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Differential density matrix overlap: an index for assessment of electron correlation in atoms and molecules

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Summary. A new index, called the differential density matrix overlap (DDMO), is proposed for assessment of the electron correlation effects in atoms and molecules. DDMO can be easily calculated as the negative value of the correlation energy derivative with respect to the relative position of the occupied and virtual orbitals. DDMO is transparent to physical interpretation. It can serve as a tool for analyzing the accuracy of approximate electron correlation methods and the validity of the Hartree–Fock wavefunction as the zeroth-order approximation. The properties of DDMO are discussed using test calculations on 11 atoms and molecules as an example.

Key words: First-order density matrix – Electron correlation – Molecular similarity

1. Introduction

During the last decade, quantum chemistry has witnessed a substantial progress in the electron correlation methods [1–7]. The Møller–Plesset perturbation theory has been implemented up to the fifth order (MP5) [2]. Calculations with the coupled cluster method including triple excitations (CCSDT) have been carried out [3, 4]. Several new computer implementations of the previously known methods have emerged, including the quadratic configuration interaction (QCI) [5] and the Brueckner doubles (BD) approach [6, 7].

Although the electron correlation methods vary with respect to their sensitivity to the (pseudo-)degeneracy effects, the importance of assessing the validity of the Hartree–Fock wavefunction as the zeroth-order approximation was recognized a long time ago. The index of almost idempotency (IAI), defined as:

$$\mathrm{IAI} = \sum_i n_i(1 - n_i), \tag{1}$$

where n_i is the occupation number of the i-th natural spinorbital, was proposed in 1965 [8] as a measure of the electron correlation effects. The same index has been recently used in the localization of the natural orbitals [9]. Recently, Lee et al. have proposed [10, 11] the Euclidean norm of the vector of t_1 (single excitation) amplitudes:

$$T_1 = N^{-1/2}\|\vec{t}_1\|, \tag{2}$$

where N is the number of electrons, as a diagnostic for the *a priori* prediction of the validity of a single-determinantal wavefunction. However, applicability of the T_1 index to assessing the multi-reference character is in doubt as the major role played by the $\hat{T}_1$ operator is rotation of spinorbitals (Thouless' theorem [12]). Instead, magnitudes of selected T_2 amplitudes seem to be more suitable for such a diagnostic.

Another application of the electron correlation indices is that of assessing the accuracy of approximate electron correlation methods. The accuracy is usually measured as the difference between the computed electron correlation energies and those obtained within a given basis set from a full configuration interaction (FCI) procedure. One might argue that the accuracy of the corresponding wavefunctions or density matrices could be assessed by computing several first-order properties, such as dipole and quadrupole moments, energy gradients, etc. and comparing them with those obtained within the FCI method. Such approach, however, would introduce an unnecessary bias, as different properties are sensitive to errors pertinent to different portions of the first-order density matrix. For example, errors in the valence natural orbitals are likely to affect the computed values of dipole moments, whereas those in the core orbitals will primarily influence the computed electron densities at nuclei. It is therefore obvious that *an average measure* of the quality of the first-order density matrix is needed. It is desirable that the same measure allows one to break down the electron correlation effects into contributions from individual occupied orbitals.

2. Theory

Electronic wavefunctions can be compared in several different ways. The simplest idea involves calculation of the overlap between the wavefunctions. This diagnostic, known as the reference configuration coefficient (C_0), has been routinely used by quantum chemists for over three decades. Unfortunately, this approach is hampered by the fact that the overlap itself is not a size extensive quantity and that only systems with the same number of elecrons can be compared. It has been repeatedly demonstrated in the literature [11, 12] that C_0 is not a good measure of the magnitude of electron correlation effects. These difficulties are alleviated in calculation of the (normalized) overlap between the respective electron densities. This approach, which was proposed some time ago by Carbo et al. [13] for the purpose of assessment of molecular similarity, suffers from the necessity of calculating four-center integrals, which makes it computationally very expensive. It is also difficult to interpret the resulting unnormalized density overlaps, since they do not represent any physical quantity.

Recently, we have proposed a new similarity index [14], called the number of overlapping electrons (NOEL), which is both computationally frugal and transparent to interpretation. Let $\Gamma_A(\vec{x}, \vec{x}')$ and $\Gamma_B(\vec{x}, \vec{x}')$ denote two first-order reduced density matrices [15], corresponding to the wavefunctions under comparison. They can represent two different systems, the same system described at two different levels of theory, or even two different geometries or different states of the same system. The NOEL similarity index is given by:

$$(A, B) = \int \int \Gamma_A^*(\vec{x}, \vec{x}')\Gamma_B(\vec{x}, \vec{x}')\, d\vec{x}\, d\vec{x}', \tag{3}$$

where $\vec{x}$ denotes both the Cartesian and spin coordinates.

When applied to two systems described at the Hartree–Fock (*HF*) level, Eq. (3) yields the number of the electrons in the overlapping fragments of the molecules. In particular:

$$(A_{HF}, A_{HF}) = N_A, \tag{4}$$

where A_{HF} denotes an atom or a molecule A, possessing N_A electrons, described at the *HF* level. Let A_{corr} stand for an atom or a molecule A with more than one electron and some approximate correlated electron method "corr". The inequality:

$$(A_{HF}, A_{\text{corr}}) < N_A \tag{5}$$

is always satisfied. The difference:

$$n_A = N_A - (A_{HF}, A_{\text{corr}}), \tag{6}$$

which we call the differential density matrix overlap (DDMO), is a measure of the extend of electron correlation in A as described by a particular approximate electron correlation method.

Before discussing practical ways of calculating DDMO we describe its properties. DDMO is always non-negative. It is size extensive and size consistent when calculated from size consistent wavefunctions. From its definition it is clear that DDMO is equal to the difference between the total number of electrons and the partial trace (over $N_A/2$ diagonal elements corresponding to the doubly occupied *HF* orbitals) of the correlated density matrix in the basis of *HF* orbitals. Therefore for a CI wavefunction in which k-tuply excited configurations have a cumulative weight of w_k:

$$n_A = \sum_k k w_k. \tag{7}$$

Equation (7) not only allows one to readily calculate DDMO for the systems described within the CI formalism, but also hints at some of its properties. For an idealized system with $N_A - 2k$ totally uncorrelated electrons and the remaining $2k$ electrons describing k fully dissociated single bonds (or $k/2$ double bonds, etc.), it is easy to prove that $n_A = k$ provided the system is described within a size consistent method. However, for a truncated CI wavefunction with at most k-tuple excitations, $n_A \leqslant k$ for a system of any size. This (surprising) result is just another manifestation of the well-known lack of size consistency of the truncated CI method.

To calculate DDMO within a particular electron correlation method it is convenient to rewrite Eqs. (3) and (6) as:

$$n_A = N_A - \langle \hat{\Gamma}_{HF} \rangle, \tag{8}$$

where $\langle \hat{\Gamma}_{HF} \rangle$ is the expectation value of the one-electron *HF* density matrix operator for A calculated at the correlated level. The expectation value can be calculated even for the correlation methods that do not produce corresponding wavefunctions. To accomplish that, one has to invoke the concept of effective "relaxed" density matrices [15, 16]. The total electronic energy resulting from any electron correlation method that uses single-reference wavefunction can be written as:

$$E = E_{HF} + E_{\text{corr}}[\{\epsilon_i\}, \{\phi_i\}, \{\epsilon_a\}, \{\phi_a\}], \tag{9}$$

where E_{HF} is the *HF* energy. The correlation energy, E_{corr}, is a functional of only the occupied (virtual) *HF* orbitals, ϕ_i (ϕ_a), and the corresponding orbital energies, ϵ_i (ϵ_a). Within the effective density matrix approach, the expectation value $\langle \hat{O} \rangle$ is obtained by perturbing the electronic Hamiltonian by $\lambda\hat{O}$ and taking the derivative of the corresponding energy, $E(\lambda)$:

$$\langle \hat{O} \rangle = \left.\frac{\partial E(\lambda)}{\partial \lambda}\right|_{\lambda=0}. \tag{10}$$

One should point out that, in general, the perturbation affects both the orbital energies and the *HF* orbitals.

Let us now calculate the expectation value $\langle \hat{\Gamma}_{HF} \rangle$. Since $\hat{\Gamma}_{HF}$ is a projector onto the occupied *HF* space, one has:

$$\left.\frac{\partial E_{HF}(\lambda)}{\partial \lambda}\right|_{\lambda=0} = N_A. \tag{11}$$

Also, since the perturbation $\lambda\hat{\Gamma}_{HF}$ leaves all the *HF* orbitals, and the orbital energies of the virtual orbitals unchanged:

$$\left.\frac{\partial E_{\text{corr}}(\lambda)}{\partial \lambda}\right|_{\lambda=0} = \left.\frac{\partial E_{\text{corr}}[\{\epsilon_i + \lambda\}, \{\phi_i\}, \{\epsilon_a\}, \{\phi_a\}]}{\partial \lambda}\right|_{\lambda=0}. \tag{12}$$

Combining Eqs. (8)–(12) we obtain:

$$n_A = -\left.\frac{\partial E_{\text{corr}}[\{\epsilon_i + \lambda\}, \{\phi_i\}, \{\epsilon_a\}, \{\phi_a\}]}{\partial \lambda}\right|_{\lambda=0}. \tag{13}$$

Thus DDMO can be also interpreted as the sensitivity of the correlation energy to the relative positions of the occupied and virtual spaces.

Equation (13) suggests a practical way of calculating DDMO. Since the derivative, Eq. (13), does not involve orbital relaxation, it can be easily programmed for any of the known electron correlation methods. Alternatively, one can calculate DDMO by numerical differentiation at the cost of two calculations of the correlation energy. One should remark that for iterative methods, such as CCSD, the second calculation would require only a fraction of the computational effort associated with the first one. It is so because the converged amplitudes from the first calculation can be used as a very efficient guess for the second one.

3. Sample calculations

The values of DDMO were calculated with the 6-311G** basis set for 11 atoms and molecules. The T_1 diagnostics were reported previously by Lee et al. [10] for 9 of these systems. All electrons were correlated. The indices were computed by two-point finite differences using a step of 10^{-5} [au]. This methodology was found to produce the values of DDMO with an accuracy of at least four digits. The calculations required a trivial modification of link 801 of the GAUSSIAN 88

Table 1. Calculated values of DDMO per electron for selected atoms and molecules

System	Geometry[a]	N[b]	DDMO[c]						
			MP2	MP3	MP4DQ	MP4SDQ	MP4	QCISD	QCISD(T)
He		2	0.0048	0.0069	0.0075	0.0075	0.0075	0.0077	0.0077
H_2	1.361	2	0.0089	0.0133	0.0150	0.0151	0.0151	0.0161	0.0161
Be		4	0.0145	0.0265	0.0348	0.0349	0.0350	0.0462	0.0468
He_2	5.610	4	0.0048	0.0068	0.0074	0.0075	0.0075	0.0077	0.0077
Li_2	5.110	6	0.0113	0.0194	0.0246	0.0247	0.0248	0.0313	0.0320
HF	1.734	10	0.0083	0.0082	0.0084	0.0086	0.0092	0.0087	0.0092
H_2O	1.809/104.8	10	0.0105	0.0108	0.0112	0.0114	0.0122	0.0114	0.0122
CH_4	2.052	10	0.0119	0.0146	0.0149	0.0152	0.0162	0.0155	0.0166
Ne		10	0.0056	0.0055	0.0056	0.0057	0.0059	0.0057	0.0059
N_2	2.074	14	0.0159	0.0145	0.0153	0.0162	0.0189	0.0161	0.0184
CO	2.132	14	0.0136	0.0131	0.0139	0.0153	0.0180	0.0154	0.0173

[a] bond lengths in atomic units
[b] number of electrons
[c] calculated with the 6-311G** basis set by two-point numerical differences with a shift equal to 10^{-5}

suite of programs [18]. The DDMOs were calculated at the MP2, MP3, MP4DQ, MP4SDQ, full MP4, QCISD and QCISD(T) [5] levels. The computed values of DDMOs per electron (n_A/N_A) are presented in Table 1. For comparison, in Table 2 we quote values of the T_1 index taken from Ref. [10].

First, we comment on the similarities between the observed trends in the computed values of n_A/N_A and the magnitudes of the T_1 indices. In both cases, the systems with a considerable multiconfigurational character, namely Be and Li_2, have the corresponding values of correlation indices much larger than the other systems studied. Interestingly, the magnitudes of the T_1 indices for He and H_2 are much smaller than for other systems that are reasonably well described by a single Slater determinant. This is not the case with the normalized DDMO indices. This discrepancy can be simply explained by noticing that the T_1 diagnostics puts artificially large emphasis on the single excitations. In an

Table 2. Values of the T_1 index for selected atoms and molecules[a]

System[b]	Method[c]	T_1
He	FCI	0.0029
H_2	FCI	0.0050
Be	FCI	0.0210
He_2	FCI	0.0029
Li_2	FCI	0.0165
HF	CISD	0.0096
CH_4	CISD	0.0073
Ne	CISD	0.0065

[a] Ref. [10]
[b] see Table 1 for molecular geometries
[c] see Ref. [10] for the basis sets used

extreme case of two-electron systems described by just one occupied and one virtual orbital, the T_1 index is expected to be exactly equal to zero, whereas the normalized DDMO index is not. At the present time, it is unclear how this feature of the T_1 diagnostics is going to affect its predictive value.

Our second comment concerns the convergence of the MP results. Three distinct patterns are present. The indices for the He and Ne atoms and the H_2, He_2, HF, H_2O, and CH_4 molecules exhibit in general a monotonic convergence, although in the case of the HF and Ne species the MP3 indices are slightly smaller than the MP2 ones. The full MP4 indices are close to those computed at the QCISD(T) level, whereas the MP4SDQ indices follow the QCISD ones. The size extensivity of DDMO is clearly demonstrated by comparing the indices of He and the weakly interacting He_2. The second category encompasses the N_2 and CO molecules. There is an oscillatory convergence of the DDMOs. Despite this, the MP4 values are not very different from the QCISD(T) ones. Finally, for the Be atom and the Li_2 molecule a very slow convergence of the MP series is observed.

The line that demarcates the first two categories from the third one is the value of DDMO per electron. The systems belonging to the first two classes have their values of DDMO per electron (calculated at the QCISD(T) level) in the range of 0.0077–0.0166. The respective values for the third class are 0.0468 (Be) and 0.0320 (Li_2). It is clear that one cannot expect the systems with DDMO per electron greater than ca. 0.02 to be well described with the *HF* wavefunction as the zeroth-order approximation.

One should point out that the normalized values of DDMO express, like their T_1 counterparts, only an *average* extent of the correlation effects per electron. Although large values of the normalized DDMO indicate a substantial multiconfigurational character, small values do not imply that the contributions from individual orbitals are all small. Such situation can be well illustrated by the example of a large biradicaloid molecule in which only one occupied orbital is highly correlated. In such a case it is important to look at contributions to n_A from "suspicious" occupied orbitals. Let $n_{A(i)}$ denote the negative derivative of the correlation energy with respect to the orbital energy of the i-th occupied orbital. Obviously, (see Eq. (13)):

$$n_A = \sum_{i=1}^{N_A/2} n_{A(i)}. \tag{14}$$

$n_{A(i)}$, which is calculated as easily as n_A itself, can be regarded as a contribution from the i-th occupied *HF* orbital to the error in the first-order density matrix. It assumes values between 0 and 1. To illustrate the differences between the magnitudes of individual $n_{A(i)}$ and their averages, we computed these indices for the CH_4 and CO molecules at the QCISD(T) level. The indices are given in Table 3.

There are marked differences between the orbital contributions to DDMOs in these two molecules, although the respective averages are very similar. In CH_4, which has one core and four valence occupied orbitals, the largest contribution originates from the σ HOMO and amounts to 0.0518. On the other hand, in the CO molecule, there are two core and five valence occupied orbitals. In this case, the largest contributions come from the two degenerate HOMO-1 π-orbitals and are substantially larger than the largest contributions in CH_4.

Table 3. Orbital contributions to DDMO in the CH_4 and CO molecules (at the QCISD(T) level)[a]

	CH_4			CO	
Orbital i	Orbital energy ϵ_i [au]	Contribution to DDMO, $n_{A(i)}$	Orbital i	Orbital energy ϵ_i [au]	Contribution to DDMO, $n_{A(i)}$
$1\ A'$	-11.20582	0.0009	$1\ \sigma$	-20.66437	0.0001
$2\ A'$	-0.96292	0.0270	$2\ \sigma$	-11.36067	0.0002
$3\ A''$	-0.59915	0.0429	$3\ \sigma$	-1.52354	0.0184
$4\ A'$	-0.56615	0.0436	$4\ \sigma$	-0.80343	0.0343
$5\ A'$	-0.44107	0.0518	$5\ \pi$	-0.63819	0.0664
			$6\ \pi$	-0.63819	0.0664
	Total	0.1662	$7\ \sigma$	-0.55281	0.0563
				Total	0.2421

[a] calculated with the 6-311G** basis set by two-point numerical differences with a shift equal to 10^{-5}

What do we learn from Table 3? the spatial extent of π-orbitals is usually larger than that of (especially core) σ-orbitals. This means that, despite similar normalized values of DDMO, one may expect much larger errors in such quantities as multipole moments for the CO molecule than for the CH_4 one. This explains why CO is usually regarded to be a "problem" molecule whereas CH_4 is not. One should note, however, that the core orbital contributions are much larger in CH_4 than in CO. This means that inclusion of electron correlation effects is going to affect the computed values of such observables as the density at nuclei or the average reciprocal distance from the nucleus much more in the case of CH_4 than in CO. Obviously, different observables are sensitive to different portions of the first-order density matrix.

4. Discussion

The DDMO index has several advantages. It can be computed easily with the *HF* spin orbitals (Eq. (13)). It is invariant with respect to orbital rotations (although one has to use Eqs. (3) and (6) for non-canonical orbitals) and it has a transparent physical interpretation. It parallels the NOEL similarity index and therefore it allows for a more unified description of the electronic structure of atoms and molecules. Since it does not rely on the single excitations alone, it is more general than the t_1 diagnostic. There are two potential applications of DDMO. First, it can be used as a diagnostic for the magnitude of the electron correlation effects in a given system. Second, it can be utilized for assessing the accuracy of approximate electron correlation methods. The values of DDMO calculated within a given method can be compared with those obtained from the FCI calculations. In this way DDMO can serve as an index complementary to the correlation energy. In this respect, DDMO provides more information than the correlation energy alone, since it is sensitive to the quality of wavefunction, rather than energy. The traditional way of assessing the accuracy of the wavefunction by comparing the calculated dipole moments, optimized geometries, and vibrational frequencies [19] is less desirable, since it introduces bias toward particular electronic properties.

This particular application of DDMO is well illustrated in Figs. 1 and 2 in which we display the dependence of the 6-311G** correlation energies and DDMOs calculated at different levels of approximation as a function of the nuclear separation in the hydrogen molecule. It is evident that upon bond stretching the quality of the wavefunction (and therefore the computed properties) is expected to deteriorate much quicker than the quality of correlation energy. Figure 2 also nicely illustrates the FCI limit of DDMO as R goes to infinity. The value of unity is attained as expected.

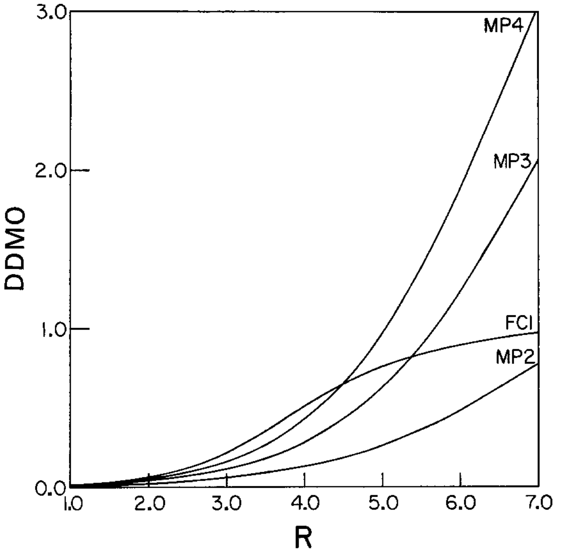

Fig. 1. The DDMO index as a function of the nuclear separation, R, in the H_2 molecule

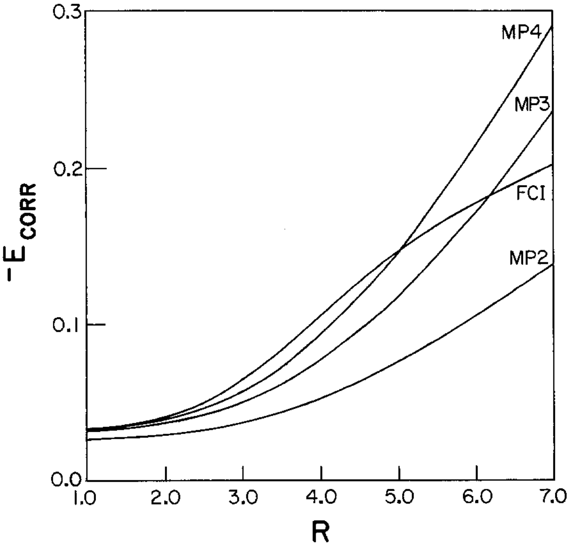

Fig. 2. The correlation energy as a function of the nuclear separation, R, in the H_2 molecule

Summing up, we believe that both the (normalized) DDMO and the orbital contributions to it have the potential of becoming useful tools in assessing the extent of electron correlation and judging the accuracy of approximate quantum-chemical methods.

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