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Electron correlation effects in third-order densities†

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The electronic energy of a system of fermions can be obtained from the second-order reduced density matrix through the contracted Schrödinger equation or its anti-Hermitian counterpart. Both energy expressions depend on the third-order reduced density matrix (3-RDM) which is usually approximated from lower-order densities. The accuracy of these methods depends critically on the set of N -representability conditions enforced in the calculation and the quality of the approximate 3-RDM. There are no benchmark studies including most 3-RDM approximations and, thus far, no assessment of the deterioration of the approximations with correlation effects has been performed. In this paper we introduce a series of tests to assess the performance of 3-RDM approximations in a model system with varying electron correlation effects, the three-electron harmonium atom. The results of this work put forward several limitations of the currently most used 3-RDM approximations for systems with important electron correlation effects.

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1 Introduction

The equations to calculate the electronic energy of an N -electron system have been known for a long time, however, their exact application leads to equations much too complicated to be solved.¹ Indeed, the energy is a well-known functional of the wavefunction and there exist a plethora of methods to construct increasingly accurate wavefunctions leading to corresponding approximations of the electronic energy. The complex structure of a wavefunction complicates the practical solutions of the underlying mathematical equations and, therefore, many wavefunction methods can only be applied to molecules of modest size. Conversely, there are robust theorems assessing the existence of energy functionals of the density² and the first-order reduced density matrix (1-RDM),³ however, the exact functional is not known and the accuracy of the corresponding approximations is not so easily assessed.

A completely different set of approximations is obtained if the working ansatz is the second-order reduced density matrix (2-RDM). For a system of fermions subject to one and two-particle forces

the exact energy can be completely expressed in terms of the 2-RDM.^{4–7} Many authors have attempted the calculation of the ground-state energy from the 2-RDM because it is a much simpler object than the electronic wavefunction and, therefore, it entails a reduced computational cost. The use of the variational method to calculate the energy of a system involves the modification of the 2-RDM subject to the N -representability conditions (see Section 2.2). Although a complete set of N -representability conditions of the 2-RDM is nowadays known,⁸ a practical solution to the problem remains to be found. Besides, the N -representability problem of n -order reduced density matrices (n -RDM), for $n > 2$, is still unsolved.

Notwithstanding, the contracted Schrödinger equation (CSE)^{9–17} and the anti-Hermitian counterpart (ACSE)¹⁸ have rekindled the interest in methods that use the 2-RDM and higher-order densities.¹⁹ Both CSE and ACSE energy expressions depend on the 3-RDM (the CSE depends also on the 4-RDM),^{20,21} which is usually approximated from lower-order densities.^{22–24} The accuracy of these methods depends critically on the set of N -representability conditions enforced in the calculation and the quality of the approximate 3-RDM.^{7,19} There are not many approximations to the 3-RDM,^{18,22,23,25} and, to our knowledge, very few benchmark tests have been performed in order to compare these approximations.^{24,26–29} Moreover, no assessment of the deterioration of the approximations upon inclusion of electron correlation has been carried out.

n -RDMs are also used in the context of density matrix functional theory (DMFT)^{30,31}—where the 2-RDM is approximated from the exact 1-RDM—and in some variations of the density matrix renormalization group (DMRG) that use up to the 5-RDM.³²

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The 3-RDM and higher orders are also used to calculate particle number distributions in domains^{33–37} and to construct several electronic structure descriptors such as multicenter indices³⁸ and aromaticity descriptors.^{39–43}

In this paper we submit the four most employed 3-RDM approximations (the single-determinant approximation,⁴⁴ Valdemoro's,²² Nakatsuji's²³ and Mazziotti's²⁴) to a series of constrictive tests that will put forward some important limitations of these approximations and suggest new means to construct more robust ones. We will employ highly-accurate full-configuration-interaction (FCI) benchmark data for the three-electron harmonium atom, a model system that permits us to test methods under varying electron correlation regimes and has been successfully used in the past to test DMFT⁴⁵ and DFT methods.^{46–49} The present set of tests does not involve electronic energies and, therefore, it is not biased towards providing most accurate energies. In this sense, they add to the list of benchmark tests that assess the other properties of RDMs⁵⁰ and can be used to complement the many existing energy-based benchmarking tools.

2 Methodology

2.1 Density matrices

The n -order reduced density matrix (n -RDM) of an N -electron system is obtained from the wavefunction upon integration over $N - n$ coordinates (see ref. 51 for notation),⁶

$$\rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) = \binom{N}{n} n! \int d\mathbf{n}_{n+1} \dots d\mathbf{n}_N \Psi(\mathbf{1}', \dots, \mathbf{n}', \mathbf{n}, \mathbf{n}_{n+1}, \dots, \mathbf{n}_N) \Psi^*(\mathbf{1}, \dots, \mathbf{n}) \quad (1)$$

where Ψ is the wavefunction describing the system and we have assumed the McWeeny normalization.⁵² The n -density function (n -DF, hereafter) corresponds to the diagonal part of the n -RDM, *i.e.*,

$$\rho_n(\mathbf{1}, \dots, \mathbf{n}) = \int d\mathbf{1}' \dots d\mathbf{n}' \rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) \delta(\mathbf{1}' - \mathbf{1}) \dots \delta(\mathbf{n}' - \mathbf{n}) \quad (2)$$

The n -RDM can be expanded in terms of a set of M orbitals, $\{\phi_i(\mathbf{1})\}_{i=1, M}$, giving

$$\rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) = \sum_{\substack{i_1 \dots i_n \\ j_1 \dots j_n}}^M {}^n D_{j_1 \dots j_n}^{i_1 \dots i_n} \phi_{i_1}^*(\mathbf{1}') \dots \phi_{i_n}^*(\mathbf{n}') \times \phi_{j_1}(\mathbf{1}) \dots \phi_{j_n}(\mathbf{n}) \quad (3)$$

where ${}^n D_{j_1 \dots j_n}^{i_1 \dots i_n}$ are the elements of ${}^n \mathbf{D}$, which is the n -th order density matrix (n -DM hereafter). In the following we will assume that n -DM is expressed on the basis of canonical molecular orbitals obtained from a Hartree–Fock calculation, unless otherwise specified.

In practice, the calculation of the n -DM carries a large computational cost and it is common to resort to approximate n -DM constructed from lower-order matrices. Namely, for the

3-DM there exist four well-known approximations: the single-determinant (SD) approximation (also referred as $n = 1$, *vide infra*),

$${}^3 \mathbf{D}^{\text{SD}} = {}^1 \mathbf{D} \wedge {}^1 \mathbf{D} \wedge {}^1 \mathbf{D} = {}^1 \mathbf{D}^3, \quad (4)$$

Valdemoro's approximation,²²

$${}^3 \mathbf{D}^{\text{VAL}} = 3! \left[\frac{3}{2} {}^2 \mathbf{D} - 2 {}^1 \mathbf{D}^2 \right] \wedge {}^1 \mathbf{D} = 9 {}^2 \mathbf{D} \wedge {}^1 \mathbf{D} - 12 {}^1 \mathbf{D}^3, \quad (5)$$

Nakatsuji's approximation,²³

$$[{}^3 \mathbf{D}^{\text{NAK}}]_{ijk}^{pqs} = [{}^3 \mathbf{D}^{\text{VAL}}]_{ijk}^{pqs} + \sum_l \sigma_l \hat{A} \left({}^2 \Delta_{ij}^{pl} {}^2 \Delta_{lk}^{qs} \right), \quad (6)$$

and Mazziotti's approximation,¹⁸

$$[{}^3 \mathbf{D}^{\text{MAZ}}]_{ijk}^{pqs} = [{}^3 \mathbf{D}^{\text{VAL}}]_{ijk}^{pqs} - \frac{1}{\chi_{ijk}^{pqs} - 3} \sum_l \hat{A} \left({}^2 \Delta_{ij}^{pl} {}^2 \Delta_{lk}^{qs} \right) \quad (7)$$

where ${}^2 \Delta = {}^2 \mathbf{D} - {}^1 \mathbf{D}^2$ is the cumulant of the 2-DM,⁵³ \hat{A} performs the antisymmetric summation of all superindices and all subindices (without mixing superindices and subindices) excluding l , $\sigma_l = 1$ for orbitals below the Fermi level and -1 otherwise, and $\chi_{ijk}^{pqs} = {}^1 D_i^p + {}^1 D_j^q + {}^1 D_k^s + {}^1 D_p^q + {}^1 D_q^s + {}^1 D_k^s$. The latter expressions (eqn (4)–(7)) use Grassmann algebra (notice the wedge product, \wedge),⁵⁴ as introduced by Mazziotti to provide a compact representation of these approximations.^{24,55–58}

2.2 N -Representability conditions

For a quantum-mechanical system of N identical fermions, the N -representability problem is the problem of recognizing whether, for a given n -RDM, there exists an antisymmetric N -particle wavefunction fulfilling eqn (1). The N -representability problem, therefore, concerns the determination of conditions (constraints), the N -representability conditions, to be imposed on the approximate n -RDM to guarantee the fulfillment of eqn (1).⁵ If the equality holds the n -RDM is said to be N -representable. The full set of sufficient conditions for N -representability of the n -RDM is only known for the 1-RDM⁵ and the 2-RDM,⁸ the latter set carrying a large computational cost.

The use of non- N -representable n -RDM can lead to spurious results such as non-variational electronic energies.⁶ Therefore, methods that use approximate 2-RDM and higher-order densities such as DMFT, CSE, ACSE or DMRG need to impose the necessary N -representable conditions that are available. In this work we are concerned with the assessment of the 3-RDM, and therefore we will consider the following N -representability conditions that the 3-DM should satisfy:^{6,59}

D (or P) condition:

$${}^3 D_{ijk}^{ijk} \geq 0 \quad (8)$$

G condition (I):

$${}^2 D_{ij}^{ij} - {}^3 D_{ijk}^{ijk} \geq 0 \quad (9)$$

G condition (II):

$${}^1 D_i^i - {}^2 D_{ij}^{ij} - {}^2 D_{ik}^{ik} + {}^3 D_{ijk}^{ijk} \geq 0 \quad (10)$$

Q condition:

$$1 - {}^1 D_i^i - {}^1 D_j^j - {}^1 D_k^k + {}^2 D_{ij}^{ij} + {}^2 D_{ik}^{ik} + {}^2 D_{jk}^{jk} - {}^3 D_{ijk}^{ijk} \geq 0 \quad (11)$$

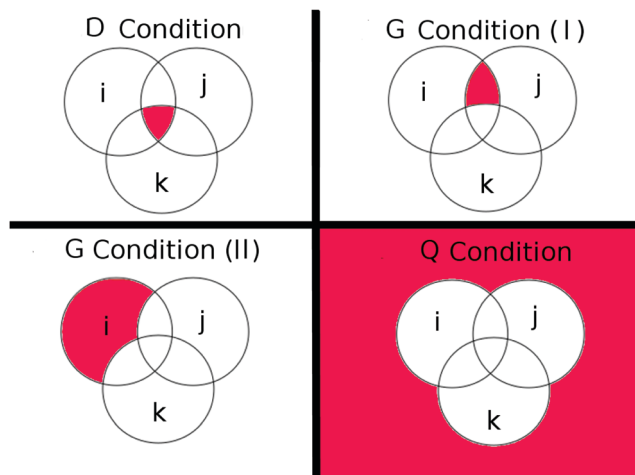


Fig. 1 Venn diagrams representing the probabilities of occupying orbitals i , j and k , according to the D, G-I, G-II and Q conditions of the 3-DM.

These N -representability conditions are related to the probability of finding groups of three electrons in different orbitals and, therefore, they can be easily illustrated with Venn diagrams (see Fig. 1). D condition accounts for the probability of finding three electrons occupying orbitals i , j and k , Q condition is related to the probability that neither i , j nor k are occupied, whereas G conditions I and II concern the probability of finding the three electrons in i and j but not in k and the probability of finding the electrons in i but not in j or k , respectively. These conditions hold for an arbitrary orthonormal orbital basis and, therefore, the full validation of eqn (8)–(11) involves the positive definiteness condition of the underlying operators.⁶⁰ The simplest way to check these conditions consists in finding the diagonal form of the corresponding operators and check that each associated eigenvalue is nonnegative. For a 3-DM this procedure involves the very costly procedure of constructing the natural 3-states.⁶ In this paper we restrict ourselves to a less constrictive test that consists in checking the D, G-I, G-II and Q conditions on the basis of canonical molecular orbitals. 3-DM approximations that fail to fulfill a given condition on this basis set obviously fail to satisfy the most general condition.

Apart from these conditions, the 3-DM should satisfy the symmetry

$${}^3D_{lmn}^{ijk} = {}^3D_{ijk}^{lmn} \quad (12)$$

and antisymmetry conditions

$${}^3D_{lmn}^{ijk} = -{}^3D_{lmn}^{jik} = {}^3D_{lmn}^{kji} = \dots \quad (13)$$

as well as the sum rule imposed by eqn (1), *i.e.*,

$$\text{Tr}[\mathbf{D}] = \sum_{ijk} {}^3D_{ijk}^{ijk} = N(N-1)(N-2) \quad (14)$$

2.3 Multicenter indices

The n -DF can be used to calculate the so-called n -center electron sharing indices (nc -ESI),⁶⁴ through the following formula:

$$\delta(A_1, A_2, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \int_{A_1} d\mathbf{1} \int_{A_2} d\mathbf{2} \dots \int_{A_n} d\mathbf{n} \gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}), \quad (15)$$

where

$$\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = \langle (\hat{\rho}_1 - \bar{\rho}_1)(\hat{\rho}_2 - \bar{\rho}_2) \dots (\hat{\rho}_n - \bar{\rho}_n) \rangle, \quad (16)$$

$\hat{\rho}$ stands for the density operator⁶ (see eqn (17) and (19)) and $\bar{\rho}$ is its average value, *i.e.*, $\bar{\rho}_A = \langle \hat{\rho} \rangle_A$. From $\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})$, 2^n terms arise and the computationally most expensive one involves the n -DF,

$$\langle \hat{\rho}_1 \dots \hat{\rho}_n \rangle_{A_1 \dots A_n} = \int_{A_1} d\mathbf{1} \dots \int_{A_n} d\mathbf{n} \rho_n(\mathbf{1}, \dots, \mathbf{n}), \quad (17)$$

and the lower-order DF in a set of three-dimensional space regions. $\delta(A_1, \dots, A_n)$ is invariant with respect to the order of the atoms in the string and is proportional to the n -central moment of the n -variate probability distribution, n -DF, integrated into the atomic basins A_1, \dots, A_n :⁶²

$$\delta(A_1, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \left\langle \prod_{i=1}^n (\hat{N}_{A_i} - \bar{N}_{A_i}) \right\rangle \quad (18)$$

where \hat{N}_A is the particle operator applied to region A and \bar{N}_A is the average number of electrons in A (or population of A):

$$\bar{N}_A = \langle \hat{\rho}_1 \rangle_A = \int_{A_1} d\mathbf{1} \hat{N}_A \rho(\mathbf{1}) \equiv \int_A d\mathbf{1} \rho(\mathbf{1}). \quad (19)$$

The large cost associated with the 3c-ESI is mostly due to the computation of the exact 3-DF, which by itself is a huge computational task for non-single-determinant wavefunctions. The 3c-ESI is thus often computed from approximate 3-DF.^{43,63,64} In a recent work⁶⁵ we have put forward two new approximations to the 3-DF that have been used to calculate the 3c-ESI in a series of molecules. Our approximations were compared against the Valdemoro,²² Nakatsuji²³ and Mazziotti²⁴ approximations, showing that one of our proposals was clearly superior to the others.^{65,66} This 3-DF expression was named cube root (CR) or $n = 1/3$ approximation, it is exact for single-determinant wavefunctions and is the only approximation to satisfy the sum rule, eqn (14). It can be obtained by setting $a = 1/3$ in the following general expression

$$\rho_3^a(\mathbf{1}, \mathbf{2}, \mathbf{3}) = \gamma^a(\mathbf{1}, \mathbf{2}, \mathbf{3}) - 2\rho(\mathbf{1})\rho(\mathbf{2})\rho(\mathbf{3}) + \hat{\pi}_1^3 \rho_2(\mathbf{1}, \mathbf{2})\rho(\mathbf{3}), \quad (20)$$

where $\hat{\pi}_1^3$ is an operator which generates the two possible subsets of indices of sizes 1 and 2 from the elements in the set $\{\mathbf{1}, \mathbf{2}, \mathbf{3}\}$, ρ_2 is the 2-density function (2-DF) and

$$\gamma^a(\mathbf{1}, \mathbf{2}, \mathbf{3}) = 2 \sum_{ijk} (n_i n_j n_k)^a \eta_i^*(\mathbf{1}) \eta_j(\mathbf{1}) \eta_k(\mathbf{2}) \eta_j^*(\mathbf{2}) \eta_i(\mathbf{3}) \eta_k^*(\mathbf{3}), \quad (21)$$

where $\eta(\mathbf{1})$ is a natural orbital and n_i its occupation number. The CR approximation of the 3-DF bears a close resemblance with Müller's approximation of the 2-DF⁶⁷ and provides a simple expression to calculate the 3c-ESI only in terms of natural orbitals:

$$\tilde{\delta}^{\text{CR}}(A_1, A_2, A_3) = 4 \sum_{ijk} (n_i n_j n_k)^{1/3} S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3), \quad (22)$$

where $S_{ij}(A_1)$ is the atomic overlap matrix (AOM) of atom A_1 ,

$$S_{ij}(A_1) = \int_{A_1} d\mathbf{r} \eta_i^*(\mathbf{r}) \eta_j(\mathbf{r}). \quad (23)$$

In the tests of this paper we include the 3c-ESI using two approximations we have recently suggested,^{65,66} the latter eqn (22) and

$$\tilde{\delta}^{\text{SR}}(A_1, A_2, A_3) = 4 \sum_{i,j,k} (n_i n_j n_k)^{1/2} S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3). \quad (24)$$

which is also indicated as $n = 1/2$. These approximations, as well as the single-determinant approximation ($n = 1$), *i.e.*, eqn (4) substituted in eqn (15),

$$\tilde{\delta}^{\text{SD}}(A_1, A_2, A_3) = 4 \sum_{i,j,k} n_i n_j n_k S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3), \quad (25)$$

only require the calculation of the natural orbitals and their occupancies and, therefore, bear a very reduced computational cost (unlike the 3-DM formulations of Valdemoro, Mazziotti and Nakatsuji that generate 3c-ESI approximations that implicitly depend on the exact 2-DM). Conversely, the 3-DF approximations in eqn (20) for $a = 1$, $a = 1/2$ and $a = 1/3$ are referred to as SD ($n = 1$), SR ($n = 1/2$) and CR ($n = 1/3$), and depend on natural orbitals and the 2-DF. Except in the case of the SD approximation, no 3-DM can be constructed from the latter formulae and, therefore, some of the benchmark tests suggested in this paper cannot be applied. For single-determinant wavefunctions all the approximations analyzed in this study reduce to the exact formulation.

2.4 Harmonium atom

Our working system is the harmonium atom (HA),⁶⁸ where the electrons are confined on a parabolic potential, $\frac{1}{2}\omega^2 \mathbf{r}^2$, and whose Hamiltonian reads

$$\hat{H} = \sum_i \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \omega^2 \mathbf{r}_i^2 \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (26)$$

where ω is the confinement strength. This model allows an easy tuning of the amount of correlation by playing with the ω parameter. For large values of ω electrons are in a low-correlation regime, whereas the small- ω region corresponds to highly correlated systems. The two-electron harmonium has been widely used in calibration and benchmarking of electronic structure methods^{45–49,69–75} due to the availability of analytical^{76–78} and very accurate results.^{79–82}

In the present study we have taken the lowest-lying quartet ($S = 3/2$) and doublet ($S = 1/2$) states of the three-electron HA for several values of the ω parameter ($\omega \in [0.1, 1000]$). FCI calculations of quartet and doublet 3e-HA from a previous study⁴⁹ have been used to generate the exact 3-DM and various approximations. For the reader's reference, let us note that the correlation energy of the helium atom is very similar to the correlation energy of two-electron harmonium at $\omega = 1/2$.

3 Computational details

FCI calculations were performed on the two lowest-lying states (doublet and quartet) of the three-electron HA for 12 values of

the confinement parameter, ω , namely 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 5.0, 10.0, 100.0, and 1000.0. We used a modified version of the code developed by Knowles^{83,84} and a variationally-optimized even-tempered basis set consisting of seven S, P, D and F Gaussian functions, amounting a total of 112 basis functions.⁴⁹ 1-DM, 2-DM and 3-DM were calculated from the FCI expansion coefficients using the DMN code⁸⁵ developed in our group. The approximate 3-DMs were also generated with the DMN code.

In this work we will test four 3-DM expressions, namely, Valdemoro's (eqn (5)), Nakatsuji's (eqn (6)), Mazziotti's (eqn (7)), and the single-determinant approximation (eqn (4)). A series of four tests will be used to analyze the performance of these 3-DM approximations: (i) fulfillment of the sum rule, eqn (14), (ii) attainment of the D-, G-I, G-II and Q conditions of the 3-DM, eqn (8)–(11) (see Fig. 1), (iii) calculation of the 3c-ESI between three regions of the Cartesian space and (iv) a termwise assessment, *i.e.*,

$$Tw[{}^3\mathbf{D}^X] = \sum_{(i < j < k) \leq (l < m < n)} \left| [{}^3D^X]_{lmn}^{ijk} - {}^3D_{lmn}^{ijk} \right|. \quad (27)$$

For the sake of completeness, in tests (i) and (iii) we have also included the calculation of the two approximate 3-DF obtained from eqn (20) by setting $a = 1/2$ and $a = 1/3$ (*vide supra*).

The 3c-ESI calculations were performed over several three-region partitions of the Cartesian space occupied by the HA. In the end, among many partitions tested we have decided for the partition that was most affected by correlation effects and, therefore, poses the most stringent test to the 3-DM approximations. Namely, the Cartesian space is partitioned by two concentric spheres with radii r_1 and r_2 , which are selected in such a way that there is one electron in each of the three resulting regions. Obviously, r_1 and r_2 vary for each value of ω and each spin state, their values being collected in Table 1. The calculation of the corresponding overlap matrices, eqn (23), was performed with the in-house RHO_OPS code.⁸⁶ The 3c-ESI values were computed with the ESI-3D^{87–89} code developed in our group.

Table 1 Values of r_1 and r_2 that define the partition of the 3e-HA in three regions of the Cartesian space

ω	$S = 1/2$		$S = 3/2$	
	$r_1/\text{a.u.}$	$r_2/\text{a.u.}$	$r_1/\text{a.u.}$	$r_2/\text{a.u.}$
0.10	4.03	5.66	4.35	5.92
0.15	3.25	4.54	3.45	4.70
0.20	2.75	3.86	2.93	4.03
0.30	2.17	3.07	2.33	3.21
0.40	1.84	2.62	1.99	2.74
0.50	1.62	2.31	1.76	2.43
1.0	1.10	1.59	1.21	1.68
2.0	0.76	1.10	0.84	1.17
5.0	0.47	0.68	0.52	0.73
10.0	0.33	0.47	0.37	0.52
100.0	0.10	0.15	0.11	0.16
1000.0	0.03	0.04	0.04	0.05

4 Results

4.1 The sum rule

The plots in Fig. 2 correspond to the difference between the trace of ${}^3\mathbf{D}$ obtained from the different approximations *via* eqn (14) and the trace of the exact 3-DM (which for a three-electron system equals six) against the inverse of the confinement strength, ω . The $n = 1/3$ approximation has not been included because it satisfies the sum rule. The smaller the ω value, the more important the correlation effects in the HA. For large values of ω , all the approximations provide trace values very close to the exact result. However, as ω decreases, most approximations show significant deviations. The single-determinant approximation gives a very poor estimate of the trace with more than 50% of the error for the doublet state at $\omega = 0.1$. Mazziotti's 3-DM only performs marginally better than the single-determinant approximation in this case. Valdemoro's approximation systematically underestimates the value of the trace, but provides very accurate results. On the other hand, Nakatsuji's 3-DM and $n = 1/2$ (eqn (24)) approximation also provide quite accurate trace values but show larger errors than Valdemoro's. The quartet state poses a less serious test for the approximations, giving significantly smaller errors in the calculation of the trace. In this case, Mazziotti's 3-DM provides quite accurate results, improving Nakatsuji's values. Again, the Valdemoro approximation provides trace values systematically below the exact ones but more accurate than any other approximation.

4.2 N -Representability

We have assessed the deviation from the N -representability conditions introduced in Section 2.2 by summing the l.h.s. of eqn (8)–(11) on the basis of canonical molecular orbitals. The resulting numbers are plotted against ω^{-1} in Fig. 3. As expected, a more significant deviation from the N -representability conditions is observed as the confinement strength is weakened.

The single-determinant approximation of the 3-DM satisfies the D condition, however, it presents significant errors in the other N -representability conditions for low values of ω . Valdemoro's 3-DM presents the largest deviations from the D condition for

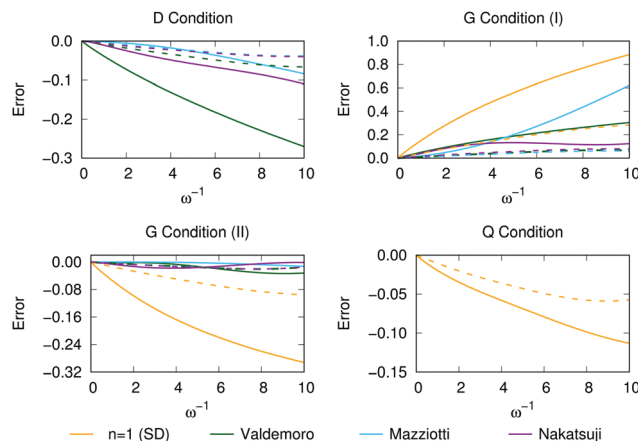


Fig. 3 Errors associated with the N -representability conditions. Solid lines are used for the doublet state and dashed lines are used for the quartet state.

both states, in line with the fact that it is the only approximation that underestimates the trace value of ${}^3\mathbf{D}$. In addition, it presents non-negligible deviations in the G conditions for the doublet state. Mazziotti's approximation shows the smallest errors in the D condition upon inclusion of electron correlation and, with the exception of the G-I condition in the doublet state, it presents the smallest deviations from N -representability conditions. Therefore, in the case of Mazziotti's approximation, the large errors in the sum rule (eqn (14)) seem to be connected to the satisfaction of the G-I condition. Interestingly, Nakatsuji's 3-DM presents the smallest deviations in the G-I condition for the doublet state and it does not perform better than Mazziotti's approximation in the other N -representability conditions. Although there is no apparent reason for that, on the basis of canonical molecular orbitals, the Q condition is attained by all the approximate 3-DM, excepting the single-determinant formulation.

4.3 3c-ESI

The 3c-ESI between regions A, B and C is a measure of the simultaneous electron sharing between these regions.^{38,88} The partition has been constructed to contain one electron in each of its parts. Upon reduction of the confinement parameter the electron distribution spreads and, consequently, regions A and B increase their size. The 3c-ESI decreases with ω , showing values between 0.38 and 0.33 for both spin states, which indicate that there is substantial electron sharing between the three regions.

The difference between the approximate 3c-ESI and the exact ones is plotted against the logarithm of the confinement parameter in Fig. 4. In general, the approximations correctly provide the gross electron sharing, with the exception of Mazziotti's in the doublet state. The latter always overestimates the actual 3c-ESI and, as we have seen in previous tests, it presents a very large error for low- ω values of the doublet state, whereas it gives very good estimates of the quartet state. For both states, Valdemoro's approximation systematically underestimates the 3c-ESI but it provides the most accurate values. Excepting the doublet state at the strong correlation regime, Nakatsuji's 3-DM

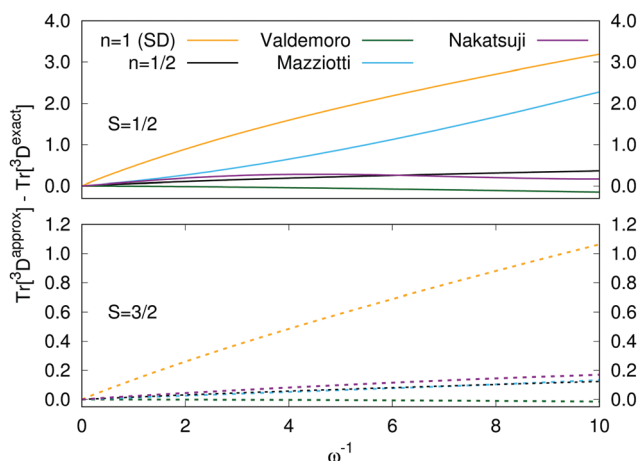


Fig. 2 Error in the trace of the 3-DM against the inverse of ω for the doublet (top) and quartet (bottom) states of three-electron harmonium.

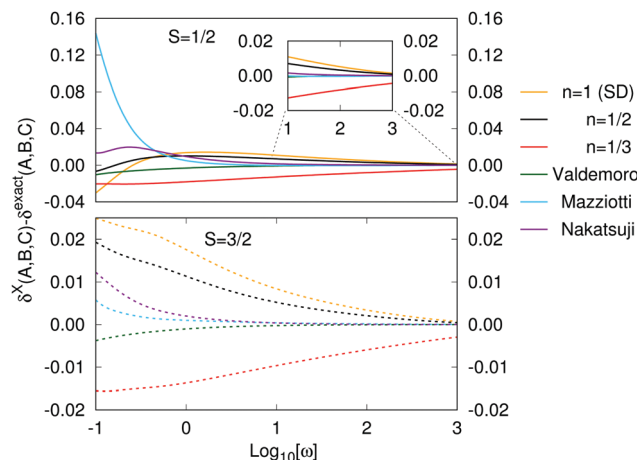


Fig. 4 3c-ESI errors of the approximate 3-DM for the doublet (above) and quartet (below) states of 3e-HA plotted against the logarithm of ω .

provides results that are usually worse than Mazziotti's. The 3-DF obtained from $a = 1/3$ and $a = 1/2$ gives better results than the single-determinant approximation ($a = 1$) and, for both states, the $n = 1/3$ approximation error seems to reach an asymptotic value.

4.4 Termwise error

Thus far, we have examined the performance of 3-DM approximations in the properties that depend only on the diagonal part of the 3-DM. In Fig. 5 we find the accumulated termwise error of the 3D , eqn (27), for the different 3-DM used in this work. Upon decrease of the confinement strength, the electron correlation enhances (especially in the doublet state) and the matrices present larger termwise deviations, as expected. Indeed, for the quartet state, the single-determinant approximation shows the worst results, while the other three approximations show similar errors. Surprisingly, the largest deviations (even larger than the single-determinant approximation for low- ω values) of the doublet state are presented by Valdemoro's formulation. Mazziotti's 3-DM performs only marginally better and Nakatsuji's provides the

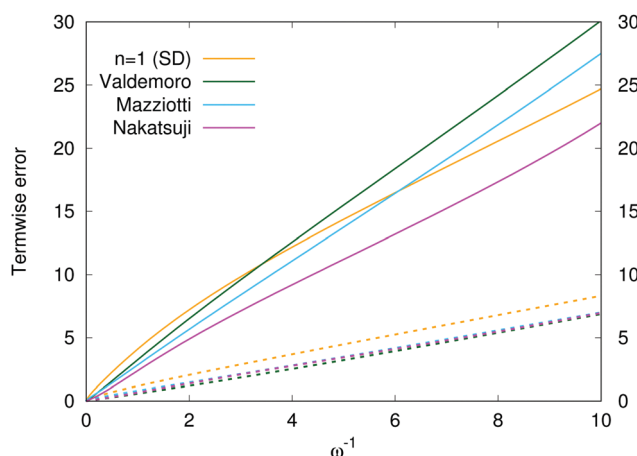


Fig. 5 Termwise errors of the 3-DM approximations for the doublet (solid) and quartet (dashed) states plotted against the inverse of ω .

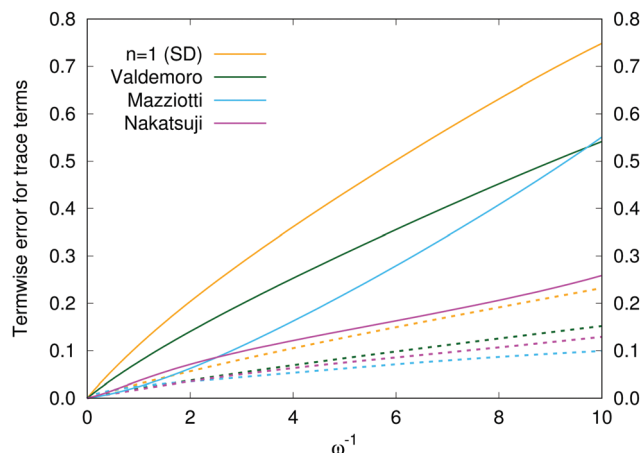


Fig. 6 Termwise errors of the diagonal elements of the 3-DM approximations for the doublet (solid) and quartet (dashed) states plotted against the inverse of ω .

best results for the range of ω values considered in this work. However, the trends in Fig. 5 suggest that for very low ω values the total errors will be worse than the poor single-determinant approximation. Finally, it is worth mentioning that the termwise error increases as ω^{-1} in all cases. On the other hand, the termwise error of the diagonal elements of the 3-DM is not too large in most approximations, except for the single-determinant one (see Fig. 6). Nakatsuji's approximation shows the smallest errors at the weak confinement regime.

5 Conclusions

We have introduced a series of four tests for 3-DM approximations that can be readily computed in a model three-electron system with varying electron correlation effects. The results of this work put forward several limitations of the currently most used 3-DM approximations for systems with important electron correlation effects. Our results show that most of the properties evaluated show errors of the 3-DM approximations that increase as ω^{-1} in the three-electron harmonium atom. Although the approximations perform reasonably well in accounting for the 3c-ESI, they fail to satisfy several N -representability conditions. In addition, they also show significant deviations from the trace numbers upon inclusion of electron correlation.

The comparison of the quartet and doublet states permits the analysis of the Coulomb correlation, which is only present in the doublet state. For this reason, this state poses a most serious challenge for the 3-DM approximations. Indeed, Mazziotti's 3-DM performs remarkably bad for the low-spin state if we compare it against Nakatsuji's approximation, which provides better 3c-ESI values and trace numbers for small values of the confinement parameter. Since Mazziotti's approximation gives small deviations for all the tested N -representability conditions but G-I, one is prompted to attribute the erratic behavior of this 3-DM approximation to the violation of the G-I condition. Furthermore, Nakatsuji's approximation performs reasonably well for this state and, therefore, one is tempted to conclude that the phase

factor σ_l of eqn (6) is responsible for this fact. Investigation along these lines is currently being pursued in our laboratory.

Finally, one should mention that analytical solutions of two- and three-electron harmonium atoms at $\omega \rightarrow 0$ have recently become available and could be used to calibrate 3-DM approximations at this highly correlated limit.⁹⁰

In general, it is advisable to use approximations other than the single-determinant formulations, which provide the largest errors for most tests. However, for large correlation effects, all approximations fail to satisfy at least one of the tests, suggesting caution when using the current 3-DM approximations in this context. In this sense, we expect that the construction of new 3-DM approximations will benefit from the deficiencies shown by the present test set.

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References

- 1 P. A. M. Dirac, *Proc. R. Soc. London, Ser. A*, 1929, **123**, 714–733.
- 2 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864–B871.
- 3 T. Gilbert, *Phys. Rev. B: Solid State*, 1975, **12**, 2111.
- 4 K. Husimi, *Nippon Sugaku-Buturigakkwai Kizi Dai 3 Ki*, 1940, **22**, 264–314.
- 5 A. J. Coleman, *Rev. Mod. Phys.*, 1963, **35**, 668–687.
- 6 A. J. Coleman and V. I. Yukalov, *Reduced density matrices: Coulson's challenge*, Springer Verlag, Berlin, 2000, vol. 72.
- 7 D. A. Mazziotti, *Chem. Rev.*, 2012, **112**, 244–262.
- 8 D. A. Mazziotti, *Phys. Rev. Lett.*, 2012, **108**, 263002.
- 9 H. Nakatsuji, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1976, **14**, 41–50.
- 10 F. Colmenero, C. P. del Valle and C. Valdemoro, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1993, **47**, 971.
- 11 F. Colmenero and C. Valdemoro, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1993, **47**, 979.
- 12 C. Valdemoro, L. Tel and E. Pérez-Romero, *Adv. Quantum Chem.*, 1997, **28**, 33–46.
- 13 K. Yasuda and H. Nakatsuji, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1997, **56**, 2648–2657.
- 14 M. Ehara, M. Nakata, H. Kou, K. Yasuda and H. Nakatsuji, *Chem. Phys. Lett.*, 1999, **305**, 483–488.
- 15 M. Nakata, M. Ehara, K. Yasuda and H. Nakatsuji, *J. Chem. Phys.*, 2000, **112**, 8772–8778.
- 16 J. Cioslowski, *Many-electron densities and reduced density matrices*, Kluwer Academic, New York, 2000.
- 17 B. Verstichel, H. van Aggelen, D. Van Neck, P. W. Ayers and P. Bultinck, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2009, **80**, 032508.
- 18 D. A. Mazziotti, *Phys. Rev. Lett.*, 2006, **97**, 143002.
- 19 D. A. Mazziotti, *Acc. Chem. Res.*, 2006, **39**, 207–215.
- 20 J. J. Foley IV, A. E. Rothman and D. A. Mazziotti, *J. Chem. Phys.*, 2011, **134**, 034111.
- 21 J. W. Snyder Jr and D. A. Mazziotti, *J. Chem. Phys.*, 2011, **135**, 024107.
- 22 F. Colmenero and C. Valdemoro, *Int. J. Quantum Chem.*, 1994, **51**, 369–388.
- 23 H. Nakatsuji and K. Yasuda, *Phys. Rev. Lett.*, 1996, **76**, 1039–1042.
- 24 D. A. Mazziotti, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1999, **60**, 4396.
- 25 D. R. Alcoba, C. Valdemoro and L. M. Tel, *Comput. Theor. Chem.*, 2013, **1003**, 55–61.
- 26 C. Valdemoro, L. Tel and E. Pérez-Romero, *Many-Electron Densities and Reduced Density Matrices*, Springer, 2000, pp. 117–137.
- 27 H. Nakatsuji, *Many-Electron Densities and Reduced Density Matrices*, Springer, 2000, pp. 85–116.
- 28 D. A. Mazziotti, *Many-Electron Densities and Reduced Density Matrices*, Springer, 2000, pp. 139–163.
- 29 G. Gidofalvi and D. A. Mazziotti, *J. Chem. Phys.*, 2007, **126**, 024105.
- 30 M. Piris and J. Ugalde, *Int. J. Quantum Chem.*, 2014, **114**, 1169–1175.
- 31 K. Pernal and K. J. H. Giesbertz, *Top. Curr. Chem.*, 2015, **368**, 125.
- 32 T. Yanai, Y. Kurashige, W. Mizukami, J. Chalupsky, T. N. Lan and M. Saitow, *Int. J. Quantum Chem.*, 2015, **115**, 283–299.
- 33 C. Aslangul, R. Constanciel, R. Daudel and P. Kottis, *Advances in Quantum Chemistry*, Academic Press, New York, 1972, vol. 6, pp. 93–141.
- 34 R. Daudel, R. F. W. Bader, M. E. Stephens and D. S. Borrett, *Can. J. Chem.*, 1974, **52**, 1310–1320.
- 35 P. Ziesche, *Many-Electron Densities and Reduced Density Matrices*, Springer, 2000, pp. 33–56.
- 36 E. Francisco, A. M. Pendás and M. A. Blanco, *J. Chem. Phys.*, 2007, **126**, 094102.
- 37 A. M. Pendás, E. Francisco and M. Blanco, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1087–1092.
- 38 K. C. Mundim, M. Giambiagi and M. S. de Giambiagi, *J. Phys. Chem.*, 1994, **98**, 6118–6119.
- 39 M. Giambiagi, M. S. de Giambiagi, C. D. dos Santos Silva and A. P. de Figueiredo, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3381–3392.
- 40 P. Bultinck, R. Ponc and S. Van Damme, *J. Phys. Org. Chem.*, 2005, **18**, 706–718.
- 41 F. Feixas, E. Matito, J. Poater and M. Solà, *Chem. Soc. Rev.*, 2015, **44**, 6389–6646.
- 42 E. Matito and M. Solà, *Coord. Chem. Rev.*, 2009, **253**, 647–665.
- 43 J. Cioslowski, E. Matito and M. Solà, *J. Phys. Chem. A*, 2007, **111**, 6521–6525.
- 44 P.-O. Löwdin, *Phys. Rev.*, 1955, **97**, 1474–1489.
- 45 J. Cioslowski, M. Piris and E. Matito, *J. Chem. Phys.*, 2015, **143**, 214101.
- 46 S. Ivanov, K. Burke and M. Levy, *J. Chem. Phys.*, 1999, **110**, 10262.
- 47 Z. Qian and V. Sahni, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1998, **57**, 2527.

- 48 M. Taut, A. Ernst and H. Eschrig, *J. Phys. B: At., Mol. Opt. Phys.*, 1998, **31**, 2689.
- 49 J. Cioslowski and E. Matito, *J. Chem. Theory Comput.*, 2011, **7**, 915.
- 50 E. Ramos-Cordoba, P. Salvador, M. Piris and E. Matito, *J. Chem. Phys.*, 2014, **141**, 234101.
- 51 In the following we will indicate the coordinates of the electron using the short-hand notation $\mathbf{1} \equiv (\vec{r}_1, \sigma_1)$ and $\mathbf{d}_1 \equiv d\vec{r}_1 d\sigma_1$ for the derivatives. A semicolon (;) will be used to separate l.h.s. coordinates from r.h.s. coordinates. The absence of the semicolon indicates the diagonal elements of the matrix.
- 52 R. McWeeny, *Rev. Mod. Phys.*, 1960, **32**, 335–369.
- 53 W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.*, 1999, **110**, 2800–2809.
- 54 The Grassman or wedge product between two tensors a and b is given by
- $$(a \wedge b)_{j_1 j_2 j_3 \dots j_n}^{i_1 i_2 i_3 \dots i_n} = \left(\frac{1}{n!}\right)^2 \sum_{\pi} \sum_{\sigma} \varepsilon(\pi) \varepsilon(\sigma) \hat{\pi} \hat{\sigma} a_{j_1 \dots j_p}^{i_1 \dots i_p} b_{j_{p+1} \dots j_n}^{i_{p+1} \dots i_n} \quad (28)$$
- where $\hat{\pi}$ permutes all the superindices, $\hat{\sigma}$ permutes all the subindices, $\varepsilon(\pi)$ and $\varepsilon(\sigma)$ return 1 (–1) for even (odd) permutations.
- 55 D. A. Mazziotti, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1998, **57**, 4219–4234.
- 56 D. A. Mazziotti, *Chem. Phys. Lett.*, 1998, **289**, 419–427.
- 57 A. E. DePrince III and D. A. Mazziotti, *J. Chem. Phys.*, 2007, **127**, 104104.
- 58 D. A. Mazziotti, *Chem. Phys. Lett.*, 2000, **326**, 212–218.
- 59 P. W. Ayers and E. R. Davidson, *Adv. Chem. Phys.*, 2007, **134**, 443–483.
- 60 D. A. Mazziotti and R. M. Erdahl, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2001, **63**, 042113.
- 61 M. Giambiagi, M. S. de Giambiagi and K. C. Mundim, *Struct. Chem.*, 1990, **1**, 423–427.
- 62 The expectation values do not include the self-pairing of electrons (explicitly forbidden by Pauli's exclusion principle).
- 63 J. M. Mercero, E. Matito, F. Ruipérez, I. Infante, X. Lopez and J. M. Ugalde, *Chem. – Eur. J.*, 2015, **21**, 9610–9614.
- 64 F. Feixas, J. Vandenbussche, P. Bultinck, E. Matito and M. Solà, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20690–20703.
- 65 F. Feixas, M. Solà, J. M. Barroso, J. M. Ugalde and E. Matito, *J. Chem. Theory Comput.*, 2014, **10**, 3055–3065.
- 66 F. Feixas, M. Rodríguez-Mayorga, E. Matito and M. Solà, *Comput. Theor. Chem.*, 2015, **1053**, 173–179.
- 67 A. M. K. Müller, *Phys. Lett.*, 1984, **105A**, 446–452.
- 68 N. R. Kestner and O. Sinanoglu, *Phys. Rev.*, 1962, **128**, 2687.
- 69 P. M. Laufer and J. B. Krieger, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1986, **33**, 1480–1491.
- 70 S. Kais, D. R. Hersbach, N. C. Handy, C. W. Murray and G. J. Laming, *J. Chem. Phys.*, 1993, **99**, 417.
- 71 C. Filippi, C. J. Umrigar and M. Taut, *J. Chem. Phys.*, 1994, **100**, 1290.
- 72 C.-J. Huang and C. J. Umrigar, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1997, **56**, 290.
- 73 P. Hessler, J. Park and K. Burke, *Phys. Rev. Lett.*, 1999, **82**, 378.
- 74 W. M. Zhu and S. B. Trickey, *J. Chem. Phys.*, 2006, **125**, 094317.
- 75 E. V. Ludeña, V. Karasiev, A. Artemiev and D. Gómez, in *Functional N-representability in density Matrix and Density Functional Theory: An illustration for Hooke's Atom*, ed. J. Cioslowski, Kluwer Academic/Plenum Publishers, New York, 2000, ch. 10.
- 76 E. Santos, *An. R. Soc. Esp. Fis. Quim.*, 1968, **64**, 177.
- 77 M. Taut, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1993, **48**, 3561.
- 78 J. Cioslowski and E. Matito, *J. Chem. Phys.*, 2011, **134**, 116101.
- 79 J. Cioslowski and K. Pernal, *J. Chem. Phys.*, 2000, **113**, 8434.
- 80 E. Matito, J. Cioslowski and S. F. Vyboishchikov, *Phys. Chem. Chem. Phys.*, 2010, **12**, 6712.
- 81 J. Cioslowski, K. Strasburger and E. Matito, *J. Chem. Phys.*, 2012, **136**, 194112.
- 82 J. Cioslowski, K. Strasburger and E. Matito, *J. Chem. Phys.*, 2014, **141**, 044128.
- 83 P. J. Knowles and N. C. Handy, *Comput. Phys. Commun.*, 1989, **54**, 75.
- 84 P. J. Knowles and N. C. Handy, *Chem. Phys. Lett.*, 1984, **111**, 315–321.
- 85 E. Matito and F. Feixas, *DMn program*, University of Girona (Spain) and University of Szczecin (Poland), 2009.
- 86 M. Rodríguez-Mayorga, *RHO-OPS: Density Operations*, Institute of Computational Chemistry and Catalysis, University of Girona, Catalonia, Spain, 2015.
- 87 E. Matito, *ESI-3D: Electron Sharing Indices Program for 3D Molecular Space Partitioning*, Institute of Computational Chemistry and Catalysis, University of Girona, Catalonia, Spain, 2015.
- 88 E. Matito, M. Solà, P. Salvador and M. Duran, *Faraday Discuss.*, 2007, **135**, 325–345.
- 89 E. Matito, M. Duran and M. Solà, *J. Chem. Phys.*, 2005, **122**, 014109.
- 90 J. Cioslowski, *J. Chem. Phys.*, 2015, **142**, 114104.