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Abstract

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Objetives:

- 1. (...)

Resumen

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Objetivos:

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Contents

1	Introduction	4
1.1	Second quantization	4
1.2	Reduced Density Matrix Functional Theory	5
1.3	Properties in terms of the density matrices	6
1.4	Equivalence between spin-orbital and coordinate representations	10
2	Electron repulsion functional	11
2.1	Approximations for E_{ee}	13
3	A possible new approximation	15
4	Methodology & calculations	18
4.1	One- and two-electron integrals, 1-RDM and 2-RDM	19
4.2	Approximated 2-RDMs	21
4.3	Energy calculations	21
4.4	Minkowski distance	21
5	Results	22
6	Conclusions	22

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

$$n_p = a_p^\dagger a_p. \quad (1)$$

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

$$n_p |k\rangle = a_p^\dagger a_p |k\rangle = k_p |k\rangle. \quad (2)$$

The ON operators are Hermitian

$$n_p^\dagger = \left(a_p^\dagger a_p\right)^\dagger = a_p^\dagger a_p = n_p, \quad (3)$$

commute among themselves

$$n_p n_q |k\rangle = k_p k_q |k\rangle = k_q k_p |k\rangle = n_q n_p |k\rangle, \quad (4)$$

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

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

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

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

which returns the number of electrons in an ON vector

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

Also, the δ_{pq} operator is defined as

$$\delta_{pq} = a_p a_q^\dagger + a_q^\dagger a_p, \quad (8)$$

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 [Lwdin1955quantuma], 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

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = n \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_n) d\mathbf{x}_2 \cdots d\mathbf{x}_n, \quad (9)$$

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

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

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]

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

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-electron 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

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

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

$$\text{tr}[\gamma] = \sum_p \gamma_{pp} = \sum_p n_p = n. \quad (13)$$

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

$$0 \leq n_p \leq 1 \quad \forall_p. \quad (14)$$

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]

$$E_\nu^{\text{HK}}[\gamma] = \text{tr} [\hat{h}\hat{\gamma}] + \left\langle \Psi[\gamma] \left| \hat{V}_{\text{ee}} \right| \Psi[\gamma] \right\rangle, \quad (15)$$

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}_{ext} , and the kinetic energy, \hat{T}

$$\hat{h} = \hat{T} + \hat{V}_{\text{ext}}, \quad (16)$$

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

$$\hat{V}_{\text{ee}} = \sum_{i>j}^n \frac{1}{r_{ij}}. \quad (17)$$

This functional follows the variational principle

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

where $\nu\text{-rep}$ 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

$$E_{\text{ee}}^{\text{L}}[\gamma] = \min_{\Psi \rightarrow \gamma} \left\langle \Psi \left| \hat{V}_{\text{ee}} \right| \Psi \right\rangle, \quad (19)$$

and further extended to ensemble n -representable 1-RDMs (belonging to a set “ $n\text{-rep}$ ”) by Valone [10, 11], so the exact functional reads

$$E_{\text{ee}}[\gamma] = \min_{\Gamma^{(n)} \rightarrow \gamma} \text{tr} [\hat{\mathbf{H}}\hat{\Gamma}^{(n)}], \quad (20)$$

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 $\nu\text{-rep}$, pure-state n -representable, and ensemble n -representable ($n\text{-rep}$) 1-RDMs coincide for a given external potential, \hat{V}_{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

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

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, $E_{\text{ee}} [\gamma]$

$$E [\gamma] = E_{\text{oe}} [\gamma] + E_{\text{ee}} [\gamma]. \quad (22)$$

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

$$\hat{H} = \sum_{\sigma} \sum_{pq} h_{pq}^{\sigma\sigma} a_{p\sigma}^{\dagger} a_{q\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{pqrs} \langle p\sigma r\sigma' | q\sigma s\sigma' \rangle a_{p\sigma}^{\dagger} a_{r\sigma'}^{\dagger} a_{s\sigma'} a_{q\sigma}, \quad (23)$$

where σ refers to the spin components α, β .

For the sake of simplicity, spin components are omitted for the moment. Then, the electronic molecular Hamiltonian is written as

$$\hat{H} = \sum_{pq} h_{pq} a_p^{\dagger} a_q + \frac{1}{2} \sum_{pqrs} (pq | rs) a_p^{\dagger} a_q^{\dagger} a_s a_r. \quad (24)$$

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

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^{\dagger} a_{q\sigma}, \quad (25)$$

such that

$$[E_{pq}, E_{rs}] = \delta_{qr} E_{ps} - \delta_{ps} E_{qr}. \quad (26)$$

Then, the Hamiltonian can be written as

$$\hat{H} = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} (pq | rs) (E_{pq} E_{rs} - \delta_{qr} E_{ps}). \quad (27)$$

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

$$|0\rangle = \sum_k c_k |k\rangle, \quad \langle 0 | 0 \rangle = 1, \quad (28)$$

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

$$E_0 = \langle 0 | \hat{H} | 0 \rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} (pq | rs) (d_{pqrs} - \delta_{qr} D_{ps}), \quad (29)$$

where

$$d_{pqrs} = \langle 0 | E_{pq} E_{rs} | 0 \rangle, \quad (30)$$

and

$$D_{pq} = \langle 0 | E_{pq} | 0 \rangle \equiv D_{pq}^{(1)}, \quad (31)$$

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

$$D_{pq}^* = \langle 0 | a_p^\dagger a_q | 0 \rangle = \langle 0 | a_q^\dagger a_p | 0 \rangle = D_{qp}, \quad (32)$$

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 $F(m, n)$

$$\omega_p = D_{pp}^{(1)} = \langle 0 | n_p | 0 \rangle. \quad (33)$$

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

$$\langle k | n_p | k \rangle = k_p. \quad (34)$$

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

$$n_p | 0 \rangle = \sum_k k_p c_k | k \rangle, \quad (35)$$

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

$$\omega_p = \langle 0 | n_p n_p | 0 \rangle = \sum_k k_p |c_k|^2. \quad (36)$$

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

$$\text{tr } \mathbf{D}^{(1)} = \sum_p \omega_p = \sum_p \langle 0 | n_p | 0 \rangle = n. \quad (37)$$

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

$$\mathbf{D}^{(1)} = \mathbf{U} \lambda \mathbf{U}^\dagger. \quad (38)$$

The eigenvalues, λ_p , are real numbers

$$0 \leq \lambda_p \leq 1, \quad (39)$$

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

$$\sum_p \lambda_p = n. \quad (40)$$

A new set of spin orbitals, the natural spin orbitals, are obtained from the eigenvectors, the columns of \mathbf{U} , resulted from eq. (38).

Following the idea given in eq. (20) and with the definition of the one-electron density matrix given in eq. (31), eq. (29) can be further simplified introducing the *two-electron spin-orbital density matrix*

$$D_{pqrs}^{(2)} = d_{pqrs} - \delta_{qr} D_{ps}, \quad (41)$$

as

$$E_0 = \sum_{pq} h_{pq} D_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} D_{pqrs}^{(2)} (pq | rs), \quad (42)$$

and written explicitly with the spin components as

$$E_0 = \sum_{\sigma} \sum_{pq} h_{pq}^{\sigma\sigma} \gamma_{pq}^{\sigma\sigma} + \sum_{\sigma\sigma'} \sum_{pqrs} \Gamma_{pqrs}^{\sigma\sigma'\sigma\sigma'} \langle \psi_{p\sigma} \psi_{r\sigma'} | \psi_{q\sigma} \psi_{s\sigma'} \rangle. \quad (43)$$

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

$$E_{ee}[\gamma] = \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs} [\{n_t\}] \langle pq | rs \rangle, \quad (44)$$

where the 2-RDM is formally defined as

$$D_{pqrs}^{(2)} = \langle 0 | a_r^\dagger a_s^\dagger a_q a_p | 0 \rangle. \quad (45)$$

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

$$D_{pqrs}^{(2)} = -D_{rqp s}^{(2)} = -D_{psrq}^{(2)} = D_{rspq}^{(2)}. \quad (46)$$

Also, in accordance with the Pauli principle

$$D_{pqps}^{(2)} = D_{pqrq}^{(2)} = D_{pqpp}^{(2)} = 0. \quad (47)$$

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

$$T_{pq,rs} = \langle 0 | a_p^\dagger a_q^\dagger a_s a_r | 0 \rangle, \quad p > q, \quad r > s, \quad (48)$$

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

$$T_{pq,rs} = D_{prqs}^{(2)}, \quad p > q, \quad r > s. \quad (49)$$

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

$$\omega_{pq} = T_{pq,pq} = \langle 0 | a_p^\dagger a_q^\dagger a_q a_p | 0 \rangle = \langle 0 | n_p n_q | 0 \rangle, \quad (50)$$

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

$$0 \leq \omega_{pq} \leq \min[\omega_p, \omega_q] \leq 1. \quad (51)$$

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

$$\text{tr}[\mathbf{T}] = \sum_{p>q} \langle 0 | n_p n_q | 0 \rangle = \frac{1}{2} \sum_{pq} \langle 0 | n_p n_q | 0 \rangle = \frac{1}{2} \sum_p \langle 0 | n_p | 0 \rangle = \frac{1}{2} n(n-1). \quad (52)$$

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

$$T_{pq,rs}^{[k]} = D_{pq}^{[k]} D_{qs}^{[k]}. \quad (53)$$

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

$$D_{pq}^{(1)} = \frac{1}{N-1} \sum_r D_{prqr}^{(2)}. \quad (54)$$

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. (38), $\mathbf{D}^{(2)}$ 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 $n(n-1)/2$ electron pairs are distributed among the $m(m-1)/2$ 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

$$\langle 0 | \hat{g} | 0 \rangle = \sum_{pq} D_{pq}^{(1)} g_{pq}, \quad (55)$$

with the g_{pq} integrals

$$g_{pq} = \int \varphi_p(\mathbf{x}_1)^* g(\mathbf{x}_1) \varphi_q(\mathbf{x}_1) d\mathbf{x}_1. \quad (56)$$

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. (31) via the expansion theorem, as

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{pq} D_{pq}^{(1)} \varphi_p^*(\mathbf{x}'_1) \varphi_q(\mathbf{x}_1). \quad (57)$$

Similarly, the following relationship between the two-electron density matrix in the coordinate representation (eq. (10)) and that in the spin-orbital representation (eq. (41)) may be established

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = \frac{1}{2} \sum_{pqrs} D_{pqrs}^{(2)} \varphi_p^*(\mathbf{x}'_1) \varphi_q(\mathbf{x}_1) \varphi_r^*(\mathbf{x}'_2) \varphi_s(\mathbf{x}_2). \quad (58)$$

2 Electron repulsion functional

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

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

$$\hat{\gamma}^2 = \hat{\gamma} \Leftrightarrow n_p = 0 \vee n_p = 1 \quad \forall p. \quad (59)$$

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

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = n(n-1) \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_n) \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_n) d\mathbf{x}_3 \cdots d\mathbf{x}_n, \quad (60)$$

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

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1) \gamma(\mathbf{x}_2, \mathbf{x}'_2) - \gamma(\mathbf{x}_1, \mathbf{x}'_2) \gamma(\mathbf{x}_2, \mathbf{x}'_1). \quad (61)$$

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

$$E_{ee}^{\text{HF}}[\gamma] = E_{\text{H}}[\gamma] + E_{\text{x}}[\gamma], \quad (62)$$

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

$$E_H[\gamma] = \frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}) \gamma(\mathbf{x}', \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}', \quad (63)$$

whereas the exchange functional, E_x , reads

$$E_x[\gamma] = -\frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}'. \quad (64)$$

Using the Hartree-Fock approximation stated in eq. (61), where Γ in the representation of the natural spin-orbitals is given solely in terms of the occupation numbers

$$\Gamma_{pqrs}^{\text{HF}} = n_p n_q (\delta_{pr} \delta_{qs} - \delta_{ps} \delta_{qr}), \quad (65)$$

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

$$\psi^{\text{LS}} = \sum_p c_p |\varphi_p \varphi_{\bar{p}}|, \quad (66)$$

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

$$n_p = c_p^2 \quad \forall p. \quad (67)$$

The energy is given by

$$E = \langle \psi^{\text{LS}} | \hat{H} | \psi^{\text{LS}} \rangle = \sum_p c_p^2 h_{pp} + \frac{1}{2} \sum_{pq} c_p c_q \langle pp | qq \rangle, \quad (68)$$

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

By minimizing the energy with respect to $\{c_p\}$ and $\{\varphi_p\}$, an exact electron interaction density

matrix functional can be immediately written as

$$E_{\text{ee}}^{\text{LS}}[\gamma] = \frac{1}{2} \min_{\{f_p\}} \sum_{pq} f_p f_q \sqrt{n_p n_q} \langle pq | qp \rangle, \quad (69)$$

with

$$f_p = \pm 1 \quad \forall_p, \quad (70)$$

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 ($n_p < \frac{1}{2}$) 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

$$\tilde{E}_{\text{ee}}^{\text{LS}}[\gamma] = \frac{1}{2} \sum_{pq} G_{pq}^{\text{LS}} \langle pq | qp \rangle, \quad (71)$$

with

$$G_{pq}^{\text{LS}} = \begin{cases} n_p & p = q \\ -\sqrt{n_p n_q} & p = 1, q > 1 \text{ or } p > 1, q = 1, \\ \sqrt{n_p n_q} & \text{otherwise} \end{cases} \quad (72)$$

which, although not always fully equivalent to the exact LS functional given in eq. (69), 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]

$$E_{\text{ee}}^{\text{BBC}}[\gamma] = \frac{1}{2} \sum_{pq} n_p n_q \langle pp | qq \rangle + \frac{1}{2} \sum_{pq} G_{pq}^{\text{BBC}} \langle pq | qp \rangle, \quad (73)$$

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

$$G_{pq}^{\text{BBC1}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (74)$$

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

$$G_{pq}^{\text{BBC2}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (75)$$

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.

$$G_{pq}^{\text{BBC3}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ \sqrt{n_p n_q} & (p \in W \wedge q \in F_W) \vee (p \in F_W \wedge q \in W), \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S \wedge q \in F) \vee (p \in F \wedge q \in S), \\ -n_p^2 & p = q \wedge p \notin F, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (76)$$

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

$$G_{pq}^{\text{BBC3}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S_c \wedge q \in W_a) \vee (p \in W_a \wedge q \in S_c), \\ -n_p^2 & p \neq q \wedge p, q \in S_c \cup W_h, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (77)$$

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

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

$$D_{pqrs}^{(2)} = \sum_{ijkl} C_{pqrs,ijkl} D_{ij}^{(1)} D_{kl}^{(1)}, \quad (78)$$

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

In principle, recalling eq. (41), a similar expression for d_{pqrs} should also hold

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} D_{ij}^{(1)} D_{kl}^{(1)}. \quad (79)$$

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

$$D_{pq}^{(1)} = \nu_p \delta_{pq}, \quad (80)$$

such that d_{pqrs} in eq. (79) is rewritten as

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} = \sum_{ik} C'_{pqrs,ikk} \nu_i \nu_k. \quad (81)$$

The energy, expanding the $\frac{1}{2} (pq | rs)$ factor of eq. (29), reads

$$E_0 = \sum_{pq} h_{pq} D_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} (pq | rs) d_{pqrs} - \frac{1}{2} \sum_{pqrs} (pq | rs) D_{ps}^{(1)} \delta_{qr}, \quad (82)$$

and with eqs. (80) and (81)

$$E_0 = \sum_{pq} h_{pq} \nu_p \delta_{pq} + \frac{1}{2} \sum_{pqrs} \sum_{ijkl} (pq | rs) C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} - \frac{1}{2} \sum_{pqrs} (pq | rs) \nu_p \delta_{ps} \delta_{qr}. \quad (83)$$

Therefore, the energy is given by

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pqrs} \lambda_{pqrs} (pq | rs) - \frac{1}{2} \sum_{pq} (pq | qp) \nu_p, \quad (84)$$

where

$$\lambda_{pqrs} = \sum_{ij} C'_{pqrs,ij} \nu_i \nu_j. \quad (85)$$

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 λ , proposed by Alfredo, is given as follows.

Looking at eq. (79), 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. (44)), this energy functional could be splitted into Coulomb ($pp|qq$) and Exchange ($pq|qp$) contributions. And, so for, λ

$$\lambda_{pqrs} (pq|rs) \leftarrow \tilde{\lambda}_{pqrs} (pp|qq) + \tilde{\lambda}_{pqrs} (pq|qp). \quad (86)$$

Then, a possible parametrization for λ might be

$$\lambda_{pqrs} = \alpha_{pqrs} - \beta_{pqrs}, \quad (87)$$

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

$$\alpha_{pqrs} = \mu_{pq} D_{pq}^{(1)} \mu_{rs} D_{rs}^{(1)}, \quad (88)$$

and β_{pqrs} to the exchange contributions

$$\beta_{pqrs} = \mu'_{ps} D_{ps}^{(1)} \mu'_{rq} D_{rq}^{(1)}. \quad (89)$$

Therefore, in the natural basis, λ reads

$$\lambda_{pqrs} = \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} - \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr}. \quad (90)$$

Then, in eq. (84)

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pqrs} \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} (pq|rs) - \frac{1}{2} \sum_{pqrs} \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr} (pq|rs) - \frac{1}{2} \sum_{pq} (pq|qp) \nu_p, \quad (91)$$

and

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pq} \mu_{pq} \nu_p \nu_q (pp|qq) - \frac{1}{2} \sum_{pq} \mu'_{pq} \nu_p \nu_q (pq|qp) - \frac{1}{2} \sum_{pq} (pq|qp) \nu_p. \quad (92)$$

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

$$\therefore E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pq} \nu_p \nu_q [\mu_{pq} (pp|qq) - \mu'_{pq} (pq|pq)] - \frac{1}{2} \sum_{pq} (pq|pq) \nu_p, \quad (93)$$

and the 2-RDM, recalling eq. (41), by

$$\therefore D_{pqrs}^{(2)} = \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} - \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr} - \nu_p \delta_{qr} \delta_{ps}. \quad (94)$$

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 (MO) basis, correspond to

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

$$0 \leq \nu_p \leq 2 \quad \forall p, \quad (95)$$

- The normalization condition must be fulfilled, such that

$$\sum_i \nu_i = n, \quad (96)$$

and

$$\sum_{ij} D_{ijij}^{(2)} = n(n-1), \quad (97)$$

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

$$\mathbf{D}^{(2)} \succeq 0 \Leftrightarrow \langle \Psi | D^{(2)} | \Psi \rangle \geq 0, \quad (98)$$

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

There are more complex conditions, as the two- and three-index conditions [28]. Here, the main definitions for the two-index conditions [29] are given as:

- 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

$$\mathcal{Q} \succeq 0, \quad \mathcal{Q}_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \langle \Psi_i | a_\alpha a_\beta a_\delta^\dagger a_\gamma^\dagger | \Psi_i \rangle, \quad (99)$$

which can be rewritten as the following linear matrix mapping

$$\mathcal{Q}(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\beta\gamma} \delta_{\alpha\delta} + \Gamma_{\alpha\beta;\gamma\delta} - (\delta_{\alpha\gamma} \gamma_{\beta\delta} - \delta_{\alpha\delta} \gamma_{\beta\gamma} - \delta_{\beta\gamma} \gamma_{\alpha\delta} + \delta_{\beta\delta} \gamma_{\alpha\gamma}), \quad (100)$$

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

$$\mathcal{G}_1 \succeq 0, \quad (\mathcal{Q}_1)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \langle \Psi_i | a_\alpha^\dagger a_\beta a_\delta^\dagger a_\gamma | \Psi_i \rangle, \quad (101)$$

which can be rewritten using anticommutation relations as

$$\mathcal{G}_1(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\beta\delta} \gamma_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta}. \quad (102)$$

The combined conditions \mathcal{IQG}_1 are known as the standard two-index conditions, which already lead to very good approximations for some systems.

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

$$\mathcal{G}_2 \succeq 0, \quad (\mathcal{Q}_2)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \left| a_\alpha a_\beta^\dagger a_\delta a_\gamma^\dagger \right| \Psi_i \right\rangle, \quad (103)$$

as a function of Γ

$$\mathcal{G}_2(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\beta}\gamma_{\gamma\delta} - \delta_{\gamma\delta}\gamma_{\alpha\beta} + \delta_{\alpha\gamma}\gamma_{\beta\delta} - \Gamma_{\alpha\delta;\gamma\beta}. \quad (104)$$

There are stronger conditions as the three-index conditions $\mathcal{T}_1\mathcal{T}_2\mathcal{T}_3$, the primed conditions [28, 30, 31] $\mathcal{G}'\mathcal{T}'_2$, and non-standard conditions [29].

This optimization would, ideally, be done formally. One approach is to decompose the 2-RDM Γ_{pqrs} or, for simplicity, the packed matrix $\tilde{\Gamma}_{pq,rs}$ with composite indexes pq, rs . The objective is to define μ, μ' such that the N -representability conditions are satisfied. Any higher-order singular value decomposition (HOSVD) method as, for example, the Tucker decomposition [32, 33] could be used to decompose Γ or, simply, any singular value decomposition (SVD) method as the Cholesky decomposition [34] for $\tilde{\Gamma}$.

However, it can be done variationally such that the variational parameters μ, μ' minimize the energy. This method, referred as v2DM, can be formally defined as a semidesemidefinite programming (SDP) problem following the N -representability constraints [29].

Also, it can be done finding a function $Q(\nu_p, \nu_q, \nu_r, \nu_s)$ 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

$$Q(\nu_p, \nu_q, \nu_r, \nu_s) = \frac{\sum_{j=0}^m a_j \nu_p^j \nu_q^j \nu_r^j \nu_s^j}{1 + \sum_{k=1}^n b_k \nu_p^k \nu_q^k \nu_r^k \nu_s^k} = \frac{a_0 + a_1 \nu_p \nu_q \nu_r \nu_s + \dots + a_m \nu_p^m \nu_q^m \nu_r^m \nu_s^m}{1 + b_1 \nu_p \nu_q \nu_r \nu_s + \dots + b_n \nu_p^n \nu_q^n \nu_r^n \nu_s^n}. \quad (105)$$

This approach has already been used to find a fully empirically function by Marques and Lathiotakis (ML) [35] using a Padé approximant depending on a variable $x = n_p n_q$.

4 Methodology & calculations

The objective is to create a program to test the approximations described in this document. The intention is to establish a testing environment for future parametrization of the proposed approximation discussed in the previous section.

The entire program can be found on [Github](#). The user must be warned that the program is still in development and, at this point, not intended to be efficient.

The testing is performed by comparing properties dependent of the RDMs with CASSCF and FCI calculations. In this case, the ground state energy and the Minkowski distance, which serves as a direct metric for the approximated 2-RDMs.

4.1 One- and two-electron integrals, exact 1-RDM and 2-RDM

The one-electron integrals matrix, h_{pq} , is extracted from the AOONEINT file with the ONEHAMIL label from the Dalton software [36]. Leaving the technical parts behind, the lower triangular is readen in the atomic orbital (AO) basis packed by symmetry, and later unpacked to obtain the full matrix and symmetrized as $h_{ji} = h_{ij}$. It is converted from atomic orbital basis, \tilde{h}_{ab} , to the molecular orbital basis, h_{ij} , as

$$\mathbf{h} = \mathbf{C}^\dagger \tilde{\mathbf{h}} \mathbf{C} \implies h_{ij} = C_{ai}^\dagger \tilde{h}_{ab} C_{bj}, \quad (106)$$

where \mathbf{C} is the MO coefficients matrix.

The two-electron integrals matrix, $(pq|rs)$, is extracted from the MOTWOINT with the MOLTWOEL label already in the MO basis and written in the Mulliken (chemistry) notation, with the equivalence $(ij|kl) \equiv \langle ik|jl \rangle$ in the Dirac notation. Similarly, it is unpacked to full dimension and symmetrized considering the 8-fold symmetry

$$(ij|kl) = (ij|lk) = (ji|kl) = (ji|lk) = (kl|ij) = (kl|ji) = (lk|ij) = (lk|ji). \quad (107)$$

Then, along other data, the density matrices $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$ are extracted from the interface SIRIFC file similarly to the integrals matrices. Once symmytrized, since the density matrices are already in the (molecular) spacial orbitals, they are refered to as $\boldsymbol{\gamma}$ and $\boldsymbol{\Gamma}$.

For the CASSCF calculations, the complete 1-RDM is constructed by block matrices corresponding to each -inactive, active, virtual- subspace

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma^{i-i} & \gamma^{i-a} & \gamma^{i-v} \\ (\gamma^{i-a})^\dagger & \gamma^{a-a} & \gamma^{a-v} \\ (\gamma^{i-v})^\dagger & (\gamma^{a-v})^\dagger & (\gamma^{v-v})^\dagger \end{pmatrix}, \quad (108)$$

where i,a,v superindexes correspond to inactive, active and virtual orbitals, respectively. Also, $\boldsymbol{\gamma}^\dagger = \boldsymbol{\gamma}$ as all its elements are real.

Since the inactive orbitals are totally occupied, the inactive-inactive block matrix is a diagonal matrix with diagonal elements equal to the total occupation, with a value of two considering double occupation

$$\gamma_{ij}^{i-i} = 2\delta_{ij} \implies \boldsymbol{\gamma}^{i-i} = 2\mathbf{I}, \quad (109)$$

where \mathbf{I} is the identity matrix. Then, $\boldsymbol{\gamma}^{i-i}$ is already symmetric.

The active-active block matrix is the one obtained from Dalton which is, similarly to \mathbf{h} , symmytrized as $D_{ji}^{(1)} = D_{ij}^{(1)} \equiv \gamma_{ij}^{a-a}$.

Since the virtual orbitals are not occupied, both the diagonal virtual-virtual block matrix and the crossed virtual-inactive and virtual-active block matrices are zero

$$\boldsymbol{\gamma}^{v-v} = \boldsymbol{\gamma}^{i-v} = \boldsymbol{\gamma}^{v-i} = 0, \quad (110)$$

and, also, the inactive-active block matrix is zero assuming that there is no direct correlation between

inactive and active orbitals

$$\gamma^{i-a} = 0. \quad (111)$$

Therefore, the complete 1-RDM given in eq. (108) reads

$$\gamma = \begin{pmatrix} 2\mathbf{I} & 0 & 0 \\ 0 & \gamma^{a-a} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (112)$$

Analogously, the complete 2-RDM must be constructed and symmetrized to be consistent with the 8-fold symmetry of the two-electron integrals (see eq. (107)). It must fulfill the following symmetry conditions

$$\Gamma_{\beta\alpha\gamma\delta} = \Gamma_{\alpha\beta\gamma\delta}, \quad \alpha\text{-}\beta \text{ swapping}, \quad (113)$$

$$\Gamma_{\beta\alpha\delta\gamma} = \Gamma_{\alpha\beta\gamma\delta}, \quad \gamma\text{-}\delta \text{ swapping}, \quad (114)$$

$$\Gamma_{\gamma\delta\alpha\beta} = \Gamma_{\alpha\beta\gamma\delta}, \quad \alpha\beta\text{-}\gamma\delta \text{ swapping}, \quad (115)$$

for any index $\alpha, \beta, \gamma, \delta$. To simplify the formulation, the definitions for the non-zero elements are directly given [37], where inactive orbitals are indexed with i, j, k, l and active orbitals with t, u, v, w .

The elements of the 2-RDM involving only inactive orbitals are given by

$$D_{ijkl}^{(2)} = 2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk}, \quad (116)$$

which are then symmetrized as

$$\Gamma_{ijkl} = \frac{1}{2} \left(D_{ijkl}^{(2)} + D_{jikl}^{(2)} \right), \quad (117)$$

fulfilling eqs. (113) to (115), $_{ijkl} = \Gamma_{jilk} = \Gamma_{lkij} = \Gamma_{ijkl}$.

The elements of the 2-RDM involving only active orbitals are obtained from Dalton, where a packed matrix $\tilde{D}_{tu,vw}^{(2)}$ with composite indexes tu, vw is constructed as half of the values obtained from Dalton¹ and then unpacked to full dimension $D_{tuvw}^{(2)}$. It should already be symmetrized by Dalton, $\Gamma_{tuvw} = \Gamma_{uvwt}$, and must fulfill $\Gamma_{utvw} = \Gamma_{tuwv} = \Gamma_{vwtu} = \Gamma_{tuvw}$.

The elements with two active-two inactive orbitals are proportional to the 1-RDM for the active orbitals and correspond to Coulomb and exchange terms. The Coulomb terms are given by

$$D_{ijtu}^{(2)} = D_{tuij}^{(2)} = 2\gamma_{tu}\delta_{ij}, \quad (118)$$

which are symmetrized as

$$\Gamma_{tuij} = \Gamma_{ijtu} = \frac{1}{2} \left(D_{tuij}^{(2)} + D_{ijtu}^{(2)} \right), \quad (119)$$

and fulfill $\Gamma_{utij} = \Gamma_{tují} = \Gamma_{ijtu} = \Gamma_{tuij}$.

And the exchange terms by

$$D_{ituj}^{(2)} = D_{tjiu}^{(2)} = -\gamma_{tu}\delta_{ij}, \quad (120)$$

¹A computational detail is that Dalton writes $\tilde{\mathbf{D}}^{(2)}$ multiplied by two to reduce the dimensions of the loops taking advantage of the symmetry of the integrals (see eq. (107)) and of $\tilde{\mathbf{D}}^{(2)}$, as $\tilde{D}_{tu,vw}^{(2)} = \tilde{D}_{vw,ut}^{(2)}$, to sum only over the lower triangular part of $\tilde{\mathbf{D}}^{(2)}$.

symmetrized as

$$\Gamma_{tjiu} = \Gamma_{jtiu} = \frac{1}{2} \left(D_{tjiu}^{(2)} + D_{jtiu}^{(2)} \right), \quad (121)$$

and fulfill $\Gamma_{utij} = \Gamma_{tuji} = \Gamma_{ijtu} = \Gamma_{tuij}$.

The 2 and -1 factors for the Coulomb term, Γ_{ijtu} (eq. (118)), and exchange, Γ_{iutj} (eq. (120)), differ in this case from the 1, $-\frac{1}{2}$ factors given by Maradzike [37].

4.2 Approximated 2-RDMs

The expression for the approximated 2-RDMs can be recovered, recalling eq. (44), from the expressions for the given approximated electron-electron interaction functional.

TODO: revisar indices para que esten en base a integrales en notacion Mulliken para respetar simetria con integrales

For the LS functional, eq. (71) can be rewritten as

$$E_{ee}^{LS} = \frac{1}{2} \sum_{pqrs} G_{pq}^{LS} \delta_{pr} \delta_{qs} \langle pq | rs \rangle, \quad (122)$$

and, by comparing it with eq. (44), the approximated 2-RDM for the LS approximation is directly recovered as

$$\Gamma_{pqrs}^{LS} = G_{pq}^{LS} \delta_{pr} \delta_{qs}. \quad (123)$$

where G_{pq}^{LS} is given by eq. (72).

The BBC functional given in eq. (73) can also be rewritten as

$$E_{ee}^{BBC}[\gamma] = \frac{1}{2} \sum_{pqrs} (n_p n_q \delta_{pq} \delta_{rs} + G_{pq}^{BBC} \delta_{qr} \delta_{ps}) \langle pq | rs \rangle, \quad (124)$$

resulting in the approximated 2-RDM

$$\Gamma_{pqrs}^{BBC} = n_p n_q \delta_{pq} \delta_{rs} + G_{pq}^{BBC} \delta_{qr} \delta_{ps}, \quad (125)$$

with G_{pq}^{BBC} given by eqs. (74) to (77) for BBC1, BBC2, BBC3 and BBC3M, respectively.

4.3 Energy calculations

The ground state energy, with eq. (42), is computed as

$$E_0 = \sum_{pq} h_{pq} \gamma_{pq} + \sum_{pqrs} \Gamma_{pqrs} (pq | rs) + V_{\text{nuc}}, \quad (126)$$

where V_{nuc} is the nuclear repulsion potential.

4.4 Minkowski distance

Also, a second metric is computed to directly compare the approximated 2-RDMs. Taking one element of one 2-RDM as a point in the high-dimensional 4D space, the Minkowski distance can be computed between a point in the 4D space given by the exact 2-RDM and a point by the approximated 2-RDM.

The Minkowski distance (metric) of order p for an approximated 2-RDM, $\tilde{\Gamma}$, with respect to the exact 2-RDM, Γ , is given by

$$d(\Gamma, \tilde{\Gamma}) = \left(\sum_{pqrs} |\Gamma_{pqrs} - \tilde{\Gamma}_{pqrs}|^p \right)^{\frac{1}{p}}, \quad (127)$$

which reduces to the Manhattan distance for $p = 1$, to the Euclidean distance for $p = 2$ and, in the limit, to the Chebyshev distance for $p \rightarrow \infty$.

Therefore, the Minkowski distance is a direct metric to test any approximated 2-RDM, resulting in a good approximation if $d \rightarrow 0$, and a bad approximation for larger d 's. In this sense, this metric has no value if only one approximated 2-RDM is tested, as this distance has to be compared with other distances in order to establish the quality of the approximation.

5 Results

(...)

6 Conclusions

(...)