The derivative discontinuity in the strong-interaction limit of density functional theory

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We generalize the exact strong-interaction limit of the exchange-correlation energy of Kohn-Sham density functional theory to open systems with fluctuating particle numbers. When used in the self-consistent Kohn-Sham procedure on strongly-correlated systems, this functional yields exact features crucial for important applications such as electronic transport. In particular, the step-like structure of the highest-occupied Kohn-Sham eigenvalue is very well captured, with accurate quantitative agreement with exact many-body chemical potentials. Whilst it can be shown that a sharp derivative discontinuity is only present in the infinitely strong-correlated limit, at finite correlation regimes we observe a slightly-smoothened discontinuity, with qualitative and quantitative features that improve with increasing correlation. From the fundamental point of view, our results obtain the derivative discontinuity without making the assumptions used in its standard derivation, offering independent support for its existence.

First-principles calculations of many-electron systems such as solids, molecules, and nanostructures are based, to a very large extent, on Kohn-Sham (KS) [1] density functional theory (DFT) [2]. KS DFT is, in principle, an exact theory, in which the ground-state energy and density of an interacting many-electron system are mapped into a problem of non-interacting electrons moving in the effective one-body KS potential. In practice, KS DFT relies on approximations for the exchange-correlation energy that, although successful in very many cases, have still deficiencies that hamper its overall usefulness [3].

Exact KS DFT has many weird and counterintuitive features often missed by the available approximations. One of the weirdest and most elusive of these features is the derivative discontinuity of the exact exchange-correlation energy functional at integer particle numbers $N$ [1], which has been an incredibly long-debated issue [5,12]. This discontinuity makes the exact KS potential “jump” by a constant $\Delta_{xc}$ when we add to an $N$-electron system even a very tiny fraction of an electron, aligning the chemical potential of the non-interacting KS system to the exact, interacting, one, as schematically illustrated in Fig. 1. The derivative discontinuity has crucial physical consequences. For example, it accounts for the difference between the KS and the physical fundamental gaps [13,15], it allows a correct KS DFT description of molecular dissociation [4,16], and it should improve the description of charge-transfer excitations in time-dependent DFT [17,19]. It also plays a fundamental role in nanotransport, especially to capture the physics of the Coulomb blockade [20,23]. Not surprisingly, these are all cases in which the currently available approximations, which miss this discontinuity, work poorly.

Recently, it has been shown [24,25] that the exact strong-interaction limit of DFT provides a non-local density functional, called “strictly-correlated electrons” (SCE) [26,28], which can be used to approximate the exchange-correlation energy of KS DFT, and captures key features of strong correlation such as charge localization in low-density quantum wires without any artificial symmetry breaking [21,25]. This approximation becomes asymptotically exact in the very low-density (or infinitely strong correlation) limit [24,25]. The purpose of this Letter is to generalize the SCE functional to the case of fractional particle numbers, yielding an exchange-correlation functional for open systems that becomes more and more accurate as correlation increases, and that can be already used for calculations on low-density quantum wires and quantum dots. From a fundamental point of view, our formalism supports the assumptions that were made to derive the existence of the derivative discontinuity [4], and provides new insight for the construction of approximate functionals.

The Letter is organized as follows. After briefly reviewing the extension of KS DFT to open systems and the exact strong-interaction limit of DFT, we present the rigorous generalization of the SCE functional to fractional electron numbers. We then perform self-consistent KS calculations with the SCE functional varying the particle number in a continuous way, finding the expected exact features when correlation is very strong. Finally, we draw our conclusions and discuss some perspectives.

Hartree (effective) atomic units are used throughout.

Fractional particle numbers in KS DFT—At zero temperature, open systems with fluctuating particle number have been first analyzed in the KS framework by considering statistical mixtures [4]. When dealing with DFT for quantum mechanical systems, it is also possible to consider pure states in which a degenerate system is composed by well separated fragments, and one focuses on the energy and density of one of the fragments alone [29,30]. A very simple example is a stretched H$_2^+$ molecule, in which on each proton we find, on average, $\frac{1}{2}$ electron [10,14]. A key point to prove the existence
of the derivative discontinuity is the (empirical) observation that, for integer particle numbers \(N\), the energy \(E_N\) of a \(N\)-electron system in a given external potential is a concave-up function, i.e., \(E_N \leq \frac{1}{2}(E_{N+1} + E_{N-1})\). This implies that for fractional electron numbers \(Q = N + \eta\) (with \(0 \leq \eta \leq 1\)) the exact many-electron ground-state energy \(E_Q\) and density \(\rho_Q(r)\) lay on the line connecting the values at the two adjacent integers:

\[
E_{N+\eta} = (1-\eta)E_N + \eta E_{N+1} \\
\rho_{N+\eta}(r) = (1-\eta)\rho_N(r) + \eta \rho_{N+1}(r).
\] (1, 2)

In KS DFT, one usually aims at obtaining the exact quantities of Eqs. (1)-(2) by means of a non-interacting system of \(Q = N + \eta\) electrons in the effective single-particle KS potential \(v_s(r; |\rho_Q|)\), which necessarily changes as we change \(Q\). The energy is then minimized by giving integer occupation to the \(N\) single particle KS spin-orbitals with lowest eigenvalues and fractional occupation \(\eta\) to the frontier orbital(s), often called HOMO (highest occupied molecular orbital) \([31, 32]\).

In the exact KS theory, the HOMO eigenvalue \(\epsilon_{\text{HOMO}}\) is the derivative of the total energy of Eq. (1) with respect to the particle number \(Q\), \(\frac{dE}{dQ} = \epsilon_{\text{HOMO}}\) \([31, 32]\). Thus, the exact \(\epsilon_{\text{HOMO}}\) is constant between any two adjacent integers (say, \(N\) and \(N + 1\)) and equal to the interacting chemical potential \(E_{N+1} - E_N\), jumping to a different value when crossing an integer. This “step-like” behavior of the KS \(\epsilon_{\text{HOMO}}\) is not captured by the available approximate functionals (see, e.g., Refs. \([32-34]\)). The alignment of the KS HOMO eigenvalue with the interacting chemical potential implies that the exact KS one-body potential must jump by a constant \(\Delta_{xc}\) (the derivative discontinuity) when crossing an integer, \(v_s(r; |\rho_{N+1}|) - v_s(r; |\rho_N|) = \Delta_{xc}\) (see Fig. 1).

Strong-interaction limit - The strong-interaction limit of DFT is given by the SCE functional \(V_{\text{SCE}}[\rho]\), defined as \(26, 28, 33, 36\):

\[
V_{\text{SCE}}[\rho] = \min_{A} \langle \Psi | V_{\text{ee}} | \Psi \rangle,
\] (3)

where, the minimum of the electronic interaction alone over all the wave functions yielding the density \(\rho\). It can be shown \(24, 37, 38\) that in the low-density (or strong-interaction) limit the exact Hartree and exchange-correlation functional \(E_{\text{Hxc}}[\rho]\) of KS theory approaches asymptotically \(V_{\text{SCE}}[\rho]\).

Physically, the functional \(V_{\text{SCE}}[\rho]\) portrays the strict correlation regime, where the position \(r\) of one electron determines all the other \(N-1\) electronic positions \(r_i\) through the so-called co-motion functions, \(r_i = f_i[\rho](r)\), some non-local functionals of the density \(26, 27, 30, 40\). Therefore, the net repulsion on an electron at position \(r\) due to the other \(N-1\) electrons depends on \(r\) alone. Its effect can then be exactly represented \(25, 26, 30, 40\) by a local one-body potential with a transparent physical meaning,

\[
\nabla \tilde{v}_{\text{SCE}}[\rho](r) = -\sum_{i=2}^{N} \frac{r - f_i[\rho](r)}{|r - f_i[\rho](r)|^3},
\] (4)

which is also the functional derivative of \(V_{\text{SCE}}[\rho]\),

\[
\frac{dV_{\text{SCE}}[\rho]}{d\rho(r)} = \tilde{v}_{\text{SCE}}[\rho](r) \quad (24, 25)
\]

In terms of the co-motion functions we have \(26\)

\[
V_{\text{SCE}}[\rho] = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \int dr \rho(r) \frac{1}{N |f_i[\rho](r) - f_j[\rho](r)|}.
\] (5)

SCE for fractional particle numbers - The generalization of the SCE formalism to non-integer particle numbers \(Q\) is not obvious, because in Eqs. (1)-(2) the sum runs over the integer number of electrons \(N\). We can, however, gain insight by thinking in terms of a well separated fragment inside a degenerate system with total integer electron number \(M\) \([3, 10, 16, 29, 30]\). The fragment can then have on average a non-integer number \(Q\) of electrons, as schematically illustrated in Fig. 2.

Actually, from Eq. (5) it is not evident that \(V_{\text{SCE}}[\rho]\) separates into the simple sum of the contributions of the isolated fragments, because the interaction \(|f_i[\rho](r) - f_j[\rho](r)|^{-1}\) between two electrons on a given fragment...
cent strictly-correlated positions $f_i(x)$ of the other 4 electrons as a function of the position $x$ of the first electron. The two black circles represent the "local" SCE solution on each fragment.

We start from (quasi) one-dimensional systems, for which we can deduce the SCE solution for fractional electron numbers: we have solved the SCE problem for $M = 5$ electrons, for which we find only 2 particles (the third electron is in the other fragment). Similarly, we find that the general SCE solution for a density integrating to $Q = N + \eta$ electrons can be easily obtained from Eq. (7). From now on, we consider the fragment alone, and we set the origin of the $x$ axis in the center of the density $\rho_Q(x)$ [which, for simplicity, is assumed to be symmetric, $\rho_Q(-x) = \rho_Q(x)$]. The co-motion functions read

$$f_i(x) = \begin{cases} N^{-1}[(N_\varepsilon(x) + 2i] & x < a_{N-2i+\eta} \\ N^{-1}[(N_\varepsilon(x) - 2(N+1-i)] & x > a_{N+2-2i-\eta} \\ \infty & \text{otherwise}, \end{cases}$$

where the function $N_\varepsilon(x)$ is defined via the density $\rho_Q(x)$,

$$N_\varepsilon(x) = 2 \int_0^x \rho_Q(x')dx',$$

and $a_k = N^{-1}(k)$. Here $x$ and $f_i(x)$ are positive and measure the distance from the center of the density. The minimization of $V_{ee}^{SCE}[\rho_Q]$ determines whether $f_i(x)$ is at the left or at the right of the origin. We then have values of $x$ with $N + 1$ electrons in the density, and values of $x$ for which we find only $N$ strictly-correlated positions (the $N + 1$th electron is at infinity; in the supramolecular system it would be in the other fragment).

**Self-consistent KS SCE for $N + \eta$ electrons** – From Eqs. (7), (6) and (4) we can now construct the SCE functional $V_{ee}^{SCE}[\rho_Q]$ and its functional derivative $\delta_{SCE}[\rho_Q](r)$ for any one-dimensional density integrating to a non-integer particle number $Q$. We then consider $Q$ electrons in the quasi-one-dimensional model quantum wire of Refs. [43] [44], in which the effective electron-electron interaction is obtained by integrating the Coulomb repulsion on the lateral degrees of freedom [45] [46], and is given by $v_{ee}(x) = \frac{\sqrt{2\pi}}{\pi} \exp\left(\frac{x^2}{4\pi}\right) \text{erfc}\left(\frac{x}{\sqrt{2\pi}}\right)$. The parameter $b$ fixes the thickness of the wire, set to $b = 0.1$ throughout this work, and $\text{erfc}(x)$ is the complementary error function. As in Ref. [43], we consider an external harmonic confinement $v_{ext}(x) = \frac{1}{2}\omega^2x^2$ in the direction of motion of the electrons, which for small $\omega$ yields bound states with very low density, where the functional $V_{ee}^{SCE}[\rho]$ becomes closer and closer to the exact $E_{KS}[\rho]$.

We have then performed self-consistent, spin-restricted (each spatial orbital is doubly occupied), KS calculations with the SCE potential, as in Refs. [24] [25], this time

$$\int_{f_i(x)}^{f_{i+1}(x)} \rho(x')dx' = 1,$$
by giving fractional occupation to the KS HOMO orbital \[^{31, 32}\]. The SCE potential \(\hat{v}_{\text{SCE}}[\rho Q](x)\), representing the approximate Hartree plus exchange-correlation potentials in our KS SCE calculations, is obtained by integrating the 1D analogue of Eq. (4), with boundary condition \(\hat{v}_{\text{SCE}}[\rho Q](|x| \to \infty) = 0\), using the co-motion functions of Eq. (8).

In Fig. 3 we show our self-consistent KS SCE results for the HOMO eigenvalue as a function of the particle number \(Q\) for a quasi-1D quantum wire with harmonic confinement along the direction of motion of the electrons, \(v_{\text{ext}}(x) = \frac{1}{2} \omega^2 x^2\), and \(\omega = \frac{1}{L^{\frac{1}{2}}}\). The KS SCE results are compared with the standard KS LDA and with the exact chemical potential \(E_{N+1} - E_N\) from full CI calculations \[^{25}\].

In Fig. 4, we also show the result for a three-dimensional electronic system in the external harmonic potential, \(v_{\text{ext}}(r) = \frac{1}{2} \omega^2 r^2\), with \(\omega = 10^{-5}\). The KS SCE results are compared with the exact chemical potential \(E_{N+1} - E_N\) \[^{17, 48}\].

Concluding remarks and perspectives—The ability of the self-consistent KS SCE, in a spin-restricted formalism, to yield the right discontinuity in the HOMO for open shell systems (case in the upper panel of Fig. 1), is not just a unique result, but also an independent proof that the exact KS formalism should have this feature. In fact, in our construction we have computed the exact \(V_{\text{SCE}}[\rho Q]\) and used it in the KS self-consistent procedure, without imposing any other condition on our functional. Until now, this feature had only been captured by approximations in the context of lattice hamiltonians \[^{49}\], or by imposing it \textit{a priori} (as, e.g., in Refs. \[^{33, 50}\]).

From a practical point of view, our results could already be used to model transport through a correlated quantum wire or quantum dot, going beyond the lattice calculations of Refs. \[^{22, 23}\]. From a fundamental point of view, our findings provide novel insight and guidance...
for the construction of approximate exchange-correlation functionals: the challenge is now to transfer this exact behavior into approximations for the intermediate correlation regimes (similar to the case $L = 1$ of Fig. 3) relevant for solid-state physics and chemistry.

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