One-Particle Density Matrix Functional for Correlation in Molecular Systems

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Received 16 October 2002; accepted 8 May 2003
DOI 10.1002/qua.10707

ABSTRACT: Based on the analysis of the general properties for the one- and two-particle reduced density matrices, a new natural orbital functional is obtained. It is shown that by partitioning the two-particle reduced density matrix in an antisymmeterized product of one-particle reduced density matrices and a correction \( \Gamma \) we can derive a corrected Hartree–Fock theory. The spin structure of the correction term from the improved Bardeen–Cooper–Schrieffer theory is considered to take into account the correlation between pairs of electrons with antiparallel spins. The analysis affords a nonidempotent condition for the one-particle reduced density matrix. Test calculations of the correlation energy and the dipole moment of several molecules in the ground state demonstrate the reliability of the formalism. © 2003 Wiley Periodicals, Inc. Int J Quantum Chem 94: 317–323, 2003

Key words: reduced density matrix; density matrix functional; natural orbital functional; electron correlation; dipole moment

Introduction

The most accurate methods available today for calculating the ground-state energy in molecular systems, e.g., the configuration interaction (CI) method [1] or the coupled cluster (CC) method [1], are computationally too expensive to be applied to large systems. Rather than dealing directly with the many-body wave function, we can alternatively determine the ground-state energy by minimizing an energy functional with respect to the electronic charge density [2]. Unfortunately, this functional is not known exactly and attempts to construct it have not been successful due to the strong nonlocality of the kinetic energy term.

Because the interactions between electrons are pairwise within the Hamiltonian, the energy may be determined exactly from a knowledge of the two-particle reduced density matrix (2-RDM). Although this functional is known, the 2-RDM has not replaced the wave function as the fundamental quantity of electronic structure because a simple set of necessary and sufficient conditions for ensuring...
that the 2-RDM corresponds to an \( N \)-particle wave function is not known (the \( N \)-representability problem) [3]. The minimization of the energy with respect to a 2-RDM constrained by the well-known \( D \), \( Q \), and \( G \) necessary conditions [3, 4] has been recently presented [5] with accurate results. The contracted Schrödinger equation (CSE), also known as the density equation, offers a nonvariational approach to constrain the 2-RDM to be approximately \( N \)-representable [6]. The difficulty with this method lies in the need for the 3- and 4-RDMs that have to be reconstructed from the 2-RDM. The number of elements in the 2-RDM in general is still large.

In this article we consider a theory focused on the one-particle reduced density matrix (1-RDM). The properties of the total energy functional of the 1-RDM are well known [7]. A major advantage of a density matrix formulation is that the kinetic energy and the exchange energy are explicitly defined using the one-matrix and do not require the construction of a functional. The unknown functional in a 1-RDM theory only needs to incorporate electron correlation. It does not rely on the concept of a fictitious noninteracting system. Consequently, density matrix schemes are not expected to suffer from the numerous problems of Kohn–Sham (KS) methods [8] based upon approximate exchange correlation energies in contrast to the GU functional. Yasuda [14] obtained a correlation energy functional (GU) [10] proposed a simple functional without the spin structure that we used in the improved Bardeen–Cooper–Schrieffer (IBCS) approximation [19], but introduce a new spatially dependence in the correction term of the 2-RDM. The reliability of this natural orbital functional (NOF) is then established by applying it to several molecules.

**Functional**

For a system of \( N \) electrons, the exact energy functional of the 1- and 2-RDMs is

\[
E = \sum_{q,\sigma,q',\sigma'} \langle q\sigma| h | q'\sigma' \rangle \Gamma_{q',\sigma';q,\sigma} + \sum_{q,\sigma,q_1,\sigma_1,q_2,\sigma_2} \times \langle q_1\sigma_1, q_2\sigma_2 | q_1'\sigma_1', q_2'\sigma_2' \rangle \Gamma_{q_1',\sigma_1';q_2,\sigma_2} \Gamma_{q_2',\sigma_2';q_1,\sigma_1} \quad (1)
\]

in which \( q\sigma \) is the matrix element of the kinetic energy and nuclear attraction terms and \( \langle q_1\sigma_1, q_2\sigma_2 | q_1'\sigma_1', q_2'\sigma_2' \rangle \) are the electronic repulsion integrals. The states \( | q\sigma \rangle \) constitute a complete orthonormal set of single-particle wave functions, where \( q \) denotes the orbital and \( \sigma \) is the sign of the spin projection (it takes two values: +1 and −1). The matrices \( 1\Gamma_{q',\sigma';q,\sigma} \) and \( 2\Gamma_{q_1',\sigma_1';q_2,\sigma_2} \Gamma_{q_2',\sigma_2';q_1,\sigma_1} \) are the 1- and 2-RDM, respectively, both in the \( (q\sigma) \)-representation.

The RDMs satisfy important sum rules. The trace of the 1-RDM equals the number of electrons

\[
\sum_{q,\sigma} 1\Gamma_{q,\sigma} = N \quad (2)
\]

and the trace of the 2-RDM gives the number of electron pairs in the system.
\[
\sum_{q,q',q''} 2\Gamma_{q'q''q''} = \frac{N(N-1)}{2}.
\]  

(3)

Their diagonal elements are always nonnegative because \(\Gamma_{qq''} \) is related to the probability of finding one electron at \( (q) \) and \( 2\Gamma_{q'q''q''} \) is related to the probability of finding one electron at \( (q) \) and another at \( (q') \).

Attempts to determine the energy by minimizing expression (1) are complicated by the fact that the \( N \)-representability conditions for the 2-RDM are not known. Consequently, the energy obtained may not be an upper bound to the true energy. The 2-RDM can be partitioned into an antisymmetrized product of the 1-RDMs, which is simply the Hartree-Fock (HF) approximation, and a correction \( \Gamma^c \) to it,

\[
2\Gamma_{q'q''q''q''} = \frac{1}{2} (\Gamma_{q'q''q''} \Gamma_{q'q''q''} - \Gamma_{q'q''q''} \Gamma_{q''q'q''} - \Gamma_{q'q''q''} \Gamma_{q''q'q''}).
\]

(4)

This decomposition of the 2-RDM is well known from the cumulant theory. \( \Gamma^c \) is the cumulant matrix [20] or the connected part [14, 21] of the 2-RDM but with the opposite sign. Note that \( \Gamma^c \) cannot be decomposed into terms that depend only on 1-RDM elements because it arises from interactions in the Hamiltonian.

The first two terms on the right side of Eq. (4) together satisfy general properties of the 2-RDM: the Hermiticity, the particle permutational symmetry, and the fermionic antisymmetry [22]. Therefore, our correction \( \Gamma^c \) to the HF approximation should satisfy these relations.

There is an important contraction relation between 1- and 2-RDMs that is in agreement with the previous normalization:

\[
\Gamma_{q'q''} = \frac{2}{N-1} \sum_{i,s} 2\Gamma_{q'q''i'sq'is}.
\]

(5)

It can be shown from Eq. (5), taking into account the normalization condition for the 1-RDM (2), that the corrected 1-RDM satisfies then the following nonidempotent condition:

\[
\sum_{i,s} (\Gamma^c_{q'q''i's} + \Gamma^c_{s'q''q'r}) = \Gamma_{q'q''}.
\]

(6)

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This condition guarantees also the normalization condition (3) for the 2-RDM if the normalization condition for the 1-RDM is imposed. Equation (6) generalizes our previous used nonidempotent condition [19] and is equivalent to the partial trace relation involving the two-particle cumulant matrix and the 1-RDM obtained by Mukherjee and Kutzelnigg [23].

It is well known that the HF approximation accounts for most of the correlation effects between electrons with parallel spins. The unknown functional in a corrected RDM theory only needs in principle to incorporate correlation effects between electrons with antiparallel spins. Therefore, we can obtain a suitable approximation for \( \Gamma^c \) in the IBCS form:

\[
\Gamma^c_{q'q''q''q} = \sigma_1 \sigma_3 \left\{ \delta_{q'q''q} \delta_{q'q''q} - \delta_{q'q''q} \delta_{q'q''q} \right\}.
\]

(7)

where the spinless correction \( \Gamma^c_{q'q''q''q} \) must be a Hermitian matrix and satisfies the following symmetry properties:

\[
\Gamma^c_{q'q''q''q} = \Gamma^c_{q'q''q''q} = \Gamma^c_{q'q''q''q} = \Gamma^c_{q'q''q''q}.
\]

(8)

A large number of choices for the correction \( \Gamma^c \) is possible. It has a dependence of four indices and direct computation with such magnitudes is too expensive to be applied to large systems. We want to maximize the physical content of \( \Gamma^c \) to a few number of terms. Considering the symmetry properties (8), we express \( \Gamma^c \) by means of a two-index Hermitian matrix \( \gamma_{q'q} \):

\[
\Gamma^c_{q'q''q''q} = \gamma_{q'q}(\delta_{q'q'q} \delta_{q'q''q} + \delta_{q'q''q} \delta_{q'q''q}).
\]

(9)

Let us now consider that our single-particle wave functions \( \langle q|q'\rangle \) are the natural spin orbitals:

\[
\Gamma^c_{q'q''q''q} = n_q \delta_{q'q} \delta_{q'q''}.
\]

(10)

According to expression (6) matrix \( \gamma \) must satisfy the relation

\[
\gamma_{ql} + \sum_i \gamma_{li} = n_q (1 - n_q).
\]

(11)

The dependence of \( \gamma_{qq} \) on the indices \( q \) and \( q' \) is perhaps a difficult one. We propose a simple dependence where indices are separated, satisfying always the above nonidempotent set of conditions (11),
The electronic energy functional will then be
\[ \gamma_{qq} = f_q f_q - g_q g_q + \frac{1}{2} \delta_{qq} \]
\[ \times \left[ n_q(1-n_q) + g_q^2 - f_q^2 = S \cdot f_q \right] \tag{12} \]
in which
\[ S = \sum_q f_q \]
and the functions \( g_q \) are compelled to obey the constraint
\[ \sum_q g_q = 0. \tag{13} \]

The electronic energy functional will then be
\[ E([|q\rangle],\{n_q\}) \]
\[ = 2 \sum_q \langle q|\langle q|n_q + \sum_{qq'} [2\langle qq'|qq' \rangle
- \langle qq'|q'q \rangle n_q n_{q'} - \sum_{q'} [\langle qq'|qq' \rangle
+ \langle qq'|q'q \rangle [f_q f_{q'} - g_q g_{q'}]

+ \sum_q \langle qq|qq\rangle [f_q^2 + S \cdot f_q - n_q(1-n_q) - g_q^2]. \tag{15} \]

In this equation, the first term is the sum of the kinetic and electron-nuclei potential energies. It can be seen that the electron correlation modifies this term directly because the value of \( n_q \) may now be fractional. The second term is the well-known sum of the Coulomb and exchange energies. The last two terms are energies that adjust the correlation of particles with antiparallel spins.

Concerning the choice of the type of the correlation functions \( f_q \) and \( g_q \), we think that they should depend on the product of the level occupation \( n_q \) and the level vacancy \( 1-n_q \) to annihilate the correlation corrections for the HF case. The exact functional forms of them are probably complicated, requiring a distinction between occupied and virtual HF orbitals [22]. Moreover, we consider a different functional form for the lower occupied levels. To be specific we propose the following potential dependences for the occupied HF levels:

\[ f_q = -n_q^{120000+10^{-13}c^2} (1-n_q)^{0.22}, \]
\[ g_q = [n_q(1-n_q)]^{0.9}, \quad e_q < e_{cf} \tag{16} \]
\[ f_q = n_q^{-20e^q}(1-n_q)^{0.22}, \quad g_q = -[n_q(1-n_q)]^{0.9}, \]
\[ e_q > e_{cf} \tag{17} \]

where \( e_q \) is the one-particle orbital energy of the level \( q \) and \( e_{cf} \) is the value of the energy where the functions \( f_q \) and \( g_q \) change their signs. For the case of virtual HF orbitals the exponent values of function \( f_q \) must be set equal to unity:

\[ f_q = n_q(1-n_q), \quad g_q = [n_q(1-n_q)]^{0.9}. \tag{18} \]

The exponential values are critical to fulfill the 2-RDM nonnegativity condition (D-condition). We fixed their values to obtain the CI total energy with inclusion of single, double, triple, and quadruple excitations (CI-SDTQ) for the water molecule. It is well known that this kind of calculation on this molecule yields more than 99% of the basis set correlation energy [1]. The huge values for the exponents in Eq. (16) are necessary to guarantee that occupations for the lower occupied levels approach to unity.

The functions \( f_q \) and \( g_q \) obtained with these exponents are appropriate ones. They fulfill all properties of the RDMs imposed before and give a good description of the occupation numbers. We recall that all occupation numbers must be fractional to guarantee that all orbitals have the same chemical potential.

**Results**

Applying the well-known procedure of taking molecular orbitals as linear combination of atomic orbitals (MO-LCAO), Eq. (15) becomes the functional \( E([c_q],\{n_q\}) \). One has to calculate the gradient of the functional both with respect to natural orbitals coefficients \( [c_q] \) and the occupation numbers \( \{n_q\} \). Because the minimization with respect to occupations is much cheaper than with respect to the orbitals, one can adopt the procedure used by us in the IBCS method. In the inner loop we find the optimal occupation numbers for a given set of orbitals. In the outer loop we minimize with respect to the orbital coefficients. The iterative procedure is repeated until convergence not only for \( [c_q] \) but also for \( \{n_q\} \) is reached.
The constraints that have to be satisfied simultaneously in the minimization process are:

1. The constant number of particles \(2 \sum q n_q = N\).

2. The \(N\)-representability condition of the 1-RDM [3]: \(0 \leq n_q \leq 1\).

3. The consequence of the nonidempotent condition \(\sum g_q = 0\).

4. The orthonormality condition \(C^* SC = I\) (S is the overlap matrix).

Figure 1 shows a typical solution for \([n_q]\) of the variational problem. As we can see, due to the correlation, the electrons partially occupy molecular orbitals outside of the Fermi surface. The valence orbitals closer to the Fermi level have the largest contribution to the electronic correlation because their occupations differ more from the HF values. For the lower occupied levels, occupations approach to unity whereas for the higher virtual levels they approach to zero.

In Table I we report the values obtained for the total energies of several molecules, employing the experimental geometry [24]. These values were computed using contracted Gaussian basis sets 6-31G** [25]. For comparison, we included in this table the total energies calculated with the Gaussian

TABLE I ______________________________________________________________________________________________

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF(^a)</th>
<th>CCD(^b)</th>
<th>NOF(^c)</th>
<th>G3(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>−100.0098</td>
<td>−100.1959</td>
<td>−100.2145</td>
<td>−100.4011</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>−76.0226</td>
<td>−76.2256</td>
<td>−76.2271</td>
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</tr>
<tr>
<td>NH(_3)</td>
<td>−56.1950</td>
<td>−56.3960</td>
<td>−56.3965</td>
<td>−56.5070</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>−40.2014</td>
<td>−40.3851</td>
<td>−40.3921</td>
<td>−40.4576</td>
</tr>
<tr>
<td>LiF</td>
<td>−106.9337</td>
<td>−107.1222</td>
<td>−107.2523</td>
<td>−107.3675</td>
</tr>
<tr>
<td>BeO</td>
<td>−89.4066</td>
<td>−89.6330</td>
<td>−89.7498</td>
<td>−89.8465</td>
</tr>
<tr>
<td>C(_2)</td>
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<td>−75.6828</td>
<td>−75.7647</td>
<td>−75.8896</td>
</tr>
<tr>
<td>BF</td>
<td>−124.1006</td>
<td>−124.3431</td>
<td>−124.4966</td>
<td>—</td>
</tr>
<tr>
<td>CO</td>
<td>−112.7360</td>
<td>−113.0188</td>
<td>−113.1716</td>
<td>−113.2674</td>
</tr>
<tr>
<td>N(_2)</td>
<td>−108.9408</td>
<td>−109.2520</td>
<td>−109.3896</td>
<td>−109.4840</td>
</tr>
<tr>
<td>HCN</td>
<td>−92.8752</td>
<td>−93.1661</td>
<td>−93.2914</td>
<td>−93.3754</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>−76.8206</td>
<td>−77.0937</td>
<td>−77.2255</td>
<td>−77.2760</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>−78.0377</td>
<td>−78.3461</td>
<td>−78.4644</td>
<td>−78.5074</td>
</tr>
<tr>
<td>H(_2)CO</td>
<td>−113.8679</td>
<td>−114.1898</td>
<td>−114.3857</td>
<td>−114.4310</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>−398.6733</td>
<td>−398.8287</td>
<td>−399.0667</td>
<td>−399.2384</td>
</tr>
<tr>
<td>PH(_3)</td>
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</tr>
<tr>
<td>HCl</td>
<td>−460.0643</td>
<td>−460.2215</td>
<td>−460.4863</td>
<td>−460.6546</td>
</tr>
<tr>
<td>CH(_2)F</td>
<td>−139.0378</td>
<td>−139.3735</td>
<td>−139.5431</td>
<td>−139.6496</td>
</tr>
<tr>
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<td>−199.0316</td>
<td>−199.3710</td>
<td>−199.4261</td>
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<tr>
<td>ClF</td>
<td>−558.8160</td>
<td>−559.1394</td>
<td>−559.6950</td>
<td>−559.7701</td>
</tr>
</tbody>
</table>

\(^a\) HF total energies.
\(^b\) Coupled cluster doubles total energies.
\(^c\) Natural orbital functional total energies computed in this work.
\(^d\) G3 total energies.

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94 system of programs [26] at the coupled cluster doubles (CCD) level. We also included in Table I the total energies obtained with the Gaussian-3 (G3) theory [27]. This composite technique is designed to arrive at a total energy of a given molecular system.

According to Table I, the values we obtained are in general lower than those obtained with the CCD method. Our NOF calculations on 10-electron molecules (HF, H₂O, NH₃, CH₄) give total energies close to the CCD ones, which are accurate results for the basis set correlation energies. Note that the percentage of the correlation energy obtained by CCD decreases as the size of the molecule increases, whereas our functional keeps giving a substantial portion of the correlation energy (see, e.g., the HCL molecule). Note that the energy improvement is not lower than the G3 theory.

For molecules with reported experimental values [28] of the dipole moment, we also evaluated this property (Table II). The results clearly underline the importance of the correlation effects. An important case is the CO molecule, for which the HF approximation gives a dipole moment in the wrong direction, whereas correlation methods approach it to the experimental value. In the case of LiF, we have to mention that with all methods the dipole moment is decreased with respect to the HF result, whereas the experiment yields a higher value.

### Table II

Dipole moments ($\mu$) in Debyes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HFa</th>
<th>CCDb</th>
<th>NOFc</th>
<th>Exp.d</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.97</td>
<td>1.88</td>
<td>1.82</td>
<td>1.82</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.19</td>
<td>2.11</td>
<td>2.04</td>
<td>1.85</td>
</tr>
<tr>
<td>NH₃</td>
<td>1.88</td>
<td>1.83</td>
<td>1.75</td>
<td>1.47</td>
</tr>
<tr>
<td>LiF</td>
<td>6.20</td>
<td>5.96</td>
<td>5.76</td>
<td>6.33</td>
</tr>
<tr>
<td>CO</td>
<td>0.32e</td>
<td>0.01</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>HCN</td>
<td>3.23</td>
<td>2.93</td>
<td>3.08</td>
<td>2.98</td>
</tr>
<tr>
<td>H₂CO</td>
<td>2.75</td>
<td>2.69</td>
<td>2.45</td>
<td>2.33</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.39</td>
<td>1.30</td>
<td>1.22</td>
<td>0.97</td>
</tr>
<tr>
<td>PH₃</td>
<td>0.80</td>
<td>0.79</td>
<td>0.65</td>
<td>0.58</td>
</tr>
<tr>
<td>CH₃F</td>
<td>2.06</td>
<td>1.96</td>
<td>1.92</td>
<td>1.85</td>
</tr>
<tr>
<td>HCl</td>
<td>1.45</td>
<td>1.38</td>
<td>1.28</td>
<td>1.08</td>
</tr>
<tr>
<td>ClF</td>
<td>1.26</td>
<td>1.05</td>
<td>1.04</td>
<td>0.88</td>
</tr>
</tbody>
</table>

a HF dipole moments.
b Coupled cluster doubles dipole moments.
c Natural orbital functional dipole moments computed in this work.
d Experimental dipole moments.
e This value has an opposite sign relative to the experimental value.

### Conclusions

A natural orbital functional (15) that satisfies the general properties of reduced density matrices has been proposed. The approach presented is a well-comprehensible density matrix theory that does not require the introduction of a noninteracting kinetic energy functional. It is shown that by partitioning the two-particle reduced density matrix into an antisymmetrized product of one-particle reduced density matrices and a correction $\Gamma$ we can derive a corrected HF theory.

The nonidempotency of the one-particle reduced density matrix is a key aspect of many correlated systems that all exhibit occupation numbers that deviate from one or zero. The set of these conditions, Eq. (6), has been reduced to only one constraint (14) that may help in future calculations for large systems.

The resultant two-particle reduced density matrices satisfied the $D$ condition, while the one-particle reduced density matrices were exactly $N$ representable. Complementary research on $Q$ and $G$ conditions for the 2-RDM should be made. Although these necessary conditions are not sufficient, they will be useful to eliminate unphysical solutions.

The results are encouraging: A simple functional yields correlation energies as good as those obtained from the density functionals.

### Acknowledgment

The authors are grateful for the generous financial support of the Alexander von Humboldt (AvH) Foundation (AvH ID IV KUB 1071038 STP).

### References


