A 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. In the former approach the unknown part of the functional contains both a kinetic and a potential contribution whereas in the latter approach it contains only a potential energy and consequently has simpler scaling properties. 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.

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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) especially when employed with the Generalized Gradient Approximation (GGA) for the exchange-correlation energy. DFT is based on the Hohenberg-Kohn theorem 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 non-locality of the kinetic energy term. The Kohn-Sham scheme 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 of 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 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. However in spite of the enthusiasm expressed towards this approach in the early papers, 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. 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.

Let us first briefly review some basic facts about reduced density matrices. If Ψ is an arbitrary trial wave function of an N-electron system, the first and second order reduced density matrices, γ₁ and γ₂ are

\[ γ₁(x₁', x₁) = N \int ... \int \Psi(x₁', x₂, ..., xₙ) \Psi(x₁, x₂, ..., xₙ) dx₂...dxₙ, \]

\[ γ₂(x₁', x₂'; x₁, x₂) = \frac{N(N-1)}{2} \int ... \int \Psi(x₁', x₂', xₙ, ..., x₁) \Psi(x₁, x₂, ..., xₙ) dxₙ...dxₙ. \]

The variables xᵢ contain both the position coordinates rᵢ, as well as the spin coordinate sᵢ. The integration sign stands for a combined integration of the spatial coordinates and summation of the discrete spin part.

The electronic charge density ρ(r) is obtained from the diagonal part of the first-order reduced density matrix,

\[ ρ(x₁) = γ₁(x₁, x₁); \quad ρ(r₁) = \sum_{s₁} ρ(x₁). \]

The natural orbitals ϕᵢ are the eigenfunctions of the first-order reduced density matrix with eigenvalues nᵢ.

\[ \int γ₁(x₁', x₁) ϕᵢ(x₁) dx₁ = nᵢ ϕᵢ(x₁'). \]
The total energy can be written in terms of the natural orbitals and the diagonal elements of the second order reduced density matrix,

$$\sigma(x_1, x_2) = \gamma_2(x_1, x_2; x_1, x_2),$$

(5)
as

$$E = -\frac{1}{2} \sum_i n_i \int \phi_i(x) \nabla^2 \phi_i(x) dx$$

(6)

and

$$\int V(x) \rho(x) dx + \int \int \sigma(x_1, x_2) |r_1 - r_2| dx_1 dx_2.$$ 

In order to construct a natural orbital functional, it remains to find an approximation for \(\sigma\) 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 \(\sigma\) we propose has the following form:

$$\sigma\{n\}, \{\phi\} = \sum_{i,j}^\prime \frac{n_i n_j}{2} \phi_i^2(r_1) \phi_j^2(r_2)$$

(7)

$$- \sum_{i,j}^\prime \Delta_{s_i, s_j} \phi_i(r_1) \phi_j(r_1) \phi_i(r_2) \phi_j(r_2).$$

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. The functional derivatives are

$$\frac{\partial E}{\partial \phi_i(r)} = -n_i \nabla^2 \phi_i(r) + n_i V(r) \phi_i(r)$$

(8)

$$+ \sum_j n_j \phi_j(r) \int \frac{\phi_j^2(r')}{|r - r'|} dr'$$

$$- \sum_j \sqrt{n_j} \Delta_{s_i, s_j} \phi_i(r) \phi_j(r) \int \frac{\phi_j(r') \phi_i(r)}{|r - r'|} dr',$n

$$\frac{\partial E}{\partial n_i} = -\frac{1}{2} \int \phi_i(r) \nabla^2 \phi_i(r) dr + \int V(r) \phi_i^2(r) dr$$

(9)

$$+ \sum_j n_j \int \int \frac{\phi_j^2(r') \phi_i^2(r)}{|r - r'|} dr dr'$$

$$- \frac{1}{2} \sum_j \sqrt{n_j} \Delta_{s_i, s_j} \int \int \frac{\phi_j(r') \phi_i(r') \phi_i(r) \phi_j(r)}{|r - r'|} dr dr'.$$

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.

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 under a uniform scaling of the density matrix. The exchange-correlation energy, deduced from Eqs. (4) and (6), 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. (4) excludes terms with \(i = j\), but it is not perfectly electron self-interaction free. The total energy for \(H\) is therefore not correct (Table II). 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 II). In contrast LDA 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.

$$\int \int \sigma(r_1, r_2) d r_1 d r_2 = (N - 1) \rho(r_1),$$

(10)

$$\int \int \sigma(r_1, r_2) d r_1 d r_2 = \frac{N(N - 1)}{2} .$$

(11)

Our approximation for the second order reduced density matrix would satisfy these equations if the sums in Eq. (4) 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.

Hartree Fock as limiting case:

The functional coincides with the Hartree Fock (HF) functional if one imposes the additional constraint, that the occupations numbers all 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 \(\sigma_g\) 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 non-zero 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 $\mu = \partial E / \partial n_i$. 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 quasi discontinuous effect might mimic the discontinuity 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 II, the NOFT occupation numbers may differ considerably from the ones obtained from configuration interaction calculations, but the main trends are correctly reproduced. In particular, the trend in the occupation numbers of the strongly occupied 1s orbitals, going from He to H$^-$ is correct.

Accurate results:
In Table III, the NOFT occupation numbers: trends.

Any GGA functional can at best describe only one of the correlations of different origin. Both trends are correctly captured by the NOFT functional as shown in Table II. The NOFT 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. The essential point in this work is that we have used natural orbitals instead of Kohn Sham orbitals. We believe that this is essential to obtain accurate densities and kinetic energies.
TABLE I. Comparison of the errors of the quantities described in the text. Energies are in Hartree atomic units. No data are available (NA) for the non-spherical 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 come from the fact that they bind only a fraction of the additional electron.

|        | H | H$^-$ | He | Li | Be | C | Ne |
|--------|---|-------|----|----|----|---|----|
| Energy | - E | .5 | 5.278 | 2.9037 | 7.4781 | 14.6674 | 37.8450 | 128.9376 |
| LDA $\Delta E$ | 2.e-2 | 6.e-3 | 7.e-2 | 1.e-1 | 2.e-1 | 4.e-1 | 7.e-1 |
| $(\Delta \rho)^2$ | 1.e-3 | 6.e-3 | 8.e-3 | 2.e-2 | 2.e-2 | 5.e-2 | 2.e-2 |
| $\Delta \tau$ | 4.e-1 | $\infty$ | 2.e-1 | 7.e-1 | 2.e-2 | 4.e-1 | 3.e-1 |
| PBE $\Delta E$ | 8.e-5 | 2.e-3 | 1.e-2 | 2.e-2 | 4.e-2 | NA | 7.e-2 |
| $(\Delta \rho)^2$ | 2.e-4 | 6.e-3 | 1.e-3 | 3.e-3 | 3.e-3 | NA | 1.e-2 |
| $\Delta \tau$ | 2.e-1 | $\infty$ | 1.e-1 | 1.e-0 | 5.e-1 | NA | 5.e-1 |
| HF $\Delta E$ | 0 | 4.e-2 | 4.e-2 | 5.e-2 | 9.e-2 | 2.e-1 | 4.e-1 |
| $(\Delta \rho)^2$ | 0 | 1.e-3 | 1.e-4 | 7.e-4 | 8.e-4 | 5.e-4 | 6.e-3 |
| $\Delta \tau$ | 0 | 5.e-0 | 2.e-2 | 3.e-1 | 1.e-0 | 6.e-2 | 2.e-1 |
| NOFT $\Delta E$ | -2.e-2 | 1.e-2 | 6.e-3 | 1.e-3 | 2.e-2 | 3.e-2 | 5.e-2 |
| $(\Delta \rho)^2$ | 3.e-5 | 4.e-4 | 1.e-5 | 2.e-4 | 6.e-4 | 7.e-4 | 4.e-4 |
| $\Delta \tau$ | -2.e-2 | 1.e-2 | 1.e-2 | 5.e-1 | 6.e-1 | 5.e-2 | -5.e-2 |
| QCISD $\Delta E$ | 2.e-3 | 8.e-3 | 8.e-3 | 5.e-2 | 5.e-2 | 7.e-2 | 1.e-1 |

TABLE II. Correlation energies, in Hartrees, for the 2- and 4-electron series. The exact values of $-E^{Q\!C}_{HF} = E_{HF} - E^{exact}$, taken from Ref. [7], are compared to $E_{HF} = E_{NOFT}$.

| Z | $E^{Q\!C}_{HF} - E^{NOFT}$ | $E^{HF} - E^{NOFT}$ |
|---|--------------------------|---------------------|
| 1 | .040 | .031 |
| 2 | .042 | .036 | .6 | .126 | .141 |
| 4 | .044 | .040 | 8 | .154 | .171 |
| 6 | .045 | .042 | 10 | .180 | .200 |

TABLE III. Occupation numbers for the 2-electron series. Columns labelled 'E' are the almost exact numbers of Kutzelnigg [17]. Entries smaller than 1e-5 were set to zero.