

Natural Orbital Functional for the Many-Electron Problem

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The exchange-correlation energy in Kohn-Sham density functional theory is expressed as a functional of the electronic density and the Kohn-Sham orbitals. An alternative to Kohn-Sham theory is to express the energy as a functional of the reduced first-order density matrix or equivalently the natural orbitals. We present an approximate, simple, and parameter-free functional of the natural orbitals, based solely on scaling arguments and the near satisfaction of a sum rule. Our tests on atoms show that it yields on average more accurate energies and charge densities than the Hartree-Fock method, the local density approximation, and the generalized gradient approximations. [S0031-9007(98)06532-6]

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The solution of the quantum mechanical many-electron problem is one of the central problems of physics. A great number of schemes that approximate the intractable many-electron Schrödinger equation have been devised to attack this problem. Most of them map the many-body problem to a self-consistent one-particle problem. Probably the most popular method at present is density functional theory (DFT) [1] especially when employed with the generalized gradient approximation (GGA) [2,3] for the exchange-correlation energy. DFT is based on the Hohenberg-Kohn theorem [4] which asserts that the electronic charge density completely determines a many-electron system and that, in particular, the total energy is a functional of the charge density. Attempts to construct such a functional for the total energy have not been very successful because of the strong nonlocality of the kinetic energy term. The Kohn-Sham scheme [5] where the main part of the kinetic energy, the single particle kinetic energy, is calculated by solving one-particle Schrödinger equations circumvented this problem. The difference between the one-particle kinetic energy and the many-body kinetic energy is a component of the unknown exchange-correlation functional. The exchange-

correlation functional is thus a sum of a kinetic energy contribution and a potential energy contribution, and partly for this reason it does not scale homogeneously [6] under a uniform spatial scaling of the charge density.

It has been known for a long time that one can also construct a total energy functional using the first-order reduced density matrix. Several discussions of the existence and the properties of such a functional can be found in the literature [7–10]. However, no explicit functional has ever been constructed and tested on real physical systems. An important advantage of this approach is that one employs an exact expression for the many-body kinetic energy. Only the small non-Hartree-Fock-like part of the electronic repulsion is an unknown functional [9]. We propose in this paper an explicit form of such a functional in terms of the natural orbitals. The high accuracy of this natural orbital functional theory (NOFT) is then established by applying it to several atoms and ions.

If Ψ is an arbitrary trial wave function of an N -electron system, the first- and second-order reduced density matrices [11,12], γ_1 and γ_2 , are

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = N \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (1)$$

$$\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) = \frac{N(N-1)}{2} \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) d\mathbf{x}_3 \dots d\mathbf{x}_N. \quad (2)$$

The variables \mathbf{x}_i contain both the position coordinates \mathbf{r}_i as well as the spin coordinate s_i . The integration sign stands for a combined integration of the spatial coordinates and summation of the discrete spin part.

The electronic charge density $\rho(\mathbf{r})$ is obtained from the diagonal part of the first-order reduced density matrix,

$$\rho(\mathbf{x}_1) = \gamma_1(\mathbf{x}_1, \mathbf{x}_1); \quad \rho(\mathbf{r}_1) = \sum_{s_1} \rho(\mathbf{x}_1). \quad (3)$$

The natural orbitals ϕ_i are the eigenfunctions of the first-order reduced density matrix with eigenvalues n_i :

$$\int \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \phi_i(\mathbf{x}_1) d\mathbf{x}_1 = n_i \phi_i(\mathbf{x}'_1). \quad (4)$$

The natural spin orbitals and occupation numbers n_i specify the reduced first-order density matrix completely.

The total energy can be written in terms of the natural orbitals and the diagonal elements of the second-order reduced density matrix,

$$\sigma(\mathbf{x}_1, \mathbf{x}_2) = \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2), \quad (5)$$

as

$$E = -\frac{1}{2} \sum_i n_i \int \phi_i(\mathbf{x}) \nabla^2 \phi_i(\mathbf{x}) d\mathbf{x} + \int V(\mathbf{x}) \rho(\mathbf{x}) d\mathbf{x} + \iint \frac{\sigma(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{x}_1 d\mathbf{x}_2. \quad (6)$$

In order to construct a natural orbital functional, it remains to find an approximation for σ in terms of the natural orbitals and occupation numbers. In the following, we assume the standard case of a Hamiltonian that is not spin dependent. Each natural orbital can then be chosen to be either purely spin up or spin down and can be labeled by an orbital index i and a spin index s_i .

The approximate σ we propose has the following form:

$$\sigma[\{n\}, \{\phi\}] = \sum_{i,j}' \frac{n_i n_j}{2} \phi_i^2(\mathbf{r}_1) \phi_j^2(\mathbf{r}_2) - \sum_{i,j}' \frac{\sqrt{n_i n_j}}{2} \delta_{s_i, s_j} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2). \quad (7)$$

The primes indicate that the $i = j$ terms are omitted. To find the ground state, we minimize the functional with respect to both the natural orbitals and the occupation numbers, under the constraint that the natural orbitals be orthogonal [13]. The functional derivatives are

$$\begin{aligned} \frac{\partial E}{\partial \phi_i(\mathbf{r})} = & -\frac{n_i}{2} \nabla^2 \phi_i(\mathbf{r}) + n_i V(\mathbf{r}) \phi_i(\mathbf{r}) + \sum_j' n_i n_j \phi_i(\mathbf{r}) \int \frac{\phi_j^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ & - \sum_j' \sqrt{n_i n_j} \delta_{s_i, s_j} \phi_j(\mathbf{r}) \int \frac{\phi_i(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{\partial E}{\partial n_i} = & -\frac{1}{2} \int \phi_i(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \int V(\mathbf{r}) \phi_i^2(\mathbf{r}) d\mathbf{r} + \sum_j' n_j \iint \frac{\phi_j^2(\mathbf{r}') \phi_i^2(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & - \frac{1}{2} \sum_j' \sqrt{\frac{n_j}{n_i}} \delta_{s_i, s_j} \iint \frac{\phi_i(\mathbf{r}') \phi_j(\mathbf{r}') \phi_i(\mathbf{r}) \phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (9)$$

In principle an infinite number of natural orbitals must be included. For the systems studied in Table I at most 38 orbitals were needed to obtain good convergence. The occupation numbers of the core natural orbitals are restricted to be unity, while the remaining occupation numbers are allowed to vary freely and are found to lie always between zero and one, which is a necessary and sufficient condition for the density matrix to be N representable [12].

We now discuss the properties of this functional.

Homogeneous scaling of exchange-correlation energy: The exact exchange-correlation energy in first-order density matrix functional theory differs from the exact exchange-correlation energy in density functional theory and scales homogeneously [9] under a uniform scaling of the density matrix. The exchange-correlation energy, deduced from Eqs. (6) and (7), exhibits this property.

No orbital self-interactions: In the case where one has fractional occupation numbers one has to distinguish between orbital self-interactions and electron self-interactions. Our functional is free of orbital self-interactions because the sum in Eq. (7) excludes terms with $i = j$, but it is not perfectly electron self-interaction free. The total energy for H is therefore not correct

(Table I). The functional has, however, a much better cancellation of electron self-interactions than density functionals, as can be seen from the fact that negative ions are stable (Table I). In contrast LDA (local density approximation) and GGA bind only a fraction of an additional electron.

Sum rule for second order reduced density: The density and the number of electron pairs are obtained by integrating the exact second-order reduced density matrix:

$$\int \sigma(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \frac{(N-1)}{2} \rho(\mathbf{r}_1), \quad (10)$$

$$\iint \sigma(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N(N-1)}{2}. \quad (11)$$

Our approximation for the second-order reduced density matrix would satisfy these equations if the sums in Eq. (7) also included the $i = j$ terms. We omit these terms because we find that an exact cancellation of the orbital self-interactions is more important than an exact fulfillment of the sum rules in Eqs. (10) and (11). The sum rules are violated only by terms of the order of $n_i(1 - n_i)$, which for most systems are small since all the occupation numbers are close to either zero or one.

TABLE I. Comparison of errors in the energy, density, and transferability (see text) obtained from various functionals. Energies are in hartree atomic units. No data are available (NA) for the nonspherical PBE ground state of C. The large errors in $\Delta\rho$ and the infinite errors in $\Delta\tau$ for the H^- ion in LDA and PBE are because they bind only a fraction of the additional electron.

	H	H^-	He	Li	Be	C	Ne
Energy							
$-E$	0.5	0.5278	2.9037	7.4781	14.6674	37.8450	128.9376
LDA							
ΔE	2×10^{-2}	6×10^{-3}	7×10^{-2}	1×10^{-1}	2×10^{-1}	4×10^{-1}	7×10^{-1}
$(\Delta\rho)^2$	1×10^{-3}	6×10^0	8×10^{-3}	2×10^{-2}	2×10^{-2}	5×10^{-2}	2×10^{-1}
$\Delta\tau$	4×10^{-1}	∞	2×10^{-1}	-7×10^{-1}	2×10^{-2}	4×10^{-1}	3×10^{-1}
PBE							
ΔE	8×10^{-5}	2×10^{-3}	1×10^{-2}	2×10^{-2}	4×10^{-2}	NA	7×10^{-2}
$(\Delta\rho)^2$	2×10^{-4}	6×10^0	1×10^{-3}	3×10^{-3}	3×10^{-3}	NA	1×10^{-2}
$\Delta\tau$	2×10^{-1}	∞	1×10^{-1}	-1×10^0	5×10^{-1}	NA	3×10^{-1}
HF							
ΔE	0	4×10^{-2}	4×10^{-2}	5×10^{-2}	9×10^{-2}	2×10^{-1}	4×10^{-1}
$(\Delta\rho)^2$	0	1×10^{-3}	1×10^{-4}	7×10^{-5}	8×10^{-4}	5×10^{-4}	6×10^{-3}
$\Delta\tau$	0	-5×10^0	-2×10^{-2}	3×10^{-1}	1×10^0	-6×10^{-2}	-2×10^{-1}
NOFT							
ΔE	-2×10^{-2}	1×10^{-2}	6×10^{-3}	-1×10^{-3}	-2×10^{-2}	3×10^{-2}	5×10^{-2}
$(\Delta\rho)^2$	3×10^{-5}	4×10^{-4}	1×10^{-5}	2×10^{-4}	6×10^{-4}	7×10^{-4}	4×10^{-4}
$\Delta\tau$	-2×10^{-2}	1×10^2	-1×10^{-2}	-5×10^{-1}	6×10^{-1}	5×10^{-2}	-5×10^{-2}

Hartree-Fock as limiting case: The functional coincides with the Hartree-Fock (HF) functional if the occupation numbers are constrained to be 1 or 0.

No dissociation problems: Even though the functional contains terms which are similar to the HF functional, it should not suffer from some well established deficiencies of the spin restricted HF functional such as the dissociation problem of the H_2 molecule. As one separates the two H atoms, the large occupation numbers in the up- and down-spin σ_g molecular orbital get redistributed to the up-spin $1s$ atomic orbital on one atom and the down-spin $1s$ atomic orbital on the other. In the infinitely separated limit each atom has nonzero occupation numbers in either only the up-spin or only the down-spin orbitals. Consequently the energy is the sum of the energies of the individual atoms.

Transition states: In molecular calculations the effect of this functional is expected to be particularly significant for transition states, which are poorly described by LDA and HF. At transition states more than one determinant is needed for an adequate description, and releasing the HF constraint of integer occupation numbers is therefore important.

Orbital-dependent ‘‘potentials’’: The weakly occupied natural orbitals are localized in the same region of space as the highest strongly occupied natural orbitals. This is in contrast to the unoccupied Kohn-Sham and Hartree-Fock orbitals which have a larger extent than the occupied ones. The manner in which this comes about can be seen from Eq. (8) which has an orbital-dependent ‘‘potential.’’ One term in the potential goes as $\sqrt{n_i}$ —an enhancement by a factor of $1/\sqrt{n_i}$ relative to Hartree-Fock—which has the consequence that weakly occupied natural orbitals see

a more strongly negative potential than do the strongly occupied orbitals, thereby helping to localize the weakly occupied natural orbitals.

Chemical potential: All natural orbitals with fractional occupation n_i share the same chemical potential [10], $\mu = \frac{\partial E}{\partial n_i}$.

Discontinuity of the exchange-correlation potential: As one adds fractions of an electron, one finds, at occupation numbers close to integers, a rapid change in the effective potential felt by all the electrons, which is due to the jump in the chemical potential. This quasidiscontinuous effect might mimic the discontinuity [14] in the DFT exchange correlation potential, an effect missing in the LDA and GGA functionals.

Correct description of correlations of different origin: In a $1/Z$ expansion of the energy, the correlation energy of the two-electron series can be described by nondegenerate perturbation theory while the four-electron series requires degenerate perturbation theory. Consequently the correlation energy of the two-electron series tends to a constant with increasing Z , whereas it increases linearly in the four-electron case. Both trends are correctly captured by the NOFT functional as shown in Table II. Any GGA functional can at best describe only one of the trends.

Correct qualitative behavior of natural occupation numbers: As seen from Table III, the NOFT occupation numbers may differ considerably from the ones obtained from configuration interaction calculations, but the main trends are correctly reproduced.

Accurate results: In Table I, we give a compilation of the errors in the total energy ΔE and the errors in the charge densities $\Delta\rho$. The charge density errors are defined by $(\Delta\rho)^2 = \int [\rho_{\text{ex}}(\mathbf{r}) - \rho(\mathbf{r})]^2 d\mathbf{r}$, with the

TABLE II. Correlation energies, in hartrees, for the two- and four-electron series. The exact values of $-E_c^{\text{QC}} = E^{\text{HF}} - E^{\text{exact}}$, taken from Ref. [15], are compared to $E^{\text{HF}} - E^{\text{NOFT}}$.

Z	Two-electron		Z	Four-electron	
	$-E_c^{\text{QC}}$	$E^{\text{HF}} - E^{\text{NOFT}}$		$-E_c^{\text{QC}}$	$E^{\text{HF}} - E^{\text{NOFT}}$
1	0.040	0.031	4	0.094	0.110
2	0.042	0.036	6	0.126	0.141
4	0.044	0.040	8	0.154	0.171
6	0.045	0.042	10	0.180	0.200

“exact” charge densities ρ_{ex} obtained from accurate quantum Monte Carlo calculations. Both total energies and charge densities are improved on average compared to HF and DFT calculations. In particular, the improvements over the HF densities are impressive since they are known to be rather accurate. The GGA schemes yield improved total energies compared to both LDA and HF while the GGA densities are better than those from LDA but not as good as those from HF. In the case of C, the error in the spherically averaged charge density is quoted. The exact total energies were obtained from Ref. [15]. The LDA energies and densities were obtained by a standard spherical atomic program. As a representative of a GGA functional we have chosen the recent Perdew-Becke-Ernzerhof (PBE) [2] functional. All the HF and NOFT calculations were done with a nonspherical atomic program developed by the authors. All calculations were done in a spin restricted scheme. In the case of C the correct nonspherical 3P ground state was chosen. Since we do no molecular calculations, we monitor a third quantity, the transferability error $\Delta\tau$, to make predictions about the behavior of this scheme in molecular and solid state calculations. Molecular geometries are determined via the Hellmann-Feynman theorem by the charge densities in the valence region. The external potential in the valence region is modified in a molecule compared to the atomic case. We simulated this modi-

TABLE III. Deviation of the occupation numbers for the two-electron series from the Hartree-Fock values in units of 10^{-5} electrons. For each Z, the first column gives the exact values of Kutzelnigg [16] and the second column our NOFT values.

nl	Z = 1		Z = 2		Z = 4		Z = 6	
1s	-3536	-3339	-691	-566	-162	-154	-68	-65
2s	2352	1038	322	217	63	55	25	24
2p	1115	825	337	276	89	84	39	39
3s	7	1038	3	11	0	2	0	1
3p	15	174	7	23	2	5	1	0
4s	0	27	0	0	0	0	0	0
3d	37	165	16	31	5	6	2	3
4p	1	13	0	3	0	0	0	2
5s	0	8	0	0	0	0	0	0
4d	3	29	2	4	0	1	0	0
5p	1	17	0	0	0	0	0	0
6s	0	1	0	0	0	0	0	0
6p	0	3	0	0	0	0	0	0

fication by adding a confining parabolic potential to the atom. The change in the total energy due to the variation of this parabolic potential is again given by the Hellmann-Feynman theorem, and we define the transferability error $\Delta\tau$ therefore as $\Delta\tau = \int[\rho(\mathbf{r}) - \rho_{\text{ex}}(\mathbf{r})]r^2 d\mathbf{r}$.

In conclusion, we have made a first attempt at constructing an approximate total energy functional of the first-order reduced density matrix. We have listed and discussed the properties that make it superior to the HF and approximate DFT functionals and have also shown that it yields better energies and densities than HF and current DFT schemes. The high accuracy of quantities related to the charge density leads one to expect that this new functional will give accurate molecular geometries as well as accurate energy differences between different geometric configurations. In view of the fact that the functional is parameter-free and based on a few simple considerations, we think this to be a remarkable success. It is likely that it will be possible to construct even better functionals along these lines.

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