

MÁSTER ERASMUS MUNDUS EN QUÍMICA
TEÓRICA Y MODELIZACIÓN COMPUTACIONAL
UNIVERSITAT DE VALENCIA

Trabajo Fin de Máster

Título

Autor:

José Antonio QUIÑONERO
GRIS

Tutor:

Alfredo SÁNCHEZ DE-MERÁS

Departamento de Química Física
Facultad de Química
Julio de 2024

Abstract

In this thesis, the application of Reduced Density Matrix Functional Theory (RDMFT) in the context of electronic structure calculations is explored. The primary objective is to create a working environment that enables the optimization of a potentially new parameterization proposed within this document. Therefore, the viability and accuracy of using one-particle (1-RDM) and two-particle reduced density matrices (2-RDM) in place of traditional wavefunction methods is investigated. Both exact RDMs, computed from the integration of the wavefunction, and approximated RDMs are studied.

A significant advantage of RDMFT over conventional wavefunction-based methods is its ability to handle static correlation effects efficiently, making it a promising approach for systems where these effects are pronounced. Additionally, the use of reduced density matrices simplifies the treatment of the kinetic energy term and avoids the need for introducing a fictitious non-interacting system, as required in Density Functional Theory (DFT).

Despite its potential, the application of RDMFT is currently limited to small systems due to the computational complexity associated with larger systems. This limitation stems from the intricate nature of constructing and managing higher-order density matrices and the challenges in ensuring their N -representability.

Future research directions include extending the methodologies proposed in this thesis to Time-Dependent Reduced Density Matrix Functional Theory (TDRDMFT), which would enable the study of dynamic processes in electronic systems. Moreover, significant theoretical advancements have been made over the past decades, particularly with the development of contracted Schrödinger equations and higher-order reduced density matrices, which promise to further enhance the applicability and robustness of RDMFT.

In conclusion, this work provides a comprehensive framework for employing RDMFT in electronic structure calculations, demonstrating its potential advantages and outlining the challenges that need to be addressed for broader application.

Objectives:

First: Create a program integrated with the Dalton software for the obtention of exact RDMs

Second: Validate available approximations for the electron repulsion functional in terms of the 2-RDM.

Third: Develop the formalism of a possible new approximation and propose possible parametrization and optimization methods.

Fourth: Create a framework for the construction, testing and deeper study of the 2-RDM, with the computation of RDM-derived properties, as the energy, comparable with the literature and/or software calculations, and direct metrics, as the Minkowski distance, for the direct comparison of RDMs.

Resumen

Objetivos:

- 1.

Contents

1	Introduction	5
1.1	Second quantization	5
1.2	Reduced Density Matrix Functional Theory	7
1.3	Properties in terms of the density matrices	8
1.4	Equivalence between spin-orbital and coordinate representations	14
2	Electron repulsion functional	14
2.1	Approximations for E_{ee}	17
3	A possible parametrization of the 2-RDM	18
4	Methodology & calculations	22
4.1	One- and two-electron integrals, exact 1-RDM and 2-RDM	23
4.2	Approximated 2-RDMs	25
4.3	Energy calculations	26
4.4	Minkowski distance	27
5	Results and discussion	28
6	Outlook and perspectives	30
7	Appendix	36

List of Acronyms

- RDMFT: Reduced Density Matrix Functional Theory
- 1-RDM: One-particle Reduced Density Matrix
- 2-RDM: Two-particle Reduced Density Matrix
- TDRDMFT: Time-Dependent Reduced Density Matrix Functional Theory
- DFT: Density Functional Theory
- MO: Molecular Orbital
- AO: Atomic Orbital
- CASSCF: Complete Active Space Self-Consistent Field
- MP2: Møller-Plesset perturbation theory of second order
- FCI: Full Configuration Interaction
- HF: Hartree-Fock
- NEPOLD: A keyword in Dalton software related to the wave functions
- SCF: Self-Consistent Field
- CAS: Complete Active Space

1 Introduction

Second quantization formalism is used in the document. Consequently, some useful definitions [1] are recalled in this section.

Also, Dirac (braket) notation is mainly used in the document except for section 4, where the Mulliken (chemistry) notation is used.

The two-electron integrals are given, in Dirac notation, by

$$\langle pq | rs \rangle = \iint \psi_p^* (\mathbf{r}_1) \psi_q^* (\mathbf{r}_2) \psi_r (\mathbf{r}_1) \psi_s (\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (1)$$

and in Mulliken notation by

$$(pq | rs) = \iint \psi_p^* (\mathbf{r}_1) \psi_q (\mathbf{r}_1) \psi_r^* (\mathbf{r}_2) \psi_s (\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (2)$$

with the equivalence

$$\langle pq | rs \rangle = (pr | qs). \quad (3)$$

Additionally, atomic units are used all throughout the document.

1.1 Second quantization

In second quantization, an abstract linear vector space, the *Fock* space, is introduced. Each determinant in this space is represented by an *occupation-number* (ON) *vector*, $|k\rangle$

$$|k\rangle = |k_1, k_2, \dots, k_M\rangle, \quad (4)$$

with $k_P = 1$ if P is an occupied orbitals and $k_P = 0$ if P is unoccupied.

Also, the *vacuum state* is defined as a vector in the subspace $F(M, 0)$ consisting of ON vectors with no electrons

$$|\text{vac}\rangle = |0_1, 0_2, \dots, 0_M\rangle, \quad \langle \text{vac} | \text{vac} \rangle = 1. \quad (5)$$

All operators and states can be constructed from a set of elementary creation and annihilation operators, $\{a^\dagger\}$, $\{a\}$. The creation operators are defined by the relations

$$a_P^\dagger |k_1, k_2, \dots, 0_P, \dots, k_M\rangle = \Theta_P^{[k]} |k_1, k_2, \dots, 1_P, \dots, k_M\rangle, \quad (6)$$

$$a_P^\dagger |k_1, k_2, \dots, 1_P, \dots, k_M\rangle = 0, \quad (7)$$

and the annihilation operators as

$$a_P |k_1, k_2, \dots, 0_P, \dots, k_M\rangle = 0, \quad (8)$$

$$a_P |k_1, k_2, \dots, 1_P, \dots, k_M\rangle = \Theta_P^{[k]} \delta_{k_P, 1} |k_1, k_2, \dots, 0_P, \dots, k_M\rangle, \quad (9)$$

with the phase factor $\Theta_P^{[k]}$

$$\Theta_P^{[k]} = \prod_{Q=1}^{P-1} (-1)^{k_Q}, \quad (10)$$

which $\Theta_P^{[k]} = 1$ for an even number of electrons in the spin-orbitals, $Q < P$, and $\Theta_P^{[k]} = -1$ for an odd number.

The creation and annihilation operators satisfy the following anticommutation rules

$$[a_p, a_q]_+ = a_p a_q + a_q a_p = 0, \quad (11)$$

$$[a_p^\dagger, a_q^\dagger]_+ = a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0, \quad (12)$$

$$[a_q, a_q^\dagger]_+ = a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}, \quad (13)$$

which guarantees that the Antisymmetry Principle is fulfilled.

For this set of creation and annihilation operators, the ON operators are defined as

$$n_p = a_p^\dagger a_p. \quad (14)$$

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

$$n_p |k\rangle = a_p^\dagger a_p |k\rangle = k_p |k\rangle. \quad (15)$$

The ON operators are Hermitian

$$n_p^\dagger = (a_p^\dagger a_p)^\dagger = a_p^\dagger a_p = n_p, \quad (16)$$

commute among themselves

$$n_p n_q |k\rangle = k_p k_q |k\rangle = k_q k_p |k\rangle = n_q n_p |k\rangle, \quad (17)$$

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

$$n_p^2 = n_p n_p = a_p^\dagger a_p a_p^\dagger a_p = a_p^\dagger (1 - a_p^\dagger a_p) a_p = a_p^\dagger a_p = n_p. \quad (18)$$

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

$$\hat{N} = \sum_{p=1}^m a_p^\dagger a_p, \quad (19)$$

which returns the number of electrons in an ON vector

$$\hat{N} |k\rangle = \sum_{p=1}^m k_p |k\rangle = n |k\rangle. \quad (20)$$

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 [lowdin1955quantu] 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

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = n \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_n) d\mathbf{x}_2 \cdots d\mathbf{x}_n, \quad (21)$$

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

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = \frac{n(n-1)}{2} \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_n) \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_n) d\mathbf{x}_3 \cdots d\mathbf{x}_n, \quad (22)$$

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. (21), allows for its spectral representation [3]

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_p n_p \varphi_p(\mathbf{x}) \varphi_p^*(\mathbf{x}'). \quad (23)$$

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

$$\int \varphi_p^*(\mathbf{x}) \varphi_q(\mathbf{x}) = \delta_{pq} \quad \forall_{p,q}. \quad (24)$$

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

$$\text{tr} [\gamma] = \sum_p \gamma_{pp} = \sum_p n_p = n. \quad (25)$$

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

$$0 \leq n_p \leq 1 \quad \forall_p. \quad (26)$$

1.3 Properties in terms of the density matrices

Gilbert theorem [5] states 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 has been proved that there is a 1-RDM functional [5, 6] such that the Hohenberg-Kohn theorems is extended to nonlocal potentials [5, 7]

$$E_\nu^{\text{HK}}[\gamma] = \text{tr} [\hat{h}\gamma] + \left\langle \Psi[\gamma] \left| \hat{V}_{\text{ee}} \right| \Psi[\gamma] \right\rangle, \quad (27)$$

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}

$$\hat{h} = \hat{T} + \hat{V}_{\text{ext}}, \quad (28)$$

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

$$\hat{V}_{\text{ee}} = \sum_{i>j}^n \frac{1}{r_{ij}}. \quad (29)$$

This functional follows the variational principle

$$E_\nu[\gamma] \geq E_0 \quad \forall_{\gamma \in \nu\text{-rep}}, \quad (30)$$

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

$$E_{\text{ee}}^{\text{L}}[\gamma] = \min_{\Psi \rightarrow \gamma} \left\langle \Psi \left| \hat{V}_{\text{ee}} \right| \Psi \right\rangle, \quad (31)$$

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

$$E_{\text{ee}}[\gamma] = \min_{\Gamma^{(n)} \rightarrow \gamma} \text{tr} \left[\hat{\mathbf{H}} \hat{\Gamma}^{(n)} \right], \quad (32)$$

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. (31), the Hohenberg-Kohn functional given in eq. (27), and that defined in eq. (32), respectively for ν -rep, pure-state n -representable, and ensemble n -representable (n -rep) 1-RDMs coincide for a given external potential, \hat{V}_{ext} [10, 12]. Thus, considering the variational principle given in eq. (30), it can be concluded that a ground state energy at minimum is produced by a functional defined for n -rep 1-RDMs

$$E_0 = \min_{\gamma \in n\text{-rep}} \left\{ \text{tr} \left[\hat{h} \hat{\gamma} \right] + E_{\text{ee}}[\gamma] \right\}. \quad (33)$$

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

$$E[\gamma] = E_{\text{oe}}[\gamma] + E_{\text{ee}}[\gamma]. \quad (34)$$

Indeed, eqs. (24) to (26) and (33) are the foundation for RDMFT.

Therefore, the 2-RDM is formally a functional of the 1-RDM, which agrees to Hohenberg-Kohn theorem.

Now, rewriting eq. (64) in the spin-orbital basis, the nonrelativistic and spin-free molecular electronic Hamiltonian is given by

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} \langle pq | rs \rangle a_p^\dagger a_q^\dagger a_s a_r. \quad (35)$$

Introducing now the *one-electron spin-orbital density matrix*

$$\bar{D}_{pq}^{(1)} = \langle 0 | a_p^\dagger a_q | 0 \rangle, \quad (36)$$

and the *two-electron spin-orbital density matrix*

$$\bar{D}_{pqrs}^{(2)} = \langle 0 | a_p^\dagger a_q^\dagger a_s a_r | 0 \rangle, \quad (37)$$

the ground state energy, from eq. (35), is given in the spin-orbital basis by

$$E_0 = \langle 0 | \hat{H} | 0 \rangle = \sum_{pq} h_{pq} \bar{D}_{pq}^{(1)} + \sum_{pqrs} \bar{D}_{pqrs}^{(2)} \langle pq | rs \rangle. \quad (38)$$

The one-electron spin-orbital density matrix is an Hermitian matrix, since

$$(\bar{D}_{pq}^{(1)})^\dagger = (\langle 0 | a_p^\dagger a_q | 0 \rangle)^\dagger = \langle 0 | a_q^\dagger a_p | 0 \rangle = \bar{D}_{qp}^{(1)}, \quad (39)$$

which is also symmetric for real wave functions.

Since the elements of $\bar{\mathbf{D}}^{(1)}$ 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 $\bar{\mathbf{D}}^{(1)}$, i.e. the expectation values of the occupation-number operators, n_p , in $F(m, n)$

$$\omega_p = \bar{D}_{pp}^{(1)} = \langle 0 | n_p | 0 \rangle. \quad (40)$$

The diagonal elements of $\bar{\mathbf{D}}^{(1)}$ 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

$$\langle k | n_p | k \rangle = k_p. \quad (41)$$

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

$$n_p | 0 \rangle = \sum_k k_p c_k | k \rangle, \quad (42)$$

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

$$\omega_p = \langle 0 | n_p n_p | 0 \rangle = \sum_k k_p |c_k|^2. \quad (43)$$

Recalling the N -representability conditions (eqs. (25) and (26)), 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

$$\text{tr } \bar{\mathbf{D}}^{(1)} = \sum_p \omega_p = \sum_p \langle 0 | n_p | 0 \rangle = n. \quad (44)$$

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

$$\bar{\mathbf{D}}^{(1)} = \mathbf{U} \boldsymbol{\lambda} \mathbf{U}^\dagger. \quad (45)$$

The eigenvalues, λ_p , are real numbers

$$0 \leq \lambda_p \leq 1, \quad (46)$$

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

$$\sum_p \lambda_p = n. \quad (47)$$

A new set of spin orbitals, the natural spin orbitals, are obtained from the eigenvectors, the columns of \mathbf{U} , resulted from eq. (45).

Now, the elements of $\mathbf{D}^{(2)}$ are not all independent because of the anticommutation

relations between the creation and annihilation operators

$$\bar{D}_{pqrs}^{(2)} = -\bar{D}_{rqp s}^{(2)} = -\bar{D}_{psrq}^{(2)} = \bar{D}_{rspq}^{(2)}. \quad (48)$$

Also, in accordance with the Pauli principle

$$\bar{D}_{pqps}^{(2)} = \bar{D}_{pqrq}^{(2)} = \bar{D}_{pqpq}^{(2)} = 0. \quad (49)$$

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

$$\bar{T}_{pq,rs} = \langle 0 | a_p^\dagger a_q^\dagger a_s a_r | 0 \rangle, \quad p > q, \quad r > s, \quad (50)$$

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

$$\bar{T}_{pq,rs} = \bar{D}_{prqs}^{(2)}, \quad p > q, \quad r > s. \quad (51)$$

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

$$\omega_{pq} = \bar{T}_{pq,pq} = \langle 0 | a_p^\dagger a_q^\dagger a_q a_p | 0 \rangle = \langle 0 | n_p n_q | 0 \rangle, \quad (52)$$

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

$$0 \leq \omega_{pq} \leq \min[\omega_p, \omega_q] \leq 1. \quad (53)$$

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

$$\text{tr}[\bar{\mathbf{T}}] = \sum_{p>q} \langle 0 | n_p n_q | 0 \rangle = \frac{1}{2} \sum_{pq} \langle 0 | n_p n_q | 0 \rangle - \frac{1}{2} \sum_p \langle 0 | n_p | 0 \rangle = \frac{1}{2} n(n-1). \quad (54)$$

There are more complex conditions, as the two- and three-index conditions [13]. Here, the main definitions for the two-index conditions [14] 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

$$\mathcal{Q} \succeq 0, \quad \mathcal{Q}_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \langle \Psi_i | a_\alpha a_\beta a_\delta^\dagger a_\gamma^\dagger | \Psi_i \rangle, \quad (55)$$

which can be rewritten as the following linear matrix mapping

$$\mathcal{Q}(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\beta\gamma}\delta_{\alpha\delta} + \Gamma_{\alpha\beta;\gamma\delta} - (\delta_{\alpha\gamma}\gamma_{\beta\delta} - \delta_{\alpha\delta}\gamma_{\beta\gamma} - \delta_{\beta\gamma}\gamma_{\alpha\delta} + \delta_{\beta\delta}\gamma_{\alpha\gamma}), \quad (56)$$

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

$$\mathcal{G}_1 \succeq 0, \quad (\mathcal{Q}_1)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \left| a_\alpha^\dagger a_\beta a_\delta^\dagger a_\gamma \right| \Psi_i \right\rangle, \quad (57)$$

which can be rewritten using anticommutation relations as

$$\mathcal{G}_1(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\beta\delta}\gamma_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta}. \quad (58)$$

The combined conditions $\mathcal{I}\mathcal{Q}\mathcal{G}_1$ 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

$$\mathcal{G}_2 \succeq 0, \quad (\mathcal{Q}_2)_{\alpha\beta;\gamma\delta} = \sum_i \omega_i \left\langle \Psi_i \left| a_\alpha a_\beta^\dagger a_\delta a_\gamma^\dagger \right| \Psi_i \right\rangle, \quad (59)$$

as a function of Γ

$$\mathcal{G}_2(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\beta}\gamma_{\gamma\delta} - \delta_{\gamma\delta}\gamma_{\alpha\beta} + \delta_{\alpha\gamma}\gamma_{\beta\delta} - \Gamma_{\alpha\delta;\gamma\beta}. \quad (60)$$

There are stronger conditions as the three-index conditions $\mathcal{T}_1\mathcal{T}_2\mathcal{T}_3$, the primed conditions [13, 15, 16] $\mathcal{G}'\mathcal{T}'_2$, and non-standard conditions [14].

Therefore, the $\bar{\mathbf{T}}$ 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

$$\bar{T}_{pq,rs}^{[k]} = (\bar{D}_{pr}^{(1)} \bar{D}_{qs}^{(1)})_{|k\rangle}. \quad (61)$$

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

Then, due to the two-particle nature of the electron interaction functional given in eq. (32), the contraction of the 2-RDM matrix components, $D_{pqrs}^{(2)}$, with two-electron integrals $\langle pq | rs \rangle$, the electronic repulsion energy E_{ee} may be approximated as

$$E_{ee}[\gamma] = \frac{1}{2} \sum_{pqrs} \Gamma_{pqrs}[\{n_t\}] \langle pq | rs \rangle. \quad (62)$$

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

$$\bar{D}_{pq}^{(1)} = \frac{1}{n-1} \sum_r \bar{D}_{prqr}^{(2)}. \quad (63)$$

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, $\bar{\mathbf{T}}$ 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. (45), $\bar{\mathbf{D}}^{(2)}$ 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].

From a computational point of view, when using restricted spin orbitals is more convenient to write the Hamiltonian as

$$\hat{H} = \sum_{\sigma} \sum_{pq} h_{pq}^{\sigma\sigma} a_{p\sigma}^{\dagger} a_{q\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{pqrs} (p\sigma q\sigma | r\sigma' s\sigma') a_{p\sigma}^{\dagger} a_{r\sigma'}^{\dagger} a_{s\sigma'} a_{q\sigma}, \quad (64)$$

where σ refers to the spin components α, β . The use of Mulliken notation should be noted.

And, defining the operators

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^{\dagger} a_{q\sigma}, \quad (65)$$

such that

$$[E_{pq}, E_{rs}] = \delta_{qr} E_{ps} - \delta_{ps} E_{qr}. \quad (66)$$

Then, the molecular electronic Hamiltonian in eq. (64) be written as

$$\hat{H} = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} (pq | rs) (E_{pq} E_{rs} - \delta_{qr} E_{ps}). \quad (67)$$

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

$$|0\rangle = \sum_k c_k |k\rangle, \quad \langle 0 | 0 \rangle = 1, \quad (68)$$

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

$$E_0 = \langle 0 | \hat{H} | 0 \rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} (pq | rs) (d_{pqrs} - \delta_{qr} D_{ps}), \quad (69)$$

where

$$d_{pqrs} = \langle 0 | E_{pq} E_{rs} | 0 \rangle, \quad (70)$$

and

$$D_{pq} = \langle 0 | E_{pq} | 0 \rangle \equiv D_{pq}^{(1)}, \quad (71)$$

are the elements (densities) of an $m \times m$ Hermitian matrix, the *one-electron density matrix*, $\mathbf{D}^{(1)}$, in the MO basis.

Following the idea given in eq. (32), eq. (69) can be further simplified introducing the *two-electron density matrix*

$$D_{pqrs}^{(2)} = d_{pqrs} - \delta_{qr} D_{ps}^{(1)}, \quad (72)$$

as

$$E_0 = \sum_{pq} h_{pq} D_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} (pq | rs) D_{pqrs}^{(2)}, \quad (73)$$

in the molecular orbitals basis.

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

$$\langle 0 | \hat{g} | 0 \rangle = \sum_{pq} D_{pq}^{(1)} g_{pq}, \quad (74)$$

with the g_{pq} integrals

$$g_{pq} = \int \varphi_p(\mathbf{x}_1)^* g(\mathbf{x}_1) \varphi_q(\mathbf{x}_1) d\mathbf{x}_1. \quad (75)$$

Combining both, the 1-RDM in the coordinates representation given in eq. (21) can be written in terms of the one-electron density matrix in the spin-orbital representation given in eq. (71) via the expansion theorem, as

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{pq} D_{pq}^{(1)} \varphi_p^*(\mathbf{x}'_1) \varphi_q(\mathbf{x}_1). \quad (76)$$

Similarly, the following relationship between the two-electron density matrix in the coordinate representation (eq. (22)) and that in the spin-orbital representation (eq. (72)) may be established

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = \frac{1}{2} \sum_{pqrs} D_{pqrs}^{(2)} \varphi_p^*(\mathbf{x}'_1) \varphi_q(\mathbf{x}_1) \varphi_r^*(\mathbf{x}'_2) \varphi_s(\mathbf{x}_2). \quad (77)$$

2 Electron repulsion functional

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

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

$$\hat{\gamma}^2 = \hat{\gamma} \Leftrightarrow n_p = 0 \vee n_p = 1 \quad \forall_p. \quad (78)$$

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

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = n(n-1) \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_n) \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_n) d\mathbf{x}_3 \cdots d\mathbf{x}_n, \quad (79)$$

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

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1) \gamma(\mathbf{x}_2, \mathbf{x}'_2) - \gamma(\mathbf{x}_1, \mathbf{x}'_2) \gamma(\mathbf{x}_2, \mathbf{x}'_1). \quad (80)$$

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

$$E_{\text{ee}}^{\text{HF}}[\gamma] = E_{\text{H}}[\gamma] + E_{\text{x}}[\gamma], \quad (81)$$

referred to as the Hartree-Fock functional as the HF equations' solution coincides with an idempotent density matrix that results from functional optimization [17]. The Hartree functional, E_{H} , describes the classical part of electron interaction

$$E_{\text{H}}[\gamma] = \frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}) \gamma(\mathbf{x}', \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}', \quad (82)$$

whereas the exchange functional, E_{x} , reads

$$E_{\text{x}}[\gamma] = -\frac{1}{2} \iint \frac{\gamma(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}'. \quad (83)$$

Using the Hartree-Fock approximation stated in eq. (80), where Γ in the representation of the natural spin-orbitals is given solely in terms of the occupation numbers

$$\Gamma_{pqrs}^{\text{HF}} = n_p n_q (\delta_{pr} \delta_{qs} - \delta_{ps} \delta_{qr}), \quad (84)$$

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 [18, 19].

Based on the work of Löwdin and Shull (LS) [20], 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

$$\psi^{\text{LS}} = \sum_p c_p |\varphi_p \varphi_{\bar{p}}|, \quad (85)$$

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

$$n_p = c_p^2 \quad \forall p. \quad (86)$$

The energy is given by

$$E = \langle \psi^{\text{LS}} | \hat{H} | \psi^{\text{LS}} \rangle = \sum_p c_p^2 h_{pp} + \frac{1}{2} \sum_{pq} c_p c_q \langle pp | qq \rangle, \quad (87)$$

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

$$E_{\text{ee}}^{\text{LS}}[\gamma] = \frac{1}{2} \min_{\{f_q\}} \sum_{pq} f_p f_q \sqrt{n_p n_q} \langle pq | qp \rangle, \quad (88)$$

with

$$f_p = \pm 1 \quad \forall p, \quad (89)$$

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 [18].

There are known cases when this condition is violated [18, 21–23], in which a two-electron functional that depends explicitly on the occupation numbers is defined as

$$\tilde{E}_{\text{ee}}^{\text{LS}}[\gamma] = \frac{1}{2} \sum_{pq} G_{pq}^{\text{LS}} \langle pq | qp \rangle, \quad (90)$$

with

$$G_{pq}^{\text{LS}} = \begin{cases} n_p & p = q \\ -\sqrt{n_p n_q} & p = 1, q > 1 \text{ or } p > 1, q = 1, \\ \sqrt{n_p n_q} & \text{otherwise} \end{cases} \quad (91)$$

which, although not always fully equivalent to the exact LS functional given in

eq. (88), 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 [24, 25] 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 [26] and, independently, by Buijse and Baerends [27, 28]. It was later corrected resulting in the BB-corrected (BBC) functionals [29]

$$E_{ee}^{\text{BBC}}[\gamma] = \frac{1}{2} \sum_{pq} n_p n_q \langle pp | qq \rangle + \frac{1}{2} \sum_{pq} G_{pq}^{\text{BBC}} \langle pq | qp \rangle, \quad (92)$$

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

$$G_{pq}^{\text{BBC1}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (93)$$

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 [29].

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

$$G_{pq}^{\text{BBC2}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (94)$$

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.

$$G_{pq}^{\text{BBC3}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ \sqrt{n_p n_q} & (p \in W \wedge q \in F_W) \vee (p \in F_W \wedge q \in W), \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S \wedge q \in F) \vee (p \in F \wedge q \in S), \\ -n_p^2 & p = q \wedge p \notin F, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (95)$$

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.* [30].

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 [31] 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

$$G_{pq}^{\text{BBC3M}} = \begin{cases} \sqrt{n_p n_q} & p \neq q \wedge p, q \in W, \\ -n_p n_q & p \neq q \wedge p, q \in S, \\ -n_p n_q & (p \in S_c \wedge q \in W_a) \vee (p \in W_a \wedge q \in S_c), \\ -n_p^2 & p \neq q \wedge p, q \in S_c \cup W_h, \\ -\sqrt{n_p n_q} & \text{otherwise,} \end{cases} \quad (96)$$

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

3 A possible parametrization of the 2-RDM

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

$$D_{pqrs}^{(2)} = \sum_{ijkl} C_{pqrs,ijkl} D_{ij}^{(1)} D_{kl}^{(1)}, \quad (97)$$

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

In principle, recalling eq. (72), a similar expression for d_{pqrs} should also hold

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} D_{ij}^{(1)} D_{kl}^{(1)}. \quad (98)$$

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

$$D_{pq}^{(1)} = \nu_p \delta_{pq}, \quad (99)$$

such that d_{pqrs} in eq. (98) is rewritten as

$$d_{pqrs} = \sum_{ijkl} C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} = \sum_{ik} C'_{pqrs,ii kk} \nu_i \nu_k. \quad (100)$$

The energy, expanding the $\frac{1}{2} (pq | rs)$ factor of eq. (69), reads

$$E_0 = \sum_{pq} h_{pq} D_{pq}^{(1)} + \frac{1}{2} \sum_{pqrs} (pq | rs) d_{pqrs} - \frac{1}{2} \sum_{pqrs} (pq | rs) D_{ps}^{(1)} \delta_{qr}, \quad (101)$$

and with eqs. (99) and (100)

$$E_0 = \sum_{pq} h_{pq} \nu_p \delta_{pq} + \frac{1}{2} \sum_{pqrs} \sum_{ijkl} (pq | rs) C'_{pqrs,ijkl} \nu_i \nu_k \delta_{ij} \delta_{kl} - \frac{1}{2} \sum_{pqrs} (pq | rs) \nu_p \delta_{ps} \delta_{qr}. \quad (102)$$

Therefore, the energy is given by

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pqrs} \lambda_{pqrs} (pq | rs) - \frac{1}{2} \sum_{pq} (pq | qp) \nu_p, \quad (103)$$

where

$$\lambda_{pqrs} = \sum_{ij} C'_{pqrs,ii jj} \nu_i \nu_j. \quad (104)$$

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 our group, is given as follows.

Looking at eq. (98), 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. (62)), this energy functional could be splitted into Coulomb $(pp | qq)$ and Exchange $(pq | qp)$ contributions. And, so for, $\boldsymbol{\lambda}$

$$\lambda_{pqrs} (pq | rs) \leftarrow \tilde{\lambda}_{pqrs} (pp | qq) + \tilde{\lambda}_{pqrs} (pq | qp). \quad (105)$$

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

$$\lambda_{pqrs} = \alpha_{pqrs} - \beta_{pqrs}, \quad (106)$$

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

$$\alpha_{pqrs} = \mu_{pq} D_{pq}^{(1)} \mu_{rs} D_{rs}^{(1)}, \quad (107)$$

and β_{pqrs} to the exchange contributions

$$\beta_{pqrs} = \mu'_{ps} D_{ps}^{(1)} \mu'_{rq} D_{rq}^{(1)}. \quad (108)$$

Therefore, in the natural basis, λ reads

$$\lambda_{pqrs} = \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} - \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr}. \quad (109)$$

Then, in eq. (103)

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pqrs} \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} (pq | rs) - \frac{1}{2} \sum_{pqrs} \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr} (pq | rs) - \frac{1}{2} \sum_{pq} (pq | qp) \nu_p, \quad (110)$$

and

$$E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pq} \mu_{pq} \nu_p \nu_q (pp | qq) - \frac{1}{2} \sum_{pq} \mu'_{pq} \nu_p \nu_q (pq | qp) - \frac{1}{2} \sum_{pq} (pq | qp) \nu_p. \quad (111)$$

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

$$\therefore E_0 = \sum_p h_{pp} \nu_p + \frac{1}{2} \sum_{pq} \nu_p \nu_q [\mu_{pq} (pp | qq) - \mu'_{pq} (pq | qp)] - \frac{1}{2} \sum_{pq} (pq | pq) \nu_p, \quad (112)$$

and the 2-RDM, recalling eq. (72), by

$$\therefore D_{pqrs}^{(2)} = \mu_{pr} \nu_p \nu_r \delta_{pq} \delta_{rs} - \mu'_{pq} \nu_p \nu_q \delta_{ps} \delta_{qr} - \nu_p \delta_{qr} \delta_{ps}. \quad (113)$$

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

$$0 \leq \nu_p \leq 2 \quad \forall p, \quad (114)$$

- The normalization condition must be fulfilled, such that

$$\sum_i \nu_i = n, \quad (115)$$

and

$$\sum_{ij} D_{ijij}^{(2)} = \frac{n(n-1)}{2}, \quad (116)$$

- $\mathbf{D}^{(2)}$ 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}

$$\mathbf{D}^{(2)} \succeq 0 \Leftrightarrow \langle \Psi | \mathbf{D}^{(2)} | \Psi \rangle \geq 0, \quad (117)$$

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

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

The optimization can be done variationally taking μ, μ' as variational parameters, which can be formally defined as a semidesemidefinite programming (SDP) problem following the N -representability constraints. Although another formulation has been used in this document, the optimization problem is, basically, the v2DM problem [14].

Therefore, the algorithm algorithm 1 is proposed. For a given set of orbitals, a 2-RDM is obtained with eq. (113) for the μ, ν parameters, along with the MO coefficients, C . Then

1. μ, ν are optimized such that the 2-RDM is constrained to the normalization conditions eqs. (115) and (116).
2. Purification.

Since, to this point, the N -representability conditions are not fulfilled, the 2-RDM is decomposed with the Cholesky decomposition algorithm until a block with negative diagonal elements is found, which correspond to the negative semidefinite block of 2-RDM. Therefore, the rest correspond to a new positive semidefinite 2-RDM, which must be re-scaled and normalized.

The 2-RDM is not positive semidefinite in the MO basis. Therefore, the purification process could very probably be more effective in the spin-orbital basis.

3. Reoptimize the orbitals with the rest of μ, ν fixed.

Basically, it results in a HF-like optimization.

Also, it can be solved 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

$$Q(\nu_p, \nu_q, \nu_r, \nu_s) = \frac{\sum_{j=0}^m a_j \nu_p^j \nu_q^j \nu_r^j \nu_s^j}{1 + \sum_{k=1}^n b_k \nu_p^k \nu_q^k \nu_r^k \nu_s^k} = \frac{a_0 + a_1 \nu_p \nu_q \nu_r \nu_s + \dots + a_m \nu_p^m \nu_q^m \nu_r^m \nu_s^m}{1 + b_1 \nu_p \nu_q \nu_r \nu_s + \dots + b_n \nu_p^n \nu_q^n \nu_r^n \nu_s^n}, \quad (118)$$

which is the best approximation to Q near x of a given order, as the approximant's power series agrees with the power series of the function it is approximating.

Algorithm 1 2-RDM optimization algorithm.

Require: $n, \mu, \nu, \mathbf{C}_{\text{MO}}$

```
1: for  $\mu_p \in \{\mu\}, \nu_p \in \{\nu\}$  do
2:   while  $\hat{\Gamma} \neq n(n-1)/2$  do
3:     Build  $\mathbf{\Gamma}$  with  $\mu_p, \nu_p$ 
4:     Compute the norm  $\hat{\Gamma} = \sum_{ij} \Gamma_{ijij}$ 
5:     Vary  $\mu_p, \nu_p$  constrained to  $\nu_p + \sum_{i \neq p} \nu_i = n$ 
6:   Decompose  $\mathbf{\Gamma} = \mathbf{L}\mathbf{L}^T \implies \Gamma_{ij,kl} = \sum_J L_{ij}^J L_{kl}^J$  by Cholesky:
7:   for  $J = 1, \text{range}(\mathbf{\Gamma})$  do
8:     Compute  $L_{ij}^J = \Gamma_{ij,J}^{(J-1)} \left( \Gamma_{J,J}^{(J-1)} \right)^{-1/2}$ 
9:     Update  $\mathbf{\Gamma}^{(J)} = \mathbf{\Gamma}^{(J-1)} - \mathbf{L}^J (\mathbf{L}^J)^T$ 
10:    if  $\Gamma_{J+1,J+1}^{(J)} < 0$  then
11:      Reorder  $\mathbf{\Gamma}^{(J)}$  to move  $\Gamma_{J+1,J+1}^{(J)}$  into the next diagonal element
12:    Extract the positive semidefinite block of  $\mathbf{\Gamma}, \tilde{\mathbf{\Gamma}}$ 
13:    Scale  $\tilde{\mathbf{\Gamma}}$  to full dimension and re-normalize,  $\mathbf{\Gamma} \leftarrow \tilde{\mathbf{\Gamma}}$ 
14:    Re-optimize  $\mathbf{C}_{\text{MO}}$  with fixed  $\mu_i \in \{\mu\} \ \forall_{i \neq p}$  and  $\nu_i \in \{\nu\} \ \forall_{i \neq p}$ 
15: return  $\mathbf{\Gamma}$ 
```

This approach has already been used to find a fully empirically function by Marques and Lathiotakis (ML) [35] using a [1/1] Padé approximant depending on a variable $x = n_p n_q$

$$f^{\text{ML}}(n_j, n_k) = x \frac{a_0 + a_1 x}{1 + b_1 x}, \quad (119)$$

where the parameters a_1 and b_1 are optimized to minimize the energy. The function is multiplied by x to ensure that the contribution of completely empty states ($n_j = 0$) to the exchange-correlation energy is zero. The functional is also forced to $f^{\text{ML}}(1) = 1$ by setting $a_0 = 1 + b_1 - a_1$ to recover the Hartree-Fock limit in the case of an idempotent density matrix.

A similar algorithm to algorithm 1 could be use to optimize a_1 and b_1 .

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, MP2 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.

It should be noted that, since the part of the program specified in this section is done in MO basis, both integrals and density matrices are expressed in Mulliken notation (see

eq. (2)).

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

The one-electron integrals matrix, h_{pq} , is extracted from the A00NEINT file with the ONEHAMIL label from the Dalton software[36]. Leaving the technical parts behind, the lower triangular is read 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

$$\mathbf{h} = \mathbf{C}^\dagger \tilde{\mathbf{h}} \mathbf{C} \implies h_{ij} = C_{ai}^\dagger \tilde{h}_{ab} C_{bj}, \quad (120)$$

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. Similarly, it is unpacked to full dimension and symmetrized considering the 8-fold symmetry

$$(ij|kl) = (ij|lk) = (ji|kl) = (ji|lk) = (kl|ij) = (kl|ji) = (lk|ij) = (lk|ji). \quad (121)$$

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 symmetrized, since the density matrices are already in the (molecular) spacial orbitals, they are referred 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

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma^{i-i} & \gamma^{i-a} & \gamma^{i-v} \\ (\gamma^{i-a})^\dagger & \gamma^{a-a} & \gamma^{a-v} \\ (\gamma^{i-v})^\dagger & (\gamma^{a-v})^\dagger & (\gamma^{v-v})^\dagger \end{pmatrix}, \quad (122)$$

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

$$\gamma_{ij}^{i-i} = 2\delta_{ij} \implies \boldsymbol{\gamma}^{i-i} = 2\mathbf{I}, \quad (123)$$

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} , symmetrized 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

$$\gamma^{v-v} = \gamma^{i-v} = \gamma^{v-i} = 0, \quad (124)$$

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

$$\gamma^{i-a} = 0. \quad (125)$$

Therefore, the complete 1-RDM given in eq. (122) reads

$$\gamma = \begin{pmatrix} 2\mathbf{I} & 0 & 0 \\ 0 & \gamma^{a-a} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (126)$$

In principle, γ is already diagonal, as γ^{a-a} is already diagonalized in Dalton. To generalize, a Jacobi diagonalization routine is implemented to diagonalize γ if it is not diagonal. But, an unitary transformation of the integral matrices with the eigenvectors in order to work with the natural orbitals basis has not been implemented yet. Then, in addition to the symmetry restrictions, the normalization condition (eq. (25)) is assured to be fulfilled.

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. (121))

$$\Gamma_{\alpha\beta\gamma\delta} = \Gamma_{\alpha\beta\delta\gamma} = \Gamma_{\beta\alpha\gamma\delta} = \Gamma_{\beta\alpha\delta\gamma} = \Gamma_{\gamma\delta\alpha\beta} = \Gamma_{\gamma\delta\beta\alpha} = \Gamma_{\delta\gamma\alpha\beta} = \Gamma_{\delta\gamma\beta\alpha}. \quad (127)$$

It must fulfill the following symmetry conditions

$$\Gamma_{\beta\alpha\gamma\delta} = \Gamma_{\alpha\beta\gamma\delta}, \quad \alpha \leftrightarrow \beta, \quad (128)$$

$$\Gamma_{\beta\alpha\delta\gamma} = \Gamma_{\alpha\beta\gamma\delta}, \quad \gamma \leftrightarrow \delta, \quad (129)$$

$$\Gamma_{\gamma\delta\alpha\beta} = \Gamma_{\alpha\beta\gamma\delta}, \quad \alpha\beta \leftrightarrow \gamma\delta, \quad (130)$$

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

$$D_{ijkl}^{(2)} = 2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk}, \quad (131)$$

which are then symmetrized as

$$\Gamma_{ijkl} = \frac{1}{2} \left(D_{ijkl}^{(2)} + D_{jikl}^{(2)} \right), \quad (132)$$

fulfilling eqs. (128) to (130), $\Gamma_{jikl} = \Gamma_{jilk} = \Gamma_{lkij} = \Gamma_{ijkl}$.

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

$$D_{ijtu}^{(2)} = D_{tuij}^{(2)} = 2\gamma_{tu}\delta_{ij}, \quad (133)$$

which are symmetrized as

$$\Gamma_{tuij} = \Gamma_{ijtu} = \frac{1}{2} \left(D_{tuij}^{(2)} + D_{ijtu}^{(2)} \right), \quad (134)$$

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

And the exchange terms by

$$D_{iutj}^{(2)} = D_{tjiu}^{(2)} = -\gamma_{tu}\delta_{ij}, \quad (135)$$

symmetrized as

$$\Gamma_{tjiu} = \Gamma_{jtiu} = \frac{1}{2} \left(D_{tjiu}^{(2)} + D_{jtiu}^{(2)} \right), \quad (136)$$

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

The 2 and -1 factors for the Coulomb term, Γ_{ijtu} (eq. (133)), and exchange, Γ_{iutj} (eq. (135)), differ in this case from the 1, $-\frac{1}{2}$ factors given by Maradzike [37].

In addition to the symmetry restrictions, the normalization conditions in eqs. (25) and (116) are assured to be fulfilled.

4.2 Approximated 2-RDMs

The expression for the approximated 2-RDMs can be recovered, recalling eq. (62), from the expressions for the given approximated electron-electron interaction functionals.

For the LS functional, eq. (90) can be rewritten as

$$E_{ee}^{LS} = \frac{1}{2} \sum_{pqrs} G_{pq}^{LS} \delta_{qr} \delta_{ps} (pq | rs), \quad (137)$$

and, by comparing it with eq. (62), the approximated 2-RDM for the LS approximation is directly recovered as

$$\Gamma_{pqrs}^{LS} = G_{pq}^{LS} \delta_{qr} \delta_{ps}. \quad (138)$$

where G_{pq}^{LS} is given by eq. (91).

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. (121)) 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 $\tilde{\mathbf{D}}^{(2)}$.

The BBC functional given in eq. (92) can also be rewritten as

$$E_{\text{ee}}^{\text{BBC}}[\gamma] = \frac{1}{2} \sum_{pqrs} (n_p n_q \delta_{pr} \delta_{qs} + G_{pq}^{\text{BBC}} \delta_{qr} \delta_{ps}) (pq | rs), \quad (139)$$

resulting in the approximated 2-RDM

$$\Gamma_{pqrs}^{\text{BBC}} = n_p n_q \delta_{pr} \delta_{qs} + G_{pq}^{\text{BBC}} \delta_{qr} \delta_{ps}, \quad (140)$$

with G_{pq}^{BBC} given by eqs. (93) to (96) for BBC1, BBC2, BBC3 and BBC3M, respectively.

Also, the approximated 2-RDMs are checked to be consistent to the symmetry restrictions (eq. (127)) and the normalization condition (eq. (116)).

4.3 Energy calculations

The ground state energy, with eq. (73), is computed as

$$E_0 = \sum_{pq} h_{pq} \gamma_{pq} + \sum_{pqrs} \Gamma_{pqrs} (pq | rs) + V_{\text{nuc}}, \quad (141)$$

where V_{nuc} is the nuclear repulsion potential.

In order to have a better understanding, the energy is splitted into the inactive, active-inactive (cross) and active contributions

$$E_0 = E_{\text{ina}} + E_{\text{i-a}} + E_{\text{act}} + V_{\text{nuc}}. \quad (142)$$

Considering the one- and two-electron contributions separately, as

$$E_0 = E_{\text{oe}} + E_{\text{ee}} + V_{\text{nuc}}, \quad (143)$$

the one-electron and two-electron functionals are splitted independently as

$$E_{\text{oe}} = E_{\text{oe}}^{\text{ina}} + E_{\text{oe}}^{\text{i-a}} + E_{\text{oe}}^{\text{act}}, \quad (144)$$

with

$$E_{\text{oe}}^{\text{ina}} = \sum_{ij}^{n_{\text{io}}} h_{ij} \gamma_{ij}, \quad (145)$$

$$E_{\text{oe}}^{\text{i-a}} = \sum_i^{n_{\text{io}}} \sum_t^{n_{\text{ao}}} h_{it} \gamma_{it}, \quad (146)$$

$$E_{\text{oe}}^{\text{act}} = \sum_{tu}^{n_{\text{ao}}} h_{tu} \gamma_{tu}, \quad (147)$$

where n_{io} and n_{ao} are the number of inactive and active orbitals, respectively. In this case, although, $E_{\text{oe}}^{\text{i-a}} = 0$.

And, similarly for the two-electron contributions

$$E_{ee} = E_{ee}^{\text{ina}} + E_{ee}^{\text{i-a}} + E_{ee}^{\text{act}} \quad (148)$$

with

$$E_{ee}^{\text{ina}} = \sum_{ijkl}^{n_{io}} P_{ijkl}, \quad (149)$$

$$E_{ee}^{\text{i-a}} = \sum_{ij}^{n_{io}} \sum_{tu}^{n_{ao}} (P_{ijtu} + P_{tuij} + P_{tjiu} + P_{jtiu} + P_{tjui} + P_{jtui}), \quad (150)$$

$$E_{ee}^{\text{act}} = \sum_{tuvw}^{n_{ao}} P_{tuvw}, \quad (151)$$

where $P_{ijkl} = \Gamma_{ijkl}(ij|kl)$ for the symmetrized Γ .

Lastly, the following relations between eqs. (144) and (148) with eq. (142) hold

$$E_{\text{ina}} = E_{\text{oe}}^{\text{i-a}} + E_{ee}^{\text{i-a}}, \quad (152)$$

$$E_{\text{i-a}} = E_{\text{oe}}^{\text{act}} + E_{ee}^{\text{i-a}}, \quad (153)$$

$$E_{\text{act}} = E_{\text{i-a}} + E_{ee}^{\text{act}} = E_{\text{oe}}^{\text{act}} + E_{ee}^{\text{i-a}} + E_{ee}^{\text{act}}. \quad (154)$$

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

$$d(\Gamma, \tilde{\Gamma}) = \left(\sum_{pqrs} |\Gamma_{pqrs} - \tilde{\Gamma}_{pqrs}|^p \right)^{\frac{1}{p}}, \quad (155)$$

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 $p \rightarrow \infty$. In practice, several orders should be tried for each case, looking for the order that results in larger differences between the distances that are being compared.

Similarly to the energy, the Minkowski distance can be splitted into inactive, active and cross contributions by adjusting the indexes

$$d(\Gamma, \tilde{\Gamma}) = d_{\text{ina}} + d_{\text{i-a}} + d_{\text{act}} = \left(\sum_{ijkl}^{n_{io}} |\Delta\Gamma_{ijkl}|^p \right)^{\frac{1}{p}} + \left(\sum_{ij}^{n_{io}} \sum_{tu}^{n_{ao}} |\Delta\Gamma_{ijtu}|^p \right)^{\frac{1}{p}} + \left(\sum_{tuvw}^{n_{ao}} |\Delta\Gamma_{tuvw}|^p \right)^{\frac{1}{p}}, \quad (156)$$

in order to have a better understanding of each block.

Therefore, the Minkowski distance is a direct metric to test any approximated 2-RDM, resulting in a similar 2-RDM if $d \rightarrow 0$, and a non-similar 2-RDM 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. Also, it is not a direct metric of the performance of a 2-RDM.

5 Results and discussion

In table 1, the MCSCF energies computed with each approximated 2-RDM given in section 4.2, together with the absolute errors, are tabulated for the CASSCF calculation corresponding to the input file (file 1) of the Appendix. The performed calculations for this input correspond to CASSCF(8,8)/cc-pVDZ with 1 inactive orbital. The energy error is a direct measurement of the performance of each approximation.

Also, the Minkowski distances of order $p = 4$ computed with eq. (155) are tabulated in table 2. This metric serves as a direct way to compare each approximated 2-RDM with the exact one which, along with the MCSCF energy, serves to gut the functioning of the 2-RDMs.

Upon examining table 1, the first thing the reader may notice is the low errors obtained for the different approximations. This implies two things: first, that the approximations, at least in this case, work very well; second, considering that all the approximate 2-RDMs are constructed based on the ONs, i.e. the 1-RDMs, it suggests that the 1-RDMs used in these calculations are of high quality, which makes sense considering the setup and performance of the CASSCF calculation performed in this case.

This can also be seen in fig. 1, where the MCSCF energies, absolute errors and Minkowski distances of order $p = 4$ are shown. In the first subfigure, it can be seen that all the energies are real close to the exact energy except for one: the BBC3 approximation. It can also be seen in the second subfigure, where the errors corresponding to BBC3 go up to $\sim 10^{10}$ times the errors corresponding to the rest of approximations.

This is the result of the main problem discussed in section 2.1, the assignment of

Table 1: CASSCF energies and absolute errors, in hartrees, for the LS, BBC1, BBC2, BBC3 and BBC3M approximations.

$d, \text{\AA}$	LS		BBC1		BBC2		BBC3		BBC3M	
	E, Ha	ΔE	E, Ha	ΔE	E, Ha	ΔE	E, Ha	ΔE	E, Ha	ΔE
0.5	-60.2947	0.13e-09	-60.2947	0.13e-09	-60.2947	0.13e-09	-64.8410	0.45e+01	-60.2947	0.13e-09
1.0	-69.9020	0.33e-10	-69.9020	0.33e-10	-69.9020	0.33e-10	-74.5575	0.47e+01	-69.9020	0.33e-10
1.5	-71.9914	0.13e-11	-71.9914	0.13e-11	-71.9914	0.13e-11	-76.6761	0.47e+01	-71.9914	0.13e-11
2.0	-72.8738	0.15e-10	-72.8738	0.15e-10	-72.8738	0.15e-10	-77.5792	0.47e+01	-72.8738	0.15e-10
2.5	-73.2204	0.35e-11	-73.2204	0.35e-11	-73.2204	0.35e-11	-77.9279	0.47e+01	-73.2204	0.35e-11
3.0	-73.3153	0.46e-10	-73.3153	0.46e-10	-73.3153	0.46e-10	-78.0228	0.47e+01	-73.3153	0.46e-10
3.5	-73.2969	0.50e-10	-73.2969	0.50e-10	-73.2969	0.50e-10	-78.0176	0.47e+01	-73.2969	0.50e-10
4.0	-73.2486	0.37e-10	-73.2486	0.37e-10	-73.2486	0.37e-10	-77.9760	0.47e+01	-73.2486	0.37e-10

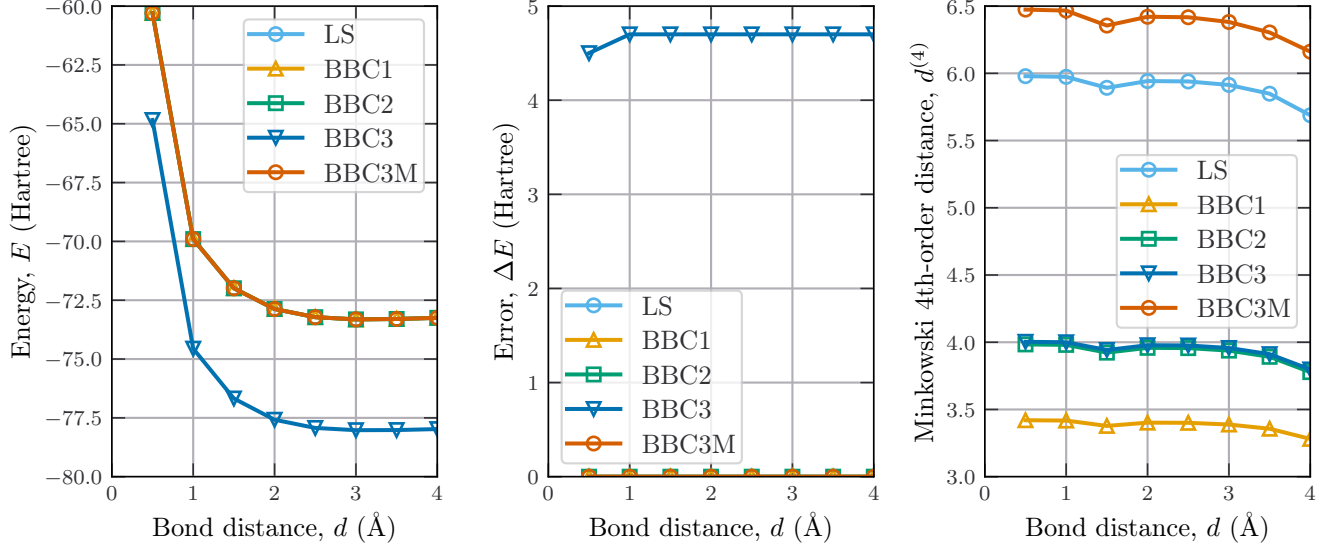


Figure 1: CASSCF energies, absolute errors and Minkowski distances of order $p = 4$ for the LS, BBC1, BBC2, BBC3 and BBC3M approximations.

frontier orbitals. In this case, no automatized function was used. An orbital p was selected as antibonding if $0 \leq n_p \leq 0.1$, and as bonding if $0.9 \leq n_p \leq 1$. Looking at the results, it can be concluded that this criteria does not perform well, but was improved with the modification applied in BBC3M. This improvement is noticeable in the third subfigure, where the Minkowski distance for BBC3 and BBC3M is noticeable different and, furthermore, the difference between BBC2 and BBC3 is not noticeable, meaning that the corrections applied to BBC2 leading to BBC3 are not well implemented. Also, the BBC3 2-RDM was the only approximated 2-RDM to not fulfill the normalization condition, which is a clear indication that important contributions were lost with this classification criteria.

Table 2: Minkowski distances of order $p = 4$ for the LS, BBC1, BBC2, BBC3 and BBC3M approximations.

d , Å	LS	BBC1	BBC2	BBC3	BBC3M
0.5	5.9788	3.4199	3.9839	4.0034	6.4741
1.0	5.9738	3.4174	3.9804	3.9999	6.4664
1.5	5.8923	3.3777	3.9228	3.9424	6.3552
2.0	5.9424	3.4021	3.9584	3.9779	6.4207
2.5	5.9397	3.4008	3.9564	3.9759	6.4170
3.0	5.9135	3.3880	3.9379	3.9574	6.3819
3.5	5.8485	3.3566	3.8917	3.9114	6.3039
4.0	5.6882	3.2811	3.7779	3.7978	6.1611

One possible improvement for the classification of bonding and antibonding orbitals would be to use the CI coefficients, such that the high-occupation orbitals of a relevant configuration (large CI coefficient), associated with a decrease of the energy, would be classified as bonding. Similarly, a low-occupation orbital of a relevant configuration, associated with an increase in the energy, would be classified as antibonding.

With table 2, and looking at the third subplot of fig. 1, different values of the Minkowski distance can be observed, even though the energy errors are pretty close between all approximations. In fact, the Minkowski distance corresponding to BBC3 is lower than that corresponding to BBC3M and LS, although the BBC3 approximation is the worst-performing approximation. This is the main reason why the Minkowski distance is not a performance metric. Also, the Minkowski distance for BBC3M is ~ 4 times larger than that of BBC1, which means that both perform well in this case while being constructed differently.

Different order Minkowski distances were computed, with equivalent results. The order $p = 4$ is included because, in this case, all distances were $0 \leq d \leq 10$ which is convenient to not work with big number.

6 Outlook and perspectives

In this thesis, the application of Reduced Density Matrix Functional Theory (RDMFT) for electronic structure calculations has been extensively explored. The primary goal was to create a working environment that enables the following optimization of the possible new parameterization proposed in this work.

Several key findings emerged from this study:

First. Validation of approximations: Established approximations for the electron repulsion functional in terms of the two-particle reduced density matrix (2-RDM) have been validated. These approximations have shown promise in accurately capturing electron correlation effects in small sized systems, as in this case, H_2O .

Second. Possible new parameterizations A possible new parameterization of the 2-RDM was proposed, providing possible approaches and algorithms for a future optimization.

Third. Computational implementation: The methodologies proposed were implemented and tested through various level of theory calculations, and is extensible to other systems simply changing the Dalton input. Their feasibility and effectiveness in practical applications was demonstrated.

Reduced Density Matrix Functional Theory presents a promising improvement in computational cost to wavefunction-based methods. Therefore, the study of reduced density matrices and their applications presents multiple avenues for future research. One of the promising directions is the development of new approximations and improvement of

existing approximations for the electron repulsion functional, specially for its application to larger systems.

The development of more precise approximated reduced density matrices and efficient methods directly repercute in accurately describing electronic properties, which has significant implications in fields such as computational chemistry and solid-state physics.

There are a vast of interdisciplinary applications of RDMFT, such as to molecular biology with the study of quantum-level interactions in biomolecules. Along those practical applications, RDMFT is used in theoretical physics to provide new insights into the nature of electronic interactions in strongly correlated systems.

The principal advantage of using reduced density matrices over classical wavefunction methods lies in their ability to capture electronic correlation without an explicit representation of the full many-body wavefunction, which removes exponential grow with the number of electrons and orbitals. The 2-RDM carries all the relevant information if one is interested in expectation values of one- and two-particle operators, which is almost always the case. Therefore, the 2-RDM is a much more compact and economic storage of information than the N -particle wave function. This reduction in complexity could make such methods computationally feasible for larger systems and provide a more efficient means of handling electron correlation effects. By using functionals of the reduced density matrices, RDMFT can offer a balance between accuracy and computational feasibility, making it a powerful tool for studying complex electronic systems.

One of the main challenges is that the 2-RDM has to obey complicated N -representability conditions in order to correspond its formal definition (eq. (22)), while the wave function only has to be antisymmetric and normalized to unity. This results in a high computational complexity problem associated with accurate approximations of reduced density matrices. Additionally, one of the main downsides of current methods is their application primarily to small systems, for which approximated functionals have been parametrized. This limitation arises due to the exponential increase in computational resources required as the system size grows, specially for the 2-RDM as it is constructed as a 4-dimensional tensor. For larger systems, the computational cost becomes prohibitive because the number of possible electronic configurations increases dramatically.

However, with advances in quantum computing and machine learning algorithms, there is a significant opportunity to overcome these limitations. For example, the optimization of parametrization factors, such as μ and μ' in eq. (113), with type-algorithms as those proposed in this work involve expensive methods and algorithms as matrix and tensor decompositions and diagonalization. Therefore, the integration of this variational-type methods in quantum computing, which is a currently developing area, would overcome this problems. Also, the integration of machine learning techniques to this kind of parametrizations and optimizations could improve the cost and, more importantly, the application to larger and more complex systems.

Over the past few decades, there has been extensive theoretical development around reduced density matrices. This includes the formulation and refinement of the contracted Schrödinger equations (CSE), which offer a framework for approximating the many-body

problem by considering only the RDMs of interest.

While this document has primarily focused on the 1-RDM and 2-RDM due to their importance, physical significance and relatively simpler formal definitions, there have been substantial theoretical advancements concerning higher-order reduced density matrices, such as the 3-RDM and 4-RDM, which are of the most practical interest. Also, analogously to the reconstruction of the 1-RDM from the 2-RDM given in eq. (63), lower-order RDMs can be reconstructed from higher-order ones by tracing over a dimension. These higher-order RDMs provide even more detailed information about electronic interactions but come with increased complexity in both definition and computational demand. Exploring these higher-order RDMs can potentially lead to more accurate descriptions of electronic systems and new insights into many-body quantum phenomena.

The primary future vision for this work is for the potentially new approximation proposed in this document to be verified and optimized. By achieving this, the program is intended to be enhanced, generalized, and made more efficient, ultimately seeking its possible integration with existing software such as Dalton.

Additionally, since no time-dependence has been considered in this work, an important extension would be the development and application to Time-Dependent Reduced Density Matrix Functional Theory (TDRDMFT), which is a relatively young extension of RDMFT and represent a significant future research direction. TDRDMFT can provide insights into the dynamic behavior of electronic systems under various external perturbations, enhancing our understanding of time-dependent processes in complex quantum systems with the advantage of RDMFT.

Looking forward, several future research directions have been identified:

- Time-Dependent Extensions: Extending the current methodologies to Time-Dependent Reduced Density Matrix Functional Theory (TDRDMFT) could provide valuable insights into dynamic processes in electronic systems.
- Theoretical Advancements: Optimization of the proposed parametrization and testing.
- Integration with Existing Software: Integration of the program with existing software such as Dalton.

In conclusion, this thesis provides a comprehensive framework for employing reduced density matrices in electronic structure calculations, highlighting both its potential and the challenges that need to be addressed. The field of Reduced Density Matrix Functional Theory and RDM approximations is full of opportunities and challenges. It is essential to continue improving existing approximations and methodologies and exploring new techniques that can overcome current limitations. With the convergence of different disciplines and the use of emerging technologies, the future of this field promises to be exciting and full of innovative discoveries. The advancements made here lay the groundwork for further study of the possible new approximation proposed in this work, and for future studies in the theory.

References

1. Helgaker, T.; Jørgensen, P.; Olsen, J. in *Molecular Electronic-Structure Theory* John Wiley & Sons, Ltd: 2000, **pages** 1–33, DOI: [10.1002/9781119019572.ch1](https://doi.org/10.1002/9781119019572.ch1).
2. Kollmar, C.; Heß, B. A. [The Structure of the Second-Order Reduced Density Matrix in Density Matrix Functional Theory and Its Construction from Formal Criteria.](#) *The Journal of Chemical Physics* **2004**, *120*, 3158–3171.
3. Löwdin, P.-O. [Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction.](#) *Physical Review* **1955**, *97*, 1474–1489.
4. Coleman, A. J. [Structure of Fermion Density Matrices.](#) *Reviews of Modern Physics* **1963**, *35*, 668–686.
5. Gilbert, T. L. [Hohenberg-Kohn Theorem for Nonlocal External Potentials.](#) *Physical Review B* **1975**, *12*, 2111–2120.
6. Hohenberg, P.; Kohn, W. [Inhomogeneous Electron Gas.](#) *Physical Review* **1964**, *136*, B864–B871.
7. Donnelly, R. A.; Parr, R. G. [Elementary Properties of an Energy Functional of the First-order Reduced Density Matrix.](#) *The Journal of Chemical Physics* **1978**, *69*, 4431–4439.
8. Mel Levy [Universal Variational Functionals of Electron Densities, First-Order Density Matrices, and Natural Spin-Orbitals and Solution of the \$N^N\$ -Representability Problem.](#) *Proceedings of the National Academy of Sciences* **1979**, *76*, 6062–6065.
9. Levy, M. in *Density Matrices and Density Functionals* **by** Erdahl, R.; Smith, V. H., Springer Netherlands: Dordrecht, 1987, **pages** 479–498, DOI: [10.1007/978-94-009-3855-7_25](https://doi.org/10.1007/978-94-009-3855-7_25).
10. Valone, S. M. [Consequences of Extending 1-matrix Energy Functionals from Pure-State Representable to All Ensemble Representable 1 Matrices.](#) *The Journal of Chemical Physics* **2008**, *73*, 1344–1349.
11. Valone, S. M. [A One-to-one Mapping between One-particle Densities and Some \$N^N\$ -particle Ensembles.](#) *The Journal of Chemical Physics* **2008**, *73*, 4653–4655.
12. Nguyen-Dang, T. T.; Ludena, E. V.; Tal, Y. [Variation of the Energy Functional of the Reduced First-Order Density Operator.](#) *Journal of Molecular Structure: THEOCHEM* **1985**, *120*, 247–264.
13. Garrod, C.; Percus, J. K. [Reduction of the \$N^N\$ -Particle Variational Problem.](#) *Journal of Mathematical Physics* **1964**, *5*, 1756–1776.
14. Verstichel, B. [Variational Determination of the Two-Particle Density Matrix as a Quantum Many-Body Technique](#) **seen 25 june 2024**, preprint.
15. [Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules](#), 1 **edition**; Mazziotti, D. A., **editor**; Advances in Chemical Physics, **volume** 134; Wiley: **2007**.
16. Mazziotti, D. A. [Variational Reduced-Density-Matrix Method Using Three-Particle \$N^N\$ -Representability Conditions with Application to Many-Electron Molecules.](#) *Physical Review A* **2006**, *74*, 032501.

17. Lieb, E. H. [Variational Principle for Many-Fermion Systems](#). *Physical Review Letters* **1981**, *46*, 457–459.
18. Goedecker, S.; Umrigar, C. J. [Natural Orbital Functional for the Many-Electron Problem](#). *Physical Review Letters* **1998**, *81*, 866–869.
19. Kutzelnigg, W. [Die Lösung des quantenmechanischen Zwei-Elektronenproblems durch unmittelbare Bestimmung der natürlichen Einelektronenfunktionen](#). *Theoretica chimica acta* **1963**, *1*, 327–342.
20. Shull, H.; Löwdin, P. [Correlation Splitting in Helium-Like Ions](#). *The Journal of Chemical Physics* **1956**, *25*, 1035–1040.
21. Sheng, X. W.; Mentel, M.; Gritsenko, O. V.; Baerends, E. J. [A Natural Orbital Analysis of the Long Range Behavior of Chemical Bonding and van Der Waals Interaction in Singlet H₂: The Issue of Zero Natural Orbital Occupation Numbers](#). *The Journal of Chemical Physics* **2013**, *138*, 164105.
22. Giesbertz, K. J. H.; family=Leeuwen given=Robert, p. u. [Long-Range Interactions and the Sign of Natural Amplitudes in Two-Electron Systems](#). *The Journal of Chemical Physics* **2013**, *139*, 104110.
23. Cioslowski, J.; Pernal, K. [The Ground State of Harmonium](#). *The Journal of Chemical Physics* **2000**, *113*, 8434–8443.
24. Pernal, K.; Cioslowski, J. [Phase Dilemma in Density Matrix Functional Theory](#). *The Journal of Chemical Physics* **2004**, *120*, 5987–5992.
25. Mentel, M.; family=Meer given=R., p. u.; Gritsenko, O. V.; Baerends, E. J. [The Density Matrix Functional Approach to Electron Correlation: Dynamic and Nondynamic Correlation along the Full Dissociation Coordinate](#). *The Journal of Chemical Physics* **2014**, *140*, 214105.
26. Müller, A. M. K. [Explicit Approximate Relation between Reduced Two- and One-Particle Density Matrices](#). *Physics Letters A* **1984**, *105*, 446–452.
27. BUIJSE, M. A.; BAERENDS, E. J. [An Approximate Exchange-Correlation Hole Density as a Functional of the Natural Orbitals](#). *Molecular Physics* **2002**.
28. Buijse, M. A. [Electron Correlation Fermi and Coulomb Holes Dynamical and Nondynamical Correlation](#), Vrije Universiteit, 1991.
29. Gritsenko, O.; Pernal, K.; Baerends, E. J. [An Improved Density Matrix Functional by Physically Motivated Repulsive Corrections](#). *The Journal of Chemical Physics* **2005**, *122*, 204102.
30. Rohr, D. R.; Pernal, K.; Gritsenko, O. V.; Baerends, E. J. [A Density Matrix Functional with Occupation Number Driven Treatment of Dynamical and Nondynamical Correlation](#). *The Journal of Chemical Physics* **2008**, *129*, 164105.
31. Lathiotakis, N. N.; Marques, M. A. L. [Benchmark Calculations for Reduced Density-Matrix Functional Theory](#). *The Journal of Chemical Physics* **2008**, *128*, 184103.
32. Hitchcock, F. L. [The Expression of a Tensor or a Polyadic as a Sum of Products](#). *Journal of Mathematics and Physics* **1927**, *6*, 164–189.
33. Tucker, L. R. [Some Mathematical Notes on Three-Mode Factor Analysis](#). *Psychometrika* **1966**, *31*, 279–311.

34. [Note Sur Une Méthode de Résolution des équations Normales Provenant de L'Application de la Méthode des Moindres Carrés a un Système D'équations Linéaires en Nombre Inférieur a Celui des Inconnues. — Application de la Méthode a la Résolution D'un Système Défini D'éQuations LinéAires.](#) *Bulletin géodésique* **1924**, *2*, 67–77.
35. Marques, M. A. L.; Lathiotakis, N. N. [Empirical Functionals for Reduced-Density-Matrix-Functional Theory.](#) *Physical Review A* **2008**, *77*, 032509.
36. Aidas, K. **and others** [The Dalton Quantum Chemistry Program System.](#) *WIREs Computational Molecular Science* **2014**, *4*, 269–284.
37. Maradzike, E.; Gidofalvi, G.; Turney, J. M.; Schaefer, H. F. I.; DePrince, A. E. I. [Analytic Energy Gradients for Variational Two-Electron Reduced-Density-Matrix-Driven Complete Active Space Self-Consistent Field Theory.](#) *Journal of Chemical Theory and Computation* **2017**, *13*, 4113–4122.

7 Appendix

Listing 1: Dalton input file for the CASSCF(8,8) with 1 inactive orbital calculations for H₂O.

```
1 **DALTON INPUT
2 .RUN WAVE
3 **WAVE FUNCTIONS
4 .HF
5 .MP2
6 .MCSCF
7 .NEPOLD
8 *SCF INPUT
9 .DOUBLY OCCUPIED
10 3 1 1 0
11 *CONFIGURATION INPUT
12 .SYMMETRY
13 1
14 .SPIN MULTIPLLCITY
15 1
16 .INACTIVE
17 1 0 0 0
18 .CAS SPACE
19 8 0 0 0
20 .ELECTRONS
21 8
22 **END OF DALTON INPUT
```
