Elimination of the asymptotic fractional dissociation problem in Kohn-Sham density-functional theory using the ensemble-generalization approach

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Many approximations within density-functional theory spuriously predict that a many-electron system can dissociate into fractionally charged fragments. Here, we revisit the case of dissociated diatomic molecules, known to exhibit this problem when studied within standard approaches, including the local spin-density approximation (LSDA). By employing our recently proposed [E. Kraisler and L. Kronik, Phys. Rev. Lett. **110**, 126403 (2013)] ensemble generalization we find that asymptotic fractional dissociation is eliminated in all systems examined, even if the underlying exchange correlation (xc) is still the LSDA. Furthermore, as a result of the ensemble-generalization procedure, the Kohn-Sham potential develops a spatial step between the dissociated atoms, reflecting the emergence of the derivative discontinuity in the xc energy functional. This step, predicted in the past for the exact Kohn-Sham potential and observed in some of its more advanced approximate forms, is a desired feature that prevents any fractional charge transfer between the system's fragments. It is usually believed that simple xc approximations such as the LSDA cannot develop this step. Our findings show, however, that ensemble generalization to fractional electron densities automatically introduces the desired step even to the most simple approximate xc functionals and correctly predicts asymptotic integer dissociation.

I. INTRODUCTION

Density-functional theory (DFT) [1–9] is a widely used theoretical framework for studying the electronic properties of matter. It is usually employed by mapping the original N interacting-electron system into an equivalent Kohn-Sham (KS) system of N noninteracting particles subject to a common effective potential, such that the ground-state electron density $n(\mathbf{r})$ is reproduced. While exact in principle, this mapping involves the exchange-correlation (xc) density functional, $E_{xc}[n(\mathbf{r})]$, whose exact form is unknown. Therefore, it is always approximate in practice.

Present-day density-functional approximations (DFAs) already make it widely applicable to a variety of many-electron systems in physics, chemistry, and materials science [10–15]. However, there remain numerous challenges that common DFAs fail to meet. A significant problem, which has both formal and practical implications, is the so-called *problem of fractional dissociation*. It is most easily demonstrated when considering a neutral diatomic molecule, AB. Upon dissociation, the molecule must break up into two neutral atoms, A and B, with an *integer* number of electrons, N_A^0 and N_B^0, on each [16]. This observation is known as the *principle of integer preference* [17]. This fundamental principle is not reproduced by many DFAs. Instead, one finds that a system of two well-separated atoms often reaches its energy minimum when the number of electrons on each of the atoms is fractional: $N_A^0 + q$ electrons on atom A and $N_B^0 - q$ electrons on atom B, with $q \in (-1,1)$ [17–26].

The significance of this failure lies beyond the accurate description of dissociation in diatomic systems. It indicates that common DFAs may fail to describe charge transfer in molecules and materials (see, e.g., [27–35] and references therein). Furthermore, theoretical analysis of the problem of fractional dissociation allowed an understanding of fundamental properties of many-electron systems [18,36,37]: If N is allowed to be fractional, the total energy $E(N)$

of a many-electron system must possess a piecewise-linear dependence on N. As a result [38–45], $E_{xc}[n(\mathbf{r})]$ may exhibit a discontinuity in its derivative at integer N.

It has been shown [18,23,46] that the fractional dissociation problem occurs in approximate DFAs due to the deviation of their energy curves from piecewise linearity: Standard (semi-)local calculations for atoms show a convex behavior of the energy $E_a(N_a^0 + q)$, where $a \in \{A,B\}$. As a result, the total energy of a well-separated diatomic molecule, which can be expressed as

$$E_{A\cdots B}(q) = E_A\left(N_A^0 + q\right) + E_B\left(N_B^0 - q\right), \tag{1}$$

may reach an unphysical minimum at $q \neq 0$ (see Fig. 1 below). This failure has been discovered as early as 1982 by Perdew *et al.* [18], for an infinitely stretched LiH molecule treated within the local density approximation, and has since been found in various molecules with different DFAs [17,19–26,47]. Perdew *et al.* [18] have shown that this would not have happened had the atomic energy curves, and as a result the molecular energy curve, been exactly piecewise linear. Then, in terms of the total energy, the molecular energy curve $E_{A\cdots B}(q)$ would have possessed a nonanalytical minimum at $q = 0$, obeying the principle of integer preference. In terms of the KS potential, a "plateau" in the vicinity of one of the atoms would have emerged, shifting the KS potential and the energy levels associated with that atom [17,34,48–53]. Because all these desired features are absent in the standard local density approximation, spurious transfer of fractional charge is not precluded.

Recently, we have proposed an approximate ensemble generalization of the Hartree-exchange-correlation (Hxc) functional [54]. In contrast to the usual approach, in the generalized approach one does not insert the ensemble density, which integrates to a fractional N, into the standard form of the approximate Hxc functional chosen. Instead, the Hxc energy is now evaluated as a weighted sum of Hxc energies
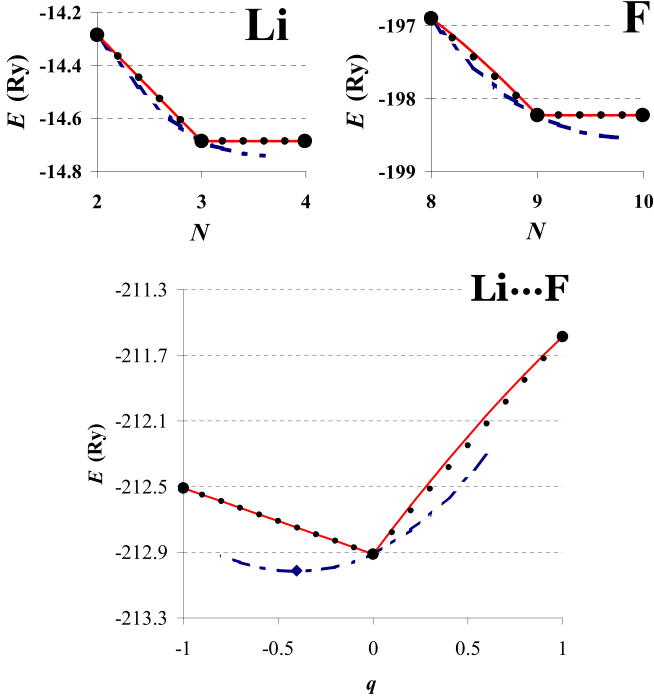
FIG. 1. (Color online) Total energy of the Li and F atoms as a function of N (top) and energy of the dissociated Li$\cdots$F molecule as a function of q (bottom), computed with LSDA (dash-dotted line) and eLSDA (solid line), compared to the expected piecewise-linear (dotted line) behavior (the latter is obtained by linear interpolation of the eLSDA energies at integer electron values).

obtained using two auxiliary densities, which integrate to integer N's. These are derived from the same self-consistent KS potential by choosing the highest, partially occupied KS energy level as either fully occupied or completely unoccupied. We have shown [54–56] that this ensemble generalization restores, to a large extent, the piecewise-linearity property in the energy and simultaneously introduces an appropriate derivative discontinuity into the xc potential in a natural manner, even when the underlying xc functional is as simple as the local spin-density approximation (LSDA). All this is achieved while neither introducing empiricism nor changing the underlying functional form. This generalization would appear to be of direct relevance to the question of asymptotic fractional dissociation. It is therefore of much interest to examine whether and how it affects this important problem.

Here we employ the ensemble-generalized LSDA, denoted by eLSDA, to well-separated diatomic molecules. We find that spurious asymptotic fractional dissociation is eliminated in all systems examined. Furthermore, the KS potential develops the desired spatial step, which explains the absence of spurious fractional charge transfer also from the potential perspective. This shows that, contrary to conventional wisdom, the asymptotic fractional dissociation problem can be eliminated even with simple xc functionals, as long as an appropriate ensemble generalization is used.

II. METHODOLOGY

In the dissociation limit, a diatomic molecule can be described as two atoms with a possibly fractional electrical charge on each [Eq. (1)] [18]. Generally, a closed system with a fractional number of electrons, $N = N_0 + \alpha$, where $N_0 \in \mathbb{N}$ and $\alpha \in (0,1)$ is not physical, in the sense that electrons do not fracture in chemical systems. A fractional electron number may, however, arise as a time average of an open system, which is free to exchange electrons with its surroundings. Such a system can no longer be described by a pure quantum-mechanical state. Instead, it must be considered as a statistical mixture, or ensemble, of pure (integer electron) states [18]. Specifically, in our case—Coulomb systems at zero temperature—this ensemble state is a linear combination of the pure ground states for N_0 and $N_0 + 1$ electrons, with the statistical weights of $(1 - \alpha)$ and α, respectively [4,57,58], [59,60].

For describing a quantum system with fractional N in KS-DFT, recall that in KS-DFT one maps the original many-electron system to a fictitious noninteracting one, such that the overall density is retained. In particular, the number of particles in the KS system must equal the number of electrons in the real system. Therefore, the KS density must also integrate to a fractional number of particles and the KS ground state must be an ensemble of N_0- and $N_0 + 1$-states, i.e., $\hat{\Lambda}_{\mathrm{KS}} = (1 - \alpha)|\Phi_{N_0}^{(\alpha)}\rangle\langle\Phi_{N_0}^{(\alpha)}| + \alpha|\Phi_{N_0+1}^{(\alpha)}\rangle\langle\Phi_{N_0+1}^{(\alpha)}|$. Both $|\Phi_{N_0}^{(\alpha)}\rangle$ and $|\Phi_{N_0+1}^{(\alpha)}\rangle$ are Slater determinants constructed from one-electron KS orbitals, $\varphi_i^{(\alpha)}(\mathbf{r})$, arising from the *same* KS potential. The difference between the two determinants is that $|\Phi_{N_0}^{(\alpha)}\rangle$ is constructed from N_0 orbitals, whereas $|\Phi_{N_0+1}^{(\alpha)}\rangle$ is constructed from $N_0 + 1$ orbitals.

The above-discussed mapping is enforced by the KS potential, which is the common potential "felt" by all KS particles. Therefore, when changing the number of electrons, i.e., changing α, the KS potential itself can change because the nature of the mapping is changing. Significant variation of the KS potential with α have been indeed found for both the exact KS potential and various approximations to it (see [61] and references therein). As a result, the KS orbitals, $\varphi_i^{(\alpha)}(\mathbf{r})$, and all the quantities derived from them [including $\rho_p^{(\alpha)}(\mathbf{r})$ and $n^{(\alpha)}(\mathbf{r})$ that are introduced below], are generally α dependent. Here we emphasize this by including the superscript (α) explicitly.

The usual approach to the KS-DFT treatment of systems with fractional N is based on the construction of the electron density as

$$n^{(\alpha)}(\mathbf{r}) = \sum_{i=1}^{N_0} \left|\varphi_i^{(\alpha)}(\mathbf{r})\right|^2 + \alpha\left|\varphi_{N_0+1}^{(\alpha)}(\mathbf{r})\right|^2, \qquad (2)$$

i.e., on occupying the first N_0 levels fully but occupying the next one by the electron fraction α, so as to obtain $N_0 + \alpha$ electrons overall. This density can be equivalently expressed as $n^{(\alpha)}(\mathbf{r}) = (1 - \alpha)\rho_0^{(\alpha)}(\mathbf{r}) + \alpha\rho_1^{(\alpha)}(\mathbf{r})$, where $\rho_p^{(\alpha)}(\mathbf{r})$ is defined as the density due to the first $N_0 + p$ KS orbitals: $\rho_p^{(\alpha)}(\mathbf{r}) = \sum_{i=1}^{N_0+p} |\varphi_i^{(\alpha)}(\mathbf{r})|^2$, where $p = 0$ or 1. In other words, the overall density is the weighted sum of the two auxiliary densities obtained from taking the partially occupied orbital as either completely empty or completely full [62]. These two auxiliary

densities are not to be confused with the true densities of the N_0 and $N_0 + 1$ electron systems. In the usual approach, the overall density $n^{(\alpha)}(\mathbf{r})$ is then employed *directly* in the evaluation of the approximate Hxc energy functional $E_{\mathrm{Hxc}}[n]$, by inserting $n^{(\alpha)}(\mathbf{r})$ into the the functional form used for the description of systems with integer N.

Recently, we have shown [54,55] that this usual approach, i.e., using the integer Hxc form for systems with fractional N, contributes significantly to the spurious deviation from piecewise linearity in the total energy discussed above. To address this problem, we proposed an approximate ensemble-based generalization of the Hxc functional to fractional N. For completeness, we provide a short overview of this generalization. Its basic idea is that by considering the ensemble average of the many-electron Coulomb operator, $\hat{W} = \frac{1}{2} \sum_i \sum_{j \neq i} |\mathbf{r}_i - \mathbf{r}_j|^{-1}$, in the KS system, the Hxc energy can be generalized as follows:

$$E_{e-\mathrm{Hxc}}[n^{(\alpha)}] = (1-\alpha)E_{\mathrm{Hxc}}\big[\rho_0^{(\alpha)}\big] + \alpha E_{\mathrm{Hxc}}\big[\rho_1^{(\alpha)}\big]. \quad (3)$$

Here, the index $e-$ signifies that the functional is ensemble generalized; E_{Hxc} is the pure-state Hxc functional mentioned above. The essential difference between the ensemble-generalized functional $E_{e-\mathrm{Hxc}}[n^{(\alpha)}]$ and the usual pure-state $E_{\mathrm{Hxc}}[n^{(\alpha)}]$ is that we do not linearly combine the pure state densities $\rho_p^{(\alpha)}(\mathbf{r})$ first, and then insert the result in the Hxc functional. Instead, following the ensemble approach, we first evaluate the Hxc for the pure-state densities separately, then linearly combine the two ensuing $E_{\mathrm{Hxc}}[\rho_p^{(\alpha)}(\mathbf{r})]$ energies. These two procedures are *not* the same mathematically, because the Hxc functional is not linear with respect to the density. Only at integer N does the Hxc energy reduce to the same form, namely that of the underlying pure-state Hxc functional. Because at fractional N the Hxc functional is explicitly dependent on $\rho_p^{(\alpha)}(\mathbf{r})$, i.e., it is explicitly orbital dependent; treatment within the optimized effective potential (OEP) formalism [7,63,64] is required. This is true even if the underlying xc functional is explicitly density dependent, as is the case with the LSDA.

The generalization in Eq. (3) is applicable to *any* functional and makes the total energy *explicitly* linear in α. However, there may still remain an *implicit* nonlinear dependence of the energy on α because of the α-dependent KS orbitals. In practice, the ensemble generalization of Eq. (3) has already been shown to significantly improve, but not completely eliminate, deviations from piecewise linearity in the energy of simple atoms and molecules [54].

Here we focus on infinitely separated diatomic molecules, which can be constructed from the atoms H, Li, C, and F, namely H $\cdots$ H, Li $\cdots$ H, C $\cdots$ H, F $\cdots$ H, Li $\cdots$ Li, Li $\cdots$ F, C $\cdots$ C, C $\cdots$ F, and F $\cdots$ F, as well as their ions. All calculations are performed within the LSDA and eLSDA, while varying the number of electrons on each of the constituent atoms, using the DARSEC code [65]. This code allows for spin-polarized all-electron DFT calculations for single atoms and diatomic molecules, using a real-space prolate-spheroidal grid. In all calculations the total energy and the highest occupied (ho) eigenvalue have been obtained with an accuracy of 0.001 Ry. For all fractional densities, eLSDA calculations were performed within the optimized effective potential (OEP) formalism [7,63,64], usually in the Krieger-Li-Iafrate (KLI)

approximation [66]. A special case that required employment of the S-iteration method [67,68] for solving the full OEP equation is discussed in the Supplemental Material [69]. LSDA results are presented only if the obtained system is bound, which is not always the case for (fractionally) negatively charged ions. For eLSDA, where negative ions were never found to be bound, their energy is taken to be equal to that of a neutral system (plus a fraction of an electron at infinity, whose contribution is zero), [42,70]—as elaborated in the Supplemental Material [69].

III. RESULTS AND DISCUSSION

We first consider the total energy of neutral molecules, $E_{A\cdots B}(q)$, as a function of q—the amount of negative charge transferred from B to A. Figure 1 presents the total energy of the Li and F atoms as a function of N and the total energy curve of the dissociated molecule Li $\cdots$ F as a function of q. The latter curve is obtained from the combination of the atomic curves, according to Eq. (1). For the atoms, a clear improvement in restoring piecewise linearity with eLSDA is observed, comparing to LSDA. For the dissociated molecule Li $\cdots$ F, the LSDA produces a convex energy curve, which is far from the expected piecewise-linear behavior, and with a spurious minimum at $q_0 = -0.4$, in agreement with Ref. [19]. In contrast, the eLSDA yields a result that is much closer to the piecewise-linear one, being a combination of two slightly concave curves. It possesses no spurious minimum, but rather a nonanalytical minimum at 0, as required. Similar spurious minima are obtained with LSDA for the neutral Li $\cdots$ H, F $\cdots$ H, and C $\cdots$ F molecules, with $q_0 = -0.05$, 0.12, and -0.20, respectively, all removed by using eLSDA. These additional cases are shown in the Supplemental Material [69]. Importantly, close inspection of Fig. 1 (and its analogs in the Supplemental Material) reveals that the energy curves obtained with eLSDA are not perfectly linear but rather are slightly convex. This is a consequence of the remaining implicit α dependence of the e-Hxc functional, owing to the above-discussed α dependence of the KS orbitals, $\varphi_i^{(\alpha)}(\mathbf{r})$. Also for ionized molecules of the type $(A \cdots B)^+$, where $q = 0$ corresponds to the state $A^+ \cdots B$ and $q = 1$ to $A \cdots B^+$, with LSDA we find $(C \cdots H)^+$, $(F \cdots H)^+$, and $(C \cdots F)^+$ to possess spurious minima at $q_0 = 0.43$, 0.67, and 0.27, respectively. With eLSDA all these minima are eliminated. For the homoatomic molecules H $\cdots$ H, Li $\cdots$ Li, C $\cdots$ C, and F $\cdots$ F, as well as for C $\cdots$ H, $(Li \cdots H)^+$, $(Li \cdots F)^+$, no spurious minima occur even with the LSDA, but again the eLSDA energy curve is much closer to piecewise linearity.

Of particular interest are the $E(q)$ curves for homoatomic ionized molecules $(A \cdots A)^+$ [46,71–73]. For these systems we expect the energy to be the sum of the energies of the atom A and the ion A^+, independently of q. However, here the LSDA incorrectly prefers the state with $q = 0.5$, where the electron density is strongly delocalized, i.e., it is present on both nuclei. This is demonstrated, using $(H \cdots H)^+$ and $(F \cdots F)^+$ as examples, in Fig. 2, with more examples given in the Supplemental Material [69]. With LSDA, the energy for the $q = 0.5$ state is too low by 0.20 and 0.29 Ry, respectively. The eLSDA cures this problem completely for $(H \cdots H)^+$, producing a flat energy curve, as required. For $(F \cdots F)^+$, the
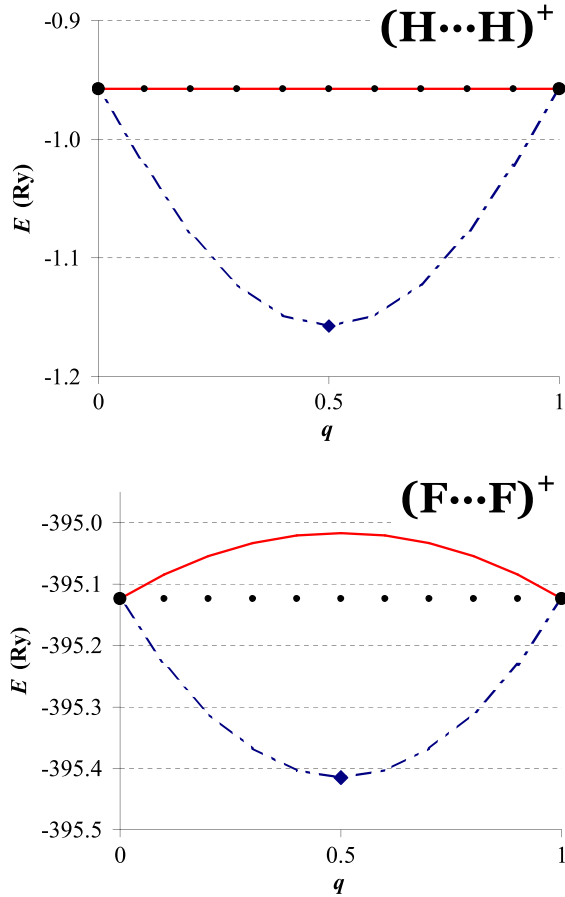
FIG. 2. (Color online) Total energy of the $(H\cdots H)^+$ and $(F\cdots F)^+$ molecules as a function of q computed with the LSDA (dash-dotted line) and eLSDA (solid line) functionals, compared to the expected piecewise-linear (dotted line) behavior.

eLSDA results in a somewhat concave curve, which has its minima at $q = 0$ and 1, being too high by 0.1 Ry at $q = 0.5$. Thus, integer preference is again enforced. In fact it is "over-enforced", in the sense that the integral states at $q = 0$ and 1 are preferred over those with fractional q, instead of being iso-energetic with them. This is a consequence of the remaining deviation of the energy curve from a horizontal line, which is again traced to the implicit α dependence of the e-Hxc functional. Still, spurious delocalization is completely eliminated.

Fractional dissociation and its elimination can be further understood by examining $dE_{A\cdots B}/dq$. From Eq. (1) it follows that $dE_{A\cdots B}/dq = \mu_A(q) - \mu_B(q)$, where $\mu_a := dE_a/dN$ is the chemical potential of the ath atom. From the property of piecewise linearity of the exact $E(N)$ we expect $\mu_A - \mu_B$ to be a stair-step function of q. The dependence of $\mu_A - \mu_B$ on q for $Li\cdots F$ is shown in Fig. 3. With LSDA we find that for low enough values of q, $\mu_A < \mu_B$. This suggests that charge has to be moved from B to A, thereby increasing q. By doing so, we reach a chemical equilibrium for $q_0 = -0.4$, with $\mu_A = \mu_B$ [18]. For higher values of q, $\mu_A > \mu_B$, which suggests moving charge back from A to B, returning to the equilibrium at q_0. For eLSDA we find a completely different behavior: $\mu_A(q) - \mu_B(q)$ is negative for negative q's,
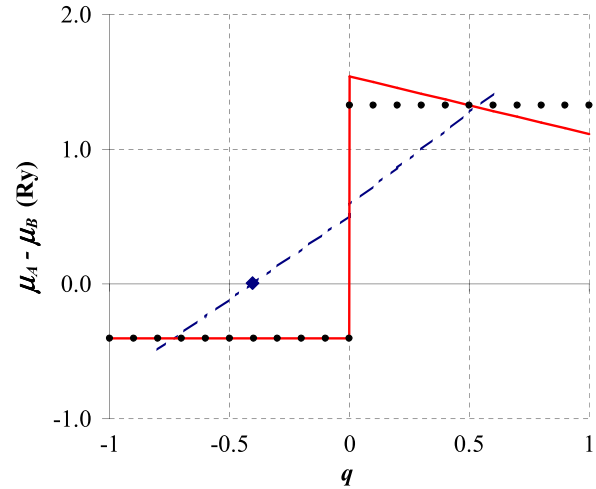

FIG. 3. (Color online) Dependence of $\mu_A(q) - \mu_B(q)$ on q for the $Li\cdots F$ molecule, computed with LSDA (dash-dotted line) and eLSDA (solid line), compared to the expected discontinuous stair-step (dotted line) behavior.

suggesting a transfer of charge from B to A, i.e., increasing q, until reaching 0, where a discontinuous change is observed and $\mu_A(q) - \mu_B(q)$ becomes positive, suggesting decreasing q back. This illustrates the fact that $E(q)$ exhibits a nonanalytic minimum: While the system reaches its energy minimum at $q = 0$, the two atoms are, strictly speaking, never in chemical equilibrium, because $\mu_A \neq \mu_B$. An infinitesimal increase of q above $q = 0$ results in an abrupt jump, which indicates that q has to be decreased, and vice versa. Note that the deviation of the eLSDA from the expected stepwise form in Fig. 3 originates from the residual convexity of the $E(q)$ in Fig. 1.

The energy considerations presented above are also reflected in the KS potential. For an infinitely separated diatomic molecule, the molecular potential coincides with the atomic potential in the vicinity of each of the nuclei. Therefore, here it is obtained by combination of the two KS atomic potentials obtained from two separate atomic calculations.

As a result of the ensemble generalization to the energy [Eq. (3)], the KS potential is generalized as well. Taking the functional derivative of $E_{e-Hxc}[n]$ with respect to n, while recalling that the ensemble-generalized functional is both α and orbital dependent [64], one reveals a peculiar property of the KS potential [54]: It does not necessarily tend asymptotically to 0, but rather to a finite spatial constant v_∞. We stress that this constant is well defined and can be analytically expressed in terms of the KS orbitals and Hxc potential [54,55]. It must be taken into account in order for the ho KS eigenvalue to equal $\partial E/\partial N$, i.e., to obey Janak's theorem [74]. Indeed, including this constant significantly improves [54,56] the prediction of the ionization potential (IP) from the ho KS eigenvalue via the IP theorem [18,75–79]. In the current context, we emphasize that v_∞ is system dependent and may change discontinuously with N across an integer point.

To illustrate how the ensemble generalization prevents spurious charge transfer from the potential perspective, we use the $(C\cdots F)^{++}$ molecule. We prefer it to the $Li\cdots F$ used above
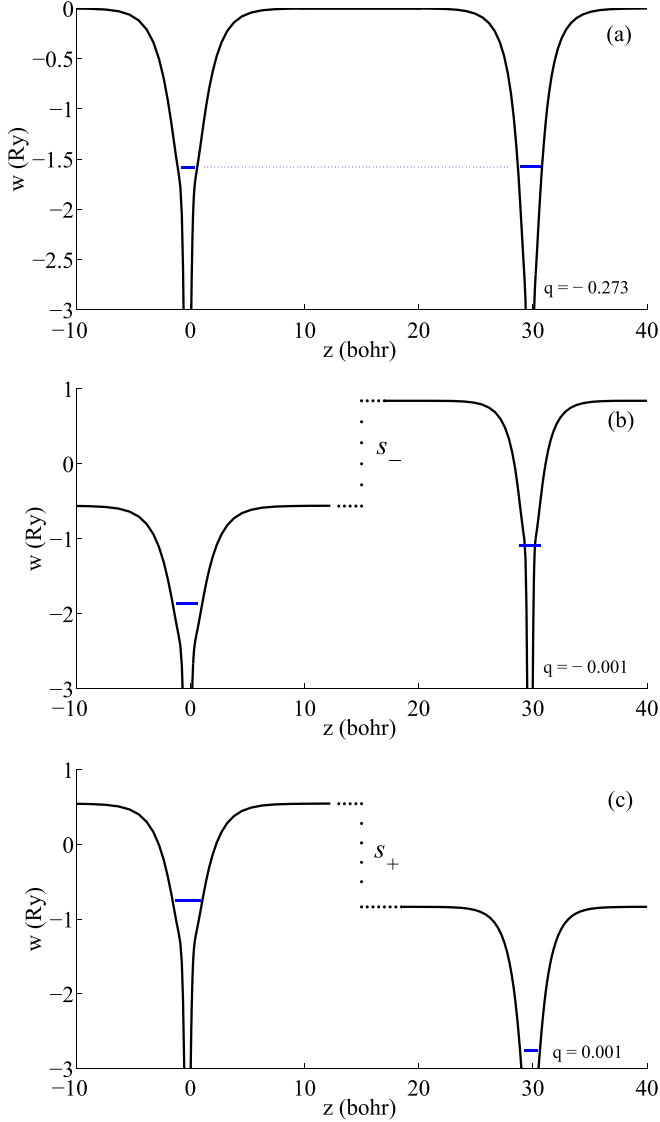
FIG. 4. (Color online) The potential $w(\mathbf{r})$ for the system $C^{1-q} \cdots F^{1+q}$ plotted against the interatomic axis z: (a) with LSDA, at $q = q_0 = -0.273$; (b) with eLSDA, at $q = -0.001$; (c) with eLSDA, at $q = +0.001$. The ho levels of both ions are marked with horizontal lines.

to confine ourselves to a system with strictly bound states (see the Supplemental Material [69] for a complete discussion).

The energy curve of the system $C^{1-q} \cdots F^{1+q}$ is qualitatively similar to the one shown in Fig. 1, with a spurious minimum at $q_0 = -0.273$ for LSDA and a nonanalytic minimum at 0 for eLSDA. In the following, we discuss the quantity $w(\mathbf{r})$, which equals the ↓-KS potential, minus the external and the Hartree potentials. The latter do not possess any discontinuity and therefore are subtracted for clarity. We stress that Fig. 4 that depicts $w(\mathbf{r})$ is not at all a schematic drawing. It is obtained by combining two KS potentials obtained from two separate atomic calculations, for C^{1-q} and F^{1+q}, while preserving their asymptotic values [80].

For LSDA [Fig. 4(a)], $w(\mathbf{r})$ essentially differs from 0 only near the two nuclei and decays to 0 elsewhere. For $q < q_0$, the ho level of the C ion is lower than the ho level of the F ion.

The levels approach each other gradually as q approaches q_0, indicating chemical equilibrium. Further increase of q makes the levels gradually separate. Therefore, chemical equilibrium is achieved by a spurious transfer of a fraction of an electron from the C ion to the F ion, contrary to the principle of integer preference. For eLSDA [Figs. 4(b) and 4(c)], the situation is radically different. Since the ensemble-generalized KS potential tends asymptotically to a nonzero system-dependent constant v_∞, the potential experiences a step between the two well-separated ions. Moreover, since v_∞ is discontinuous when N passes through an integer, the value of the step will abruptly change around an integer q. For $q < 0$, we observe a positive step, s_-, so the ho of the C ion is always lower than that of the F ion, suggesting that q should be increased. However, for $q > 0$, the step s_+ is negative and the ho of the C ion is higher than that of the F ion, suggesting that q should be decreased. This *mechanism of negative reaction* to charge transfer assures that the well-separated subsystems will always be occupied by an integer number of electrons, as expected. The height of the steps can be expressed analytically in KS quantities of the subsystems A and B with integral N: $s_- = v_B^0 - v_A^0 + \Delta_B$; $s_+ = v_B^0 - v_A^0 - \Delta_A$, where [55]

$$v_a^0 = E_{\text{Hxc}}[n_a] - E_{\text{Hxc}}\big[n_a - \big|\varphi_{\text{ho},a}^{(1)}\big|^2\big]$$
$$- \int d^3r \big|\varphi_{\text{ho},a}^{(1)}(\mathbf{r})\big|^2 v_{\text{Hxc}}[n_a](\mathbf{r}) \tag{4}$$

is the ensemble-KS-potential asymptote for $N_a \to (N_a^0)^-$ (i.e., $\alpha \to 1^-$) [81], and

$$\Delta_a = E_{\text{Hxc}}\big[n_a + \big|\varphi_{lu,a}^{(1)}\big|^2\big] - 2E_{\text{Hxc}}[n_a] + E_{\text{Hxc}}\big[n_a - \big|\varphi_{\text{ho},a}^{(1)}\big|^2\big]$$
$$+ \int d^3r \big(\big|\varphi_{\text{ho},a}^{(1)}(\mathbf{r})\big|^2 - \big|\varphi_{lu,a}^{(1)}(\mathbf{r})\big|^2\big) v_{\text{Hxc}}[n_a](\mathbf{r}) \tag{5}$$

is the ensemble derivative discontinuity of the ath system ($a \in \{A,B\}$) that occurs as N crosses the integer value N_a^0. Note that for the exact functional $v_a^0 = 0$, i.e., the asymptotic potential tends to zero, and therefore $s_- = \Delta_B$ and $s_+ = -\Delta_A$.

Importantly, we note that here we only addressed infinitely separated molecules, by treating their constituent atoms independently. Naive application of the above-formulated ensemble generalization to finite bond-length molecules is not useful as the overall number of electrons in the system is still integer, instigating no ensemble correction. Further generalization of the approach, possibly by employing partition DFT to address subsystems (see, e.g., [82] and references therein), so as to overcome this difficulty will be discussed elsewhere.

IV. CONCLUSIONS

In conclusion, from an energy perspective the problem of asymptotic fractional dissociation in DFT emerges owing to significant convexity in the energy versus fractional electron number curves. Here, we have shown that this convexity is replaced by much smaller concavity by employing the ensemble generalization [54], thereby restoring integer dissociation, even when the underlying xc functional is the simple LSDA.

From a potential perspective, spurious fractional charge transfer between well-separated molecular fragments occurs

in standard approximations because they lack a "plateau" in the KS potential. This "plateau" is naturally introduced by the ensemble generalization. Therefore, the ensemble generalization enforces the physical integer dissociation limit in both the energy and the potential pictures, without introducing empiricism or altering the underlying functional form. Finally, we note that integer dissociation is recovered by this procedure despite the fact that both LSDA and eLSDA suffer from one-electron self-interaction. We therefore conclude that the connection between fractional dissociation and one-electron self-interaction [17,83,84] is not a straightforward one. In our opinion, self-interaction correction [85] schemes can indeed remedy fractional dissociation, but this is because they produce a concave energy curve. We expect that the ensemble-generalization perspective can bring significant improvement in the description of charge transfer processes, even with currently existing xc functionals.

ACKNOWLEDGMENTS

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