Occupation numbers in the density functional calculations.

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Abstract

It is the intention of this paper to rigorously clarify the role of the occupation numbers in the current practical applications of the density functional formalism. In these calculations one has to decide how to distribute a given, fixed number of electrons over a set of single-particle orbitals. The conventional choice is to have single-particle orbitals below the Fermi level completely occupied (with possible fractional occupations at the Fermi level) and the orbitals above the Fermi level empty. Although there is a certain confusion in the literature why this choice is superior to any others, the general belief is that it can be justified by treating the occupation numbers as variational parameters and then applying Janak’s theorem or similar reasoning. We demonstrate that there is a serious flaw in those arguments, mainly the kinetic energy functional and therefore the exchange-correlation functional are not differentiable with respect to the density for arbitrary occupation numbers. It is rigorously shown that in the present context of the density functional calculations there is no freedom to vary the occupation numbers. The occupation numbers cannot be considered as variational parameters.
I. INTRODUCTION.

Predicting properties of real materials from first principles has been an important goal of solid state physics from the early days, going back to Thomas, Fermi and others. During the past few decades, density functional theory (DFT) within the local density approximation (LDA) has been quite successful in this regard. This method has no adjustable parameters and the only significant approximation is the local density approximation. However this method also relies heavily on the variational nature of the ground state total energy and this paper is concerned with concepts and misconcepts related to this variational property.

Nonvariational nature of the energy functional with variable occupation numbers has been noticed recently by Weinert and Davenport. However we will rigorously prove that the differentiability of the energy functional with respect to the density depends critically on the choice of the occupation numbers and that there is no freedom to vary these without sacrificing the differentiability of the energy functional, i.e. a variational principle does not exist for any arbitrary choice of occupation numbers within the current framework of the density functional calculations. As we show later this means that Janak’s theorem cannot exist within the current framework of density functional calculations. To our knowledge the variational nature of the occupation numbers has never been studied in this fashion. The significance and relevance of the above statements should be judged in the context of the references made to this problem over the past two decades.

Original Hohenberg-Kohn-Sham theory (HKS) rests on the assumption that the ground state density of the interacting system is simultaneously a ground state density of the non-interacting system with suitably chosen external potential. The ground state for the non-interacting system can always be obtained by completely filling the lowest single-particle orbitals. The occupation numbers in this approach are well defined (except for the case when the topmost level is degenerate) and any other choice would be in direct violation with the original HKS assumption. In order to make any rigorous statements about this particular choice for the occupation numbers one has to define more general energy func-
tional with the domain that includes densities which are not the ground state densities of any noninteracting system. Such energy functional can be defined by using the constrained search approach proposed by Levy.

II. CONSTRAINED SEARCH APPROACH.

Constrained search approach defines the energy functional in a very simple and a physically appealing way. The ground state of any many-electron system can be found as

$$ E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle. $$

(1)

Here the minimization is performed over all allowable antisymmetric wave functions. To include mixed states as well as pure states one can extend the minimization from wave functions to all allowable density matrices:

$$ E_0 = \min_{\hat{\Gamma}} \text{Tr} \{ \hat{\Gamma} \hat{H} \}, $$

(2)

where

$$ \hat{\Gamma} = \sum d_i |\Psi_i\rangle \langle \Psi_i|, $$

(3)

$$ d_i = d^*_i \geq 0, \sum d_i = 1. $$

The minimization can be divided into two steps:

$$ E_0 = \min_n \{ \min_{\hat{\Gamma} \rightarrow n} \text{Tr} \{ \hat{\Gamma} \hat{H} \} \}. $$

(4)

The first minimization is performed over all allowable density matrices that lead to some fixed density $n(r)$. The result of this minimization is the functional of the density only:

$$ E_L[n] = \min_{\hat{\Gamma} \rightarrow n} \text{Tr} \{ \hat{\Gamma} \hat{H} \}. $$

(5)

According to eq. (4) once we have found this functional, the ground state energy as well as the ground state density can be found by minimizing eq. (5) with respect to the density, i.e.
The Hamiltonian for the many-electron system in general can be written as

\[ \hat{H} = \hat{T} + \hat{W} + \hat{V}, \]  

where

\[ \hat{T} = -\frac{1}{2} \int \nabla^2 \psi^*(r) \psi(r) \, dr \]  

is the kinetic energy term,

\[ \hat{W} = \frac{1}{2} \int \frac{1}{|r - r'|} \psi^*(r) \psi^*(r') \psi(r') \psi(r) \, dr \]  

is the electron-electron interaction term,

\[ \hat{V} = \int v(r) \psi^*(r) \psi(r) \, dr \]  

is the external field interaction term. According to eq.(5) this leads to

\[ E_L[n] = F_L[n] + \int v(r) n(r) \, dr. \]  

All the complexities of many-electron system are now hidden in the functional \( F_L[n] \):

\[ F_L[n] = \min_{\Gamma \rightarrow n} Tr\{\hat{\Gamma} \hat{T} + \hat{\Gamma} \hat{W}\}. \]  

It was shown by Lieb that \( F_L[n] \) and therefore \( E_L[n] \) are convex functionals. This means that \( E_L[n] \) has no extrema above its absolute minimum.

The following important theorem by H. Englisch and R. Englisch is central to our conclusion and deals with the issue of the differentiability of \( F_L[n] \).

**Theorem 1:** The functional

\[ F_L[n] = \min_{\Gamma \rightarrow n} Tr\{\hat{\Gamma} \hat{T} + \hat{\Gamma} \hat{W}\} \]

is differentiable nowhere else but on the following set of densities:
\[ n(r) = \sum_k \lambda_k n_k(r), \]

with \( \sum_k \lambda_k = 1 \), \( \lambda_k \geq 0 \), and \( n_k(r) = \int |\psi_k(r, r_2, \ldots, r_N)|^2 dr_2 \ldots dr_N \), where \( \psi_k \) are the orthonormal, degenerate ground states of the Hamiltonian given by (7). Moreover the choice for the external potential is unique (up to some additive constant) for a given density.

As a corollary to the above theorem one can prove the following statement:

**Proposition 1:** The functional

\[ T_J[n] = \min_{\sum_i f_i |\phi_i|^2 \to n} \sum_i f_i \int \phi_i^*(r) \left( -\frac{\nabla^2}{2} + v(r) \right) \phi_i(r) dr \]

(13)

is differentiable nowhere else but on the following set of densities:

\[ n(r) = \sum_i f_i |\phi_i(r)|^2, \]

where

\[ \left( -\frac{\nabla^2}{2} + v(r) \right) \phi_i(r) = \epsilon_i \phi_i(r), \]

and \( \sum f_i = N \),

\[ f_i = \begin{cases} 
 1 & \text{for } \epsilon_i < \epsilon_F \\
 0 & \text{for } \epsilon_i > \epsilon_F \\
 x & \text{for } \epsilon_i = \epsilon_F \text{, where } 0 \leq x \leq 1 
\end{cases} \]

(14)

The proof of the above statement follows from the fact that ensemble-N-representable first order density matrix (i.e. derivable from N-particle density matrix \( \Gamma \)) can always be written as

\[ \gamma(r, r') = \sum_i f_i \phi_i^*(r') \phi_i(r), \]

(15)

where \( 0 \leq f_i \leq 1 \), \( \sum f_i = N \) and \( \phi_i \)'s are orthonormal. Since the expectation value of the kinetic energy depends only on the first order density matrix it follows that

\[ T_J[n] = \min_{\Gamma \to n} Tr\{\hat{T}\}. \]
Once this equivalence has been established, we can now apply Theorem 1 (with \( \hat{W} \) set to zero) to the functional \( T_J[n] \). In this case \( \psi_k \)'s are the ground states of the following Hamiltonian

\[
H_0 = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N} v(r_i)
\]

and can be represented as single determinants built from \( N \) lowest single particle orbitals \( \phi(r) \):

\[
(-\frac{1}{2} \nabla^2 + v(r))\phi_i(r) = \epsilon_i \phi_i(r) \quad \epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \ldots
\]

The only case where we have degenerate many-particle ground state is when there is a degenerate single particle level \( \epsilon_k \) \((k \leq N)\) with degeneracy \( m > N - k + 1 \). This energy level \( \epsilon_k \) is the Fermi level \( (\epsilon_k = \epsilon_f) \). Then

\[
n_k(r) = \int |\psi_k(r, r_2, \ldots, r_N)|^2 dr_2 \ldots dr_N = \sum_{\epsilon_i < \epsilon_F} |\phi_i(r)|^2 + \sum_{\epsilon_{ik} = \epsilon_F} |\phi_{ik}(r)|^2.
\]

The densities where the functional \( T_J[n] \) is differentiable are given by:

\[
n(r) = \sum_k \lambda_k n_k(r) = \sum_k \lambda_k \sum_{\epsilon_i < \epsilon_F} |\phi_i(r)|^2 + \sum_k \lambda_k \sum_{\epsilon_{ik} = \epsilon_F} |\phi_{ik}(r)|^2
\]

\[
= \sum_{\epsilon_i < \epsilon_F} |\phi_i(r)|^2 + \sum_{\epsilon_i = \epsilon_F} f_i |\phi_i(r)|^2,
\]

where

\[
f_i = \sum_k \delta_{ik,i} \lambda_k \leq 1 \quad \text{Q.E.D.}
\]

**III. JANAK’S THEOREM.**

It is obvious that the energy functional (11) is of little help when it comes to practical applications. Further simplifications are needed. Following the HKS strategy one usually partitions the functional \( F_L[n] \) in the following fashion:

\[
F_L[n] = T_J[n] + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} dr dr' + E_{Lxc}[n].
\]
This results in the following energy functional

\[ E[n] = T_J[n] + \int v(r)n(r) dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} dr dr' + E_{Lxc}[n]. \] (18)

If the above functional was differentiable for any choice of the occupation numbers, its subsequent minimization with respect to density would lead to the following results:

\[ \left(-\nabla^2 + v_{eff}(r)\right) \phi_i(r) = \epsilon_i \phi_i(r), \] (19)

where

\[ v_{eff}(r) = v(r) + \int \frac{n(r')}{|r - r'|} dr' + \frac{\delta E_{Lxc}[n]}{\delta n(r)} , \quad n(r) = \sum_i f_i |\phi_i(r)|^2, \]

and

\[ \frac{\delta E[n]}{\delta f_i} = \epsilon_i. \] (20)

The last result was first obtained by Janak before the advent of the constrained search formulation and is known as Janak’s theorem. This theorem is usually regarded as a justification for occupying only the single particle orbitals below the Fermi level.

Nevertheless, the flaw in the above derivation is obvious. According to Proposition 1, once the partition (17) has been performed we have immediate restrictions on the occupation numbers. Any choice other than the conventional one, makes functionals \( T_J[n] \) and \( E_{Lxc}[n] \) (since \( E_{Lxc}[n] \) implicitly contains the kinetic energy term \( T_J[n] \)) nondifferentiable with respect to density. Therefore we cannot vary the energy functional (18) for some arbitrary choice of the of the occupation numbers \( \{ f_i \} \). Hence equation (19) is not valid for the occupation numbers other than the ones specified in Proposition 1. Obviously, in this case eq. (20) is not valid since we no longer have the freedom to choose arbitrary occupation numbers. In particular this means that there is no room for the Janak’s theorem within the current framework of density functional calculations.

The question now arises how to occupy the topmost degenerate levels (if any). As previously mentioned, the functional \( E_L[n] \) is convex and there are no extrema above its
absolute minimum. Therefore any fractional occupations at the Fermi level that conserve the degeneracy (i.e. the functionals $T_J[n]$ and $E_{Lxc}[n]$ remain differentiable) and leave eq. (17) intact (i.e. deliver the extremum of the functional $E_L[n]$) should give the same total energy. This of course may not be true in practice because of our approximations to the exchange-correlation energy.

**IV. CONCLUSION.**

The functionals $T_J[n]$ and $E_{Lxc}[n]$ appear as a direct consequence of the attempt to map the interacting system into the noninteracting one. We have demonstrated that these functionals are differentiable only on a certain domain of densities. It is only there that we are allowed to vary the energy functional. It is shown that in order for density to belong to this domain there is a certain restriction on the occupation numbers, i.e. single-particle orbitals below the Fermi level are completely occupied (with possible fractional occupations at the Fermi level) and the orbitals above the Fermi level are empty. Any other choice of the occupation numbers will make the functionals $T_J[n]$ and $E_{Lxc}[n]$ lose their differentiability with respect to density – a property which is imperative for the variational principle. Note that even though the approximate forms for the exchange-correlation energy currently being used might appear differentiable with respect to density regardless of the choice of the occupation numbers, one can hardly claim that these approximations will hold for an arbitrary set of the occupation numbers.

The main conclusion is that the occupation numbers cannot be considered as variational parameters. It means that there is no apriori justification for using the conventional set of the occupation numbers in the current density functional calculations. The only reason we resort to this set of the occupation numbers is because any other choice would make the variational principle inapplicable.
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