

Piecewise Linearity of Approximate Density Functionals Revisited: Implications for Frontier Orbital Energies

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In the exact Kohn-Sham density-functional theory, the total energy versus the number of electrons is a series of linear segments between integer points. However, commonly used approximate density functionals produce total energies that do not exhibit this piecewise-linear behavior. As a result, the ionization potential theorem, equating the highest occupied eigenvalue with the ionization potential, is grossly disobeyed. Here, we show that, contrary to conventional wisdom, most of the required piecewise linearity of an arbitrary approximate density functional can be restored by careful consideration of the ensemble generalization of density-functional theory. Furthermore, the resulting formulation introduces the desired derivative discontinuity to any approximate exchange-correlation functional, even one that is explicitly density dependent. This opens the door to calculations of the ionization potential and electron affinity, even without explicit electron removal or addition. All these advances are achieved while neither introducing empiricism nor changing the underlying functional form. The power of the approach is demonstrated on benchmark systems using the local density approximation as an illustrative example.

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Density-functional theory (DFT) is a widely popular approach to the many-electron problem [1–6]. It is based on mapping the interacting-electron system into a noninteracting one. DFT is exact in principle, but the exchange-correlation (xc) density functional $E_{xc}[n(\vec{r})]$ remains unknown and is always approximated in practice.

Many constraints that the exact $E_{xc}[n(\vec{r})]$ has to satisfy have been formulated. Of particular interest here is the piecewise-linearity property: Using a zero-temperature ensemble of integer-electron states [7,8], the realm of DFT has been extended to fractional-electron numbers ($N = N_0 + \alpha$, where $N_0 \in \mathbb{N}$ and $\alpha \in [0, 1]$). It has been shown [9] that the total ground-state energy E is given by

$$E(N) = (1 - \alpha)E(N_0) + \alpha E(N_0 + 1). \quad (1)$$

An important manifestation of piecewise linearity [9–13] is the relation between the highest occupied orbital energy ε_{ho} and the ionization potential (IP) $I \equiv E(N_0) - E(N_0 + 1)$. If piecewise linearity is maintained, $\varepsilon_{\text{ho}} = -I$, a result known as the IP theorem [9,14].

Despite the importance of piecewise linearity, it has long been known that commonly used functional classes, such as the local density approximation, the generalized gradient approximation, or the conventional hybrid functional approximation, grossly disobey this condition. Instead, a typically convex $E(N)$ curve is obtained (see, e.g., Refs. [10,13,15–19]), and, correspondingly, the discrepancy between ε_{ho} and $-I$ can easily be as large as a factor of 2 [20–23].

Two main approaches have emerged in response to this problem. In one approach, various correction terms are

imposed on existing underlying xc functionals [24–31]. In another approach, piecewise linearity is explicitly enforced in the construction of novel range-separated hybrid functionals [32–37].

The above considerations on piecewise linearity, or lack thereof, are all based on a description of fractional-electron systems by insertion of a density $n(\vec{r})$, which integrates to a fractional N , into a density functional developed originally for pure states. One may question whether this straightforward application is at all optimal. Indeed, Gidopoulos *et al.* [38] have observed, in the context of an excited-state ensemble, that straightforward application of the Hartree term leads to an unphysical “ghost contribution.” More recently, Gould and Dobson [39] have made similar observations of “ghost interactions” in the context of the exact-exchange (EXX) functional with fractional spin densities and used ensemble definitions to propose an improved, linearized EXX functional.

Here, we offer an ensemble generalization of all energy terms of an arbitrary density functional to systems with fractional N . Using the simplest functional of all, the local density approximation, on example systems, we find that this generalization greatly reduces the problem of the energy curve convexity, significantly restores the IP theorem, and concomitantly introduces an appropriate derivative discontinuity into the xc potential in a natural manner. All this is achieved while neither introducing empiricism nor changing the underlying functional form.

Our considerations start with the ground state of a zero-temperature interacting-electron system with fractional N , described by an ensemble state $\hat{\Lambda} = (1 - \alpha)|\Psi_{N_0}\rangle\langle\Psi_{N_0}| + \alpha|\Psi_{N_0+1}\rangle\langle\Psi_{N_0+1}|$, where $|\Psi_{N_0+p}\rangle$

is a (pure) many-electron ground state with $N_0 + p$ electrons and p is 0 or 1 [40]. The electron density is then obtained using the density operator $\hat{n}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$ as

$$n(\vec{r}) = \text{Tr}\{\hat{\Lambda} \hat{n}\} = (1 - \alpha)n_0(\vec{r}) + \alpha n_1(\vec{r}). \quad (2)$$

$n_0(\vec{r})$ and $n_1(\vec{r})$ are the densities of the interacting systems with N_0 and $N_0 + 1$ electrons, respectively. As a result, the total energy E is obtained as in Eq. (1).

In the Kohn-Sham (KS) formulation of DFT, the interacting-electron system is mapped into *one* KS system of noninteracting electrons with a fractional number of particles N . Therefore, its ground state must also be an ensemble state, given by $\hat{\Lambda}_{\text{KS}} = (1 - \alpha)|\Phi_{N_0}^{(\alpha)}\rangle\langle\Phi_{N_0}^{(\alpha)}| + \alpha|\Phi_{N_0+1}^{(\alpha)}\rangle\langle\Phi_{N_0+1}^{(\alpha)}|$, where $|\Phi_{N_0+p}^{(\alpha)}\rangle$ are pure KS ground states, with $N_0 + p$ electrons, respectively, [2,40,41]. Each pure ground state is described as a Slater determinant of single-electron orbitals $\{\varphi_i^{(\alpha)}\}$, corresponding to the *same*, α -dependent KS potential. In contrast to the quantities $|\Psi_{N_0+p}\rangle$ and n_p , all quantities of the KS ensemble are α dependent, a fact we emphasize via the superscript (α). Hence, in addition to the explicit dependence of $\hat{\Lambda}_{\text{KS}}$ on α , there also exists an implicit dependence through $\{\varphi_i^{(\alpha)}\}$.

Similarly to Eq. (2), the KS density is obtained as $n_{\text{KS}}^{(\alpha)}(\vec{r}) = \text{Tr}\{\hat{\Lambda}_{\text{KS}} \hat{n}\} = (1 - \alpha)\rho_0^{(\alpha)}(\vec{r}) + \alpha\rho_1^{(\alpha)}(\vec{r}) = \sum_{i=1}^{\infty} g_i |\varphi_i^{(\alpha)}(\vec{r})|^2$, where $\rho_p^{(\alpha)}(\vec{r}) := \langle\Phi_{N_0+p}^{(\alpha)}|\hat{n}|\Phi_{N_0+p}^{(\alpha)}\rangle = \sum_{i=1}^{N_0+p} |\varphi_i^{(\alpha)}(\vec{r})|^2$ and

$$g_i = \begin{cases} 1 & i \leq N_0 \\ \alpha & i = N_0 + 1 \\ 0 & i > N_0 + 1 \end{cases} \quad (3)$$

are the occupation numbers of the KS levels. While $n_{\text{KS}}^{(\alpha)}(\vec{r})$ is required to equal $n(\vec{r})$ by construction, we stress that $\rho_p^{(\alpha)}(\vec{r})$ need not equal $n_p(\vec{r})$. Moreover, because $n_0(\vec{r})$, $n_1(\vec{r})$ and $n(\vec{r})$ can all be obtained independently from each other by considering systems with different N , Eq. (2) can be viewed as a linearity criterion for the density, complementing Eq. (1).

We now examine the ensemble properties of the Coulomb energy of the KS system, associated with the operator $\hat{W} = \frac{1}{2} \sum_i \sum_{j \neq i} |\vec{r}_i - \vec{r}_j|^{-1}$. By definition [3], the Coulomb functional $W = \text{Tr}\{\hat{\Lambda}_{\text{KS}} \hat{W}\} = W_H + W_x$ is comprised of a Hartree (H) and an exchange (x) term. Performing the Tr operation, we can express the ensemble terms W_H and W_x by means of the standard, pure-state definitions of the Hartree and EXX functionals (see the Supplemental Material [42]). We obtain

$$W_H = (1 - \alpha)E_H[\rho_0^{(\alpha)}] + \alpha E_H[\rho_1^{(\alpha)}], \quad (4)$$

$$W_x = (1 - \alpha)E_x[\rho_0^{(\alpha)}] + \alpha E_x[\rho_1^{(\alpha)}], \quad (5)$$

where as usual

$$E_H[n] = \frac{1}{2} \iint d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (6)$$

and

$$E_x[n] = -\frac{1}{2} \sum_{i,j=1}^{\infty} g_i g_j \iint d^3r d^3r' \frac{\varphi_i^*(\vec{r}') \varphi_j^*(\vec{r}) \varphi_i(\vec{r}) \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (7)$$

Because $E_H[n]$ is not linear in n , it immediately follows that the required W_H of Eq. (4) is not obtained by inserting the fractional-electron density $n_{\text{KS}}^{(\alpha)}$ into Eq. (6). A similar statement is true for $E_x[n]$ and W_x [39]. Therefore, the Hartree and EXX functionals do not retain their usual forms for ensemble states. Instead, $W_H = E_H[n] + \Delta E_{eH}[\varphi_{N_0+1}^{(\alpha)}; \alpha]$ and $W_x = E_x[n] - \Delta E_{eH}[\varphi_{N_0+1}^{(\alpha)}; \alpha]$, where

$$\Delta E_{eH} = \frac{1}{2} \alpha(1 - \alpha) \iint d^3r d^3r' \frac{|\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 |\varphi_{N_0+1}^{(\alpha)}(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \quad (8)$$

is the ensemble (e) correction.

Note that, for $\alpha = 0$ or 1, W_H and W_x reduce to their usual forms (6) and (7). Thus, introduction of the term ΔE_{eH} does not affect the total energies of systems with an integer N . In addition, even at fractional N , the total energy obtained for EXX calculations with no correlation should not be affected either, as ΔE_{eH} appears with opposite signs in W_H and W_x [43]. However, the Hartree expression is usually complemented by an approximate xc functional $E_{\text{xc}}[n]$ that is not the EXX. Error cancelation is then not expected and, as shown below, not obtained. Trivially, an arbitrary $E_{\text{xc}}[n]$ is not linear in n , but it can still be made explicitly linear in α , in the same spirit as in Eqs. (4) and (5) above, yielding

$$E_{\text{exc}}[n] = (1 - \alpha)E_{\text{xc}}[\rho_0^{(\alpha)}] + \alpha E_{\text{xc}}[\rho_1^{(\alpha)}] \quad (9)$$

(see the Supplemental Material [42]). Note that, while the dependence of E_{exc} on α is now explicitly linear, there remains an implicit nonlinear dependence via the functions $\rho_p^{(\alpha)}(\vec{r})$. For the special case of the local spin density approximation (LSDA), we refer to its ensemble-generalized form, using Eq. (9), as eLSDA.

Importantly, the ensemble expressions W_H [Eq. (4)] and E_{exc} [Eq. (9)] no longer depend explicitly on the density n , even for underlying functionals that are explicitly density dependent for pure states, such as the LSDA. Ultimately, they depend on the KS orbitals (themselves a functional of n) via $\rho_p^{(\alpha)}(\vec{r})$, as well as on α itself. This affects the KS potential v_{KS} . To remain within the KS framework, it must now be evaluated using the optimized effective potential (OEP) procedure, appropriate for implicitly density-dependent functionals [22,44–47]. A complete derivation

of v_{KS} is provided in the Supplemental Material [42]. One unusual aspect of it, which we stress here, is that the explicit dependence of W_H and E_{exc} on α contributes a spatially uniform but α -dependent term to v_{KS} , given by

$$v^{(0)} = -\frac{1}{2} \iint \frac{|\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 |\varphi_{N_0+1}^{(\alpha)}(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d^3 r d^3 r' + E_{\text{xc}}[\rho_1^{(\alpha)}] - E_{\text{xc}}[\rho_0^{(\alpha)}] - \int |\varphi_{N_0+1}^{(\alpha)}(\vec{r})|^2 v_{\text{xc}}[\rho_1^{(\alpha)}] d^3 r, \quad (10)$$

where $v_{\text{xc}} = \delta E_{\text{xc}} / \delta n$ is the usual xc potential. This term involves the highest (possibly partially) occupied orbital $\varphi_{N_0+1}^{(\alpha)}$ and *does not vanish even when N is an integer*, despite the fact that for integer values the conventional and ensemble-generalized energy expressions are identical. Such a constant term, although allowed by the Hohenberg-Kohn theorem [48], is usually deemed unimportant because it does not affect the density or the total energy. However, it does shift the KS eigenvalues, a fact we show below to be crucial. Thus, all calculations now conceptually involve orbital-dependent functionals, although for integer N the term $v^{(0)}$ can be easily evaluated without performing the computationally demanding OEP calculation.

To illustrate the proposed generalization and its implications, we apply the eLSDA functional to the H_2 molecule and the C atom using DARSEC—an all-electron, real-space code [49] (numerical details are given in the Supplemental Material [42]). The total energies for the above two systems, as a function of the net charge q , are given in Fig. 1, with q ranging from -2 (doubly ionized system) to 0 (neutral system). The LSDA energy curves are, as expected, convex [10,15,17,19]. The curve for the eLSDA is, however, almost piecewise linear, being slightly concave. The strong reduction in the deviation from piecewise linearity is a significant advantage of the ensemble approach. This deviation is not fully eliminated because, while the eLSDA functional is explicitly linear in α by construction, it may still be implicitly nonlinear through $\{\varphi_i^{(\alpha)}\}$. A comparison of the eLSDA results to the EXX ones shows that the piecewise linearity of eLSDA is comparable to that of EXX. An obvious advantage of eLSDA, however, is the treatment of correlation.

eLSDA also affords a significant improvement in satisfying the density linearity criterion, Eq. (2). We consider $D(\vec{r}) := n(\vec{r}) - (1 - \alpha)n_0(\vec{r}) - \alpha n_1(\vec{r})$, which should equal 0 at all \vec{r} for the exact functional. A plot of $D(\vec{r})$ at $q = -0.5$ for H_2 , as obtained with LSDA and eLSDA, is presented in Fig. 2. Clearly, the spatial profile of $D(\vec{r})$ is smoother with eLSDA, and its average numerical value is much smaller. Specifically, $Q(q) := \int D^2(\vec{r}) d^3 r$, which is the variance of $D(\vec{r})$ per a given q , is $\sim 10^{-4} \text{ Bohr}^{-3}$ with LSDA. With eLSDA, however, it is

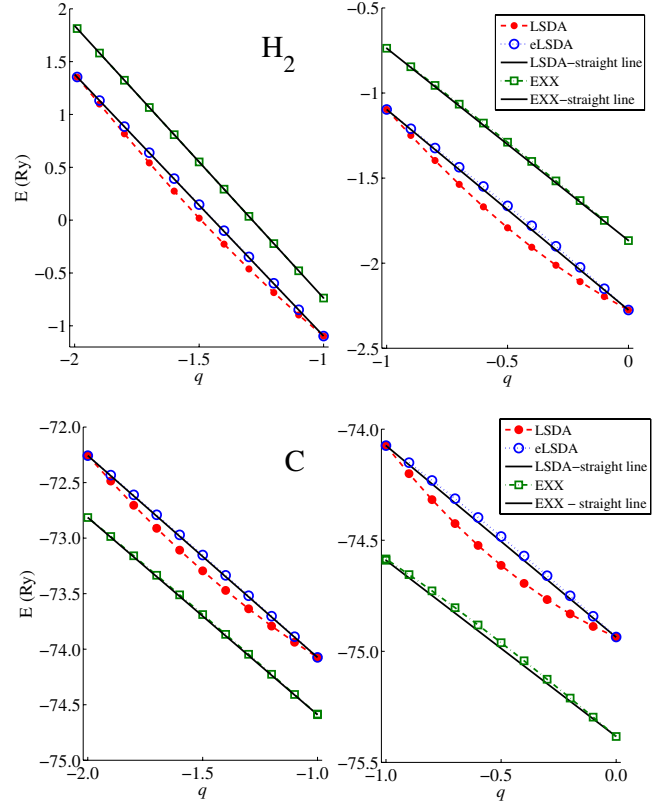


FIG. 1 (color online). Energy of the H_2 molecule (top) and of the C atom (bottom) as a function of fractional charge q for various functionals. The EXX results for H_2 have been shifted upward by 0.4 Ry for clarity. The straight solid lines connect the energies obtained at the integer value as a reference for complete piecewise linearity.

lower by 2 orders of magnitude for $q = -1, \dots, 0$ and essentially zero for $q = -2, \dots, -1$.

The great improvement in the piecewise linearity of the energy curve (Fig. 1) is directly manifested in the degree to which the IP theorem is satisfied. This is illustrated in Fig. 3. The figure shows the highest (possibly partially) occupied orbital ε_{ho} , the energy derivative $\partial E / \partial q$, and the negative of the IP $-I$ (computed from total energy

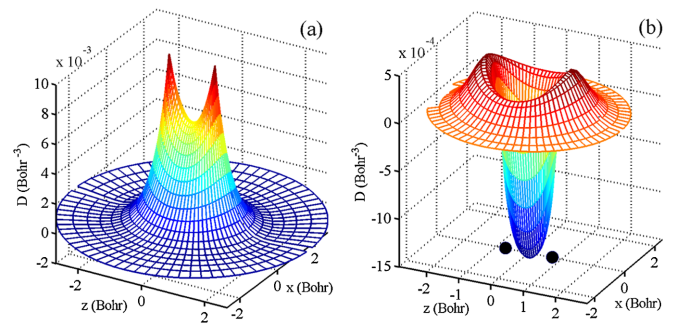


FIG. 2 (color online). Deviation from piecewise linearity in the density, $D(\vec{r})$, obtained for the H_2 molecule for $q = -0.5$ using (a) LSDA and (b) eLSDA.

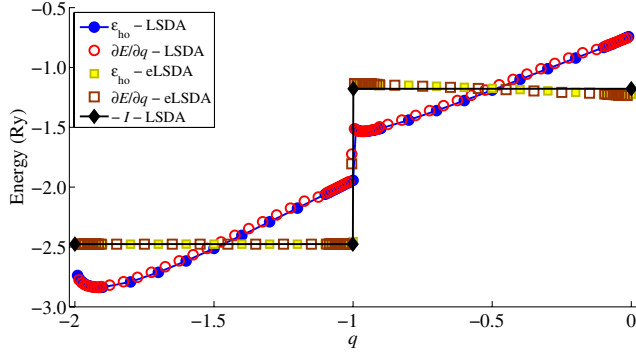


FIG. 3 (color online). Frontier orbital energy ε_{ho} , the energy derivative $\partial E/\partial q$ as a function of q , and the negative of the IP $-I$, calculated for H_2 with the LSDA and eLSDA functionals.

differences obtained at integer q values), as calculated for H_2 as a function of q with both LSDA and eLSDA. Janak’s theorem [50], which equates ε_{ho} and $\partial E/\partial q$ for any approximate functional, is indeed closely obeyed by both approximations. But, because eLSDA is much more piecewise linear, the $\varepsilon_{\text{ho}}(q)$ calculated with it is much more piecewise constant as a function of q (as it should be for the exact functional). Furthermore, ε_{ho} coincides much more closely with $-I$ when approaching an integer q from below, in agreement with the IP theorem [9,14]—a direct consequence of the constant potential $v^{(0)}$.

The satisfaction of the IP theorem is closely related to another fundamental property of the exact xc functional: As the number of electrons crosses an integer, the xc potential may “jump” by a constant, usually known as the derivative discontinuity [9]. The conventional wisdom on explicit density functionals (including LSDA) is that they do not possess this discontinuity. Recently, Stein *et al.* [13] have shown that a significant increase in the degree of piecewise linearity must be accompanied by the appearance of a discontinuity in the xc potential. Here, it emerges from $v^{(0)}$ of Eq. (10), which depends on the highest occupied orbital and is therefore different if one approaches an integer N from the left or from the right. Therefore, the derivative discontinuity of explicit density functionals arises naturally, without invoking any empiricism. This is readily observed in Fig. 3 and Table I: the fundamental gap of the ion H_2^+ , deduced from the discontinuity in ε_{ho} around $q = -1$, is much larger with eLSDA than with LSDA and corresponds much more closely to the result obtained from total energy differences (solid black line in the figure). Similar observations apply to the C atom (see Table I). Thus, our ensemble-based approach automatically identifies and restores the missing derivative discontinuity, appropriate for any underlying functional. Importantly, as the potential “jumps” by a constant at the integer-electron point, owing to the derivative discontinuity, the KS orbitals do not change at all. Therefore, the missing derivative discontinuity can be evaluated using only the Kohn-Sham eigenvalues and orbitals of the integer

TABLE I. Highest occupied orbital energy $-\varepsilon_{\text{ho}}$, compared to the IP I , and the cation fundamental gap, deduced from the discontinuity of ε_{ho} at $q = -1$, compared to the difference between the second and first IPs of the neutral system. All quantities are computed for both H_2 and C, and all energies are given in Ry. The Δ ’s correspond to the relative error between the two values positioned immediately above them.

		LSDA	eLSDA	EXX	Experiment ^a
H_2	$-\varepsilon_{\text{ho}}$	0.745	1.223	1.193	
	I	1.178	1.178	1.130	1.134
	Δ_{ho}	37%	4%	6%	
H_2^+	Gap	0.426	1.320	1.489	
	$I_2 - I_1$	1.298	1.298	1.446	1.443 ^b
	Δ_{gap}	71%	2%	3%	
C	$-\varepsilon_{\text{ho}}$	0.450	0.942	0.876	
	I	0.859	0.859	0.793	0.828
	Δ_{ho}	48%	10%	10%	
C^+	Gap	0.019	1.125	1.140	
	$I_2 - I_1$	0.962	0.962	0.982	0.965
	Δ_{gap}	98%	17%	16%	

^aReference [51].

^bFor H_2^+ , no experimental value for I_2 exists. Instead, it was obtained from EXX calculations, which yield an exact result for this system.

point itself. This opens the door to calculations of the ionization potential and electron affinity even without explicit electron removal or addition.

In conclusion, we presented a generalization of the Hartree, exchange, and correlation terms of an arbitrary density functional to systems with a fractional-electron number, based on the ensemble form of DFT. Using the local density approximation on H_2 and C as illustrative examples, we showed that this generalization significantly reduces the deviation from piecewise linearity and generates the appropriate derivative discontinuity, without introducing empiricism and with no changes to the underlying functional form. With this generalization, the total energy at integer-electron numbers remains intact but the eigenenergies change and the IP theorem is much more closely obeyed. This shows that problems that have plagued simple approximate density functionals for many years can be very strongly mitigated by rigorous employment of ensemble DFT within the OEP approach, without any further functional development. We expect this proposed generalization to be equally useful for more advanced approximate functionals, as well as for more complex systems, allowing for improvement in spectroscopic properties without any compromise on energetics.

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- [42] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.110.126403> for derivation of Eqs. (4), (5), and (8), rationale of Eq. (9), derivation of the KS potential, and numerical details.
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