Kohn-Sham potentials in exact density-functional theory at noninteger electron numbers

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Within exact electron density-functional theory, we investigate Kohn-Sham (KS) potentials, orbital energies, and noninteracting kinetic energies of the fractional ions of Li, C, and F. We use quantum Monte Carlo densities as input, which are then fitted, interpolated at noninteger electron numbers N, and inverted to produce accurate KS potentials $v_s^N(\mathbf{r})$. We study the dependence of the KS potential on N, and in particular we numerically reproduce the theoretically predicted spatially constant discontinuity of $v_s^N(\mathbf{r})$ as N passes through an integer. We further show that, for all the cases considered, the inner orbital energies and the noninteracting kinetic energy are nearly piecewise linear functions of N. This leads us to propose a simple approximation of the KS potential $v_s^N(\mathbf{r})$ at any fractional electron number N which uses only quantities of the systems with the adjacent integer electron numbers.

Over the past few decades, Kohn-Sham (KS) [1] density-functional theory (DFT) [2] has become one of the most important tools in electronic-structure theory. Given the overwhelming popularity of density-functional approximations (DFAs) (e.g., Perdew-Burke-Ernzerhof [3], hybrids [4]), surprisingly few studies have been dedicated to the detailed properties of the *exact* KS system. This is despite the fact that unusual properties [5] of the fictitious noninteracting KS system serve a vitally important role in reproducing the quantum mechanical properties of the interacting system in cases where degeneracies are present in the ground state, or where electrons are added and removed. In this paper we study exact KS DFT properties of difficult, open quantum systems with degenerate ground states—specifically open-shell atoms with noninteger electron numbers. A primary aim is to provide guidance for the construction of new DFAs.

In quantum mechanics, open electronic systems with a noninteger average number of electrons naturally arise, for example, as fragments from a molecular dissociation in entangled quantum states. In particular, in DFT the study of systems with fractional electron numbers is of great importance for a better understanding of the theory (for a recent review, see Ref. [6]). For such fractional systems, Perdew *et al.* [7] proved [8] that the energy is a piecewise linear function of the electron number between the adjacent integers. This led to the theoretical prediction of the discontinuity of the KS potential as the electron number passes through an integer, with many important physical consequences concerning the description of the fundamental gap [9,10], molecular dissociation [7], or charge-transfer excitations [11]. This also led to the explanation that the underestimation of energies obtained with the usual semilocal DFAs for delocalized densities is a consequence of their deviations from the exact piecewise linear behavior of the energy [12–16]. These understandings have guided the design of improved DFT approximations [17–22].

Although the piecewise linear energy curve and the discontinuity of the KS potential have been widely discussed in the literature, little else is known about the form of the exact KS potential as a function of the fractional electron number. In this Rapid Communication, we fill this gap by providing and analyzing accurate KS potentials as a function of the electron number for the fractional ions of Li, C, and F, exploring a range from 2 to 10 electrons. For all these systems, we numerically reproduce the discontinuity of the KS potential. We then propose a simple approximation of the KS potential at any fractional electron number which uses only quantities of the systems with the adjacent integer electron numbers.

KS DFT for fractional electron numbers. The ground-state energy of a system with a fractional number of electrons $N = M + f$ (where M is an integer and $0 \leqslant f \leqslant 1$) can be defined in the zero-temperature grand-canonical ensemble formalism as [7,22,23] (see also Refs. [24,25] for an alternative view)

$$E^N = \min_{\hat{\Gamma} \to N} \mathrm{Tr}[\hat{\Gamma}(\hat{T} + \hat{V}_{\mathrm{ext}} + \hat{W}_{\mathrm{ee}})], \qquad (1)$$

where Tr denotes the trace and the search is over all normalized ensemble fermionic density matrices $\hat{\Gamma}$ yielding N electrons, i.e., $\mathrm{Tr}[\hat{\Gamma}\hat{N}] = N$ where $\hat{N}$ is the number operator. In Eq. (1), $\hat{T}$ is the kinetic energy operator, $\hat{V}_{\mathrm{ext}}$ is the external potential operator, and $\hat{W}_{\mathrm{ee}}$ is the electron-electron interaction operator. With the usual assumption that the ground-state energy for integer electron numbers in a fixed external potential is a convex function, $E^M \leqslant (E^{M+1} + E^{M-1})/2$, the minimizing density matrix is obtained as a linear interpolation between ground-state density matrices of the M and $(M + 1)$-electron systems

$$\hat{\Gamma}^N = (1 - f)\hat{\Gamma}^M + f\hat{\Gamma}^{M+1}, \qquad (2)$$

where $\hat{\Gamma}^M = \sum_e w_e |\Psi_e^M\rangle\langle\Psi_e^M|$ (with $\sum_e w_e = 1$) is made of the possibly degenerate M-electron ground states, and similarly for $\hat{\Gamma}^{M+1}$. Equation (2) immediately implies that

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the ground-state energy and the one-electron density are also piecewise linear in f:

$$E^N = (1 - f)E^M + fE^{M+1}, \qquad (3)$$

$$n^N(\mathbf{r}) = (1 - f)n^M(\mathbf{r}) + fn^{M+1}(\mathbf{r}), \qquad (4)$$

where $n^M(\mathbf{r})$ is the density corresponding to the density matrix $\hat{\Gamma}^M$, and similarly for $n^{M+1}(\mathbf{r})$. The freedom in the choice of the ensemble weights w_e can be used to impose symmetries. For example, for atoms with an incomplete p shell, one can choose w_e so as to obtain a spherically symmetric density $n^M(r)$.

In KS DFT, a universal functional can be defined for any fractional electron density $n(\mathbf{r})$ with the constrained-search formalism [7]

$$F[n] = \min_{\hat{\Gamma} \to n} \mathrm{Tr}[\hat{\Gamma}(\hat{T} + \hat{W}_{\mathrm{ee}})], \qquad (5)$$

where $\hat{\Gamma} \to n$ refers to all normalized ensemble fermionic density matrices $\hat{\Gamma}$ yielding the density $n(\mathbf{r})$, i.e., $\mathrm{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r})$ where $\hat{n}(\mathbf{r})$ is the density operator. Decomposing this functional as

$$F[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Hxc}}[n], \qquad (6)$$

where $T_{\mathrm{s}}[n] = \min_{\hat{\Gamma} \to n} \mathrm{Tr}[\hat{\Gamma}\hat{T}]$ is the KS noninteracting kinetic-energy functional and $E_{\mathrm{Hxc}}[n]$ is the remaining Hartree-exchange-correlation functional, leads to the KS expression for the exact ground-state energy

$$E^N = \min_{\hat{\Gamma}}\{\mathrm{Tr}[\hat{\Gamma}(\hat{T} + \hat{V}_{\mathrm{ext}})] + E_{\mathrm{Hxc}}[n_{\hat{\Gamma}}]\}, \qquad (7)$$

where the functional E_{Hxc} is evaluated at the density coming from $\hat{\Gamma}$. The minimizing density matrix is assumed to have the form

$$\hat{\Gamma}_{\mathrm{s}}^N = (1 - f)\hat{\Gamma}_{\mathrm{s}}^{M,f} + f\hat{\Gamma}_{\mathrm{s}}^{M+1,f}, \qquad (8)$$

where $\hat{\Gamma}_{\mathrm{s}}^{M,f} = \sum_e w_e|\Phi_e^{M,f}\rangle\langle\Phi_e^{M,f}|$ is a density matrix made of M-electron single-determinant wave functions (which depend on f), and similarly for $\hat{\Gamma}_{\mathrm{s}}^{M+1,f}$, and again the ensemble weights w_e can be used to impose symmetries. All the M- and $(M + 1)$-electron single determinants are constructed from a common set of KS orbitals $\{\phi_i^N(\mathbf{r})\}$ determined by (in atomic units)

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{s}}^N(\mathbf{r})\right]\phi_i^N(\mathbf{r}) = \varepsilon_i^N\phi_i^N(\mathbf{r}), \qquad (9)$$

where $v_{\mathrm{s}}^N(\mathbf{r})$ is the KS potential,

$$v_{\mathrm{s}}^N(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n^N]}{\delta n(\mathbf{r})}, \qquad (10)$$

and ε_i^N are the KS orbital energies ($\varepsilon_i^N \leqslant \varepsilon_j^N$ for $i < j$). In Eq. (10), the KS potential is evaluated at the exact density $n^N(\mathbf{r})$ which is also the density given by the KS density matrix $\hat{\Gamma}_{\mathrm{s}}^N$ and can be written in terms of the KS orbitals and fractional occupation numbers $\{f_i\}$:

$$n^N(\mathbf{r}) = \sum_i f_i|\phi_i^N(\mathbf{r})|^2, \qquad (11)$$

where $f_i = 2$ for the N_{inner} lowest inner doubly occupied orbitals, $\sum_h f_h = N - 2N_{\mathrm{inner}}$ for the fractionally occupied

degenerate highest occupied orbitals (HOMOs), and $f_i = 0$ for the remaining unoccupied orbitals. Unlike other work [26,27], we use a spin-restricted open-shell formalism, and thus avoid dealing with spin dependence.

In principle, if density variations changing the electron number are allowed in the functional derivative of Eq. (10), the KS potential $v_{\mathrm{s}}^N(\mathbf{r})$ including its spatial-constant component is uniquely determined. In practice, for any fixed N, if an accurate electron density $n^N(\mathbf{r})$ is known, one can find the corresponding KS potential $v_{\mathrm{s}}^N(\mathbf{r})$ obeying $v_{\mathrm{s}}^N(|\mathbf{r}| \to \infty) = 0$ by ensuring that the orbitals satisfying Eq. (9) give the density through Eq. (11). In this work, we make use of this mapping to obtain accurate KS potentials $v_{\mathrm{s}}^N(\mathbf{r})$, orbital energies ε_i^N, and KS kinetic energies $T_{\mathrm{s}}^N \equiv T_{\mathrm{s}}[n^N]$ as a function of the fractional electron number N.

Computational method. We consider atoms with external potential $v_{\mathrm{ext}}(r) = -Z/r$. Using Eq. (4), the density for an ion with any fractional electron number between $Z - 1$ and $Z + 1$ can be obtained from the densities for $Z - 1$, Z, and $Z + 1$ electrons. We thus first calculate (spherically averaged) accurate densities $n^M(r)$ for these integer electron numbers using quantum Monte Carlo (QMC). Specifically, the densities are calculated in diffusion Monte Carlo with an improved statistical estimator [28], using Jastrow full-valence complete-active-space wave functions fully optimized at the variational Monte Carlo level [29]. As an accurate inversion requires a density to be free from statistical errors, we fit these QMC densities with a simple, yet asymptotically accurate (as $r \to \infty$) function that ensures that the density corresponds to a HOMO with the eigenenergy ε_h equal to the negative of the ionization energy, and to a KS potential with correct asymptotic behavior $v_{\mathrm{s}}^M(r \to \infty) \sim (-Z + M - 1)/r$. The fitting function and parameters given in the Supplemental Material [30] give densities that are accurate to within the QMC statistical error.

After obtaining the density at fractional electron numbers $n^N(r)$ via Eq. (4), we calculate the KS potential by using a numerically stabilized modification of Wang and Parr's iterative approach [31]. The KS potential at iteration $m + 1$ is found from the quantities at the previous iteration m through $v_{\mathrm{s}}^{N,m+1}(r) = v_{\mathrm{s}}^{N,m}(r) + Q\frac{n^N(r) - n^{N,m}(r)}{G^{N,m}(r)}$, where $G^{N,m}(r) = \sum_i f_i|\phi_m^{N,m}(r)|^2/\varepsilon_i^{N,m} + \max[0,(1/\varepsilon_h - 1/\varepsilon_h^{N,m})\{n^N(r) - n^{N,m}(r)\}]$, and $Q > 0$ is a convergence parameter. By starting from fractional LEXX [21] potentials and orbitals we achieve $\int d\mathbf{r}|n^N(\mathbf{r}) - n^{N,m}(\mathbf{r})| < 10^{-6}$, albeit with increasing errors in v_{s}^N for $N \leqslant Z - 0.8$.

Results and discussion. In Fig. 1 we show the KS potentials $v_{\mathrm{s}}^{Z+c}(r)$ (plots of its components are shown in the Supplemental Material [30]) as a function of the radial distance r and the fractional excess electron number $c = N - Z$ where $-1 \leqslant c \leqslant 1$, i.e., for ions from A^+ through A to A^- for Li, C, and F. Calculations are performed for $c \in \{-1, -0.99, -0.95, -0.8, -0.6, -0.4, -0.2, 0, 0.01, 0.05, 0.2, 0.4, 0.6, 0.8, 1\}$.

The most obvious feature of these plots is the presence of a discontinuity in the potentials as the electron number N crosses an integer. Let us concentrate on the discontinuity at $N = Z$, i.e., $c = 0$. At first sight, in Fig. 1, this discontinuity seems to be dependent on r, decreasing at large distances. To
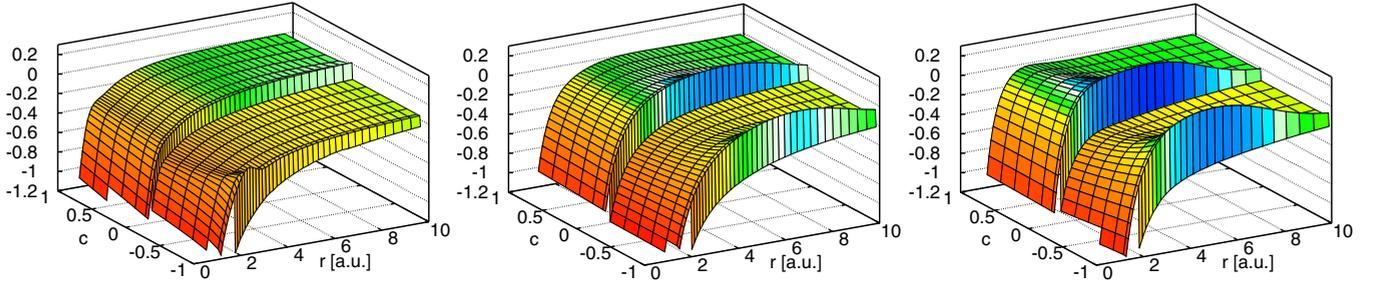
FIG. 1. (Color online) KS potentials $v_s^{Z+c}(r)$ (hartree) as a function of the radial distance r and the fractional excess electron number $c = N - Z$ for Li (left), C (middle), and F (right). Colors indicate height (from red to green for $v_s^{Z+c}(r) < 0$, white for $v_s^{Z+c}(r) \approx 0$, blue for $v_s^{Z+c}(r) > 0$).

analyze the discontinuity more precisely we plot in Fig. 2 the quantity $v_s^{Z+c}(r) - v_s^{Z^-}(r)$ as a function of c (interpolated in $-0.99 \leqslant c \leqslant 0$ and $0.01 \leqslant c \leqslant 1$) for selected values of r. It is now clear that, if we extrapolate the plots from $c > 0$ toward the limit $c \to 0^+$, the results are consistent with the KS potential having a constant discontinuity

$$\Delta^Z = v_s^{Z^+}(r) - v_s^{Z^-}(r) = I - A, \qquad (12)$$

at $N = Z$, independent of r. For the open-shell systems considered here, the discontinuity Δ^Z is equal to the difference between the ionization energy I and the electronic affinity A of the neutral atom. Therefore, the present results numerically reproduce the theoretically predicted [32,33] spatially constant discontinuity of the KS potential when the electron number N crosses an integer $M = 3$, 6, or 9, which had been so far numerically observed only for $M = 1$ [32–34]. The values of Δ^Z are found to be 0.178, 0.368, and 0.519 hartree, for Li, C, and F, respectively, very close to 0.175, 0.366, and 0.516 hartree found using $I - A$.

Besides the discontinuity, it is interesting to note that the potential is sensitive to the order of the limits $c \to 0^+$ and $r \to \infty$ [33]. It is clear from Figs. 1 and 2 that as r increases

the KS potentials go to zero in a larger and larger range of c, except near the limit $c \to 0^+$ where it becomes more and more curved. This is understandable since $v_s^{Z+c}(r) - v_s^{Z^-}(r)$ must go to Δ^Z in the limit $c \to 0^+$, but at the same time, for any finite value of c, the KS potential for $M < N \leqslant M + 1$ must have the same asymptotic behavior as the KS potential for the $(M + 1)$-electron system, $v_s^N(r \to \infty) \sim v_s^{(M+1)^-}(r) \sim (-Z + M)/r$ [35], and therefore must go to zero for large r.

In Fig. 3 we plot as a function of c the difference between the orbital energies at the fractional electron number $Z + c$ and their neutral atomic values: $\varepsilon_i^{Z+c} - \varepsilon_i^{Z^-}$. As expected, all orbital energies have a discontinuity of Δ^Z at $c = 0$. As required by theory the HOMO energy is constant, within numerical noise, between integer electron numbers: $\varepsilon_h^N = \varepsilon_h^{M^-} + \Delta^M = \varepsilon_h^{(M+1)^-}$. Interestingly, we find that the energies of the inner orbitals follow an almost piecewise linear behavior

$$\varepsilon_i^N \approx (1 - f)\big[\varepsilon_i^{M^-} + \Delta^M\big] + f\varepsilon_i^{(M+1)^-}, \qquad (13)$$

where $i \leqslant N_{\text{inner}}$. We also plot in Fig. 4 the KS kinetic energy T_s^{Z+c} and the exact kinetic energy $T^{Z+c} = -E^{Z+c}$ (by the virial theorem) as a function of c, adjusted by their neutral
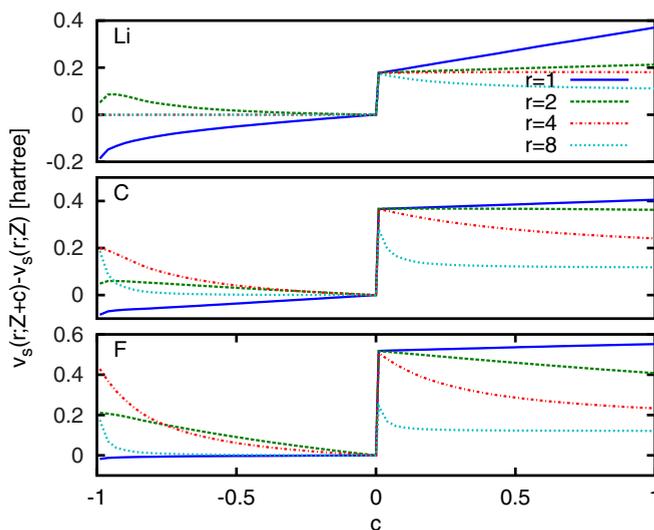

FIG. 2. (Color online) Change in Kohn-Sham potentials $v_s^{Z+c}(r) - v_s^{Z^-}(r)$ as a function of $c > -1$ for Li (top), C (middle), and F (bottom), for selected values of r.
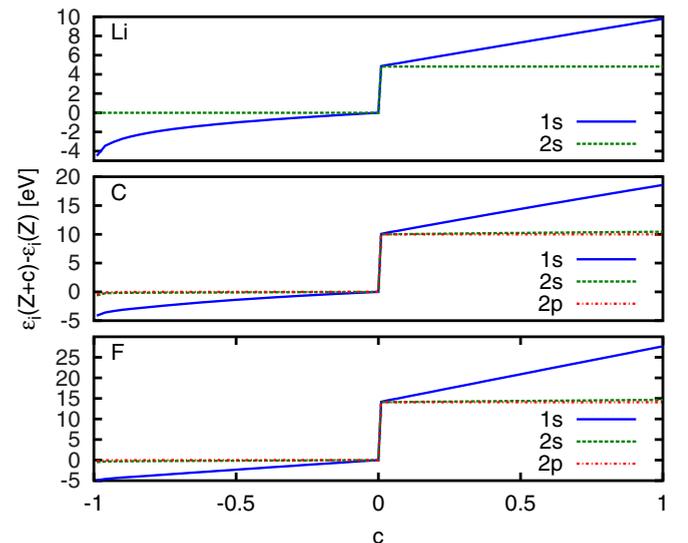

FIG. 3. (Color online) Change in Kohn-Sham orbital energies for all orbitals $\varepsilon_i^{Z+c} - \varepsilon_i^{Z^-}$ as a function of $c > -1$ for Li (top), C (middle), and F (bottom).
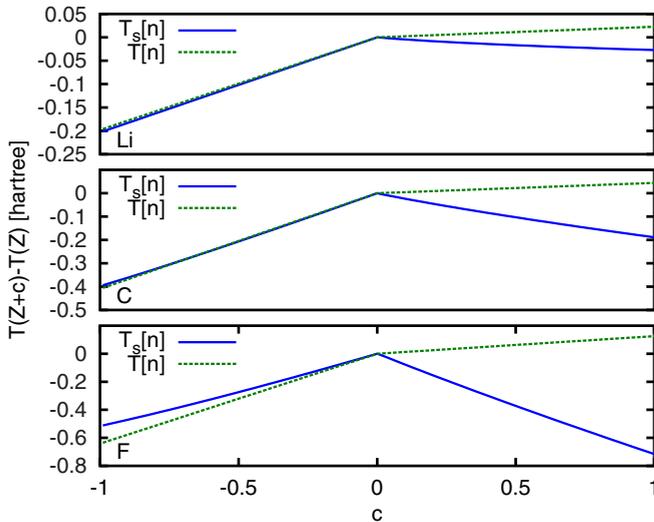
FIG. 4. (Color online) Change in Kohn-Sham kinetic energy $T_s^{Z+c} - T_s^Z$ and kinetic energy $T^{Z+c} - T^Z$ as a function of c.

atomic $c = 0$ values. Unlike T, T_s is not piecewise linear but was theoretically shown to be a convex function of f [36]. Our numerical results confirm this convex behavior. However, for all the systems studied here, T_s turns out to be remarkably close to linearity

$$T_s^N \approx (1 - f)T_s^M + f T_s^{M+1}, \qquad (14)$$

with the maximum deviation from linearity being -3.3 mhartree for $Li^{-0.4}$, -8.9 mhartree for $C^{-0.4}$, and -15.3 mhartree for $F^{+0.6}$. This near linearity was previously observed only for weakly interacting two-electron systems [37].

The near linearity of T_s^N and ε_i^N suggest that the KS orbitals change in a predictable fashion as partial electrons are added to the atoms, even in the difficult, degenerate systems considered here. If Eqs. (13) and (14) apply more generally they could provide desirable local and global constraints on new DFAs. Furthermore, since the KS kinetic energy T_s^N, the

KS potential $v_s^N(\mathbf{r})$, and the orbital energies ε_i^N are linked by the KS energy expression $T_s^N + \int n^N(\mathbf{r})v_s^N(\mathbf{r})d\mathbf{r} = \sum_i f_i \varepsilon_i^N$ at fractional electron number N, the linear approximations of Eqs. (13) and (14) suggest a linear approximation for $n^N(\mathbf{r})v_s^N(\mathbf{r})$,

$$n^N(\mathbf{r})v_s^N(\mathbf{r}) \approx (1 - f)n^M(\mathbf{r})\big[v_s^{M^-}(\mathbf{r}) + \Delta^M\big]$$
$$+ f n^{M+1}(\mathbf{r})v_s^{(M+1)^-}(\mathbf{r}). \qquad (15)$$

Indeed, we found that Eq. (15) is an excellent approximation to $v_s^N(\mathbf{r})$ for all cases studied here, especially when considered against the electronic density. Details are provided in the Supplemental Material [30]. We note that this approximation becomes exact in two limits: close to a nucleus where the KS potentials are dominated by the diverging electron-nucleus potential $v_{\text{ext}}(\mathbf{r})$, and in the asymptotic region $|\mathbf{r}| \to \infty$ where the density $n^{M+1}(\mathbf{r})$ dominates over $n^M(\mathbf{r})$ and the KS potential $v_s^N(\mathbf{r})$ reduces to $v_s^{(M+1)^-}(\mathbf{r})$. It can also be shown that this approximation is exact in the trivial case $0 \leqslant N \leqslant 1$ and in the case $1 \leqslant N \leqslant 2$ if $n^2(\mathbf{r}) = 2n^1(\mathbf{r})$. Preliminary work suggests that this approximation may be valid in a wider range of systems than those explored here.

Conclusions. We have shown that accurate KS potentials $v_s^N(\mathbf{r})$ at noninteger electron numbers N can be obtained by inversion of accurate *ab initio* electron densities. This has allowed us to numerically reproduce on systems with more than two electrons the theoretically predicted spatially constant discontinuity of the KS potential when the electron number crosses an integer. We have also found that, for all the atomic systems studied here, both the energies ε_i^N of the inner orbitals (below the HOMO) and the KS kinetic energy T_s^N are nearly piecewise linear functions of N. This has led us to propose the simple approximation of Eq. (15) for the KS potential $v_s^N(\mathbf{r})$ at any fractional electron number N which uses only quantities of the systems with adjacent integer electron numbers. This approximation appears to work very well for all the cases considered and its generality and potential application to fragment and partition DFT [38–40] will be explored in future work.

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