Approximately \( N \)-representable density functional density matrices: The case of large \( N \)

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Abstract. Density matrices approximately \( N \)-representable by a correlated determinant wavefunction (CDWF) have been previously derived. For the case of helium it had been shown how to obtain these density matrices as density functionals. Here it is shown that the same procedures, used for helium, generalize to the case for the number of electrons \( N \)-large. The result is a procedure for obtaining approximately CDWF \( N \)-representable density matrices which are functionals of the density for large \( N \).

Keywords. \( N \)-representable; density matrix; density functional; correlation energy; HK functional.

1. Introduction

The problem of \( N \)-representability (Huisimi 1940; Löwdin 1955; Mayer 1955; Tredgold 1957; McWeeny 1960; Coleman 1963) is that of finding conditions by which to recognize the reduced density matrices which are assured to be related to an \( N \)-body wavefunction according to the rule,

\[
\rho_p(1 \cdots p, 1' \cdots p') \equiv N(N-1) \cdots (N+p+1)\Psi^*(1' \cdots N)\Psi(1 \cdots N)d(p+1) \cdots N, \tag{1}
\]

where \( \Psi \) is an antisymmetric \( N \)-body wavefunction. In such cases that the above equation holds in good approximation, but not exactly, we speak of density matrices which are thus approximately \( N \)-representable.

Here, we use exact density delivering Slater determinants (Clinton and Massa 1972; Frishberg and Massa 1981; Massa et al 1985) to generate correlated-determinant wavefunctions (CDWF) (Jastrow 1955; Boys and Handy 1969; Roby 1971; Colle and Salvetti 1975). By the phrase "correlated-determinant wavefunction" we shall mean a product of a Slater determinant and a spinless correlation function of the form

\[
\Psi = \Psi_{\text{det}}(1 \cdots N)\Pi(1 - \phi(ij)). \tag{2}
\]

In a recent paper (Soirat et al 1994) we derived density matrices which are approximately \( N \)-representable by a correlated determinant wavefunction.

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The density matrices were of the form

\begin{align*}
\rho_2(12) &= \\
\rho_{2\text{det}}(12) + \{\rho_{2\text{det}}(12)b(12) + \rho_{3\text{det}}(123)[b(13) + b(23)]d3 \\
&\quad + 1/2\rho_{4\text{det}}(1234)b(34)d3d4 + \rho_{3\text{det}}(123)[b(12)b(13) + b(12)b(23)] \\
&\quad + b(13)b(23)d3 \\
&\quad + 1/2\rho_{4\text{det}}(1234)[b(13)b(14) + b(23)b(24) + b(12)b(34) + b(13)b(34)] \\
&\quad + b(14)b(34) + b(23)b(34) + b(24)b(34)d3d4 \\
&\quad + \rho_{4\text{det}}(1234)[b(13)b(24)]d3d4 \\
&\quad + 1/2\rho_{5\text{det}}(12345)[b(13)b(45) + b(23)b(45)]d3d4d5 \\
&\quad + 1/6\rho_{5\text{det}}(12345)[b(34)b(35) + b(35)b(45)]d3d4d5 \\
&\quad + 1/8\rho_{6\text{det}}(123456)[b(34)b(56)]d3d4d5d6,
\end{align*}

and

\begin{align*}
\rho_1(11') &= \\
\rho_{1\text{det}}(11') + \{\rho_{2\text{det}}(121')b(21')d2 + \rho_{3\text{det}}(123'1')[b(121') + b(132') + b(213')]d2d3 \\
&\quad + 1/2\rho_{4\text{det}}(1231'23)b(23)d2d3 \\
&\quad + 1/2\rho_{4\text{det}}(12341'234)d2d3d4 \\
&\quad + 1/6\rho_{4\text{det}}(12341'234)[b(23)b(24) + b(23)b(34) + b(24)b(34)]d2d3d4 \\
&\quad + 1/8\rho_{5\text{det}}(123451'2345)[b(23)b(45)]d2d3d4d5,
\end{align*}

where we have collected the $\phi(ij)$ according to the definition,

\begin{align*}
b(ijj') &= -\phi(ij) - \phi(i'j') + \phi(ij)\phi(i'j'),
\end{align*}

and the subscript "det" attached to a symbol for a reduced density matrix indicates it is obtained from an exact density-delivering Slater determinant.

It is convenient to write our density matrices in the following notation,

\begin{align*}
\rho_2(12) &= \rho_{2\text{det}}(12) + a_2(12), \\
\rho_1(11') &= \rho_{1\text{det}}(11') + a_1(11'),
\end{align*}

where $a_2$ and $a_1$ are given explicitly by the expressions contained in curly brackets in (3) and (4), respectively.

The correlation corrections $a_2$ and $a_1$ may be fixed entirely by the density. The exact density Slater determinant carries the very information required for its own correction. Hence, notice that according to (7)

\begin{align*}
a_1(11')|_{1\rightarrow -1} &= 0.
\end{align*}

This must be true in order for $\rho_{1\text{det}}(11')$ to satisfy its defining characteristic of delivering the exact density. This immediately places an exact condition upon the diagonal
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elements of the correction to the two-body density matrix, viz.,

\[ \int a_2(12) d^2 = 0, \]  

which may be used as a density functional condition to fix the correlation corrections to exact density determinantal qualities.

In our recent paper (Soirat et al 1994) we showed how this could be done using the helium atom as an example. Because helium contains only two electrons, the density functional condition on \( a_2 \), given by equation (9), has an approximate solution, given by Colle and Salvetti, which is readily obtained. However, for the number of electrons \( N \) large, it is clear that \( a_2 \) becomes fairly complicated and therefore so does the density functional condition it satisfies, i.e. equation (9). In fact, for \( N \) large, the density functional condition appears to be sufficiently complicated one might doubt the existence of a practical procedure for solving it. The example of helium, which we did solve, might because of its relative simplicity actually be taken to indicate that the same methods used for helium would be fraught with difficulties for a diatomic molecule or an atom with a few shells of electrons. Apparently it is not obvious that the method we previously applied in the helium atom illustration can be used to solve the density functional conditions, equation (9), for the case of large \( N \). Nonetheless, it is true that it can be so used, and the main purpose of this paper is to show this. Thus in the next section we review the case for helium. We follow that with a section which extrapolates the technique for helium to the case for \( N \) large. Finally we summarize our results and draw some conclusions.

2. The helium atom example

As an example, for the helium atom, the CDWF density matrices ((3) and (4)) simplify to the expression,

\[ P_2(12) = P_{2\text{det}}(12) + P_{2\text{d,t}}(12), \]  

and

\[ P_1(11') = P_{1\text{d.t}}(11') + \int P_{2\text{det}}(121'2)d^2. \]  

Equation (9) becomes

\[ \int P_{2\text{d.t}}(12)d^2 = 0, \]  

which must be solved for \( b \). Define the magnitude of an interparticle vector as

\[ r = |1 - 2|, \]  

and a pair center of mass vector as

\[ R = \frac{1}{2}(1 + 2). \]  

Transform 1 and 2 to the interparticle and center of mass vectors \( r \) and \( R \), in accordance with the equations above and then write (12) using variables 1 and \( r \), where 1 is held constant and \( r \) is varying. The correlation function \( b(1, 2) \) then becomes
In such a case, the volume element \( d^2 = -dr \) and (12) becomes

\[
\int \rho_{2 \text{det}}(1, 1-r)b(1, 1-r)dr = 0, \quad (15a)
\]
\[
\Rightarrow \int \rho_{2 \text{det}}(1, r)b(1, 1-r)dr = 0. \quad (15b)
\]

One expects \( b(1, 1-r) \) to vanish exponentially as \( r \) goes to \( \infty \); that is to say, when one keeps vector \( 1 \) fixed and lets vector \( r \) describe the whole space as in the latter integral, one defines a small “sphere” at the tip of vector \( 1 \) in which \( b(1, 1-r) \) is non-zero. This last remark simply states that the correlation function is non-zero when \( 1 \) is close to \( 2 \), which is characteristic of short-range correlation.

Since the density function \( \rho'_{2 \text{det}}(1, r) \) varies more slowly than the correlation function in the range of \( r \) defining the non-zero correlation “sphere,” one may, in good approximation, MacLaurin expand \( \rho'_{2 \text{det}}(1, r) \) about \( r = 0 \) (in which case \( 1 = 2 = R \)), and retain the leading term of the series. This reduces (15) to

\[
\rho_{2 \text{det}}'(1, 0) \int b(1, 1-r)dr = 0, \quad (16)
\]

which vanishes if

\[
\int b(1, 1-r)dr = 0. \quad (17)
\]

This last equation is solved for \( b \). Following Colle and Salvetti (1975) cast \( \phi(12) \) in the density functional form

\[
\phi(12) = [1 - \Phi(R)(1 + r/2)] \exp(- (\beta r)^2). \quad (18)
\]

The function \( \beta \) is defined (Colle and Salvetti 1975) through the density according to

\[
\beta = q \rho^{1/3}(R), \quad (19)
\]

where \( q \) is a constant to be determined variationally. Now the unknown function \( \Phi(R) \) may be determined by forcing it to satisfy (17) and it becomes thereby a functional of the density. Colle and Salvetti (1975) have solved (17) approximately, using (18). Thus,

\[
\int (\phi^2(12) - 2\phi(12))dr = 0, \quad (20)
\]

which may be further approximated by

\[
\int \phi(12)dr = 0. \quad (21)
\]

From the latter equation, and using (18), it follows that

\[
(1 - \Phi(R))\int \exp(- (\beta^2 r^2)dr(- \Phi(R)/2)\int r \exp(\beta^2 r^2)dr = 0. \quad (22)
\]

Evaluating the integrals analytically in (22), we get

\[
\frac{\pi^{3/2}}{\beta^3} = \Phi(R) \frac{\pi^{3/2}}{\beta^3} + \Phi(R) \frac{\pi}{\beta^4}, \quad (23)
\]

and solving for \( \Phi(R) \) yields the Colle–Salvetti (1975) density functional

\[
\Phi(R) = \frac{\pi^{1/2} \beta(R)}{1 + \pi^{1/2} \beta(R)}. \quad (24)
\]
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Now $\beta$ and $\Phi$ determine $\phi$, which in turn determines $b$, and thus $\rho_2$ and $\rho_1$ ((10) and (11), respectively) are completely defined by the density, except for the variational constant $q$.

In our previously reported helium example, energy optimized $q = 1.17$ corresponds to a calculated correlation energy $E_c = 0.0419$ \text{[a.u.]}, which compares well with the exact value $E_c = 0.0424$ \text{[a.u.]}. We pointed out that this accurate calculation of $E_c$ is partly fortuitous because of several approximations used, including the replacement of $\rho_2$ by $\rho_{2HF}$, the use of Colle and Salvetti's (1975) approximate $\Phi_1$, (24), and numerical methods for evaluation of various energy integrals. Nevertheless the helium result may certainly be taken as indicative of the plausibility of the formalism embodied in the density matrices of correlated determinant form, given by (3) and (4).

3. The case of $N$ large

Now, the same techniques as discussed in the last section for helium can be applied to solving (9) for any $N > 2$, where a sufficient condition to satisfy the equation is obtained by requiring each integral term in the equation to vanish separately. The same degree of approximation employed for helium is applied for the case $N > 2$.

For $N$ large there will be many terms in the expressions for $\rho_2$ and $\rho_1$ as given by (3) and (4). However, the only unknown function in these equations is the correlation function $b$. This is to be obtained by solving (9), just as with helium, the difference being that $a_2$ is now a more complicated object (recall that $a_2$ is the expression contained within curly brackets in (3)). It occurs, however, that the form of $b$ obtained in the helium atom case is sufficient to satisfy (9) for the more complicated case of large $N$.

Indeed, consider a more complicated term from (9) when it is in its most general form, e.g.

$$\int \rho_{3\text{det}}(123) b(13) d3d2 = 0. \quad (25)$$

One transforms 1, 3 to interparticle and center of mass vectors $r$ and $R$ in a manner analogous to that shown in (13) and (14) and then expands $\rho_{3\text{det}}(123)$ in a MacLaurin series in $r$, retaining only the zeroth order term in the expansion. The above integral then becomes

$$\int \rho_{3\text{det}}(1, 2, 1) d2 \int b(1, 1 - r) dr = 0, \quad (26)$$

which of course vanishes if

$$\int b(1, 1 - r) dr = 0. \quad (27)$$

The most difficult type of term to deal with, arising from (9), occurs when there is a shared variable between a pair of $b$ functions. As an example, a typical such term yields

$$\int \rho_{3\text{det}}(123) b(12) b(13) d3d2 = 0. \quad (28)$$

One may solve this equation as follows: first change $(1, 2)$ into $(1, 1 - r)$ as previously mentioned, obtaining

$$\int \rho_{3\text{det}}(1, 1 - r, 3) b(1, 1 - r) b(13) d3 dr = 0, \quad (29)$$
then, MacLaurin expand $\rho_{3\text{det}}$ in $r$ (in which case, $r = 0$, $R = 1 = 2$), obtaining

$$\int \rho_{3\text{det}}(1, 1, 3)b(13)d3 \int b(1, 1 - r)dr = 0,$$

(30)

which of course vanishes if

$$\int b(1, 1 - r)dr = 0.$$

(31)

In an exactly similar way, the vanishing of this last integral is sufficient for all of the terms contained in (9) to vanish when $N > 2$.

We conclude, therefore, that solving for the unknown function $b$ is no more difficult than in the case for helium, no matter what the magnitude of $N$, when $N > 2$. The same procedures applied for helium generalize for larger $N$, the principal difference being that more terms are obtained in $\rho_1$ and $\rho_2$ as given by our equations (3) and (4). Notice, however, that the list of terms is short and does not grow beyond those given explicitly in (3) and (4), no matter how large $N$ becomes.

5. Summary and conclusions

We had derived (Soirat et al. 1994) approximately $N$-representable density functional density matrices $\rho_2$ and $\rho_1$ given by (3) and (4). The unknowns in these equations were to be obtained by solving the density functional condition

$$\int a_2(1212)d2 = 0.$$  

(32)

For the helium atom, an approximate solution to (9), following Colic and Salvetti (1975) is easily obtained, and yielded a good value for the correlation energy. The question arises though, is (9) for large $N$ solved just as easily? We showed that the answer to this is yes. Indeed, the only unknown in $a_2$ is the correlation function $b$. For large $N$, a number of terms contain $b$ and various products of $b$. Still there is only one unknown function $b$, complicated though the form of $a_2$ may be. By examining the typical terms associated with $a_2$ in (9) we showed each of them vanished if $b$ is taken to be of the same form as in the helium atom case. Thus equation (9) may be solved as easily for large $N$ as for $N = 2$, contrary to expectations. The case of large $N$ is treated to the same degree of approximation as that previously applied to helium. Such approximation is characterized by use of a MacLaurin expansion of $\rho_{2\text{det}}$ about $r = 0$, which allows $\rho_{2\text{det}}$ to be removed from integrals over the variable $r$.

In an analogous way one may MacLaurin expand, in addition to $\rho_{2\text{det}}$, also $\rho_{3\text{det}}$, $\rho_{4\text{det}}$, $\rho_{5\text{det}}$, $\rho_{6\text{det}}$ in (3) and (4), thus obtaining simpler density matrices,

$$\rho_2(12) = \rho_{2\text{det}}(12)(1 + b(12)),$$

(33)

and

$$\rho_1(11') = \rho_{1\text{det}}(11') + \int \rho_{2\text{det}}(121'2)b(121'2)d2 + 1/2 \int \rho_{3\text{det}}(1231'23)b(121'2)b(131'3)d2d3,$$

(34)

which are approximately $N$-representable by a CDWF. For $N$ large, it remains to test by numerical calculation the accuracy achievable with these density matrices which are functionals of the density.

We cannot guarantee, without further numerical results, that the Colle–Salvetti
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form for $\phi$ (see (18)), used within our formalism, will give good results for neutral atoms and molecules larger than helium. We can point out that Colle and Salvetti (1975), using their form for $\phi$ have obtained very good correlation energies for a wide variety of such neutral atoms and molecules. Insofar as our formalism is inspired by and related to theirs, we might also expect good results for larger systems. But insofar as our formalism differs from theirs in certain critical respects, whether or not larger systems will in fact be well represented must remain an open question, until more numerical calculations are accomplished.

The fundamental theorem of Hohenberg and Kohn (1964), (HK), asserts that all electron properties are functionals of the electron density. Their energy for a system is given by

$$E[\rho] \equiv \int v(r)\rho(r)dr + F[\rho],$$

(35)

where $v$ is the external potential of the system, and $F$ is the unknown HK functional (Hohenberg and Kohn 1964; Parr and Yang 1989),

$$F[\rho] = \langle \psi[\rho] | T + U | \psi[\rho] \rangle,$$

(36)

where $T$ and $U$ are the system’s kinetic energy and interaction energy respectively and $\psi[\rho]$ is the ground state wavefunction of the system. The evaluation of the HK functional $F$ may be calculated approximately using CDWF density matrices, obtaining

$$F_{\text{CDWF}}[\rho] = -\frac{1}{2} \int V^2 \rho_1(11')|_{1 \rightarrow 1'} d1 + \frac{1}{2} \int \frac{\rho_2(12)}{|1-2|} d1 d2,$$

(37)

where $\rho_2(12)$ and $\rho_1(11')$ are understood to be the expressions given by (33) and (34). The point is that these may be obtained as functionals of the density and therefore, also $F_{\text{CDWF}}$. This last equation supplies an upperbound on the exact $F$, i.e.,

$$F_{\text{CDWF}}[\rho] \geq F[\rho].$$

(38)

Thus in the language of constrained search methodology (Levy 1979, 1982)

$$\min \left[ -\frac{1}{2} \int V^2 \rho(11')|_{1 \rightarrow 1'} d1 + \frac{1}{2} \int \frac{\rho_2}{|1-2|} d1 d2 \geq F[\rho] \right]$$

(39)

$$\begin{cases} \rho_2(12) \\ \rho_1(11') \rightarrow \rho \end{cases}$$

Inequalities (38) and (39) are guaranteed in the case of exact $N$-representability. For our approximate $N$-representability they are applied heuristically, as in the case of He (Soirat et al 1993) on the qualitative assumption that $N$-representability violations are small. Limits on the validity of such an heuristic procedure remains to be studied by numerical application to cases of large $N$.

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