Máster Erasmus Mundus en Química Teórica y Modelización Computacional

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Título

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Abstract

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Objetives:

1. (...)

Resumen

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Objetivos:

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1 Introduction

In the document, the second quantization formalism is used. Consequently, some useful definitions [1] are recalled in this section. Additionally, atomic units are used all throughout the document.

1.1 Second quantization

The occupation-number (ON) operators are defined for the sets of creation and annihilation operators, $\{a^\dagger\}$, $\{a\}$, as

$$n_p = a_p^\dagger a_p. \tag{1}$$

For a given ON vector $|k\rangle$, the occupation number k_p is obtained by counting the number of electrons in spin orbital p

$$n_p |k\rangle = a_p^\dagger a_p |k\rangle = k_p |k\rangle . \tag{2}$$

The ON operators are Hermitian

$$n_p^\dagger = \left(a_p^\dagger a_p\right)^\dagger = a_p^\dagger a_p = n_p, \tag{3}$$

commute among themselves

$$n_p n_q |k\rangle = k_p k_q |k\rangle = k_q k_p |k\rangle = n_q n_p |k\rangle , \tag{4}$$

and, since in the spin-orbital basis the ON operators are projection operators, they are idempotent,

$$n_p^2 = n_p n_p = a_p^\dagger a_p a_p^\dagger a_p = a_p^\dagger \left(1 - a_p^\dagger a_p\right) a_p = a_p^\dagger a_p = n_p. \tag{5}$$

Therefore, its eigenvalues can only be 0 or 1.

The particle-number operator, or simply the number operator, is the Hermitian operator resulting from adding together all ON operators in the Fock space

$$\hat{N} = \sum_{p=1}^{m} a_p^\dagger a_p, \tag{6}$$

which returns the number of electrons in an ON vector

$$\hat{N} |k\rangle = \sum_{p=1}^{m} k_p |k\rangle = n |k\rangle . \tag{7}$$

Also, the δ_{pq} operator is defined as

$$\delta_{pq} = a_p a_q^\dagger + a_q^\dagger a_p, \tag{8}$$

which is null if $p \neq q$.

1.2 Reduced Density Matrix Functional Theory

Many methods of electronic structure theory are based on variational optimization of an energy functional. An idempotent first-order reduced density matrix (1-RDM) is variationally optimized in the Hartree-Fock (HF) method [2].

The 1-RDM is determined by the natural orbitals and their occupation numbers [**lowdin1955quantuma**], leading to denote the corresponding energy functional as density matrix functional (DMF) or natural orbital functional (NOF). This is explained in detail in the following sections.

In the coordinate representation of first quantization, the *first-order reduced density matrix* (1-RDM), γ, is defined for an n-electron wavefunction, Ψ, as

$$\gamma\left(\mathbf{x}_1, \mathbf{x}_1'\right) = n \int \cdots \int \Psi\left(\mathbf{x}_1, \mathbf{x_2}, \ldots, \mathbf{x}_n\right) \Psi^*\left(\mathbf{x}_1', \mathbf{x_2}, \ldots, \mathbf{x}_n\right) \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_n \,, \tag{9}$$

and the *second-order reduced density matrix* (2-RDM), Γ, as

$$\Gamma\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2'\right) = \frac{n\left(n-1\right)}{2} \int \cdots \int \Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_n\right) \Psi^*\left(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_n\right) \mathrm{d}\mathbf{x}_3 \cdots \mathrm{d}\mathbf{x}_n \,, \tag{10}$$

where $\mathbf{x} = (\mathbf{r}, s)$ is a combined spatial and spin coordinate.

Employing the 1-RDM rather than the electron density, ρ, has the immediate advantage of making the kinetic energy an explicit functional of γ rather than ρ.

Then, introducing a fictitious noninteracting system is not necessary.

Furthermore, fractionally occupied orbitals are a feature of Reduced Density Matrix Functional Theory (RDMFT), which suggests that functionals of γ are better suited to explain static correlation.

Self-adjointness of γ, as defined in eq. (9), allows for its spectral representation [3]

$$\gamma\left(\mathbf{x}, \mathbf{x}'\right) = \sum_p n_p \varphi_p\left(\mathbf{x}\right) \varphi_p^*\left(\mathbf{x}'\right) . \tag{11}$$

The eigenvalues of 1-RDM are called natural occupation numbers, $\{n_p\}$, and the eigenfunctions are known as natural spin-orbitals, $\{\varphi_p\}$. By convention, natural spin-orbitals are denoted by the indices p, q, r, and s, and arbitrary one-eletron functions by the indices a, b, c, and d.

The ensemble n-representability conditions, which are some properties of the natural spin-orbitals and occupation numbers, have a particularly simple form [4] and read:

1. Self-adjointness of γ: implies orthonormality of the natural orbitals

$$\int \varphi_p^*\left(\mathbf{x}\right) \varphi_q\left(\mathbf{x}\right) = \delta_{pq} \quad \forall_{p,q}. \tag{12}$$

2. By the Löwdin's normalization convention [3], γ is assumed to be normalized to a number of electrons, n. Therefore, the natural occupancies sum up to n

$$\mathrm{tr}\left[\gamma\right] = \sum_p \gamma_{pp} = \sum_p n_p = n. \tag{13}$$

3. Occupation number, n_p, is nonnegative and not grater than 1

$$0 \leq n_p \leq 1 \quad \forall_p. \tag{14}$$

1.3 Properties in terms of the density matrices

Gilbert theorem [5] grounded that the expectation value of any observable of a system in its ground state is a unique functional of the ground-state 1-RDM, establishing the 1-RDM as the fundamental quantity in RDMFT in place of the electronic density on which density functional theory (DFT) is based. It proved that there is a 1-RDM functional [5, 6] such that the Hohenberg-Kohn theorems extend to nonlocal potentials [5, 7]

$$E_\nu^{\mathrm{HK}}[\gamma] = \mathrm{tr}\left[\hat{h}\hat{\gamma}\right] + \left\langle \Psi[\gamma] \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi[\gamma] \right\rangle, \tag{15}$$

where a ground state wavefunction relevant to a ν-representable γ is denoted by the symbol $\Psi[\gamma]$. The one-electron Hamiltonian, $\hat{h}$, is composed of the external potential, $\hat{V}_{\mathrm{text}}$, and the kinetic energy, $\hat{T}$

$$\hat{h} = \hat{T} + \hat{V}_{\mathrm{ext}}, \tag{16}$$

and $\hat{V}_{\mathrm{ee}}$ is an electron interaction operator

$$\hat{V}_{\mathrm{ee}} = \sum_{i>j}^{n} \frac{1}{r_{ij}}. \tag{17}$$

This functional follows the variational principle

$$E_\nu[\gamma] \geq E_0 \quad \forall_{\gamma \in \nu\text{-rep}}, \tag{18}$$

where ν-rep denotes a set of pure-state ν-representable 1-RDMs.

Levy defined the electron repulsion functional [8, 9], extending the domain of a density matrix functional to all pure-state n-representable 1-RDMs

$$E_{\mathrm{ee}}^{\mathrm{L}}[\gamma] = \min_{\Psi \to \gamma} \left\langle \Psi \middle| \hat{V}_{\mathrm{ee}} \middle| \Psi \right\rangle, \tag{19}$$

and further extended to ensemble n-representable 1-RDMs (belonging to a set "n-rep") by Valone [10, 11], so the exact functional reads

$$E_{\mathrm{ee}}[\gamma] = \min_{\Gamma^{(n)} \to \gamma} \mathrm{tr}\left[\hat{\mathbf{H}}\hat{\Gamma}^{(n)}\right], \tag{20}$$

where the minimization is carried out with respect to n-electron density matrices $\Gamma^{(n)}$ that yield γ.

The minima of the Levy functional given in eq. (19), the Hohenberg-Kohn functional given in eq. (15), and that defined in eq. (20), respectively for ν-rep, pure-state n-representable, and ensemble n-representable (n-rep) 1-RDMs coincide for a given external potential, $\hat{V}_{\mathrm{ext}}$ [10, 12]. Thus, considering the variational principle given in eq. (18), it can be concluded that a ground state energy at minimum

is produced by a functional defined for n-rep 1-RDMs

$$E_0 = \min_{\gamma \in n\text{-rep}} \left\{ \operatorname{tr}\left[\hat{h}\hat{\gamma}\right] + E_{\text{ee}}\left[\gamma\right] \right\}. \tag{21}$$

The ground state energy is a functional of the 1-RDM and, therefore, it can be obtained directly from the 1-RDM for a given electron repulsion functional, $E_{\text{ee}}\left[\gamma\right]$

$$E\left[\gamma\right] = E_{\text{oe}}\left[\gamma\right] + E_{\text{ee}}\left[\gamma\right]. \tag{22}$$

Indeed, eqs. (12) to (14) and (21) are the foundation for RDMFT.

In the second quantization formalism, the electronic molecular Hamiltonian in the spin-orbital basis is given by

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} \left(pr \,|\, qs\right) a_p^\dagger a_q^\dagger a_s a_r. \tag{23}$$

Using restricted spin-orbitals, it is convenient to define the operators

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^\dagger a_{q\sigma}, \tag{24}$$

such that

$$\left[E_{pq}, E_{rs}\right] = \delta_{qr} E_{ps} - \delta_{ps} E_{qr}. \tag{25}$$

Then, the Hamiltonian can be written as

$$\hat{H} = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} \left(pq \,|\, rs\right) \left(E_{pq} E_{rs} - \delta_{qr} E_{ps}\right). \tag{26}$$

Given a normalized reference state $|0\rangle$ written as a linear combination of ON vectors

$$|0\rangle = \sum_k c_k \left|k\right\rangle, \quad \langle 0 \,|\, 0\rangle = 1, \tag{27}$$

the expectation value of $\hat{H}$ with respect to $|0\rangle$ reads

$$E_0 = \left\langle 0 \,\middle|\, \hat{H} \,\middle|\, 0 \right\rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} \left(pq \,|\, rs\right) \left(d_{pqrs} - \delta_{qr} D_{ps}\right), \tag{28}$$

where

$$d_{pqrs} = \langle 0 \,|\, E_{pq} E_{rs} \,|\, 0\rangle, \tag{29}$$

and

$$D_{pq} = \langle 0 \,|\, E_{pq} \,|\, 0\rangle \equiv D_{pq}^{(1)}, \tag{30}$$

are the elements (densities) of an $m \times m$ Hermitian matrix, the *one-electron spin-orbital density matrix*, $\mathbf{D^{(1)}}$, since

$$D_{pq}^* = \left\langle 0 \,\middle|\, a_p^\dagger a_q \,\middle|\, 0 \right\rangle = \left\langle 0 \,\middle|\, a_q^\dagger a_p \,\middle|\, 0 \right\rangle = D_{qp}, \tag{31}$$

which is also symmetric for real wave functions.

Since the elements of the one-electron density matrix are inner products of states in the subspace $F(m, n-1)$ or trivially equal to zero, the one-electron density matrix is positive semidefinite. The occupation numbers, ω_p, of the electronic state are given by the diagonal elements of $\mathbf{D^{(1)}}$, i.e. the expectation values of the occupation-number operators, n_p, in $F(m, n)$

$$\omega_p = D^{(1)}_{pp} = \langle 0 \,|\, n_p \,|\, 0 \rangle \,. \tag{32}$$

The diagonal elements of $\mathbf{D^{(1)}}$ reduce to the usual occupation numbers, k_p, whenever the reference state is an eigenfunction of the ON operators, i.e. when the reference state is an ON vector

$$\langle k \,|\, n_p \,|\, k \rangle = k_p. \tag{33}$$

Considering that the ON operators are projectors, ω_p can be written over the projected electronic state

$$n_p \,|0\rangle = \sum_k k_p c_k \,|k\rangle \,, \tag{34}$$

as the squared norm of the part of the reference state where the spin orbital φ_p is occupied in each ON vector

$$\omega_p = \langle 0 \,|\, n_p n_p \,|\, 0 \rangle = \sum_k k_p \,|c_k|^2 \,. \tag{35}$$

Recalling the n-representability conditions (eqs. (13) and (14)), the occupation numbers are real numbers between zero and one and its sum, the trace of the density matrix, is equal to the total number of electrons in the system

$$\operatorname{tr} \mathbf{D^{(1)}} = \sum_p \omega_p = \sum_p \langle 0 \,|\, n_p \,|\, 0 \rangle = n. \tag{36}$$

Since $\mathbf{D^{(1)}}$ is Hermitian, it can be diagonalized by the spectral decomposition for a unitary matrix, $\mathbf{U}$, as

$$\mathbf{D^{(1)}} = \mathbf{U} \lambda \mathbf{U}^\dagger. \tag{37}$$

The eigenvalues, λ_p, are real numbers

$$0 \leq \lambda_p \leq 1, \tag{38}$$

known as the natural-orbital occupation numbers, which also fulfill

$$\sum_p \lambda_p = n. \tag{39}$$

A new set of spin orbitals, the natural spin orbitals, are obtained from the eigenvectors, the columns of $\mathbf{U}$, resulted from eq. (37).

Following the idea given in eq. (20) and with the definition of the one-electron density matrix given in eq. (30), eq. (28) can be further simplified introducing the *two-electron spin-orbital density matrix*

$$D^{(2)}_{pqrs} = d_{pqrs} - \delta_{qr} D_{ps}, \tag{40}$$

as

$$E_0 = \sum_{pq} h_{pq} D^{(1)}_{pq} + \frac{1}{2} \sum_{pqrs} (pq \,|\, rs)\, D^{(2)}_{pqrs}. \tag{41}$$

Then, due to the two-particle nature of the electron interaction functional given in eq. (20), the contraction of the 2-RDM matrix components, $D^{(2)}_{pqrs}$, with two-electron integrals $(pq \,|\, rs)$, the electronic repulsion energy E_{ee} may be approximated as

$$E_{\text{ee}}[\gamma] = \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs}[\{n_t\}] \langle pq \,|\, rs \rangle, \tag{42}$$

where the 2-RDM is formally defined as

$$D^{(2)}_{pqrs} = \left\langle 0 \,\middle|\, a^\dagger_r a^\dagger_s a_q a_p \,\middle|\, 0 \right\rangle. \tag{43}$$

Therefore, the 2-RDM is formally a functional of the 1-RDM.

The elements of $\mathbf{D^{(2)}}$ are not all independent because of the anticommutation relations between the creation and annihilation operators

$$D^{(2)}_{pqrs} = -D^{(2)}_{rqps} = -D^{(2)}_{psrq} = D^{(2)}_{rspq}. \tag{44}$$

Also, in accordance with the Pauli principle

$$D^{(2)}_{pqps} = D^{(2)}_{pqrq} = D^{(2)}_{pqpq} = 0. \tag{45}$$

The two-electron density matrix can be rewritten as a $m(m-1)/2 \times m(m-1)/2$ matrix, $\mathbf{T}$

$$T_{pq,rs} = \left\langle 0 \,\middle|\, a^\dagger_p a^\dagger_q a_s a_r \,\middle|\, 0 \right\rangle, \quad p > q,\ r > s, \tag{46}$$

with composite indices pq, composing a subset of $\mathbf{D^{(2)}}$ by a reordering of the middle indices

$$T_{pq,rs} = D^{(2)}_{prqs}, \quad p > q,\ r > s. \tag{47}$$

The matrix $\mathbf{T}$ is also Hermitian and, therefore, symmetric for real wave functions. Furthermore, it is positive semidefinite since its elements are either zero or inner products of states in $F(m, n-2)$.

The diagonal elements of $\mathbf{T}$, considering that $p > q$ and introducing the ON operators, are given by

$$\omega_{pq} = T_{pq,pq} = \left\langle 0 \,\middle|\, a^\dagger_p a^\dagger_q a_q a_p \,\middle|\, 0 \right\rangle = \langle 0 \,|\, n_p n_q \,|\, 0 \rangle, \tag{48}$$

which can be interpreted as simultaneous occupations of pairs of spin orbitals from the part of the wave function where the spin orbitals φ_p and φ_q are simultaneously occupied. It can be simply denoted as pair occupations, and fulfill the following conditions:

1. The simultaneous occupation of a given spin-orbital cannot be greater than that of the individual spin orbitals

$$0 \leq \omega_{pq} \leq \min[\omega_p, \omega_q] \leq 1. \tag{49}$$

2. The sum of all pair occupations ω_{pq} is equal to the number of electron pairs in the system

$$\mathrm{tr}\left[\mathbf{T}\right] = \sum_{p>q} \langle 0 \,|\, n_p n_q \,|\, 0 \rangle = \frac{1}{2} \sum_{pq} \langle 0 \,|\, n_p n_q \,|\, 0 \rangle - \frac{1}{2} \sum_{p} \langle 0 \,|\, n_p \,|\, 0 \rangle = \frac{1}{2} n \left(n-1\right). \tag{50}$$

The $\mathbf{T}$ matrix for a state with a single ON vector, $|k\rangle$, has a straightforward diagonal form and may be constructed directly from the one- electron density matrix as

$$T^{|k\rangle}_{pq,rs} = D^{|k\rangle}_{pq} D^{|k\rangle}_{qs}. \tag{51}$$

Similarly, the one-electron density matrix can be used to obtain the expectation value of any one or two-electron operator.

Also, the 1-RDM can be reconstructed from the 2-RDM by taking the trace of the 2-RDM over one of the indices, i.e. summing over all the possible remaining electrons after selecting one

$$D^{(1)}_{pq} = \frac{1}{N-1} \sum_{r} D^{(2)}_{prqr}. \tag{52}$$

The picture of an uncorrelated description of the electronic system, in which the simultaneous occupations of pairs of spin orbitals are merely the products of the individual occupations, is compatible with this result. In the case of a general electronic state containing several ON vectors, $\mathbf{T}$ is generally non-diagonal and cannot be produced directly from the elements of the one electron density matrix. As demonstrated for the one-electron density matrix in eq. (37), $\mathbf{D^{(2)}}$ can be diagonalized in practice using the spectral decomposition.

Therefore, it can be stated that the one-electron density matrix probes the individual occupancies of the spin orbitals and describes how the n electrons are distributed among the m spin orbitals, whereas the two-electron density matrix probes the simultaneous occupations of the spin orbitals and describes how the $n\left(n-1\right)/2$ electron pairs are distributed among the $m\left(m-1\right)/2$ spin-orbital pairs [1].

1.4 Equivalence between spin-orbital and coordinate representations

In this section, the equivalence relations between first and second quantization formalisms for the density matrices are established.

The one-electron density matrix in the spin-orbital representation was introduced in second quantization for the evaluation of the expectation values of one-electron operators in the form

$$\langle 0 \,|\, \hat{g} \,|\, 0 \rangle = \sum_{pq} D^{(1)}_{pq} g_{pq}, \tag{53}$$

with the g_{pq} integrals

$$g_{pq} = \int \varphi_p\left(\mathbf{x}_1\right)^* g\left(\mathbf{x}_1\right) \varphi_q\left(\mathbf{x}_1\right) \mathrm{d}\mathbf{x}_1 \,. \tag{54}$$

Combining both, the 1-RDM in the coordinates representation given in eq. (9) can be written in terms of the one-electron density matrix in the spin-orbital representation given in eq. (30) via the

expansion theorem, as

$$\gamma\left(\mathbf{x}_1, \mathbf{x}_1'\right) = \sum_{pq} D_{pq}^{(1)} \varphi_p^*\left(\mathbf{x}_1'\right) \varphi_q\left(\mathbf{x}_1\right). \tag{55}$$

Similarly, the following relationship between the two-electron density matrix in the coordinate representation (eq. (10)) and that in the spin-orbital representation (eq. (40)) may be established

$$\Gamma\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2'\right) = \frac{1}{2} \sum_{pqrs} D_{pqrs}^{(2)} \varphi_p^*\left(\mathbf{x}_1'\right) \varphi_q\left(\mathbf{x}_1\right) \varphi_r^*\left(\mathbf{x}_2'\right) \varphi_s\left(\mathbf{x}_2\right). \tag{56}$$

2 Electron repulsion functional

In most approximations proposed so far, $E_{\mathrm{ee}}[\gamma]$ is an explicit function of the occupation numbers and the natural spin-orbitals.

There are two cases where the exact forms of $E_{\mathrm{ee}}[\gamma]$ are known:

1. **n-electron noninteracting systems**: the 1-RDM corresponding to a single determinant wavefunction is idempotent, which implies integer (0 or 1) values of the natural occupation numbers

$$\hat{\gamma}^2 = \hat{\gamma} \Leftrightarrow n_p = 0 \vee n_p = 1 \quad \forall_p. \tag{57}$$

In this case, a 2-RDM is defined for a general wavefunction, Ψ, as

$$\Gamma\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2'\right) = n(n-1) \int \cdots \int \Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_n\right) \Psi^*\left(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_n\right) \mathrm{d}\mathbf{x}_3 \cdots \mathrm{d}\mathbf{x}_n, \tag{58}$$

which is explicitly expressible in terms of 1-RDM if the wavefunction takes the form of a Slater determinant

$$\Gamma\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2'\right) = \gamma\left(\mathbf{x}_1, \mathbf{x}_1'\right) \gamma\left(\mathbf{x}_2, \mathbf{x}_2'\right) - \gamma\left(\mathbf{x}_1, \mathbf{x}_2'\right) \gamma\left(\mathbf{x}_2, \mathbf{x}_1'\right). \tag{59}$$

The electron interaction functional corresponding to such a noninteracting 2-RDM reads

$$E_{\mathrm{ee}}^{\mathrm{HF}}[\gamma] = E_{\mathrm{H}}[\gamma] + E_{\mathrm{x}}[\gamma], \tag{60}$$

referred to as the Hartree-Fock functional as the HF equations' solution coincides with an idempotent density matrix that results from functional optimization [13]. The Hartree functional, E_{H}, describes the classical part of electron interaction

$$E_{\mathrm{H}}[\gamma] = \frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}) \gamma(\mathbf{x}', \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}', \tag{61}$$

whereas the exchange functional, E_{x}, reads

$$E_{\mathrm{x}}[\gamma] = -\frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}'. \tag{62}$$

Using the Hartree-Fock approximation stated in eq. (59), where Γ in the representation of the

natural spin-orbitals is given solely in terms of the occupation numbers

$$\Gamma^{\mathrm{HF}}_{pqrs} = n_p n_q \left(\delta_{pr}\delta_{qs} - \delta_{ps}\delta_{qr}\right), \tag{63}$$

and assuming that the elements of Γ are functions of the natural occupation numbers, $\{n_p\}$, and the basis set is formed by natural spin-orbitals, $\{\varphi_p\}$, the entire dependence of E_{ee} on φ_p is included in two-electron integrals.

2. **Two-electron closed-shell system**: an interacting two-electron species.

   The exact density matrix functional for a two-electron system is known [14, 15].

   Based on the work of Löwdin and Shull (LS) [16], a Slater-determinant-expansion of a singlet wavefunction (assumed to be real-valued) in the natural spin-orbitals basis $\{\varphi_p\}$ is entirely given by *diagonal* determinants composed of the spin-orbitals that share spatial parts

$$\psi^{\mathrm{LS}} = \sum_p c_p \left|\varphi_p \varphi_{\bar{p}}\right|, \tag{64}$$

   where $|\varphi_p\varphi_{\bar{p}}|$ indicates a normalized Slater determinant and p and $\bar{p}$ are spin-orbitals of opposite spin. The normalization of ψ^{LS} imposes that $\sum_p c_p^2 = 1$.

   This wavefunction provides the 1-RDM directly in its spectral representation, implying that the squares of the expansion coefficients are just the natural occupation numbers

$$n_p = c_p^2 \quad \forall_p. \tag{65}$$

   The energy is given by

$$E = \left\langle \psi^{\mathrm{LS}} \middle| \hat{H} \middle| \psi^{\mathrm{LS}} \right\rangle = \sum_p c_p^2 h_{pp} + \frac{1}{2}\sum_{pq} c_p c_q \langle pp \,|\, qq\rangle, \tag{66}$$

   assuming that the coefficients corresponding to spin-orbitals of opposite spins and same spatial parts are equal.

   By minimizing the energy with respecto to $\{c_p\}$ and $\{\varphi_p\}$, an exact electron interaction density matrix functional can be immediately written as

$$E^{\mathrm{LS}}_{\mathrm{ee}}[\gamma] = \frac{1}{2}\min_{\{f_q\}} \sum_{pq} f_p f_q \sqrt{n_p n_q}\, \langle pq \,|\, qp\rangle, \tag{67}$$

   with

$$f_p = \pm 1 \quad \forall_p, \tag{68}$$

   and $\langle pp \,|\, qq\rangle = \langle pq \,|\, qp\rangle$, as the orbitals are real.

   For two-electron atoms and molecules in equilibrium geometry, it is known that the sign of the factor f_1 corresponding to the highest occupation n_1 is predominantly opposite to the signs of all other factors corresponding to weakly occupied $\left(n_p < \frac{1}{2}\right)$ orbitals [14].

There are known cases when this condition is violated [14, 17–19], in which a two-electron functional that depends explicitly on the occupation numbers is defined as

$$\tilde{E}_{\mathrm{ee}}^{\mathrm{LS}}[\gamma] = \frac{1}{2}\sum_{pq} G_{pq}^{\mathrm{LS}} \langle pq \,|\, qp \rangle \,, \tag{69}$$

with

$$G_{pq}^{\mathrm{LS}} = \begin{cases} n_p & p = q \\ -\sqrt{n_p n_q} & p = 1,\ q > 1 \text{ or } p > 1,\ q = 1 \\ \sqrt{n_p n_q} & \text{otherwise} \end{cases} , \tag{70}$$

which, although not always fully equivalent to the exact LS functional given in eq. (67), is a good approximation.

Additionally, the LS functional has been extended to include all determinants resulting from diagonal double, diagonal quadruple, etc. excitations in the more general closed-shell n (even) electron ansatz. For systems for which a set of the natural spin-orbitals can be divided into *inner* orbitals, which are localized on atoms and have occupancies close to 1, and *outer* orbitals, which include a bonding orbital and all weakly occupied orbitals, the extended Löwdin- Shull (ELS) functional [20, 21] is applicable. In order to provide a balanced description of the dynamic and static correlation, it has been developed to treat only molecules with a single bond and no lone pairs.

Therefore, exact density matrix functionals for an uncorrelated and a strongly correlated electron pair are known.

2.1 Approximations for E_{ee}

The first approximate density matrix functional was developed by Müller [22] and, independently, by Buijse and Baerends [23, 24]. It was later corrected resulting in the BB-corrected (BBC) functionals [25]

$$E_{\mathrm{ee}}^{\mathrm{BBC}}[\gamma] = \frac{1}{2}\sum_{pq} n_p n_q \langle pp \,|\, qq \rangle + \frac{1}{2}\sum_{pq} G_{pq}^{\mathrm{BBC}} \langle pq \,|\, qp \rangle \,, \tag{71}$$

where the G_{pq}^{BBC} factor of the exchange-correlation functional depends on the occupation numbers. The first correction reads

$$G_{pq}^{\mathrm{BBC1}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -\sqrt{n_p n_q} & \text{otherwise}, \end{cases} \tag{72}$$

where $p, q \in W$ means that the spin-orbitals p, q belong to the set of weakly occupied spin-orbitals, i.e. orbitals with $n_p < \frac{1}{2}$ and $n_q < \frac{1}{2}$, and $p, q \in S$ refer to strongly occupied spin-orbitals for $n_p, n_q > \frac{1}{2}$. The symbol $\wedge$ stands for the logical *and*.

The drawback of the BBC1 functional is that it overbinds diatomic molecules, indicating a need for further repulsive corrections [25].

The BBC2 functional improved BBC1 by addressing the interaction between two strongly occupied

orbitals as

$$G_{pq}^{\mathrm{BBC2}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -\sqrt{n_p n_q} & \text{otherwise}, \end{cases} \tag{73}$$

In the BBC3 functional, corrections were included for the interaction between a pair of bonding and antibonding (frontier) spinorbitals. Additionally, BBC3 eliminated self-interaction effects from all orbitals except the frontier ones.

$$G_{pq}^{\mathrm{BBC3}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ \sqrt{n_p n_q} & (p \in W \wedge q \in F_W) \vee (p \in F_W \wedge q \in W), \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S \wedge q \in F) \vee (p \in F \wedge q \in S), \\ -n_p^2 & p = q \wedge p \notin F, \\ -\sqrt{n_p n_q} & \text{otherwise}, \end{cases} \tag{74}$$

where $p \in F_W$ refers to a weakly occupied frontier orbital. The symbol $\vee$ stands for the logical *or*.

Over the practical difficulty of the need to select bonding and antibonding orbitals, BBC3 accounts for both dynamic and static correlation, providing accurate potential energy and recovering most of the correlation energy. This practical difficulty has been addressed by attempting to automate it with functions such as AC3 proposed by Rohr *et al.* [26].

One found issue is that, when applied to systems with large number of electrons, there is the possibility of degenerate bonding and antibonding orbitals which, if selected as bonding or antibonding, break the symmetry of the molecule. In order to avoid this issue, the modification by Lathiotakis and Marques [27] is used here. The S set is subdivided into two subsets: the subset S_b for the degenerate bonding orbitals and the subset S_c for the rest. The W set is subdivided into W_a for the degenerate antibonding orbitals and W_h for the rest weakly occupied orbitals

$$G_{pq}^{\mathrm{BBC3}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S_c \wedge q \in W_a) \vee (p \in W_a \wedge q \in S_c), \\ -n_p^2 & p \neq q \wedge p, q \in S_c \cup W_h, \\ -\sqrt{n_p n_q} & \text{otherwise}, \end{cases} \tag{75}$$

where the symbol $\cup$ stands for the union of two sets.

2.2 Construction of 2-RDM in terms of 1-RDM

Assuming the cumulant expansion of 2-RDM [28] which consists of writing Γ as the antisymmetrized product of γ and the cumulant part, λ, being a functional of γ

$$\Gamma_{pqrs} = n_p n_q \left(\delta_{pr}\delta_{qs} - \delta_{ps}\delta_{qr}\right) + \lambda_{pqrs}\left[\gamma\right], \tag{76}$$

one-electron density matrix functionals can be developed by finding approximations for the cumulant part imposing known conditions which the exact cumulant satisfies.

(...)

Duda: pairs of coupled orbitals para implementar PNOFi

Duda: qué funcionales más?

3 A possible new approximation

Because of Hohenberg-Kohn theorems, it should be possible to express E_0 in terms of $\mathbf{D^{(1)}}$. Then, it should be true that $\mathbf{D^{(2)}}$ can be written as

$$D^{(2)}_{pqrs} = \sum_{ijkl} C_{pqrs,ijkl} D^{(1)}_{ij} D^{(1)}_{kl}, \tag{77}$$

for a given coefficient $C_{pqrs,ijkl}$.

In principle, recalling eq. (40), a similar expression for d_{pqrs} should also hold

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} D^{(1)}_{ij} D^{(1)}_{kl}. \tag{78}$$

Then, assuming that we choose a basis diagonalizing $\mathbf{D^{(1)}}$

$$D^{(1)}_{pq} = \nu_p \delta_{pq}, \tag{79}$$

such that d_{pqrs} in eq. (78) is rewritten as

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} = \sum_{ik} C'_{pqrs,iikk} \nu_i \nu_k. \tag{80}$$

The energy, expanding the $\frac{1}{2}(pq\,|\,rs)$ factor of eq. (28), reads

$$E_0 = \sum_{pq} h_{pq} D^{(1)}_{pq} + \frac{1}{2} \sum_{pqrs} (pq\,|\,rs)\, d_{pqrs} - \frac{1}{2} \sum_{pqrs} (pq\,|\,rs)\, D^{(1)}_{ps} \delta_{qr}, \tag{81}$$

and with eqs. (79) and (80)

$$E_0 = \sum_{pq} h_{pq} \nu_p \delta_{pq} + \frac{1}{2} \sum_{pqrs} \sum_{ijkl} (pq\,|\,rs)\, C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} - \frac{1}{2} \sum_{pqrs} (pq\,|\,rs)\, \nu_p \delta_{ps} \delta_{qr}. \tag{82}$$

Therefore, the energy is given by

$$E_0 = \sum_{p} h_{pp} \nu_p + \frac{1}{2} \sum_{pqrs} \lambda_{pqrs}\, (pq\,|\,rs) - \frac{1}{2} \sum_{pq} (pq\,|\,qp)\, \nu_p, \tag{83}$$

where

$$\lambda_{pqrs} = \sum_{ij} C'_{pqrs,iijj} \nu_i \nu_j. \tag{84}$$

To this point, no approximation has been made. In fact, λ_{pqrs} is simply d_{pqrs} in the chosen natural

basis.

A possible parametrization of $\boldsymbol{\lambda}$, proposed by Alfredo, is given as follows.

Looking at eq. (78), in which $\mathbf{D^{(2)}}$ is given by products of $\mathbf{D^{(1)}}$'s, and knowing that the electron-electron interaction energy is directly given by the product of $\mathbf{D^{(2)}}$ and the two-electron integrals (see eq. (42)), this energy functional could be splitted into Coulomb $(pp\,|\,qq)$ and Exchange $(pq\,|\,qp)$ contributions. And, so for, $\boldsymbol{\lambda}$

$$\lambda_{pqrs}\,(pq\,|\,rs) \leftarrow \tilde{\lambda}_{pqrs}\,(pp\,|\,qq) + \tilde{\lambda}_{pqrs}\,(pq\,|\,qp)\,. \tag{85}$$

Then, a possible parametrization for $\boldsymbol{\lambda}$ might be

$$\lambda_{pqrs} = \alpha_{pqrs} - \beta_{pqrs}, \tag{86}$$

where α_{pqrs} refer to type products of two $\mathbf{D^{(1)}}$ for the Coulomb contribution with given μ factors

$$\alpha_{pqrs} = \mu_{pq} D^{(1)}_{pq} \mu_{rs} D^{(1)}_{rs}, \tag{87}$$

and β_{pqrs} to the exchange contributions

$$\beta_{pqrs} = \mu'_{ps} D^{(1)}_{ps} \mu'_{rq} D^{(1)}_{rq}. \tag{88}$$

Therefore, in the natural basis, $\boldsymbol{\lambda}$ reads

$$\lambda_{pqrs} = \mu_{pr}\nu_p\nu_r\delta_{pq}\delta_{rs} - \mu'_{pq}\nu_p\nu_q\delta_{ps}\delta_{qr}. \tag{89}$$

Then, in eq. (83)

$$E_0 = \sum_p h_{pp}\nu_p + \frac{1}{2}\sum_{pqrs} \mu_{pr}\nu_p\nu_r\delta_{pq}\delta_{rs}\,(pq\,|\,rs) - \frac{1}{2}\sum_{pqrs} \mu'_{pq}\nu_p\nu_q\delta_{ps}\delta_{qr}\,(pq\,|\,rs) - \frac{1}{2}\sum_{pq}(pq\,|\,qp)\,\nu_p, \tag{90}$$

and

$$E_0 = \sum_p h_{pp}\nu_p + \frac{1}{2}\sum_{pq} \mu_{pq}\nu_p\nu_q\,(pp\,|\,qq) - \frac{1}{2}\sum_{pq} \mu'_{pq}\nu_p\nu_q\,(pq\,|\,qp) - \frac{1}{2}\sum_{pq}(pq\,|\,qp)\,\nu_p. \tag{91}$$

Therefore, the ground state energy for this parametrization is given by

$$\therefore E_0 = \sum_p h_{pp}\nu_p + \frac{1}{2}\sum_{pq} \nu_p\nu_q\left[\mu_{pq}\,(pp\,|\,qq) - \mu'_{pq}\,(pq\,|\,pq)\right] - \frac{1}{2}\sum_{pq}(pq\,|\,pq)\,\nu_p, \tag{92}$$

and the 2-RDM, recalling eq. (40), by

$$\therefore D^{(2)}_{pqrs} = \mu_{pr}\nu_p\nu_r\delta_{pq}\delta_{rs} - \mu'_{pq}\nu_p\nu_q\delta_{ps}\delta_{qr} - \nu_p\delta_{qr}\delta_{ps}. \tag{93}$$

This new parametrization for $\mathbf{D^{(2)}}$ has to be optimized in order for $\mathbf{D^{(2)}}$ to be N-representable which, in the molecular orbital basis, correspond to

- Occupation numbers, ν_p, are nonnegative and not greater than 2

$$0 \leq \nu_p \leq 2 \ \forall p, \tag{94}$$

- The normalization condition must be fulfilled, such that

$$\sum_i \nu_i = n, \tag{95}$$

and

$$\sum_{ij} D^{(2)}_{ijij} = n\left(n-1\right), \tag{96}$$

- $\mathbf{D^{(2)}}$ must be positive-semidefinite, i.e. the quadratic form $\mathbf{v^{\dagger}D^{(2)}v}$ must be possitive for any vector $\mathbf{v}$

$$\mathbf{D^{(2)}} \succeq 0 \Leftrightarrow \left\langle \Psi \middle| D^{(2)} \middle| \Psi \right\rangle \geq 0, \tag{97}$$

the eigenvalues of $\mathbf{D^{(2)}}$ must be possitive

There are more complex conditions, as the two- and three-index conditions [29]. Here, the main definitions for the two-index conditions are given as [30]:

- The $\mathcal{I}$ condition: the probability of finding a two-particle pair is larger than zero.
- The $\mathcal{Q}$ condition: the probability of finding a two-hole pair has to be larger than zero

$$\mathcal{Q} \succeq 0, \quad \mathcal{Q}_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \middle| a_\alpha a_\beta a^\dagger_\delta a^\dagger_\gamma \middle| \Psi_i \right\rangle, \tag{98}$$

which can be rewritten as the followin linear matrix mapping

$$\mathcal{Q}\left(\Gamma\right)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\beta\gamma}\delta_{\alpha\delta} + \Gamma_{\alpha\beta;\gamma\delta} - \left(\delta_{\alpha\gamma}\gamma_{\beta\delta} - \delta_{\alpha\delta}\gamma_{\beta\gamma} - \delta_{\beta\gamma}\gamma_{\alpha\delta} + \delta_{\beta\delta}\gamma_{\alpha\gamma}\right), \tag{99}$$

which, together with the $\mathcal{I}$ condition, already insures the Pauli principle.

- The $\mathcal{G}_1$ condition: the probability of finding a particle-hole pair must be larger than zero

$$\mathcal{G}_1 \succeq 0, \quad \left(\mathcal{Q}_1\right)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \middle| a^\dagger_\alpha a_\beta a^\dagger_\delta a_\gamma \middle| \Psi_i \right\rangle, \tag{100}$$

which can be rewritten using anticommutation relations as

$$\mathcal{G}_1\left(\Gamma\right)_{\alpha\beta;\gamma\delta} = \delta_{\beta\delta}\gamma_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta}.. \tag{101}$$

The combined conditions $\mathcal{IQG}_\infty$ are known as the standard two-index conditions, which already lead to very good approximations form some systems.

- The $\mathcal{G}_2$ condition: the probability of finding a hole-particle pair must be positive

$$\mathcal{G}_2 \succeq 0, \quad \left(\mathcal{Q}_2\right)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \middle| a_\alpha a^\dagger_\beta a_\delta a^\dagger_\gamma \middle| \Psi_i \right\rangle, \tag{102}$$

as a function of Γ

$$\mathcal{G}_2\left(\Gamma\right)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\beta}\gamma_{\gamma\delta} - \delta_{\gamma\delta}\gamma_{\alpha\beta} + \delta_{\alpha\gamma}\gamma_{\beta\delta} - \Gamma_{\alpha\delta;\gamma\beta}. \tag{103}$$

There are stronger conditions as the three-index conditions $\mathcal{T}_1\mathcal{T}_2\mathcal{T}_3$, the primed conditions [29, 31, 32] $\mathcal{G}'\mathcal{T}_2'$, and non-standard conditions [30].

This optimization would, idially, be done formally. However, it can be done variationally such that the variational parameters μ, μ' minimize the energy. This method, refered as v2DM, can be formally defined as a semidesemidefinite programming following the N-representability constraints [30].

Also, it can be done finding a function $Q\left(\nu_p, \nu_q, \nu_r, \nu_s\right)$ for the factors μ, μ' depending on occupation numbers using, for example, a Padé approximant or any other approximant. A general Padé approximant of order $[m/n]$ around a point $x = \nu_p\nu_q\nu_r\nu_s$ is the rational function

$$Q\left(\nu_p, \nu_q, \nu_r, \nu_s\right) = \frac{\sum_{j=0}^{m} a_j \nu_p^j \nu_q^j \nu_r^j \nu_s^j}{1 + \sum_{k=1}^{n} b_k \nu_p^k \nu_q^k \nu_r^k \nu_s^k} = \frac{a_0 + a_1\nu_p\nu_q\nu_r\nu_s + \cdots + a_m \nu_p^m \nu_q^m \nu_r^m \nu_s^m}{1 + b_1\nu_p\nu_q\nu_r\nu_s + \cdots + b_n \nu_p^n \nu_q^n \nu_r^n \nu_s^n}. \tag{104}$$

This approach has already been used to find a fully empirically function by Marques and Lathiotakis (ML) [33] using a Padé approximant depending on a variable $x = n_p n_q$.

4 Methodology & calculations

(...)

5 Results

(...)

6 Conclusions

(...)