_{2N})\phi_0^\mu(\cdot)\prod_{m=1}^{N}\phi_m^\mu(\cdot)\phi_m^\mu(\cdot)\right].$$

Using again the fact that an antisymmetric polynomial is equal to a symmetric polynomial multiplied by a Vandermonde determinant [Pro07], we can write the ground-state eigenfunction of the general interacting spinned N-fermion system as:

$$\begin{aligned}
\Psi^f(x_1,\dots,x_{2N}) =\ &(\text{const.})\, e^{-\frac{\omega-\mu}{2}\xi_{2N}^2 - \frac{\mu}{2}\sum_{i=1}^{2N} r_i^2} \\
&\times \sum_{S'_{2N}} (-)^J \left[\prod_{i=1}^{N} \uparrow_{J(i)} \prod_{i=N+1}^{2N} \downarrow_{J(i)}\right] \mathcal{V}_{(J(1),\dots,J(N))}\mathcal{V}_{(J(N+1),\dots,J(2N))};
\end{aligned}$$

and the corresponding energy is $E_{\text{gs}}^f = \frac{1}{2}(\omega+\mu) + \mu(N^2-1)$. Let us define $\eta = r + r_2 + \cdots + r_N$ and $\eta' = r' + r_2 + \cdots + r_N$. To compute the one-density we use twice the Hubbard-Stratonovich identity:

$$e^{\alpha\zeta^2} = \sqrt{\frac{\alpha}{\pi}}\int_{-\infty}^{\infty} dz\, e^{-\alpha z^2 + 2\alpha z\zeta}, \quad \text{with} \quad \alpha\in\mathbb{C} \quad \text{and} \quad \operatorname{Re}(\alpha) > 0, \tag{A.12}$$

where $\zeta = r_2 + \cdots + r_N$ and $\alpha = 2b_N$. First to compute N integrals with $\zeta' = r_{N+1} + \cdots + r_{2N}$, and second to compute $N-1$ integrals with $\zeta = r_2 + \cdots + r_N$. Each diagonal element ($\gamma_1^{\uparrow\uparrow}$ and $\gamma_1^{\downarrow\downarrow}$) of the 1-RDM reads:

$$\begin{aligned}
&(\text{const.})\, e^{-a(r^2+r'^2)} \int dr_2\cdots dr_N\, e^{-2a(r_2^2+\cdots+r_N^2)+b_{2N}(\eta^2+\eta'^2)} \int dz\, e^{-2b_{2N}z^2} e^{N\frac{b_{2N}^2}{2a}(\eta+\eta'+2z)^2} \\
&\quad\times \mathcal{V}_{(r,,2,\dots,N)}\, \mathcal{V}_{(r',2,\dots,N)} \int dz_{N+1}\cdots dz_{2N}\, \mathcal{V}^2_{(z_{N+1},\dots,z_{2N})} \prod_{j=N+1}^{2N} e^{-z_j^2},
\end{aligned}$$

where $z_j := \sqrt{2a}\big[r_j - \frac{b_{2N}}{2a}(\eta + \eta' + 2z)\big]$. The full computation gives [BRTD14]:

$$\begin{aligned}\gamma_1^{\uparrow\uparrow}(r,r') = \gamma_1^{\downarrow\downarrow}(r,r') &= \frac{1}{2\pi}\frac{1}{\sqrt{N}}\sqrt{\frac{2\omega\mu}{(2N-1)\omega+\mu}} \\ &\times e^{-a'_N(r^2+r'^2)+2\tilde{c}_{2N}rr'}\int du\, e^{-u^2}\sum_{j=0}^{N-1}\frac{1}{2^j j!}H_j[\tilde{q}_{(r,r')} - \beta_{2N}u]H_j[\tilde{q}_{(r',r)} - \beta_{2N}u],\end{aligned}$$

$$\text{where}\quad \tilde{q}_{(r,r')} = \sqrt{\mu}\big[r - \tfrac{1}{2}\beta_{2N}^2(r+r')\big], \quad \tilde{c}_{2N} = \frac{(\mu-\omega)^2}{(2N-1)\omega+\mu}\frac{2N-1}{8N},$$

$$\beta_N := \sqrt{\frac{\mu-\omega}{(N-1)\omega+\mu}} \quad \text{and} \quad a'_N := a - b_{2N} - \tilde{c}_{2N},$$

with $a = \frac{\mu}{2}$ and $b_N = \frac{\mu-\omega}{2N}$.

Let us quantify the entanglement entropy of the system by means of the linear entropy associated to the one-body density:

$$S_L = 1 - 2N\,\mathrm{Tr}[\gamma_1^2] = 1 - 2N\int \gamma_1(x;x')\gamma_1(x';x)\,dx'\,dx, \tag{A.13}$$

where $2N\,\mathrm{Tr}[\rho_1^2]$ is the *purity* of the system. This entanglement measure, which is a non-negative quantity that vanishes if and only if the Slater rank of the state equals 1, has been recently used in various two-fermion systems [YPD10, MPDK10] as well as for various helium-like systems [DKY$^+$12, BSS13] in both ground and excited states. Let us also point out that the linear entropy is a linearization of the von Neumann entropy, and gives a lower bound for this logarithmic entropy. In Figures A.3 is plotted the linear entropy (A.13). The first basic observation is that for fixed $2N$ the entanglement decreases (increases) when the relative interaction strength is increasing in the negative (positive) region. Moreover, for negative values of the coupling constant, the spatial entanglement of the $2N$-fermion harmonium grows when $2N$ is increasing. For small positive values of the coupling constant (i.e., when the fermions attract each other) for very small values of δ/k the entanglement grows again with increasing $2N$. However, in the strong-coupling regime, the linear entropy decreases as the number of particles is increasing; this means that in that regime the purity increases with increasing number of particles. For instance, for $\delta/k = 10$ the purity is 0.92 for $2N = 2$ and 0.94 for $2N = 10$, whereas for $\delta/k = 1$ is 0.998 and 0.992 respectively.

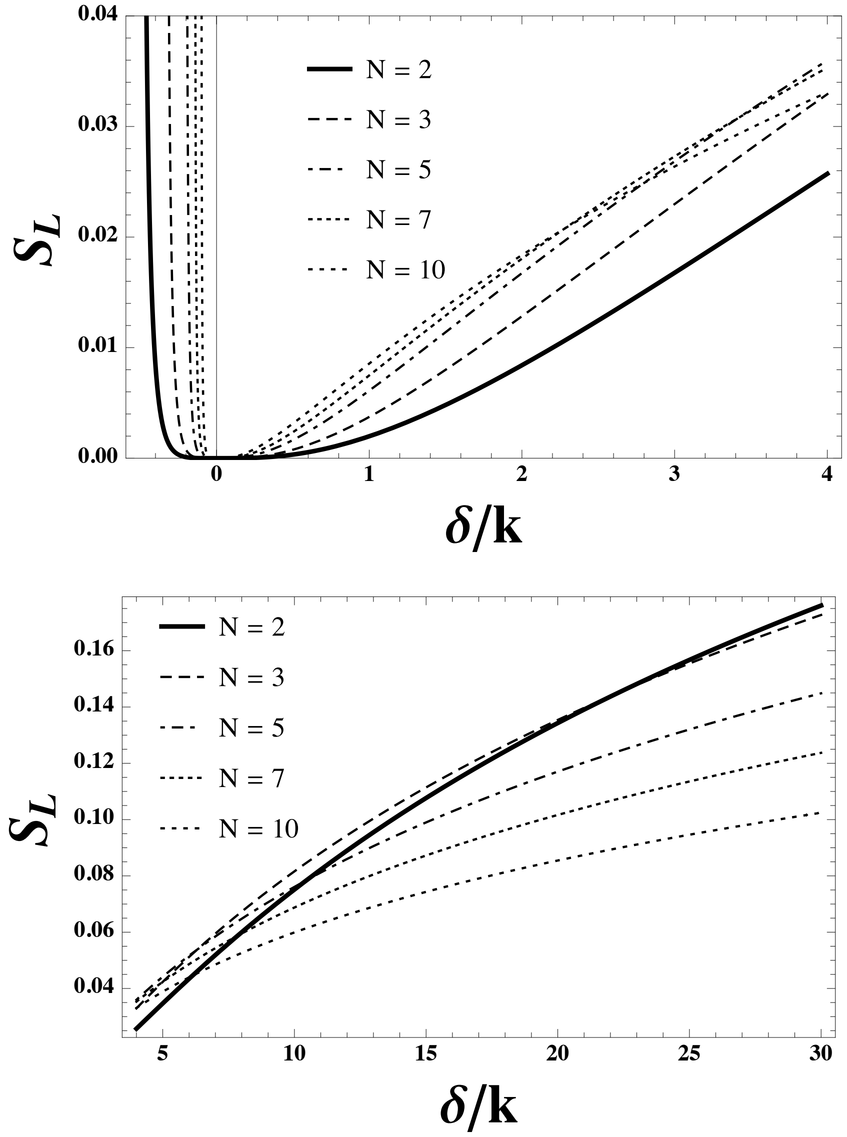

FIGURE A.3: Linear entropy of the 1-RDM of the $2N$-fermion harmonium as a function of the coupling constant for five different values of N. Note the change of behavior when the strength grows [BRTD14].

Appendix B

A note on Carlson-Keller duality

Let $|\Psi\rangle \in \wedge^{p+q}\mathcal{H}_m$, provided that $p+q \leq m$. The corresponding density matrix is given by the expression:

$$\gamma_{p+q}(\boldsymbol{x}_1, ..., \boldsymbol{x}_{p+q}; \boldsymbol{x}'_1, ..., \boldsymbol{x}'_{p+q}) = \Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_{p+q})\Psi^*(\boldsymbol{x}'_1, ..., \boldsymbol{x}'_{p+q}).$$

The q-RDM is given by the expression:

$$\gamma_q(\boldsymbol{x}_1, ..., \boldsymbol{x}_q; \boldsymbol{x}'_1, ..., \boldsymbol{x}'_q) := \tbinom{p+q}{q} \int \gamma_{p+q}(\boldsymbol{x}_1, ..., \boldsymbol{x}_q, \boldsymbol{x}_{q+1}, ..., \boldsymbol{x}_{p+q}; \\ \boldsymbol{x}'_1, ..., \boldsymbol{x}'_q, \boldsymbol{x}_{q+1}, ..., \boldsymbol{x}_{p+q})\, d\boldsymbol{x}_{q+1} \cdots d\boldsymbol{x}_{p+q}$$

and consequently the p-RDM is

$$\gamma_p(\boldsymbol{x}_1, ..., \boldsymbol{x}_p; \boldsymbol{x}'_1, ..., \boldsymbol{x}'_p) := \tbinom{p+q}{p} \int \gamma_{p+q}(\boldsymbol{x}_1, ..., \boldsymbol{x}_p, \boldsymbol{x}_{p+1}, ..., \boldsymbol{x}_{p+q}; \\ \boldsymbol{x}'_1, ..., \boldsymbol{x}'_p, \boldsymbol{x}_{p+1}, ..., \boldsymbol{x}_{p+q})\, d\boldsymbol{x}_{p+1} \cdots d\boldsymbol{x}_{p+q}.$$

Suppose that

$$\gamma_p|\alpha_j\rangle = \lambda_j|\alpha_j\rangle$$

is the spectral decomposition of this latter matrix. The eigenvectors $|\alpha_j\rangle$ are assumed to be correctly normalized to 1.

The Carlson-Keller duality points out that γ_p and γ_q share the same nonzero eigenvalues with corresponding eigenvectors, as the following theorem states.

Theorem 6. The vector

$$|\beta_j\rangle := \int \Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_q, \boldsymbol{x}_{q+1}, ..., \boldsymbol{x}_{p+q})\, \alpha_j^*(\boldsymbol{x}_{q+1}, ..., \boldsymbol{x}_{p+q})\, d\boldsymbol{x}_{q+1} \cdots d\boldsymbol{x}_{p+q}$$

is an eigenvector of γ_q, with λ_j as eigenvalue [Col63].

Proof. The proof is as follows:

$$\begin{aligned}
\gamma_q|\beta_j\rangle &= \tbinom{p+q}{q}\int \Psi(\boldsymbol{x}_1,...,\boldsymbol{x}_q,\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q})\,\Psi^*(\boldsymbol{x}'_1,...,\boldsymbol{x}'_q,\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q})\,d\boldsymbol{x}_{q+1}\cdots d\boldsymbol{x}_{p+q} \\
&\qquad\qquad \times \Psi(\boldsymbol{x}'_1,...,\boldsymbol{x}'_q,\boldsymbol{y}_{q+1},...,\boldsymbol{y}_{p+q})\,\alpha^*_j(\boldsymbol{y}_{q+1},...,\boldsymbol{y}_{p+q})\,d\boldsymbol{y}_{q+1}\cdots d\boldsymbol{y}_{p+q}\,d\boldsymbol{x}'_1\cdots d\boldsymbol{x}'_q \\
&= \int \Psi(\boldsymbol{x}_1,...,\boldsymbol{x}_q,\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q})\,\gamma_p(\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q};\boldsymbol{y}_{q+1},...,\boldsymbol{y}_{p+q}) \\
&\qquad\qquad \times \alpha^*_j(\boldsymbol{y}_{q+1},...,\boldsymbol{y}_{q+p})\,d\boldsymbol{y}_{q+1}\cdots d\boldsymbol{y}_{q+p}\,d\boldsymbol{x}_{q+1}\cdots d\boldsymbol{x}_{p+q} \\
&= \lambda_j \int \Psi(\boldsymbol{x}_1,...,\boldsymbol{x}_q,\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q})\,\alpha^*_j(\boldsymbol{x}_{q+1},...,\boldsymbol{x}_{p+q})\,d\boldsymbol{x}_{q+1}\cdots d\boldsymbol{x}_{p+q} \\
&= \lambda_j|\beta_j\rangle.
\end{aligned}$$

It is easy to see that the vector $c_j|\beta_j\rangle$, where

$$|c_j|^2 = \lambda_j^{-1}\binom{p+q}{q}$$

is correctly normalized to 1. □

To exemplify the Karlson-Keller theorem, let us choose the wave function given by the expression:

$$|\Psi\rangle = |\alpha_1\rangle \wedge (a|\alpha_2\rangle \wedge |\alpha_3\rangle + b|\alpha_4\rangle \wedge |\alpha_5\rangle) \quad \text{with} \quad |a|^2 + |b|^2 = 1.$$

It is clear that

$$\gamma_1 = |\alpha_1\rangle\langle\alpha_1| + |a|^2|\alpha_2\rangle\langle\alpha_2| + |a|^2|\alpha_3\rangle\langle\alpha_3| + |b|^2|\alpha_4\rangle\langle\alpha_4| + |b|^2|\alpha_5\rangle\langle\alpha_5|.$$

Note that

$$\gamma_2 = |\beta_1\rangle\langle\beta_1| + |a|^2|\beta_2\rangle\langle\beta_2| + |a|^2|\beta_3\rangle\langle\beta_3| + |b|^2|\beta_4\rangle\langle\beta_4| + |b|^2|\beta_5\rangle\langle\beta_5|,$$

where

$$\begin{aligned}
|\beta_1\rangle &= a|\alpha_2\rangle \wedge |\alpha_3\rangle + b|\alpha_4\rangle \wedge |\alpha_5\rangle, \\
|\beta_2\rangle &= |\alpha_1\rangle \wedge |\alpha_3\rangle, \\
|\beta_3\rangle &= |\alpha_1\rangle \wedge |\alpha_2\rangle, \\
|\beta_4\rangle &= |\alpha_1\rangle \wedge |\alpha_5\rangle, \\
|\beta_5\rangle &= |\alpha_1\rangle \wedge |\alpha_4\rangle.
\end{aligned}$$

Appendix C

Newton-Raphson method

C.1 Univariate method

In numerical analysis, the Newton-Raphson method solves the algebraic equation $f(x) = 0$ by selecting a random initial guess x_0 and following the iteration:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}, \quad \text{provided that} \quad f'(x_n) \neq 0.$$

This is the Newton-Raphson formula and can be easily derived by noting that the equation of the tangent of $f(x)$ at $x = y$ is

$$f'(x_n) = \frac{f(y) - f(x_n)}{y - x_n}$$

If y is taken to be the zero-crossing of the tangent, then $f(y) = 0$ and hence,

$$y = x_n - \frac{f(x_n)}{f'(x_n)}$$

which is closer to the desired solution than x_n. The method consists in repeating the process several times $x_{n+1}, x_{n+2}, \cdots$ which approaches the actual solution.

Sometimes the problem to solve is a optimization one in which the algebraic equation is $f'(x) = 0$. For such a case, the Newton-Raphson equations read:

$$\Delta x_n = -\frac{f'(x_n)}{f''(x_n)}.$$

C.2 Multivariate method

The above method can be easily generalized to the multi-variate case, to solve m simultaneous algebraic equations

$$f_i(\vec{x}) = 0 \quad \text{with} \quad i \in \{1, 2, \ldots, m\},$$

where

$$\vec{x} = \begin{pmatrix} x_1 \\ \vdots \\ x_m \end{pmatrix}.$$

is an m-dimensional vector. This system of equations can be represented in vector form as $\mathbf{f}(\vec{x}) = (f_1(\vec{x}), \ldots, f_m(\vec{x}))^t = 0$.

The Taylor series around $\vec{x}$ for these functions read

$$f_i(\vec{x} + \delta\vec{x}) = f_i(\vec{x}) + \sum_j \frac{\partial f_i}{\partial x_j}\delta x_j + O(\delta\vec{x}^2).$$

We ignore the terms $O(\delta\vec{x}^2)$ and higher. Therefore, if $f_i(\vec{x} + \delta\vec{x}) = 0$, we obtain:

$$\sum_j \frac{\partial f_i}{\partial x_j}\delta x_j = -f_i(\vec{x}). \tag{C.1}$$

Let us introduce the matrix $J_f(\vec{x})$, the Jacobian of the function $\mathbf{f}(\vec{x})$:

$$J_f(\vec{x}) = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_m} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_m}{\partial x_1} & \cdots & \frac{\partial f_m}{\partial x_m} \end{pmatrix}.$$

The formula (C.1) then reads $J_f(\vec{x})\delta\vec{x} = -\mathbf{f}(\vec{x})$. The Newton-Raphson formula for multivariate problem is thus:

$$\delta\vec{x} = -J_f^{-1}(\vec{x})\mathbf{f}(\vec{x}), \tag{C.2}$$

provided that the determinant of the Jacobian does exist.

C.3 Newton-Raphson method in quantum chemistry

For quantum-chemistry applications, the crucial quantity is the energy, a scalar function whose domain is a m-dimensional vector space $\mathcal{E} : \mathbb{R}^m \to \mathbb{R}$. For the purposes of this work, the problem is to find the ground state which satisfies $\frac{\partial \mathcal{E}}{\partial x_i} = 0$, $\forall i$. The Newton-Raphson requires here a column vector represented by the electronic gradient at the expansion point, namely,

$$\mathcal{E}^{(1)}(\vec{x}) = \begin{pmatrix} \frac{\partial \mathcal{E}(\vec{x})}{\partial x_1} \\ \vdots \\ \frac{\partial \mathcal{E}(\vec{x})}{\partial x_m} \end{pmatrix}$$

as well as the electronic Hessian:

$$\mathcal{E}^{(2)}(\vec{x}) = \begin{pmatrix} \frac{\partial^2 \mathcal{E}(\vec{x})}{\partial x_1 \partial x_1} & \cdots & \frac{\partial^2 \mathcal{E}(\vec{x})}{\partial x_1 \partial x_m} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 \mathcal{E}(\vec{x})}{\partial x_m \partial x_1} & \cdots & \frac{\partial^2 \mathcal{E}(\vec{x})}{\partial x_m \partial x_m} \end{pmatrix}.$$

The Newton-Raphson iterative method (C.2) reads

$$\vec{x}_{n+1} - \vec{x}_n = -[\mathcal{E}^{(2)}(\vec{x}_n)]^{-1}\mathcal{E}^{(1)}(\vec{x}_n).$$

The new parameters $\vec{x}_{n+1}$ are used to compute a new set of orbitals. New Hessian matrix and gradient vector elements are computed in this new orbital and state basis. The process is repeated until the convergence is obtained [She07].

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