Density functional theory with adaptive pair density

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(Dated: May 5, 2014)

We propose a density functional to find the ground state energy and density of interacting particles, where both the density and the pair density can adjust in the presence of an inhomogeneous potential. As a proof of principle we formulate an a priori exact functional for the inhomogeneous Hubbard model. The functional has the same form as the Gutzwiller approximation but with an unknown kinetic energy reduction factor. An approximation to the functional based on the exact solution of the uniform problem leads to a substantial improvement over the local density approximation.

PACS numbers: 71.15.Mb, 71.27.+a, 71.10.Fd

Most of our theoretical understanding of condensed matter and complex molecules stems from density functional theory (DFT) computations [1]. Practical implementations rely on the local density approximation (LDA) or its gradient generalizations which often provide accurate results at the modest cost of a Hartree like computation [2]. These methods however fail in systems at or close to the Mott insulating regime [3], when the tunneling matrix element of electrons becomes small compared with the typical electron-electron repulsion energies. This can be seen already at the level of an H2 molecule which is stretched to produce two separated H atoms. LDA performs reasonably well at the equilibrium distance, when electrons have substantial tunneling among the atoms, but fails in the molecular analog of the Mott regime, when each electron is localized on one H atom [4, 5].

Generalizing to the local spin density approximation improves the energy at the cost of an artificial breaking of the symmetry [6]. While this can be formally justified, in practice it leads to unwanted features. For example in the case of a strongly correlated metal the artificial breaking of symmetry will give rise to a Fermi surface with the wrong Luttinger volume [7].

The breakdown of unpolarized LDA in the H molecule can be traced back to the poor treatment of each H atom separately [4, 5]. The density close to the center of the H atom is 0.32 a.u. LDA essentially assumes that this portion of the system behaves as a uniform electron gas with the same density (Wigner-Seitz radius parameter \( r_s \approx 0.91 \). However the two systems have radically different pair distribution functions which leads to different electron-electron interaction energies (zero for the H atom). LDA thus introduces a spurious interaction of the electron with itself, the so-called self-interaction error [9]. A way to mitigate this problem would be to have a functional theory which depends both on the density and the pair density (DPDFT) so that it can discriminate between situations with the same density but different pair densities.

The idea to involve the pair density in electronic structure computations is older than DFT itself [10, 11]. More recently various works explored the possibility to define an energy functional based on the pair-density alone [12–15] or explore the possibility to adjust the spatially averaged pair density [16] but face serious problems on finding physically acceptable pair densities. [15] Our proposal differs in that we still keep the density as the basic variable but we use partial information on the pair density as an auxiliary variable which gives the functional more sensitivity to correlation. In this respect our functional is similar to the proposal of Ref. [7] with the difference that it does not need an artificial breaking of symmetry.

To show the feasibility and the usefulness of the formalism in strongly correlated systems we present a DPDFT for the one-dimensional Hubbard model i.e. electrons on a lattice with strong local interaction. The functional is inspired on the Gutzwiller approximation (GA) [17,18] in the same way as Kohn-Sham approach is inspired on the Hartree approximation [19]. It is thus in principle exact as Kohn-Sham theory represents the “exactification” of the Hartree approximation [1]. We develop an approximation to the unknown functional which becomes exact for uniform systems and involves local or semilocal quantities like LDA and its gradient generalizations, but which is more accurate and goes beyond LDA in the sense that it becomes highly non-local when expressed as a standard functional of the density alone.

We consider a one-dimensional inhomogeneous Hubbard model \( H = H_t + H_U + H_v \) with

\[
H = -t \sum_{x} (c_{x \uparrow}^\dagger c_{x+1 \uparrow} + H.c.) + \sum_{x} U_x n_{x \uparrow} n_{x \downarrow} + \sum_{x} v_x n_{x \sigma},
\]

where \( c_{x \sigma} \) and \( c_{x \sigma}^\dagger \) indicate the annihilation and creation operator of electrons with spin \( \sigma \) on site \( x \) and \( n_{x \sigma} \equiv c_{x \sigma}^\dagger c_{x \sigma} \). \( t \) is the nearest-neighbor hopping amplitude while \( U_x \) and \( v_x \) denote respectively the Hubbard interaction energy and the external potential on site \( x \). For reasons to become clear below we allow the interaction energy to be site dependent.

The Hohenberg and Kohn theorem [21, 22] guarantees that there exists a functional, \( E_{\nu}([\rho_{\nu}]) = F([U_x, \rho_x]) + \sum_{x} v_x \rho_x, \) which, when minimized with respect to the density provides the exact ground state en-
ergy. $F([U_x, \rho_x])$ is a “universal” functional independent of $v_x$, but depending on the $U_x$‘s, which represents the contribution of $H_I + H_U$ to the energy of a system with density $\rho_x$. A formal DP-DFT for this model can be obtained by performing the Legendre transform, \[ T([d_x, \rho_x]) = \max_{\{U_x\}} \left( F([U_x, \rho_x]) - \sum_x U_x d_x \right) \] where $d_x = (n_x \uparrow n_x \downarrow)$ is the on-site pair density or double occupancy. Identifying the last term in the brackets with the interaction energy we arrive at the conclusion that $T([d_x, \rho_x])$ is the interacting kinetic energy of the model with the specified pair density and density distributions. This is a universal functional which does not depend on the specific form of $U_x$ nor $v_x$. Below we develop an approximation for this functional.

The ground state energy of the system is obtained by minimizing the functional, \[ E_{U,v}([d_x, \rho_x]) = T([d_x, \rho_x]) + \sum_x U_x d_x + \sum_x v_x \rho_x \] with respect to $d_x$ and $\rho_x$. In the new scheme $H_I$ has become the fixed part of the Hamiltonian while both $H_U$ and $H_v$ are considered as problem dependent. We will show below that even in the conventional case in which $U_x$ is homogeneous the new functional is quite convenient.

Eq. (1) yields, \[ \frac{\partial F([U_x, \rho_x])}{\partial U_{x'}} = d_{x'}. \]

Inversion of this expression determines the set of $U_x$ a system must have to have the given $d_x$ and $\rho_x$. Since $H_v$ and $H_U$ are determined by $\rho_x$ and $d_x$, the wave-function and all physical quantities are functionals of $\rho_x$ and $d_x$.

The interacting kinetic energy can be written as \[ T = -t \sum_x (\rho_{x+1} + \rho_{x-1}), \]

where $\rho_{x',x}$ denotes the one body density matrix, $\rho_{x',x} = \sum_{\alpha,\alpha'} \langle \psi_{\alpha'} \psi_{\alpha} | \psi_{\alpha'} \psi_{\alpha} \rangle$ and is also a functional of $\rho_x$ and $d_x$.

To proceed we search for a non-interacting system satisfying the, to be determined, Kohn-Sham like equations, \[ -\sum_{d=\pm 1} t_{x,x+d} e^{-i\phi_{x,x+d}} + v_{x,x} e^{-i\phi_{x,x}} = \epsilon_{x} e^{-i\phi_{x,x}}, \]

and which has the same density of the interacting system. Defining the non-interacting one-body density matrix as the sum restricted to the occupied Kohn-Sham orbitals, \[ \rho_{x,x}^0 = \sum_{\sigma \in \text{occ.}} \phi_{\sigma}^*(x) \phi_{\sigma}(x'), \]

and the density as $\rho_x^0 = \rho_{x,x}^0$, we require thus that, $\rho_x = \rho_x^0$.

In addition we introduce the kinetic energy reduction factors which are also functionals of $d$ and $\rho$ and satisfy \[ \rho_{x,x \pm 1} = q_{x,x \pm 1}([d_x, \rho_x]) \rho_{x,x \pm 1}^0. \] With these definitions the kinetic energy functional can be written in terms of the non interacting density matrix as follows \[ T([d_x, \rho_x]) = -t \sum_{x',\delta=\pm 1} q_{x',x'+\delta}([d_x, \rho_x]) \rho_{x,x'+\delta}^0. \]

Similarly to the exchange correlation potential in the standard Kohn-Sham approach, $q$ encodes all the complication of the many-body problem in an exact way.

Minimizing Eqs. (2) with respect to the orbitals and using Eq. (6) we arrive at \[ \delta_{x,x \pm 1} = t q_{x,x \pm 1}([d_x, \rho_x]) \]

\[ v_{x,x} = v - t \sum_{x',\delta} \frac{\partial \rho_{x',x'+\delta}}{\partial \rho_{x}}. \]

Eqs. (3)-(6) define the kinetic energy reduction functional $q_{x,x \pm 1}([d_x, \rho_x])$ and the associated Kohn-Sham system.

For practical computations one needs to introduce approximations. In analogy with the Gutzwiller approximation, we assume the kinetic energy reduction functional factorizes in terms of functions of the local densities, $\rho_{x,y} = z(\rho_x, d_x) z(\rho_y, d_y)$. In the following we refer to this approximation as “factorized approximation” (FA). In the spirit of LDA we approximate the functional dependence of $z(\rho_x, d_x)$ by requesting that the functional yields the exact energy in the case of a uniform system which we obtain in one-dimension by solving numerically the exact Bethe-ansatz integral equations in (higher dimension a numerical solution can be used). Thus $z(d, \rho)$ is calculated from the condition $z(d, \rho) T_0(\rho) = T^{BA}(d, \rho)$, where $T_0(\rho)$ denotes the kinetic energy of the non-interacting uniform system. $T^{BA}(d, \rho)$ is obtained as a function of the double occupancy $d$, from the exact Bethe-ansatz energy $E(U, \rho)$ by the Legendre transform Eq. (1) for a system with uniform $U$ and density $\rho$. It is also useful to compute the function $U^P(\rho, d)$ which yields the Hubbard $U$ a uniform system with density $\rho = \rho_x$ must have, to yield the double occupancy $d_x$ of the non-uniform system at the given site. We indicate as $d(U, \rho)$ the inverse of $U^P(\rho, d)$.

The functional Eq. (2) has to be minimized with respect to the local double occupancies $d_x$ and the Kohn-Sham orbitals leading to Eq. (6). We can use the function $d(U, \rho)$ to eliminate $d_x$ in favor of a site dependent effective interaction, termed the “pseudointeraction”, $U^P$ with respect to which the minimization is actually done $[d_x \rightarrow d(\rho_x, U^P)]$. This change of variables allows us to avoid the problem of minimizing with respect to a constrained variable. In the case of a homogeneous external potential $v_x = V$, the minimum is attained when $U^P_x = U$, and one recovers the exact Bethe ansatz result.
DPDFT is a variant of DFT. Indeed once a functional for $T$ is known we can define a functional of the density alone by minimizing over $d_x$, i.e. $F[U, \rho_x] = \min_{\{d_x\}} \{T[\{d_x, \rho_x\}] + U \sum_x d_x \}$. Interestingly, as we know from previous works[26], this procedure leads to a highly non-local functional of the density starting from a nearly local functional of variables $\rho_x$, $d_x$.

In order to test the functional we solved the DPDFT-FA equations for a Hubbard chain with a binary potential $v_x = -V \delta_x \delta_y$, and compare it with standard LDA derived from the exact Bethe ansatz solution[24] and with exact results obtained by Lanczos diagonalization with the ALPS package[24].

Fig. 1 shows that DPDFT-FA performs much better than LDA when the system becomes highly inhomogeneous (a) and strongly interacting (b). The double occupancy in LDA is independent of the environment which leads to a poor approximate interaction energy for strongly inhomogeneous systems (c). In DPDFT-FA the double occupancy is allowed to adapt, so that localized electrons, for large values of the potential, tend to have a small double occupancy and a small interaction energy (c), explaining the better performance of DPDFT-FA respect to LDA. The enhanced pseudointeraction on the more charged sites [odd $x$ in (d)] leads to a reduced double occupancy and explains the small interaction energy.

The behavior of DPDFT-FA is qualitatively similar to the GA except at small $V$ where the GA is obviously not exact. The errors in other quantities like kinetic energy, potential energy and density (not shown) are also generically smaller in DPDFT-FA than in LDA.

These results suggest that the self-interaction (SI) should be strongly reduced in DPDFT-FA with respect to LDA. In order to verify that this is the case we have solved the problem of one electron with one attractive impurity site in a chain. The potential is given by $v_x = -V \delta_x \delta_y$. This is the lattice analogue of the hydrogen atom in the continuum. Being a single electron problem, the exact solution has $d_x = 0$ for all $U$ while both LDA and DPDFT-FA yield a finite $d_x$. We define the self-interaction error as the spurious interaction energy of the single electron problem, $E_{SI} = U \sum_x d_x$.

In Fig. 2(a) we plot the self-interaction error as a function of the potential strength at the impurity site, with interaction parameter $U = 4t$. For large $V$ the charge becomes localized at the impurity site with $\rho_0 \sim 1$. In LDA the interaction energy corresponds to that of a nearly half-filled uniform Hubbard model which is clearly a very bad approximation thus $E_{SI}$ (red dashed line) increases and tends to saturate at a large value. In DPDFT-FA (blue solid line) $E_{SI}$ starts with a slower increase and then decays to very small values. In this case the total double occupancy $E_{SI}/U$ becomes small showing the adaptability of the pair density to the local environment. As shown in Fig. 2(b), the reduction of the self-interaction error is large for a wide range of the interaction.

It is interesting to compare DPDFT with traditional Kohn-Sham DFT for the same model[24]. In the latter the difference between the interacting and the non-interacting kinetic energy is absorbed additively in the exchange-correlation potential. Here the correction is multiplicative and included in the kinetic energy reduction factor functional $q$. 

![FIG. 1:](image1.png)

![FIG. 2:](image2.png)
Formally the minimization in DFT has to be restricted to densities, and here also double occupancies, that correspond to a physical wave function (N-representability). While this may appear as a severe difficulty\cite{Bauer2001} it is often not a problem in practical implementations. It has indeed not hampered the development of DFT methods. In our case the problem is not more severe than in LDA because each portion of the system is approximated by a uniform system but with a modified interaction.

We have shown DPDFT at work in the lattice but a similar functional can be defined in the continuum. Ideally one would like to use the pair density, \( \gamma_{\alpha \sigma'}(r, r') = \langle \psi^\dagger_{\alpha \sigma}(r) \psi^\dagger_{\sigma'}(r') \psi_{\alpha}(r) \psi_{\sigma'}(r') \rangle \), as a variable, with \( \psi_{\alpha}(r) \) the field operator at point \( r \) with spin \( \sigma \). This, however, would be quite cumbersome as in each point a full function must be determined. A more practical approach is to impose a spatial dependent constraint on the pair density and use such a constraint to parameterize families of physical pair density functions. For example we can define,

\[
D(r) = \sum_{\sigma \sigma'} \int d^3r' \gamma_{\alpha \sigma'}(r, r') \theta(a - |r - r'|),
\]

with \( \theta \) the Heaviside function and \( a \) is an appropriately chosen cutoff radius. \( D \) measures the double occupancy probability within a sphere of radius \( a \). These or other constraints can be implemented\cite{Ohta1983} by replacing the physical interaction \( w(r, r') \) with a fictitious interaction. In the present example the fictitious interaction would read \( w(r, r') + U(r) \theta(a - |r - r'|) \). As in the lattice, the corresponding Hohenberg and Kohn functional has \( U(r) \) as a variable, \( F[n(r), U(r)] \) which allows to define the functional

\[
G[n(r), D(r)] = \max_{U(r)} \left( F[n(r), U(r)] - \int d^3r U(r) D(r) \right),
\]

leading to a theory where both \( n(r) \) and \( D(r) \) are fundamental variables similar to the lattice but with the difference that \( G \) is not the kinetic energy. Solution of the uniform problem in the presence of the fictitious interaction with a constant \( U(r) = U^p \) could serve as a basis for approximate functionals which converge to the LDA in the uniform case but have an adaptive exchange correlation hole in non-uniform situations.

We have conceptually shown how a DFT which uses the pair density as an auxiliary variable can be introduced and we have developed an approximation for the Hubbard model inspired on the GA combined with LDA ideas. Formally DPDFT can also be defined in the continuum with a local variable \( D(r) \) playing the role of the double occupancy in the lattice. Approximate functionals based on this approach should allow more control on the correlations built on the underlying wave-function respect to what LDA does, and could help to extend the success of DFT methods to strongly correlated systems where correlations are substantially different from those of the homogeneous electron gas.

We thank A. Filippetti and V. Fiorentini for useful discussions. We are in debt with P. Gori-Giorgi for a critical reading of the manuscript and many valuable suggestions. This work was supported by IIT-Seed project NEWDFESC.

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