Integer Discontinuity of Density Functional Theory

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Density functional approximations to the exchange-correlation energy of Kohn-Sham theory, such as the local density approximation and generalized gradient approximations, lack the well-known integer discontinuity, a feature that is critical to describe molecular dissociation correctly. Moreover, standard approximations to the exchange-correlation energy also fail to yield the correct linear dependence of the ground-state energy on the number of electrons when this is a non-integer number obtained from the grand canonical ensemble statistics. We present a formal framework to restore the integer discontinuity of any density functional approximation. Our formalism derives from a formula for the exact energy functional and a new constrained search functional that recovers the linear dependence of the energy on the number of electrons.

Density Functional Theory (DFT) \cite{1,2} is a useful formalism of ground-state quantum mechanics that offers a simple approach to estimate the electronic properties of molecules and solids \cite{3}. Perdew et al. \cite{4} (PPLB) considered Mermin’s extension \cite{5} of DFT to systems that adiabatically exchange electrons with a distant reservoir at zero-temperature. In this framework, the energy as a function of the electron-number is a series of straight lines interpolating the energies corresponding to those of closed systems with integer numbers of electrons. PPLB found that the exchange-correlation (XC) potential displays a derivative discontinuity (DD) that, when added to the KS band gap, yields the fundamental band gap of the system (also see Ref. \cite{5}). The DD is present in molecular dissociation: When two atoms are separated far apart they take on integer numbers of electrons to neutralize their charges, and the total energy of the system, which is nearly additive, tends to display a DD with respect to a change in the number of electrons when one atom transfers its electron to the other.

The DD of the XC energy functional and the linear dependency between discrete intervals is required to improve the physics of density functionals. The missing integer discontinuity causes problems in the estimation of ground-state properties like binding energies \cite{6} and reaction barriers \cite{8}. In time dependent density functional theory, the missing integer discontinuity is also required to improve the accuracy of density-functional approximations (DFA’s) \cite{9,10,11,12,13}, especially to describe bond-stretching processes. A strong delocalization error \cite{15} occurs due to the lack of piecewise linear dependency of the resulting fragment energies with the number of electrons. This non-linearity is pervasive and affects all calculations that use continuous XC energy functionals such as the local density approximation (LDA) \cite{16}. These known problems point to the need to develop new functionals with the correct piecewise linearity, capable of describing bond-stretching without resorting to symmetry breaking. Long-range and non-local corrections are usually added to the XC energy functional \cite{17} to solve these problems. In most cases, the corrections improve the results without completely recovering the linear behavior of the XC energy between integers and its DD.

Non-empirical functionals such as the LDA and generalized gradient approximations work well for atoms with integer numbers of electrons. Kraisler and Kronik \cite{18} explored the properties of a simple ensemble average of XC energies of pure states. They showed that the piecewise linearity is almost restored by their approach using the optimized effective potential method. Their results illustrate the plausibility of recovering the integer discontinuity of most functionals of discrete-electron states that are apparently continuous in terms of the density.

In this work we propose a formalism to restore completely the linear dependency on the electron-number between integers. We use the fact that most density functional approximations have been developed for closed systems with integer numbers of electrons. We perform an expansion of the ensemble XC energy functional in terms of XC and KS kinetic energies evaluated at closed, fully interacting discrete-electron densities that sum to the correct ensemble ground-state density. We then connect the resulting expression to an expansion of the KS kinetic energy evaluated at non-interacting discrete-electron densities that yield the same ensemble ground-state density. For density-functional approximations, a constrained search is proposed to replace the Levy-Lieb search that requires the electron-electron repulsion operator. This search assumes non-interacting \( v \)-representability of the discrete-state densities and permits to recover strictly the piecewise-defined linearity for approximate XC energy functionals and their concomitant integer discontinuities.

The PPLB density functional is defined as:

\[ E_v[n] = F[n] + \int d\mathbf{r} n(\mathbf{r})v(\mathbf{r}) , \]

where \( F[n] \) is the constrained-search functional:

\[ F[n] = \inf_{\hat{D} \to n} \text{Tr}\{ \hat{T} + \hat{W} \hat{D} \} . \]

\( \hat{T} \) is the kinetic energy operator, \( \hat{W} \) is the electron-electron repulsion operator, and \( \hat{D} \) is the density matrix operator in Fock space. The notation “\( \hat{D} \to n \)” indicates that the search for the infimum is performed over all density matrices satisfying \( \text{Tr}\{ \hat{D} n(\mathbf{r}) \} = n(\mathbf{r}) \). In order to carry out an equivalent search without requiring this density constraint, we introduce...
the Lagrange multiplier $u[n]$ as indicated below. The generalized energy $E_N[u]$, now a functional of $u[n]$, involves a search over all density matrices corresponding to $N$ electrons ($N$ is in general non-integer):

$$E_N[u] = \inf_{D \rightarrow N} \text{Tr}\{\hat{T} + \hat{W} + \int dr \, u(r)\hat{n}(r)\} + D\} . \quad (3)$$

Here, $N$ is a real number between $J$ and $J + 1$, where $J$ is a positive integer. If the convexity assumption holds, i.e.,

$$E_{J-1}[u] - E_J[u] \geq E_J[u] - E_{J+1}[u]$$

for any $J$, then $E_N[u] = (1 - \omega)E_J[u] + \omega E_{J+1}[u]$, where $\omega = \int dr \, n(r) - J$. We assume that $-1 < \omega < 1$. The search for the infimum in Eq. (3) yields a density matrix $\hat{D}[n]$ that is also a linear interpolation of integer-number density matrices, $\hat{D}_J$ and $\hat{D}_{J+1}$. For example, if the bordering systems are pure ground states then $\hat{D}_J = |\psi_M\rangle \langle \psi_M|$, $M = J, J + 1$. The densities of the pure states, that is $n_M[u](r) = \text{Tr}\{\hat{D}_M[u]\hat{n}(r)\}$, $M = J, J + 1$, satisfy the restriction:

$$n(r) = (1 - \omega)n_J[u](r) + \omega n_{J+1}[u](r) . \quad (4)$$

Because $u$ is a functional of the density, so are the densities $n_J$ and $n_{J+1}$. Inserting the minimizing density matrix $\hat{D}[n]$ into $F[n]$ we find that

$$F[n] = (1 - \omega[n])F[n_J] + \omega[n]F[n_{J+1}] \quad (5)$$

(Not: If $-1 < \omega < 0$ then we replace $\omega$ by $-\omega$, and $J$ by $J + 1$ in the above equation). For notational convenience, we introduce the average function:

$$y(x) = \begin{cases} 1 & x = 0, \\ 1 - x & 0 < x < 1, \\ 1 + x & -1 < x < 0, \\ 0 & \text{otherwise,} \end{cases} \quad (6)$$

which allows us to express $F$ (as well as the energy, density, etc.) as:

$$F[n] = \sum_M y(N - M)F[n_M] , \quad (7)$$

where $N = \int n$ is of course a density-functional as well. The functional $F[n]$ is split in the usual Kohn-Sham manner:

$$F[n] = T[n] + E_{\text{HXC}}[n] , \quad (8)$$

where $T[n] = \inf\{\text{Tr}\{\hat{T}\hat{D}_n\} | \hat{D}_n \rightarrow n\}$, and $E_{\text{HXC}}[n] = E_0[n] + E_{\text{XC}}[n]$, the Hartree and exchange-correlation energy functionals.

The ground-state energy for the auxiliary system of non-interacting electrons, $E_{s,N}$ can be thought of as a functional of $u_s(r)$, an analog of $u(r)$ introduced to carry out the non-interacting search version of Eq. (3):

$$E_{s,N}[u_s] = \inf_{\hat{D}_s \rightarrow N} \text{Tr}\{\hat{T} + \int dr \, u_s(r)\hat{n}(r)\} + D_s\} . \quad (9)$$

As in the case of $F[n]$, $T[n]$ returns two densities $n_{s,J}(r)$ and $n_{s,J+1}(r)$ that, when added together with the weight factor $y(N - M)$, yield the density $n(r)$ of the interacting system. In what follows, we will refer to $n_{s,J}(r)$ and $n_{s,J+1}(r)$ as the non-interacting bordering integer densities. We emphasize that even employing the exact exchange-correlation functional, the non-interacting integer density $n_{s,M}(r)$ is not equal to the $M$-electron density of the interacting system (see Fig. 2.a for a model system we describe later on). Rather than being the ground-state density of $M$ interacting electrons in $u(r)$ (or $M$ non-interacting electrons in $v(r)$), it is the ground-state density of $M$ non-interacting electrons in $u_s(r)$, a potential that differs from $v_s(r)$ for non-integer $M$, as illustrated in Fig. 2.b. For example, $n_{s,J}(r) = \sum_{i=1}^J |\phi_i(r)|^2$, and $n_{s,J+1}(r) = n_{s,J}(r) + |\phi_{J+1}(r)|^2$, where $\{\phi_i\}$ are single-particle orbitals that satisfy

$$\left(\hat{T} + \int dr \, u_s(r)\hat{n}(r)\right)|\phi_i\rangle = \epsilon_i|\phi_i\rangle , \quad (10)$$

and by definition $\sum_M y(N - M)n_{s,M}(r) = n(r)$. For example, $J < N < J + 1$, then using $y$ we get that $n(r) = n_{s,J} + \omega|\phi_{J+1}(r)|^2$. The non-interacting bordering integer densities $n_{s,J}(r)$ and $n_{s,J+1}(r)$ are density functionals as well. Inserting Eq. (8) on both sides of Eq. (7) and expanding $T[n]$ as $\sum_M y(N - M)T[n_M]$, we obtain the most important result of this paper:

$$E_{\text{HXC}}[n] = \sum_M y(N - M)\left\{T[n_M] - T[n_{s,M}]\right\} + E_{\text{HXC}}[n_M] \quad (11)$$

an exact relation for $E_{\text{HXC}}[n]$ in terms of quantities that describe pure quantum states, with $T_s$ evaluated at both, the interacting and non-interacting bordering integer densities. Eq. (11) is trivially true when $n(r)$ integrates to an integer number, but it is a useful identity when $J < N < J + 1$ in the context of approximate DFT, as we show next.

Let us denote as $E_{\text{HXC}}[n_{s,M}]$ an approximation for $M = 1, 2, \ldots$. Inserting this functional into Eq. (11) yields $E_{\text{HXC}}^{\text{app}}[n]$, a useful approximation to the ensemble functional. The densities $\{n_M\}$ can in principle be obtained from the search in $F[n]$, a functional we do not know. But we can circumvent the use of $F[n]$ by defining

$$G_s[n] = \inf_{\hat{n}_M \rightarrow n} \sum_M y(N - M)G_s[\hat{n}_M] , \quad (12)$$

where

$$G_s[\hat{n}_M] = \inf_{\hat{D}_s \rightarrow \hat{n}_M} \text{Tr}\{\hat{T} + \int dr \, v_{\text{HXC}}[\hat{n}_M](r)\hat{n}(r)\} + D_s\} . \quad (13)$$

By $\{\hat{n}_M\} \rightarrow n$ we refer to the constraint $\sum_M y(N - M)\hat{n}_M(r) = n(r)$. If $J < N < J + 1$, the optimal densities $\{\hat{n}_M\}$ that minimize the right hand side of Eq. (12) are obtained from solving two sets of KS equations self-consistently: one with KS potential $\tilde{v}_s[\tilde{n}_s] = v_{\text{HXC}}[\tilde{n}_s] + \tilde{u}$
and another with \( \tilde{v} \), \( \tilde{n}_{j+1} \). The orbitals arising from the KS equations with \( \tilde{v} \) and \( \tilde{n}_{j+1} \) are complex-squared and added together to yield the densities \( \tilde{n}_{j+1} \) until the constraint is satisfied. If \( \tilde{u} \) is set as the external potential of the system, \( v \), then one obtains an approximation to the ensemble ground-state density. The functional in Eq. (12) reformulates the non-interacting \( \psi \)-representability problem for an approximate XC potential. When the exact XC potential is used, then setting \( \tilde{u} = v \) and solving the two sets of KS equations produces the orbitals needed to build the exact ground-state densities \( n_j \) and \( n_{j+1} \).

The total energy of the system is

\[
E_{\text{app}}^n[u] = \sum_M g(N-M) \left( T_M[n_M] + E_{\text{HXC}}^\text{app}[n_M] \right) + \int dr \; v(r) n_M(r).
\]

The approximated ground state energy is found by setting \( E_N^\text{app}[v] = \inf_{n \rightarrow N} E_{\text{app}}^n[u] \). If the convexity assumption holds for our system of interest then

\[
E_{\text{app}}^n[v] = \sum_M g(N-M) E_{\text{app}}^n[v],
\]

where

\[
E_{\text{app}}^n[v] = \inf_{n_M} T_M[n_M] + E_{\text{HXC},M}[n_M] + \int dr v(r)n_M(r).
\]

Eq. (15) shows that it is possible to recover the piecewise linear dependence of the approximated energy. Using the analog of Eq. (4) for \( J < 1 < N < J \) and the KS equations, it can be shown that:

\[
\frac{\delta E_{\text{app}}^n}{\delta n(r')} = E_J^\text{app} - E_{J-1}^\text{app} - e_J^\text{app} + v_{\text{HXC}}^\text{app}(r') + \sum_M g(N-M) \int dr' \left( \frac{\delta E_{\text{app}}^n}{\delta n_M(r')} \right) \delta n_M(r') \delta n(r).
\]

The term \( \delta E_{\text{app}}^n / \delta n_M(r') \) is a constant at the minimum and \( \int dr' \delta n_M(r') / \delta n(r) = 0 \), which leads to (dropping the Hartree term):

\[
\frac{\delta E_{\text{app}}^n}{\delta n(r)} = -I^\text{app} - e_J^\text{app} + v_{\text{HXC}}^\text{app}(r).
\]

Since \( v_{\text{HXC}}^\text{app} = \delta E_{\text{app}}^n / \delta n \), by definition, we obtain the Janak's theorem [19] \( e_J^\text{app} = -I^\text{app} \) where \( I^\text{app} = E_{J-1}^\text{app}[u] - E_J^\text{app}[u] \) is the ionization energy of the system, and \( J < 1 < N < J \). We can also write Eq. (18) as:

\[
\frac{\delta E_{\text{app}}^n}{\delta n(r)} = -I^\text{app} - \frac{\delta T_s}{\delta n(r)} - u(r).
\]

This result allows us to calculate the XC DD as [20]:

\[
\Delta_{\chi\text{C}} = \lim_{\Delta N \to 0^+} \frac{\delta E_{\text{app}}^n}{\delta n(r)} \bigg|_{J=\Delta N} - \frac{\delta E_{\text{app}}^n}{\delta n(r)} \bigg|_{J=\Delta N} - A^\text{app} - \left( \epsilon_{\text{app}} - \epsilon_n^\text{app} \right),
\]

where \( A^\text{app} = E_J^\text{app}[u] - E_{J+1}^\text{app}[u] \) is the electron affinity of the J-electron system and \( \epsilon_n^\text{app} \) and \( \epsilon_{\text{HOMO}}^\text{app} \) are the HOMO and LUMO orbital energies of the J-electron system. The XC DD turns out to be the difference between the fundamental gap of the real system and the KS gap. However, the approximated XC DD serves the same purpose: correct the KS particle band gap.

For an ensemble DFA the Janak's theorem is valid but the ionization theorem is not, in general. For example, for a system with strictly J electrons it is known that the LDA HOMO energy does not match the ionization predicted by LDA, i.e., when \( N = J, e_J^\text{LDA} \neq -1/J^\text{LDA} \). To satisfy the Janak's theorem, a constant must be added to the approximate XC potential to replace the HOMO orbital by the DFA ionization. When \( J - 1 < N < J \), this constant is \(-I - \epsilon_n(N = J)\). At \( N = J \), however, there is no need for such correction since the functional derivative with respect to the density at this point is not defined uniquely. On the other hand, using the XC energy functional, the ionization theorem for Coulombic systems leads to the well-known expression for the DD of the XC energy functional: \( -A - \epsilon_n \).

Eq. (11) indicates that the approximation \( E_{\chi\text{C}}^\text{app}[n] = (1 - \omega) E_{\chi\text{C}}^\text{app}[n_{J-1}] + \omega E_{\chi\text{C}}^\text{app}[n_J] \) misses the different KS kinetic energy contributions leading to the piecewise linear features of the energy. (Note: It does hold for the uniform electron gas where the level spacing is negligible. The discrete-state densities returned in that case by the minimization of the kinetic energy are negligibly different from those returned by \( F \) when both are evaluated at the electron-gas density \( n \), and \( N \) is not an integer). Employing the optimized effective potential method, Kraisler and Kronik [18] showed that the linear dependency on the number of electrons is almost restored using the functional \( E_{\text{app}}^\text{XC} \). With the kinetic energy contributions of Eq. (11), it is completely restored.

To illustrate our findings, we consider the example of a system of interacting fermions [21, 22] described by the energy functional \( E_v[n_M] = T_M[n_M] + E_{\text{H}}[n_M] + E_{\text{xc}}[n_M] + \int dx \sqrt{v(x)} n(x) \) where \( E_{\text{H}}[n_M] = 1/2 \int dx x^2 \) and \( E_{\text{xc}}[n_M] = -1/4 \int dx n_M^2 x \). Suppose that \( n_M^2(x) = (NA/\pi) \text{sech}(ax) \) is a density of interest with \( N = 2.5 \) and \( a = 2 \). To find the potential \( u[n] \), we minimize the error functional:

\[
\epsilon_N^2[u] = \int \sqrt{v_n[u]} - \sqrt{n_M^2} / 2.
\]

The preset density is recovered by solving the KS equations for \( N = 2 \) and \( N = 3 \) and setting \( n_{2.5}[u](x) = \frac{1}{2} v_n[u](x) + \frac{1}{2} n_M[u](x) \). Note that the self-consistent procedure has to be applied twice, once for \( v_n[u] = -\frac{1}{2} v_n[u] \) and once for \( v_n[u] = -\frac{1}{2} n_M[u] \); in both cases, the same estimation of \( u \) is used. We represent \( u \) in a spline basis set and \( \epsilon_N^2[u] \) is minimized with the Levenberg-Marquardt algorithm [23, 24]. This procedure yields the optimal potential \( u[n_{2.5}] \) shown in Fig. 1a. Now we set that
potential as fixed $v(x) = u(x)$ and calculate the ensemble energy as a function of the number of electrons. Fig. 1b shows the results. The solid line represents the piecewise ensemble interpolation and the dashed lines result from setting $E_x[n,N] = -1/4 \int dx n^2(x)$ (which lacks the DD) to calculate the energy for any number of electrons. The solid and dashed lines look to the eye very close to each other, but their differences are made clear in Fig. 1c. This difference is small for the functional chosen. The deviation is more severe for the 3D LDA functional [7].

We stress that a functional approximation for discrete states is enough to determine, through Eq. (11), an approximation to the XC functional that is also applicable to ensembles. However, solving the linearity problem in DFA’s is not enough to solve the problem of molecular dissociation, which is caused by incorrect electron delocalization. A possible solution is to induce localization by partitioning a molecule into subsystems or a system-bath complex [26]. In such case, a functional with the correct DD is required since the theory of ensembles provides a rigorous framework for defining energy functionals of open systems. This idea follows the main argument of Ref. [4] pointing to the importance of the XC DD.

In conclusion, we presented a formal framework to extend density functional approximations of pure-state systems to be applicable to densities that integrate to fractional numbers of electrons. The main result, an exact condition, is a recursive formula relating the HXC energy with the KS kinetic energy evaluated at the non-interacting bordering densities, and the HXC and KS energies evaluated at the bordering interacting densities. However, the Hohenberg-Kohn-Mermin theorem expressing the densities $n_M[u]$ as functionals of $n(r)$ does not allow us to express $E_{xc}[n]$ as an explicit functional of $n(r)$, nor even when using explicit functionals of the discrete-electron densities. Thus, the ensemble $v_{xc}(r)$ must be accessed through inversion.

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FIG. 1. a) Preset ensemble density for $N = 2.5$ (solid line), external potential (dashed line). b) Energy as a function of $N$ (solid line), approximated energy (dashed line). c) Difference between Eq. (15) and the energy calculated using $E_x[n] = -1/4 \int dx n^2$ for any $N$. d) Ensemble exchange potential for $N = 2.0$ (solid line), $N = 2.15$ (dashed line), and $N = 2.01$ (dashed-dotted line).

FIG. 2. a) Difference between $n_M$ and $n_{\nu M}$ for $M = 3$; these densities are required to yield the density in Fig. 1a. b) Kohn-Sham potentials corresponding to $N = 2.5$ (solid line) and $N = 2.0$ (dashed line).
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