

New Approximation to the Third-Order Density. Application to the Calculation of Correlated Multicenter Indices

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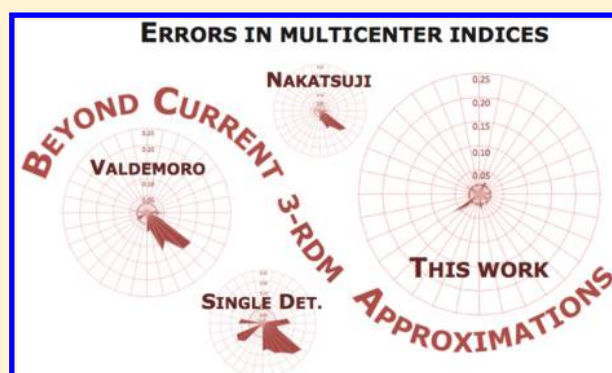
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S Supporting Information

ABSTRACT: In this work we present the formulas for the calculation of exact three-center electron sharing indices (3c-ESI) and introduce two new approximate expressions for correlated wave functions. The 3c-ESI uses the third-order density, the diagonal of the third-order reduced density matrix, but the approximations suggested in this work only involve natural orbitals and occupancies. In addition, the first calculations of 3c-ESI using Valdemoro's, Nakatsuji's and Mazzotti's approximation for the third-order reduced density matrix are also presented for comparison. Our results on a test set of molecules, including 32 3c-ESI values, prove that the new approximation based on the cubic root of natural occupancies performs the best, yielding absolute errors below 0.07 and an average absolute error of 0.015.

Furthermore, this approximation seems to be rather insensitive to the amount of electron correlation present in the system. This newly developed methodology provides a computational inexpensive method to calculate 3c-ESI from correlated wave functions and opens new avenues to approximate high-order reduced density matrices in other contexts, such as the contracted Schrödinger equation and the anti-Hermitian contracted Schrödinger equation.



1. INTRODUCTION

Lewis theory¹ has been one of a few survivors to the advent of quantum chemistry. The idea of electron pairs behind Lewis theory has been used to rationalize much of the chemistry known nowadays. Many *chemical tools* derived from quantum mechanics have actually the electron pair concept involved in its definition, as most of them rely, one way or another, on the pair density.^{2–7} Among them lists the so-called delocalization index,³ that is, the generalization of the concept of *bond order*, which gives the electron sharing number between two atoms A and B, and it is related to the covariance of their electron populations.

The delocalization index, also called the two-center electron sharing index (2c-ESI), was first developed by Bader,⁸ and it involves the calculation of the diagonal of the second-order reduced density matrix (2-RDM). The computational cost associated with the calculation of the 2-RDM is large for correlated wave functions, and therefore the number of works dealing with correlated 2c-ESI is small. Complementary definitions of the 2c-ESI relying on the first-order reduced density matrix (1-RDM) have been suggested in the past^{9–11} and some of them have been tested as approximations to the 2c-ESI, working reasonably well for the equilibrium structures of a number of molecules.^{12,13}

Remarkably, many molecular species do not fit within the model suggested by Lewis. Most of them involve interactions between more than two atoms forming a multicenter bond. For instance, diborane contains a B₂H₂ ring that is held by four electrons forming two 3-center 2-electrons bonds. Therefore, expressions that account for multicenter bonding are particularly important in order to fully characterize the electronic structure of molecules. There have been a few attempts in the past to characterize multicenter bonds but most of them rely on the molecular orbital picture¹⁴ or 2c-ESIs.¹⁵ To the best of our knowledge the first attempt to use a multicenter expression for the calculation of multicenter bonding is due to Giambiagi.¹⁶ Following the work of Giambiagi, some authors^{17–19} used similar expressions and discovered that the sign of three-center indices was an indicator of the number of electrons involved: three-center two-electron (3c-2e) bonds yield positive values and three-center four-electron (3c-4e) bonds yield negative ones (only for 3c-ESI calculated from single-determinant wave functions, vide infra).¹⁹ In 1994, Giambiagi²⁰ reformulated his definition of the multicenter

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index in terms of the n -order reduced density matrices (n -RDM), which we shall call the n -center ESI (nc -ESI).²¹

It was also Giambiagi who pointed out that multicenter indices could be used to account for the aromaticity of molecular species.²² To this aim, he renamed his index to I_{ring} and suggested it as a measure of aromaticity.²³ Afterward, Bultinck put forward a new aromaticity index, MCI, which is based on the summation of all possible I_{ring} values in a given ring.²⁴ Lately, some of us suggested a possible normalization for both I_{ring} and MCI that avoids ring-size dependency.²⁵ These expressions for multicenter bonding have been used in a number of situations such as the analysis of conjugation and hyperconjugation effects,²⁶ to characterize agostic bonds,²⁷ to understand aromaticity in organic²⁸ and all-metal compounds,^{29–32} as well as to account for electron distributions in molecules.^{33,34}

The calculation of nc -ESI, as it stands, involves the evaluation of the n -RDM, and it is thus significantly more expensive than the electronic structure calculation itself, and despite the benefit of these indices, their routine calculation is impractical for correlated wave functions. The first goal of this paper is to make these calculations inexpensive using a new approximation of the 3c-ESI in terms of natural orbitals and their occupancies. Since the 3c-ESI for correlated wave functions requires the calculation of the diagonal of the 3-RDM, implicitly, we are also suggesting a new approximation for the 3-RDM. We will analyze the accuracy of our expressions for the calculation of the 3c-ESI, and we will compare them against other approximate 3-RDMs available in the literature.

The development of new approximations for the diagonal of the 3-RDM not only provides the means to reduce the computational cost of the 3c-ESI and the calculation of three-particle distributions^{35,36} but also opens new possibilities for contracted Schrödinger equation (CSE) calculations,^{37–46} where the energy expression depends on the 3-RDM and 4-RDM, and in the anti-Hermitian contracted Schrödinger equation (ACSE) which depends only on the 3-RDM.^{47–49}

The paper is organized as follows. Next section gives a brief review on density matrices and density functions. In section 3, we show how the nc -ESI depends on density functions and give its general expression and properties. Section 4 covers the approximation of density matrices and the N -representability problem. Section 5 is devoted to the new approximations of the 3c-ESI and the implicit 3-density accompanying. The following section gives the computational details and section 7 includes the results and the discussion of the paper. Finally, section 8 summarizes the conclusions of the paper.

2. DENSITY MATRICES AND DENSITY FUNCTIONS

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 $d_1 \equiv d\vec{r}_1 d\sigma_1$ for the derivatives. A semicolon (;) will be used to separate left hand side coordinates from right hand side coordinates (i.e., they will be useful to indicate the off-diagonal terms of the matrices). The absence of the semicolon will indicate that we refer to the diagonal part of the matrix.

The N -order density matrix reads^{50,51}

$$\begin{aligned} \rho(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}'; \mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \\ = \Psi(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}') \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \end{aligned} \quad (1)$$

and describes a system of N particles, equivalently to the description given by a wave function. From the N -density

matrix we can obtain lower-rank density matrices by integration of several electronic coordinates. The n^{th} -order reduced density matrix (n -RDM) is obtained by integration of $N-n$ coordinates,

$$\begin{aligned} \rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) \\ = \binom{N}{n} n! \int d_{\mathbf{n}+1} \dots \int d_{\mathbf{N}} \Psi(\mathbf{1}', \dots, \mathbf{n}', \mathbf{n}+1, \dots, \mathbf{N}) \\ \times \Psi^*(\mathbf{1}, \dots, \mathbf{N}) \end{aligned} \quad (2)$$

where we have assumed McWeeny's normalization,⁵¹ $\binom{N}{n} n!$, instead of the Löwdin's,⁵⁰ $\binom{N}{n}$.

It is customary to work in the orbital representation, giving an expansion of the n -RDM in terms of a set of M orbitals:

$$\begin{aligned} \rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) \\ = \sum_{i_1 \dots i_n}^M {}^n D_{j_1 \dots j_n}^{i_1 \dots i_n} \varphi_{i_1}^*(\mathbf{1}') \dots \varphi_{i_n}^*(\mathbf{n}') \varphi_{j_1}(\mathbf{1}) \dots \varphi_{j_n}(\mathbf{n}) \end{aligned} \quad (3)$$

where ${}^n D$ is the n -th order density matrix and $\{\varphi_i(\mathbf{1})\}_{i=1, M}$ is a set of orbitals. Among the n -RDMs it is worth to highlight the 1-RDM and the 2-RDM, which are the only ones needed to calculate the expectation value of the energy:

$$\rho(\mathbf{1}'; \mathbf{1}) = \sum_{ij} {}^1 D_j^i \varphi_i^*(\mathbf{1}') \varphi_j(\mathbf{1}) = \sum_i n_i \chi_i^*(\mathbf{1}') \chi_i(\mathbf{1}) \quad (4)$$

and

$$\rho(\mathbf{1}', \mathbf{2}'; \mathbf{1}, \mathbf{2}) = \sum_{ijkl} {}^2 D_{kl}^{ij} \varphi_i^*(\mathbf{1}') \varphi_j^*(\mathbf{2}') \varphi_k(\mathbf{1}) \varphi_l(\mathbf{2}) \quad (5)$$

where we have also presented the diagonal representation of the 1-RDM, in terms of the so-called natural orbitals, $\{\chi_i(\mathbf{1})\}_{i=1, M}$, and their occupancies, $\{n_i\}_{i=1, M}$, which are the eigenvectors and the eigenvalues of ${}^1 D$, respectively.

The natural orbitals constitute a complete one-particle basis in terms of which to expand the wave function and all its natural p -states, $1 \leq p < N$.^{41,52} However, thus far, there is no way to solve the expansion coefficients in order to obtain an exact expression except for the two-electron case.⁵³ Löwdin's expression of the two-electron wave function in terms of natural orbitals and occupancies was used by Müller⁵⁴ to construct an approximation to the *exchange-correlation density*.

The diagonal part of the n -RDM, the n -density function or simply the n -density,

$$\begin{aligned} \rho_n(\mathbf{1}, \dots, \mathbf{n}) = \int d_{\mathbf{1}'} \dots \int d_{\mathbf{n}'} \rho(\mathbf{1}', \dots, \mathbf{n}'; \mathbf{1}, \dots, \mathbf{n}) \\ \times \delta(\mathbf{1}' - \mathbf{1}) \dots \delta(\mathbf{n}' - \mathbf{n}) \end{aligned} \quad (6)$$

measures the probability density of having simultaneously one electron at $\mathbf{1}$, another at $\mathbf{2}$, etc., regardless of how the remaining $N - n$ electrons of the system distribute in the space.

3. MULTICENTER INDICES

The n -density is used to calculate the nc -ESI through the following formula:

$$\delta(A_1, A_2, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \times \int_{A_1} d_1 \int_{A_2} d_2 \dots \int_{A_n} d_n \gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) \quad (7)$$

where γ reads

$$\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = \langle (\hat{\rho}_1 - \bar{\rho}_1)(\hat{\rho}_2 - \bar{\rho}_2) \dots (\hat{\rho}_n - \bar{\rho}_n) \rangle \quad (8)$$

Notice that $\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})$ involves the computation of the n -density

$$\langle \hat{\rho}_1 \dots \hat{\rho}_n \rangle_{A_1 \dots A_n} = \int_{A_1} d_1 \dots \int_{A_n} d_n \rho_n(\mathbf{1}, \dots, \mathbf{n}) \quad (9)$$

and the lower-order densities until $n = 1$. The $\delta(A_1, \dots, A_n)$ 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 $\rho_n(\mathbf{1}, \dots, \mathbf{n})$ integrated into the atomic basins A_1, \dots, A_n (in this expression we do not include the self-pairing of electrons (explicitly forbidden by Pauli's principle) in the calculation of expectation values):

$$\delta(A_1, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \langle \prod_{i=1}^n (\hat{N}_{A_i} - \bar{N}_{A_i}) \rangle \quad (10)$$

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

$$\bar{N}(A) = \int d_1 \hat{N}_A \rho(\mathbf{1}) \equiv \int d_1 \rho(\mathbf{1}) \quad (11)$$

The two-region expression, 2c-ESI, is known as the delocalization index³ and can be related to the covariance of the region populations:

$$\begin{aligned} \delta(A, B) &= -2 \langle (\hat{N}_A - \bar{N}_A)(\hat{N}_B - \bar{N}_B) \rangle \\ &= -2 \text{Cov}[\hat{N}_A, \hat{N}_B] \end{aligned} \quad (12)$$

$\delta(A_1, \dots, A_n)$ gives a measure of how the electron distribution is skewed from its mean, which may be related to simultaneous electron fluctuation between the atomic population of these basins (A_1, \dots, A_n). Usually these regions A_i are atoms in the molecule, but one could also use molecular fragments or other relevant regions of the space. Many atomic partitions can be used in this context, but the results of some partitions might be not as relevant as others.^{55,56} In this respect, we choose Bader's quantum theory of atoms in molecules (QTAIM) partition,⁵⁷ first used in the context of multicenter bonding by Boicchio and co-workers.⁵⁸

Giambiagi and co-workers¹⁶ developed the formula for I_{ring} ,

$$I(A_1, A_2, \dots, A_n) = 2^n \int_{A_1} d_1 \int_{A_2} d_2 \dots \int_{A_n} d_n \rho(\mathbf{1}; \mathbf{2}) \rho(\mathbf{2}; \mathbf{3}) \dots \rho(\mathbf{n}; \mathbf{1}) \quad (13)$$

that depends on the first-order reduced density matrix (1-RDM), $\rho(\mathbf{1}; \mathbf{2})$, but it can be easily expressed in terms of natural orbitals and its occupancies, cf. eq 4,

$$I(A_1, A_2, \dots, A_n) = 2^n \sum_{i_1 i_2 \dots i_n} n_{i_1} n_{i_2} \dots n_{i_n} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n) \quad (14)$$

where n_i is the occupancy of the corresponding natural orbital and $S_{ij}(A_i)$ is the atomic overlap matrix (AOM) of atom A_i , which we calculate as

$$S_{ij}(A_i) = \int_{A_i} d_1 \varphi_i^*(\mathbf{1}) \varphi_j(\mathbf{1}) \quad (15)$$

$\varphi_i(\mathbf{1})$ being the appropriate orbital. Unlike eq 10, I_{ring} depends on the particular order of the atoms in the string for $n > 3$. Excepting for a normalization factor, eqs 13 and 10 are equivalent for single-determinant wave functions when $n < 4$.

On the other hand, if we are dealing with correlated wave functions (such as those obtained from a configuration interaction or a complete active space expansion), we need to calculate the corresponding n -density (and lower orders) in order to compute the nc -ESI. The calculation of the nc -ESI for a correlated wave function is, therefore, a complicated task that bears a large computational cost, obviously associated with the calculation of the n -density. For this reason, there are actually no 4c-ESI for correlated wave functions reported in the literature to the best of our knowledge and 3c-ESI calculations are scarce.^{33,59} Some authors have attempted correlated calculations of I_{ring} , which could be regarded as an approximation to the nc -ESI values for correlated wave functions.^{25,60} Such approximation was never checked against the real nc -ESI values, which need the calculation of the corresponding n -density. In order to simplify the cost of nc -ESI in this work we suggest a few new approximations (see section 5) that we will compare against some other estimates to the n -density existing in the literature. We shall cover these approximations in the next section.

4. APPROXIMATE DENSITY MATRICES AND THE N-REPRESENTABILITY PROBLEM

There are several approximations to the 3-RDM in the literature. In this paper, we focus on those that can be calculated solely from the knowledge of the 2-RDM and the 1-RDM. Among them the simplest one consists in the calculation of the n -RDM using the exact expression for single-determinant wave functions:

$$\begin{aligned} \rho^{\text{SD}}(\mathbf{1}', \mathbf{2}', \dots, \mathbf{n}'; \mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) \\ = \begin{vmatrix} \rho(\mathbf{1}'; \mathbf{1}) & \rho(\mathbf{1}'; \mathbf{2}) & \dots & \rho(\mathbf{1}'; \mathbf{n}) \\ \rho(\mathbf{2}'; \mathbf{1}) & \rho(\mathbf{2}'; \mathbf{2}) & \dots & \rho(\mathbf{2}'; \mathbf{n}) \\ \vdots & \vdots & \ddots & \vdots \\ \rho(\mathbf{n}'; \mathbf{1}) & \rho(\mathbf{n}'; \mathbf{2}) & \dots & \rho(\mathbf{n}'; \mathbf{n}) \end{vmatrix} \end{aligned} \quad (16)$$

More sophisticated approximations for the 3-RDM include the ones of Valdemoro, Nakatsuji, and Mazziotti commonly used in CSE and ACSE. Valdemoro suggested an approximation for the 3-RDM based on the relationship between particles and holes.³⁹ Nakatsuji and Yasuda developed a systematic approach for constructing higher-order reduced density matrices using the Green function.^{43,44} Mazziotti, on the other hand, suggested his own approximation and simplified the notation for the other two estimates using Grassmann algebra (see Appendix A):^{40,61–64}

$${}^3D^{\text{VAL}} = 3! \left[\frac{3}{2} {}^2D - 2 {}^1D^2 \right] \wedge {}^1D = 9 {}^2D \wedge {}^1D - 12 {}^1D^3 \quad (17)$$

$$[{}^3D^{\text{NAK}}]_{pqs}^{ijk} = [{}^3D^{\text{VAL}}]_{pqs}^{ijk} + \sum_l \sigma_l \hat{A}(\Delta_{pq}^{il} \Delta_{ls}^{jk}) \quad (18)$$

$$[{}^3D^{\text{MAZ}}]_{pqrs}^{ijk} = [{}^3D^{\text{VAL}}]_{pqrs}^{ijk} - \frac{1}{\chi_{pqrs}^{ijk} - 3} \sum_l \hat{A}({}^2\Delta_{pq}^{il} {}^2\Delta_{ls}^{jk}) \quad (19)$$

where \hat{A} performs the antisymmetric summation over all indices excluding l , σ_l is 1 if l denotes an occupied orbital and -1 otherwise, and ${}^2\Delta$ is the second-order cumulant,

$${}^2\Delta = {}^2D - {}^1D^2 \quad (20)$$

and

$$\chi_{pqrs}^{ijk} = {}^1D_i^i + {}^1D_j^j + {}^1D_k^k + {}^1D_p^p + {}^1D_q^q + {}^1D_s^s \quad (21)$$

In Mazziotti's approximation, we have neglected the fourth-order cumulant contribution, as done in ref 63.

The single-determinant approximation, eq 16, can also be written in terms of a Grassmann product:

$${}^3D^{\text{SD}} = {}^1D^3 \quad (22)$$

Since the knowledge of the 2-RDM is sufficient to calculate the expectation value of the Hamiltonian, there has been a great interest in using this approach to calculate electronic energies, thus avoiding the wave function and its associated dimensionality problem. However, there is a major impediment to address this possibility: not all n -RDM come from an antisymmetric wave function. This complication is known as the N -representability problem and it affects all n -RDM. Fortunately, the necessary and sufficient N -representability conditions of the 1-RDM are known and easy to implement.⁶⁵ Besides, some N -representability conditions (mostly related to the orbital representation of the diagonal part of the n -RDM)⁶⁶ are known for several n -RDMs. Because in this work we concentrate on the 3-RDM, we will just focus on these conditions:

$${}^3D_{ijk}^{ijk} \geq 0 \quad (23)$$

$${}^2D_{ij}^{ij} \geq {}^3D_{ijk}^{ijk} \quad (24)$$

$${}^1D_i^i - {}^2D_{ij}^{ij} - {}^2D_{ik}^{ik} + {}^3D_{ijk}^{ijk} \geq 0 \quad (25)$$

$$1 - {}^1D_i^i - {}^1D_j^j - {}^1D_k^k + {}^2D_{ij}^{ij} + {}^2D_{ik}^{ik} + {}^2D_{jk}^{jk} - {}^3D_{ijk}^{ijk} \geq 0 \quad (26)$$

Apart from these constraints one can also check the deviation from the sum rule, $\text{Tr}({}^3D) = \binom{N}{3}3!$. Notice that these conditions only affect the diagonal part of the 3D matrix.

Therefore, we have four different approximations to the 3-RDM that we can use to calculate the nc -ESI. The errors associated with the 3c-ESI calculated using these approximate 3-RDM can be used to assess the accuracy of these approximations and complement the information given by the deviation from the N -representability constraints aforementioned.

5. NEW APPROXIMATE EXPRESSIONS FOR THE NC-ESI

The four approximations described in the last section can be applied into eq 10 to produce four approximate 3c-ESI: $\tilde{\delta}^{\text{SD}}(A,B,C)$, $\tilde{\delta}^{\text{VAL}}(A,B,C)$, $\tilde{\delta}^{\text{NAK}}(A,B,C)$, and $\tilde{\delta}^{\text{MAZ}}(A,B,C)$. In particular, the single-determinant approximation produces a quite simple expression:

$$\tilde{\delta}^{\text{SD}}(A_1, A_2, A_3) = 4 \sum_{ijk} n_i n_j n_k S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3) \quad (27)$$

Notice that this eq differs only from eq 14 on a numerical factor. Owing to the fact that this SD gives too large values (either too positive or too negative), we decided to introduce a new approximation in the spirit of Müller's approximation⁵⁴ (MUL hereafter):

$$\tilde{\delta}^{\text{MUL}}(A_1, A_2, A_3) = 4 \sum_{ijk} (n_i n_j n_k)^{1/2} S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3) \quad (28)$$

The values obtained using MUL approximation are still too large, and because eq 7 ($n = 3$) integrates to four times the number of electrons, we decided to suggest another new approximation that employs the cube root of natural occupancies (hereafter referred as CR):

$$\tilde{\delta}^{\text{CR}}(A_1, A_2, A_3) = 4 \sum_{ijk} (n_i n_j n_k)^{1/3} S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3) \quad (29)$$

In the same spirit Bultinck et al.⁶⁷ recently suggested $a = 1/6$ to calculate six-center indices but the goodness of their approximation was never tested. Equations 28 and 29, together with $\tilde{\delta}^{\text{SD}}(A,B,C)$, $\tilde{\delta}^{\text{VAL}}(A,B,C)$, $\tilde{\delta}^{\text{NAK}}(A,B,C)$, and $\tilde{\delta}^{\text{MAZ}}(A,B,C)$ are the six approximate 3c-ESI that will be used in this work. The results of the next sections will prove that these new approximations performs much better, especially CR, than the most sophisticated approximations of the 3-RDM explained in the last section. Therefore, let us examine carefully the inherent 3-density approximation taken by CR and MUL.

First of all, we write the expression of the 3-density in terms of $\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})$, eq 8,

$$\rho_3^X(\mathbf{1}, \mathbf{2}, \mathbf{3}) = \gamma^X(\mathbf{1}, \mathbf{2}, \mathbf{3}) + \rho(\mathbf{1})\rho(\mathbf{2})\rho(\mathbf{3}) - \hat{\pi}_1^3 \rho_{xc}(\mathbf{1}, \mathbf{2})\rho(\mathbf{3}) \quad (30)$$

where $\hat{\pi}_1^3$ is an operator, which generates the two possible subsets of indices of sizes 1 and 2 in the set $\{\mathbf{1}, \mathbf{2}, \mathbf{3}\}$ (see Appendix A) and ρ_{xc} is the exchange-correlation density:⁶⁸

$$\rho_{xc}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2(\mathbf{1}, \mathbf{2}) \quad (31)$$

There will be as many estimates to ρ_3^X as approximations for γ^X . If the expression of γ is exact, we recover the 3-density. SD, MUL, and CR can be casted in the following function:

$$\begin{aligned} \tilde{\gamma}^X(\mathbf{1}, \mathbf{2}, \mathbf{3}) = 2 \sum_{ijk} (n_i n_j n_k)^a \varphi_i^*(\mathbf{1}) \varphi_j(\mathbf{1}) \varphi_k(\mathbf{2}) \varphi_j^*(\mathbf{2}) \\ \times \varphi_i(\mathbf{3}) \varphi_k^*(\mathbf{3}) \end{aligned} \quad (32)$$

$a = 1$ corresponds to $X = \text{SD}$, $a = 1/2$ has been called $X = \text{MUL}$ and $a = 1/3$ is indicated as $X = \text{CR}$ in the manuscript, after cube root.

There are not so many N -representable constraints of the spatial representation of the 3-density known. Here, we will focus on three properties: (i) the sum rule, (ii) the coalescence condition, and (iii) the sequential property. The first property states that

$$\int \rho_3^X(\mathbf{1}, \mathbf{2}, \mathbf{3}) d_1 d_2 d_3 = N(N-1)(N-2) \quad (33)$$

or equivalently,

Table 1. Deviation from Idempotency (for the CASSCF Wavefunction) and 3c-ESI Values Calculated at the HF, B3LYP, and CASSCF Levels and the Six Approximations Used to Avoid the Explicit Computation of the 3-Density at the CASSCF Level^a

	multicenter	CAS(n,m)	Dev. Idemp. ^b	HF	DFT	CAS	CAS($a = 1$)	CAS($a = 1/2$)	CAS($a = 1/3$)	CAS(VAl)	CAS(NAK)	CAS(MAZ)
BeH ₂	H-Be-H	6,7	0.004	0.0104	0.0126	0.0164	0.0109	0.0145	0.0192	0.0090	0.0095	0.0271
BH ₃	H-B-H	8,7	0.004	0.0377	0.0409	0.0314	0.0346	0.0375	0.0407	0.0274	0.0277	-0.0719
NH ₃	H-N-H	8,8	0.008	0.0217	0.0248	0.0449	0.0213	0.0207	0.0196	0.0458	0.0456	0.0948
H ₂ O	H-O-H	8,8	0.007	0.0112	0.0150	0.0411	0.0123	0.0127	0.0131	0.0425	0.0425	0.0605
CH ₄	H-C-H	8,8	0.007	0.0355	0.0346	0.0285	0.0304	0.0287	0.0260	0.0246	0.0240	0.0425
H ₂ S	H-S-H	8,8	0.008	0.0709	0.0425	0.0549	0.0596	0.0567	0.0519	0.0510	0.0514	0.0586
B ₂ H ₆	B-H-B	4,6	0.005	0.0391	0.0665	0.0259	0.0418	0.0363	0.0286	0.0234	0.0235	0.0232
C ₃ H ₄ [†]	C-C-C	2,3	0.030	0.2559	0.2751	0.1025	0.2180	0.1658	0.1167	0.0841	0.0892	0.0814
C ₃ H ₅ [†]	C-C-C	6,7	0.034			0.0801	0.2114	0.1584	0.1091	0.0129	0.0024	0.1412
C ₃ H ₅ [‡]	C-C-C	4,3	0.009	-0.0725	-0.0978	-0.0017	-0.0679	-0.0306	-0.0052	0.0093	0.0117	0.0113
C ₃ H ₅ [‡]	C-C-C	8,7	0.013			0.0100	-0.0713	-0.0321	-0.0080	0.0489	0.0524	0.0274
N ₃ ⁻	N-N-N	8,6	0.068	-0.2491	-0.3056	0.0104	-0.2076	-0.0772	-0.0118	0.1672	0.1824	0.5096
N ₃ ⁻	N-N-N	12,10	0.067			-0.0242	-0.2252	-0.0944	-0.0295	0.1276	0.1260	0.1380
N ₂ O	N-N-O	8,6	0.051	-0.1530	-0.2540	0.0006	-0.1622	-0.0675	-0.0185	0.0970	0.0976	0.1819
N ₂ O	N-N-O	12,10	0.057			-0.0259	-0.1748	-0.0762	-0.0266	0.0955	0.0779	0.0797
CO ₂	O-C-O	8,6	0.020	-0.0380	-0.1333	0.0635	-0.0582	-0.0088	0.0307	0.1140	0.1161	0.1356
CO ₂	O-C-O	12,10	0.027			0.0454	-0.0816	-0.0212	0.0237	0.1034	0.1020	0.0710
CH ₂ Li ₂	Li-C-Li	8,8	0.023	0.0082	0.0108	0.0127	0.0088	0.0108	0.0135	0.0120	0.0169	0.0376
CH ₂ Li ₂	H-C-H		0.023	0.0598	0.0562	0.0477	0.0457	0.0442	0.0413	0.0441	0.0437	-0.0182
CH ₂ Li ₂	Li-C-H		0.023	0.0173	0.0199	0.0211	0.0152	0.0155	0.0155	0.0205	0.0210	0.0177
SO ₂	O-S-O	8,8	0.043	-0.0603	-0.1595	0.0378	-0.0778	-0.0252	0.0048	0.0620	0.0708	0.0699
F ₃ ⁻	F-F-F	4,4	0.261	-0.1439	-0.2156	0.0457	-0.0953	-0.0364	-0.0213	0.0796	0.0522	0.0529
F ₃ ⁻	F-F-F	8,8	0.159			0.0216	-0.1093	-0.0468	0.0133	0.0498	0.0428	0.0678
FHF ⁻	F-H-F	8,8	0.002	-0.0030	-0.0142	-0.0028	-0.0029	-0.0028	-0.0026	-0.0030	-0.0029	-0.0027
C ₃ H ₃ [†]	C-C-C	2,3	0.007	0.3936	0.3986	0.2499	0.3647	0.3140	0.2544	0.2388	0.2384	0.2390
HCNO	C-N-O	8,6	0.045	-0.0782	-0.1516	0.0129	-0.0890	-0.0398	0.0119	0.0820	0.0854	0.1480
SiC ₃	Si-C-C	8,8	0.045	0.0566	0.0792	0.0465	0.0484	0.0412	0.0347	0.0422	0.0411	0.0498
SiC ₃	C-C-C		0.045	0.3430	0.3535	0.2712	0.3138	0.2732	0.2323	0.2588	0.2574	0.3811
C ₂ B ₂ H ₄ ^c	C-B-B	8,8	0.040	0.1309	0.1395	0.1452	0.1266	0.1310	0.1369	0.1442	0.1467	0.1518
C ₄ H ₄	C-C-C	8,8	0.177	0.0629	0.0665	0.0505	0.0551	0.0511	0.0480	0.0502	0.0587	0.0356
Al ₄ ⁻	Al-Al-Al	8,7	0.240	0.2646	0.2581	0.1292	0.2001	0.1767	0.1398	0.1107	0.1312	0.1158
C ₄ H ₆ ^d	C-C-C	4,4	0.076	0.0523	0.0409	0.0414	0.0462	0.0390	0.0350	0.0413	0.0411	0.0372
MAE ^e							0.0693	0.0348	0.0139	0.0313	0.0308	0.0575
RMSE ^e							0.0955	0.0463	0.0201	0.0537	0.0542	0.1094

^aAll the quantities use au. ^bThe deviation from idempotency is calculated using the occupancies of the natural orbitals from the CASSCF wave function. ^cC_{2v} conformer. ^d1,3-butadiene. ^eMean average error (MAE) and root-mean-square error (RMSE) computed as the difference between the approximate 3c-ESI and the value calculated using the exact 3-density at the CASSCF level.

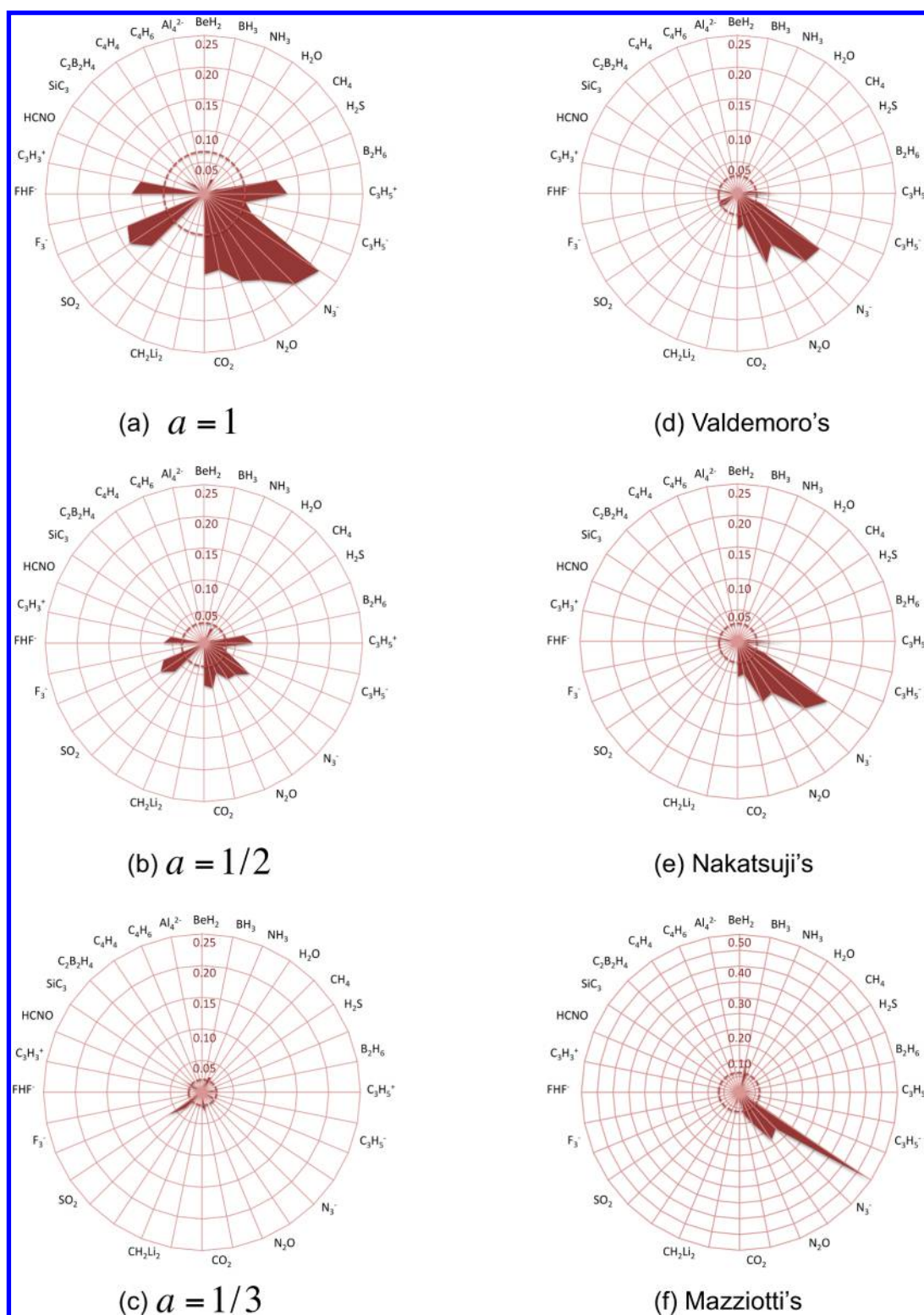


Figure 1. Absolute error distribution for the six approximations to the 3c-ESI tested. The dashed circle represents the average absolute error. Radial graphs constructed from the data in Table 1. Notice that Mazziotti's approximation uses a larger scale.

$$\int \gamma^X(1, 2, 3) d_1 d_2 d_3 = 4N \quad (34)$$

which is only fulfilled by the γ^{CR} . However, this condition is easy to impose in the other two approximations, and it does not bring any significant improvement on the 3c-ESI results (see discussion). The second condition can be written as

$$\rho_3^X(1, 1, 1) = 0 \quad (35)$$

or equivalently,

$$\gamma^X(1, 1, 1) = 2\rho(1)^3 \quad (36)$$

which is only fulfilled by the γ^{SD} . The third condition requires that the 3-density reduces to the 2-density upon integration of one coordinate:

$$\int \rho_3^X(\mathbf{1}, \mathbf{2}, \mathbf{3}) d_3 = (N - 2) \rho_2(\mathbf{1}, \mathbf{2}) \quad (37)$$

this condition cannot be recovered by any of the approximations suggested.

6. COMPUTATIONAL DETAILS

We have performed single-point B3LYP,^{69–71} Hartree–Fock (HF), and full-valence singlet closed-shell CASSCF calculations using 6-311G(d,p) within Gaussian 03 software⁷² for a series of molecules with three-center bonds of different nature, as well as some molecules without three-center bonds: BeH₂, BH₃, NH₃, H₂O, CH₄, H₂S, B₂H₆, C₃H₅⁺, C₃H₅[–], N₃[–], N₂O, CH₂Li₂, CO₂, SO₂, F₃[–], FHF[–], C₃H₃⁺, HCNO, SiC₃, C₂B₂H₄, C₄H₄, Al₄[–], C₄H₄, and C₄H₆. All molecules have been optimized at the full-valence CASSCF/6-311G(d,p) level. Additional single-point CASSCF calculations with smaller active spaces (including only π orbitals) for those molecules with valence π and σ orbitals are also included for the sake of completeness. The correlated n -densities were computed from the expansion coefficients obtained from the CASSCF calculation using an algorithm implemented in the n -densities program.⁷³ The deviation from idempotency has been calculated using the natural occupancies of the CASSCF calculation. Atomic overlap matrices (AOM) have been computed for QTAIM partition⁵⁷ with AIMPAC collection of programs.⁷⁴ These AOM and the correlated 3-RDM have been used by ESI-3D^{75,76} to compute the 3c-ESIs and their estimates. Notice that the adequacy of the level of theory used to describe the target molecular systems is not relevant in order to evaluate the goodness of the approximations suggested in this work.

7. DISCUSSION

In Table 1, we collect the 3c-ESI values for the target set of molecules calculated with B3LYP, HF, and CASSCF. The CASSCF results include the exact result and the various approximations above-mentioned. B3LYP values are obtained by assuming that the Kohn–Sham determinant can be used to retrieve n -densities as it is done for a single-determinant wave function in the HF theory. HF and B3LYP give qualitatively the same numbers, showing only large differences in the case of CO₂, N₂O, and SO₂. The agreement between both methods suggests that the amount of electron correlation included in B3LYP does not reflect in the Kohn–Sham determinant when it is treated as in HF. The same feature has been previously reported for 2c-ESIs.^{13,77} In general, both methods give pretty bad estimates of the CASSCF values. In contrast to 2c-ESI, 3c-ESI values for HF or DFT give significant differences with CASSCF even for molecules with small correlation effects such as H₂O. An interesting feature of the 3c-ESI calculated from monodeterminantal wave functions is that the sign of the index indicates whether is a 3c–2e (positive) or a 3c–4e bond (negative). Apparently, the introduction of electron correlation through CASSCF method breaks this rule.

In this work six different approximations to calculate the 3c-ESI have been used: (i) SD approximation, that is, eq 27 ($a = 1$ in eq 32), (ii) the Müller-like approach, eq 28, (iii) the $a = 1/3$ approximation, eq 29, and three methods that calculate the 3c-ESI, eq 32 for $a = 1/3$, using the exact 2-RDM and 1-RDM and an approximate 3-RDM, namely, (iv) Valdemoro's 3-RDM

approximation, eq 17, (v) Nakatsuji's approximation, eq 18, and (vi) Mazziotti's approximation, eq 19. All these approximations use the CASSCF wave function, and in the case of i–iii, they only need the natural orbitals and occupancies, while Valdemoro's, Nakatsuji's and Mazziotti's estimates need the CASSCF 2-density. (i) has been used in the past²⁵ to calculate nc -ESIs, but the other approximations are used for the first time in this work to calculate 3c-ESIs. Among all approximations used in this work, only $a = 1/3$ fulfills the sum rule. In order to improve the performance of the indices we have normalized all the components of the 3-RDM in such a way that the corresponding 3-RDM fulfills the sum rule. In the big picture, this modification does not change the results with the exception of Nakatsuji's 3c-ESIs, which are significantly improved (see the SI for unnormalized values).

Despite of being a rough estimation, the SD estimate improves the HF and the B3LYP values. Interestingly, the use of a fractional exponent for the natural occupancies (either eq 28 or eq 29) reduces the error drastically. The Müller-like approximation gives half the average error of the SD approximation and the CR approximation reduces it to less than one-fourth. Indeed, the CR approximation gives the smallest maximum error, RMSE, and average error among all the methods used.

In Figure 1, we represent the error distribution for the different approximations. The Valdemoro's and Nakatsuji's estimates to the 3-RDM performs reasonably well excepting for N₂O and N₃[–] that give errors above 0.1. Mazziotti's approximation performs somewhat worse, with errors above 0.1 also for BH₃, SiC₃, and HCNO. On the contrary, Müller's formula shows a more uniform error distribution with errors well below 0.1. The radial graphs help to identify the set of molecules that gives the largest errors. The error distribution for $a = 1$ looks like a magnified representation of the $a = 1/2$ one, indicating that both methods perform worst for the same set of molecules. Namely, the allyl cation, N₃[–], N₂O, CO₂, SO₂, F₃[–], C₃H₃⁺, and HCNO are difficult for both SD and Müller-like approximations, despite the latter performing much better. Besides, Valdemoro's and Nakatsuji's approximations fail mostly for N₃[–] and N₂O, even though the magnitude of the error is much larger than in the Müller-like approach. On top of the approximations, there is the $a = 1/3$ one, which only gives an error larger than 0.05 for F₃[–] calculated at the CASSCF level including only the π -valence orbitals in the active space.

The results obtained from the approximate 3-RDM are somewhat counterintuitive because one would expect that Mazziotti's is more accurate than Nakatsuji's, and the latter is better than Valdemoro's. In order to assess the differences between Valdemoro's, Nakatsuji's, and Mazziotti's approximation, we have computed the deviation from the constraints given by eqs 23–26 and the deviation from the sum rule (before applying the normalization). In Table 2, we collect these values. As one would expect, Mazziotti's 3-RDM is the one that best fulfils these conditions. Noteworthy, Nakatsuji's 3-RDM deviates significantly from the sum rule. In this case, the deviation seems partially responsible for the performance of this approach because upon normalization Nakatsuji's results improve significantly (compare against the unnormalized results in the SI). Altogether, deviation from the constraints in eqs 23–26 does not reflect the goodness the 3-RDM for its application in the calculation of the 3c-ESI. Therefore, the 3c-ESI puts forward the correctness of other conditions of the diagonal of ³D or its off-diagonal terms. In this sense, the

Table 2. RMSE Values Corresponding to the Deviation from the N -Representability Conditions (eqs 23–26) of the 3-RDM for Valdemoro's, Nakatsuji's, and Mazzotti's Approximations for the Set of Molecules Studied

	VAL	NAK	MAZ
sum rule	0.02	1.02	0.27
eq 23	0.04	0.02	0.02
eq 24	0.10	0.24	0.04
eq 25	0.11	0.05	0.10
eq 26	0.07	0.13	0.03

performance of 3-RDM in the calculation of the 3c-ESI provides a complementary tool to evaluate the goodness of the 3-RDMs.

Finally, we take a look at the relationship between the accuracy of the approximations and the amount of electron correlation in the CASSCF wave function. To this aim, in Figure 2, we represent the deviation from idempotency against the absolute error committed with the approximations studied. There is no clear trend but a qualitative conclusion can be extracted from this data. In general, all approaches except $a = 1/2$ and $a = 1/3$ worsen when the amount of electron correlation is important. On the other hand, the goodness of $a = 1/2$ and $a = 1/3$ approximations is essentially independent of the amount of electron correlation present in the system. It is thus remarkable that the new estimate based on $a = 1/3$ gives the smallest error and, apparently, it is also the method that is least affected by the amount of electron correlation present in the system. This finding encourages the extension of these approximations to higher-order densities, a work that is currently being developed in our laboratories. In forthcoming work, we will also use these multicenter indices on relevant

chemical problems, the description of which calls for correlated wave functions, such as those involving excited states.

8. CONCLUSIONS

In this work, we present the formulas for the calculation of the exact three-center electron sharing indices (3c-ESI) and introduce two new approximate expressions for correlated wave functions. The 3c-ESI uses a part of the third-order density but the approximations suggested in this work only involve natural orbitals and occupancies. In addition, the first calculations of 3c-ESI using Valdemoro's, Nakatsuji's, and Mazzotti's approximations for the third-order reduced density matrix are also presented for comparison. Our results on a test set of molecules, including 32 3c-ESI values, prove that our approximation based on the cubic root of natural occupancies performs the best, yielding absolute errors below 0.07 and an average absolute error of 0.015. Furthermore, this approximation seems to be rather insensitive to the amount of electron correlation present in the system. This newly developed methodology provides a computational inexpensive method to calculate 3c-ESI from correlated wave functions and opens new avenues to approximate high-order reduced density matrices in other contexts, such as the frameworks of the contracted Schrödinger equation and the anti-Hermitian contracted Schrödinger equation.

■ APPENDIX A: THE GRASSMANN PRODUCT

Also known as the wedge product, the Grassmann product (GP) is the product in an exterior algebra. Roughly speaking, this product allows the formation of n -dimensional vectors (matrices) from permutations of the indices of several q_i -dimensional vectors (matrices), so that $\sum_i q_i = n$. One can write the GP of two matrices (a and b) of dimensions p and $n-p$ as follows:

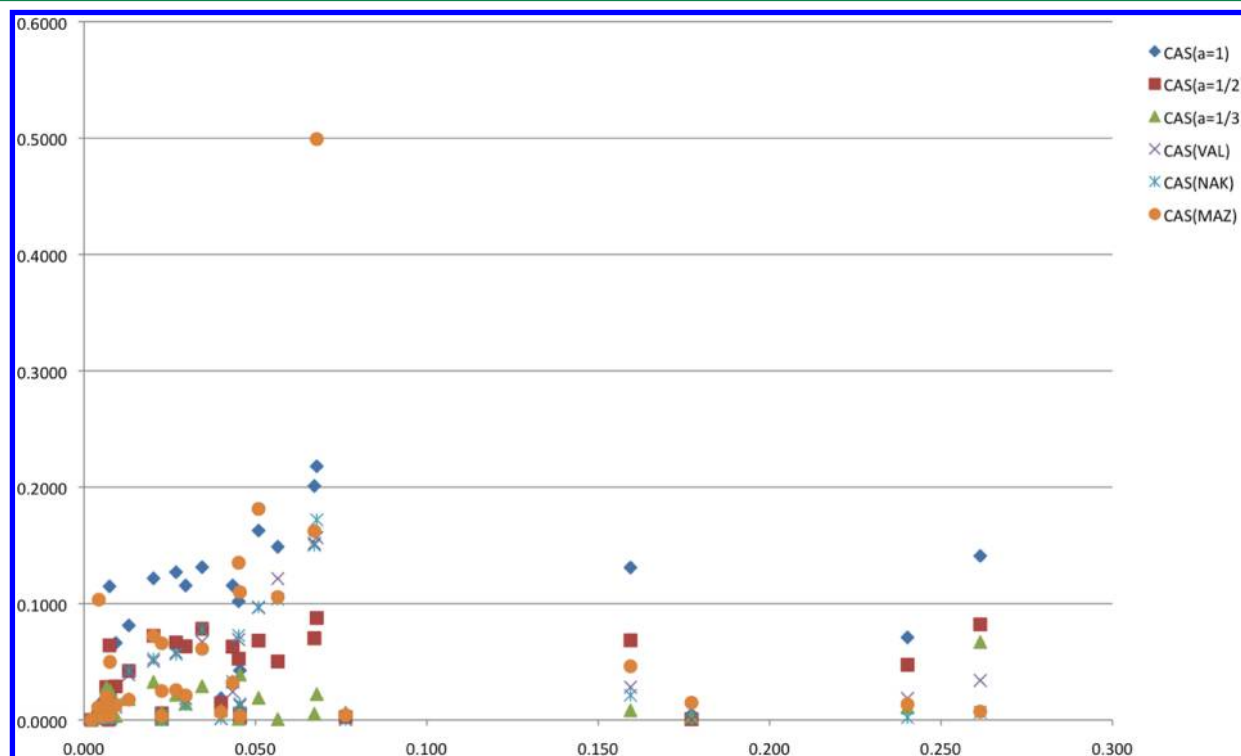


Figure 2. 3c-ESI absolute errors (y-axis) against values of the deviation from idempotency for the set of molecules studied.

$$(a \wedge b)_{i_1, i_2, \dots, i_n}^{j_1, j_2, \dots, j_n} = a_{i_1, \dots, i_p}^{j_1, \dots, j_p} \wedge b_{i_{p+1}, \dots, i_n}^{j_{p+1}, \dots, j_n} \\ = \left(\frac{1}{n!}\right)^2 \sum_{\pi} \sum_{\sigma} \varepsilon(\pi) \varepsilon(\sigma) \hat{\pi} \hat{\sigma} a_{i_1, \dots, i_p}^{j_1, \dots, j_p} b_{i_{p+1}, \dots, i_n}^{j_{p+1}, \dots, j_n} \quad (38)$$

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. The matrix power D^n is defined as n Grassmann products, for example, $D^4 = D \wedge D \wedge D \wedge D$.

If we apply these wedge product to matrices representing Fermions (such as the density matrices representing electrons), we can simplify the latter expression by using the antisymmetry of these matrices. The permutations over a group of p elements ($p!$) can be decomposed into permutations over two subsets of q and $p-q$ elements and the combinations in which we can form these two subsets $p! = \binom{p}{q} p!(p-q)!$. We shall represent this decomposition of the operator $\hat{\pi}$ (analogously for $\hat{\sigma}$) as follows:

$$\hat{\pi}_n(i_1 \dots i_n) = \hat{\pi}_p^n(i_1 \dots i_p) \hat{\pi}_{n-p}(i_{p+1} \dots i_n) \quad (39)$$

where $\hat{\pi}_p$ permutes over p indices, and $\hat{\pi}_p^n$ forms all the two possible subsets of indices of sizes p and $n-p$ (i.e., all the combinations of n elements taken p at a time). For RDMs representing Fermions we have

$$\sum_{\pi_p} \hat{\pi}_p^n \varepsilon(\pi) a_{i_1, \dots, i_p}^{j_1, \dots, j_p} = p! a_{i_1, \dots, i_p}^{j_1, \dots, j_p} \quad (40)$$

and analogously for σ . Using this property, we may write the wedge product of two (electron) density matrices as

$$a_{i_1, \dots, i_p}^{j_1, \dots, j_p} \wedge b_{i_{p+1}, \dots, i_n}^{j_{p+1}, \dots, j_n} = \binom{n}{p}^{-2} \sum_{\pi} \sum_{\sigma} \varepsilon(\pi) \varepsilon(\sigma) \hat{\pi}_p^n \hat{\sigma}_p^n a_{i_1, \dots, i_p}^{j_1, \dots, j_p} b_{i_{p+1}, \dots, i_n}^{j_{p+1}, \dots, j_n} \quad (41)$$

with the additional property that the right-hand side of this equation is such that $i_1 < i_2 < \dots < i_p$ and $i_{p+1} < \dots < i_n$ (idem for j), so that we only need to deal with the unique elements of a and b . Note that we have not used the symmetry of these matrices to simplify the formula. Obviously, we may use this recourse on the left hand side of the latter equation, where we only need to calculate the upper triangular matrix of $a \wedge b$ [$(i_1 < \dots < i_n) \leq (j_1 < \dots < j_n)$]; but on the right hand side, we shall use the full matrices and we cannot exploit their symmetry. At most, we can exclude those instances where both a and b confront the terms from the lower triangular matrix [$(i_1 < \dots < i_p) > (i_{p+1} < \dots < i_n)$ and $(j_1 < \dots < j_p) > (j_{p+1} < \dots < j_n)$], because they will not contribute to the upper triangular matrix of $a \wedge b$.

Using the previous ansatz, the associative and the bilinear properties of the Grassman product we may simplify the calculation of Valdemoro and Nakatsuji approximations,⁴⁰

$${}^3\bar{D}^{\text{VAL}} = {}^1\bar{D}^3 + 3({}^2\bar{D} - {}^1\bar{D}^2) \wedge {}^1\bar{D} \\ = [{}^1\bar{D}^2 + 3({}^2\bar{D} - {}^1\bar{D}^2)] \wedge {}^1\bar{D} = [{}^3\bar{D} - 2{}^1\bar{D}^2] \wedge {}^1\bar{D} \quad (42)$$

The simplifications obtained for the $a \wedge b$ assume that a and b are antisymmetric but $[{}^3\bar{D} - 2{}^1\bar{D}^2]$ is not antisymmetric. Therefore, we will calculate the latter as

$${}^3\bar{D}^{\text{VAL}} = {}^3\bar{D} \wedge {}^1\bar{D} - 2{}^1\bar{D}^3 \quad (43)$$

One final remark, the expressions in Mazziotti's paper⁴⁰ assume that the normalization of the n -RDM is $\text{Tr}({}^n\bar{D}) = \binom{N}{n}$, while in this work we assume that $\text{Tr}({}^nD) = \binom{N}{n} n!$. Therefore,

the formulas presented in the manuscript have been rescaled with respect to those of Mazziotti. For instance, within our normalization scheme Valdemoro's 3-RDM actually reads

$${}^3D^{\text{VAL}} = 3! \left[\frac{3}{2} {}^2D - 2 {}^1D^2 \right] \wedge {}^1D = 9 {}^2D \wedge {}^1D - 12 {}^1D^3 \quad (44)$$

■ APPENDIX B: PRACTICAL IMPLEMENTATIONS OF THE 3C-ESI FORMULA

The formula for 3c-ESI involves 3-densities of orders equal or lower than 3. In principle, one could calculate the 3c-ESI solely from the knowledge of 3-densities and using this matrix to obtain lower-order matrices by successive reductions of one index. However, such a formula is extremely expensive. The reason is that we cannot keep these matrices in memory and the strategy for the calculation of the 3c-ESI consists in the calculation three-center quantities such as $\langle \hat{\rho}_1 \hat{\rho}_2 \hat{\rho}_3 \rangle_{A,B,C}$ and sum over one atom to obtain the two-center equivalents, which are also involved in the 3c-ESI:

$$\langle \hat{\rho}_1 \hat{\rho}_2 \rangle_{A,B} = \sum_P \langle \hat{\rho}_1 \hat{\rho}_2 \hat{\rho}_3 \rangle_{A,B,P} \quad (45)$$

We need many such three-center quantities (P runs over all atoms in the molecule) in order to obtain all three-center quantities. So, even though the 3-density file is read only once, many operations need to be done for each element of the 3-density, making the calculation very time-consuming as compared to the evaluation of the only three-center quantity actually needed, $\langle \hat{\rho}_1 \hat{\rho}_2 \hat{\rho}_3 \rangle_{A,B,C}$.

It is a much wiser strategy to read lower-order n -densities files first, then calculate the lower nc -ESI and use them for the calculation of larger-order nc -ESIs. To this aim, an appropriate formula is needed. In the case of 3c-ESI, the strategy is to read first the 2-density, then calculate all 2c-ESI and the atomic populations (inexpensive), and finally read the 3-density to calculate $\langle \hat{\rho}_1 \hat{\rho}_2 \hat{\rho}_3 \rangle_{A,B,C}$. In particular, the formula reads

$$\delta(A, B, C) = 2 \langle \hat{\rho}_1 \hat{\rho}_2 \hat{\rho}_3 \rangle_{A,B,C} + \hat{\pi}_1^3 \delta(A, B) N(C) \\ - 2N(A)N(B)N(C) \quad (46)$$

where $\hat{\pi}_1^3$ is an operator which generates the combinations in the string (A,B,C) picking one and two-member sets at a time. A similar strategy can be followed to simplify the calculation of high-order ESIs, which are obviously more computationally demanding.

■ ASSOCIATED CONTENT

Supporting Information

Valdemoro's, Nakatsuji's, and Mazziotti's 3c-ESI results without the normalization factor mentioned in the manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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