Asymptotic behavior of the Hartree-exchange and correlation potentials in ensemble density functional theory

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We report on previously unnoticed features of the exact Hartree-exchange and correlation potentials for atoms and ions treated via ensemble density functional theory, demonstrated on fractional ions of Li, C, and F. We show that these potentials, when treated separately, can reach non-vanishing asymptotic constant values in the outer region of spherical, spin unpolarized atoms. In the next leading order, the potentials resemble Coulomb potentials created by effective charges which have the peculiarity of not behaving as piecewise constants as a function of the electron number. We provide analytical derivations and complement them with numerical results using the inversion of the Kohn–Sham equations for interacting densities obtained by accurate quantum Monte Carlo calculations. The present results expand on the knowledge of crucial exact properties of Kohn–Sham systems, which can guide development of advanced exchange–correlation approximations.

1 Introduction

Density-functional theory (DFT)\(^1\) is an exact reformulation of the many-body problem, which accesses the total ground-state energy of an electronic system through a variational principle based on the electron density rather than the many-body wave function. DFT is often applied within the popular Kohn–Sham (KS) approach,\(^2\) which transforms it into a problem of finding orbital solutions for non-interacting electrons in an effective potential, which is itself a functional of the density. This transforms the difficult many-electron problem into a series of simpler one-electron problems.

Both quantum mechanics and DFT can be generalised to ensembles of states with different electron numbers, thus achieving a fractional number of electrons. This can be thought of in terms of open systems weakly coupled to the environment,\(^3\) or as an asymptotic limit of a dissociation process.\(^4,5\) Such a generalisation offers insights into subtle quantum mechanical effects that are unavailable from integer systems, including into how well-separated systems behave.

Perdew, Parr, Levy and Balduz\(^3\) (PPLB) showed that the total energy, \(E\), is a piecewise linear function of the number of electrons, \(N\), and that as one crosses an integer, the slope of the \(E(N)\) curve may change. The density, and thus electron–ion energy also has this property. It is also reflected in DFT, where the sum of the non-interacting kinetic energy functional and the exact Hartree-exchange–correlation energy functional must also be a piecewise linear function of \(N\). As a consequence of the piecewise linearity of the energy, the energy of a “fractional ion” experiences derivative discontinuities as it passes through an integer.\(^1\) These derivative discontinuities give rise to surprising yet important phenomena (\(e.g., \) ref. 3–17 and references therein). They help to formalise calculations of the ionization potential, the electron affinity, and the fundamental gap.

In applications one must use various density-functional approximations (DFAs), due to the fact that the required exchange–correlation functional is, although well-defined, unknown in general. Therefore there is a strong motivation to determine properties of the exact KS system, so that approximations may be compared against them. Small systems, such as atoms and ions, can be solved within another theory such as quantum Monte-Carlo (QMC)\(^18\) or wave-function techniques like coupled-cluster theory.\(^19\) Accurate densities and energies can thereby be obtained to serve as benchmarks for testing, and hopefully improving, DFAs. (\(e.g., \) ref. 5 and 20–24). Given the density of a system, one can also
find the KS potential $v_n[r]$ through the numerical procedure of “density inversion”, [e.g., ref. 25–37] and thus provide benchmarks for effective potentials, as well as energies.

Density inversion has been applied many times to systems with integer numbers of electrons. Previous work has focused on systems without degeneracies. More rarely, inversion has been applied to systems with broken symmetries or non-integer electron number. Only very recently has inversion been applied to systems with degeneracies and fractional electron number – for the case of fractional anions and cations of Li, C, and F.

The fractional charge cases considered by Gould and Toulouse are especially difficult for approximations. They can therefore provide insights into how DFAs fail, and might be improved. However, the question of how the potential resolves into Hartree (H), exchange (x) and correlation (c) components was not addressed in their work. These terms are typically approximated separately in DFAs, making it important for us to understand how they behave separately. Here, we address the question analytically (in the asymptotic limit) and numerically, by studying and reporting Hartree-exchange (Hx) and c components of the KS potential for fractional ions of Li, C, and F.

The manuscript is organized as follows: first, we define the key properties of interest, within the framework of ensemble DFT (EDFT). Second, we derive the main analytical results, specifically that the exact Hx and c potentials can have non-zero asymptotic constants and unusual effective charges in some cases, which cancel when combined. Next, with the objective of providing insights for effective potentials, as well as energies.

2 Hartree-exchange and correlation energies in EDFT

EDFT comes in a variety of forms, each dealing with different classes of quantum state ensembles. Here, we are concerned with a form of EDFT which allows us to mix ground states with different electron numbers, as well as to treat high-symmetry densities that are associated with degeneracies. The lowest ensemble energy, $E_0[\nu_{\text{ext}}]$, for a given external potential, $\nu_{\text{ext}}(r)$, is found by minimizing an energy density functional over $N$-representable densities, $n(r)$:

$$E_0[\nu_{\text{ext}}] = \min_{n-N} \left\{ \mathcal{F}[n] + \int dr \nu_{\text{ext}}(r)n(r) \right\},$$

where the universal, ensemble-generalised functional is

$$\mathcal{F}[n] := \min_{\hat{T}=\omega} \text{Tr}[\hat{T}\left(\hat{\omega} + \hat{W}\right)] \equiv \text{Tr}[\hat{I}_f(\hat{T} + \hat{W})].$$

Here $\hat{T}$ is the usual kinetic-energy operator, and $\hat{W}$ is the Coulomb electron–electron repulsion operator. The minimisation in eqn (2) is carried out over ensemble density matrices $\hat{T}$ formed out of a set of mutually orthonormal states, possibly with different number of electrons. We denote the minimizing ensemble as $\hat{T}_f$, and $f$ indicates it is an interacting state. Note that the quantities of EDFT depend on the weights that specify the ensemble (see below). To indicate this succinctly we use calligraphic letters. All the ensemble density matrices $\hat{T}$ considered in the minimisation yield the same density, $n(r)$, i.e., $\text{Tr}[\hat{T}n(r)] = n(r)$ where $\hat{n}(r)$ is the density operator. The average electron number, $N = \langle drn(r) \rangle$, may be either integer or fractional.

By the convexity conjecture, the minimising ensemble density matrix can be written as

$$\hat{I}^N = (M + 1 - N)\hat{I}^M + (N - M)\hat{I}^{M+1}$$

and

$$\equiv (1 - c)\hat{I}^M + c\hat{I}^{M+1},$$

where $M = \lfloor N \rfloor$ is the largest integer less than $N$, and $c = N - M$ is the fractional part of the electron number. $\lfloor N \rfloor$ indicates the smallest integer greater than $N$, which is $M + 1$ when $c > 0$, but $M$ when $N$ is integer. We thus use $M + 1$ when results are the same regardless of choice (as above), but use $\lfloor N \rfloor$ when it matters. The density thus becomes

$$n^N(r) = \text{Tr}[\hat{I}^N\hat{n}(r)] = (M + 1 - N)n^M(r) + (N - M)n^{M+1}(r).$$

Traditionally, KS theory can be derived by “switching off” the electron–electron interaction and finding the energy as a functional of the density. Applying this strategy to EDFT gives the two most important energy functionals in the fashion of KS DFT: the kinetic energy functional,

$$\mathcal{F}_k[n] := \min_{\hat{I}=\omega} \text{Tr}[\hat{I}\hat{T}] = \text{Tr}[\hat{I}_f\hat{T}] = \sum_k w_k \langle \psi_k | \hat{T} | \psi_k \rangle$$

and the Hartree-exchange–correlation (Hxc) energy functional,

$$E_{\text{Hxc}}[n] := \mathcal{F}[n] - \mathcal{F}_k[n].$$

The trace on the right side of eqn (6) uses the KS non-interacting ensemble density matrix,

$$\hat{I}_s = \sum_k w_k |\psi_k\rangle \langle \psi_k|,$$

where $|\psi_{\kappa}\rangle$ is the $\kappa$th KS non-interacting state and $w_k$ is its associated ensemble weight.

The KS states $|\psi_{\kappa}\rangle$ can be chosen as single Slater determinants (SD) that are constructed from a common set of orbitals, $\{\phi_{\alpha}(r)\}$, and defined by means of the occupation factors $\{\theta_{\alpha}\}$, where $\theta_{\alpha} = 0$ or 1. For example, in Li there are four orbitals, $\{\phi_{1\alpha}^\uparrow, \phi_{1\alpha}^\downarrow, \phi_{2\alpha}^\uparrow, \phi_{2\alpha}^\downarrow\}$ which feature in two SD states, with majority up and down electrons. The two SDs are occupied according to $1s^22s^1$ (short-hand for $\{\theta_{1\alpha}^\uparrow = 1, \theta_{1\alpha}^\downarrow = 1, \theta_{2\alpha}^\uparrow = 1, \theta_{2\alpha}^\downarrow = 0\}$) and $1s^22s^2$, respectively.

The orbitals can be further separated, using $\rho_{\alpha\sigma}(r) = \phi_{\alpha}(r)\xi_{\sigma\alpha}$, into spin-independent spatial orbitals, $\phi_{\alpha}(r)$, and spin-projectors, $\xi_{\sigma\alpha}$. The spatial components $\phi_{\alpha}(r)$ obey the KS equations

$$\left[\frac{1}{2}\nabla^2 + v_s(r)\right]\phi_{\alpha}(r) = e_\alpha \phi_{\alpha}(r).$$
The electron density is then obtained as
\[ n(r) = \sum_j f_i |\phi_j(r)|^2, \quad (10) \]
where \( f_i \) are the ensemble averaged occupations of the KS orbitals, \( f_i = \sum_{\kappa a} w_{\kappa a} \delta_{\kappa a} \). In the case of Li we get \( f_1 = 2 \) and \( f_2 = 1 \), as expected.

By construction, the density from eqn (10) must yield the interacting (ensemble averaged) electron densities available from parametrised exact QMC results\(^{32}\) (see Section 4), for the systems considered. As a consequence of the underlying symmetry of atoms, the multiplicative KS effective potential \( v_s(r) \equiv v_s(r) \) is, provably, both spherically symmetric and spin independent.

The next functional to consider is the Hartree-exchange (Hx) energy \( \epsilon_{\text{Hx}} \). For closed-shell pure states, \( \epsilon_{\text{Hx}} \) is defined unambiguously. Not so for ensembles. In ensembles, the Hartree-exchange energy, and thus the correlation energy, may be defined more flexibly, although, not necessarily more conveniently. In the following discussion we shall adopt a natural and direct generalization of the ‘Hx’ energy, given by
\[ \epsilon_{\text{Hx}}[n] := \text{Tr} \left[ \hat{\mathcal{H}} \hat{W} \right] = \sum_{\kappa} w_{\kappa} \langle \kappa | \hat{W} | \kappa \rangle, \quad (11) \]
for the atomic cases we concern ourselves with here; and consistent with previous work.\(^{23,24,32,48}\) Eqn (11) may be regarded as a regular expression for the ensemble Hartree–Fock energy which, however, is here evaluated with exact KS orbitals. Correspondingly, the correlation energy can be finally extracted as follows
\[ \epsilon_c[n] := \epsilon_{\text{Hx}}[n] - \epsilon_{\text{Hx}}[n] \equiv \text{Tr}[\hat{\mathcal{H}} + \hat{W} (\hat{\mathcal{H}} - \hat{f}_s)]. \quad (12) \]

While other decompositions are possible,\(^{34,49-51}\) this particular decomposition comes with formal and practical advantages.\(^{23,24,48}\) It leads to an explicit piecewise linear dependence on \( N \) of \( \epsilon_{\text{Hx}} \) and \( \epsilon_c \) through the ensemble weights (additionally, there is an implicit piecewise non-linear dependence on \( N \), through the orbitals) and, in finite systems, to a derivative discontinuity even when using semilocal DFAs.

In this work we shall show that eqn (11) and (12), which we shall call ‘Hx’ and ‘c’ when clarity is required, can be used to uniquely define ‘Hx’ and ‘c’ potentials. The total Hxc potential is, of course, unique and thus does not need quotes for clarity. We explore formal properties of the associated potentials and thus reveal some surprises.

3 Hxc, ‘Hx’ and ‘c’ potential for ensembles

In this section we first review known facts concerning the asymptotic behaviour of the Hxc potential, \( v_{\text{Hxc}}(r) \), beginning with the properties of the KS potential, \( v_s(r) \). Then we derive our key results for its components, the Hx and c potentials, \( v_{\text{Hx}}(r) \) and \( v_c(r) \).

3.1 Behaviour of the Hxc potential: a brief review

In the traditional derivation of DFT, the KS potential \( v_s(r) \) is only defined up to a constant, due to the fact that densities could only vary up to a fixed electron number. In EDFT of open systems, we are able to vary both the spatial distribution of the density, and the number of electrons therein. Consequently, the KS potential \( v_s(r) \) associated with a density \( n(r) \) becomes a unique potential (i.e., the additive constant is determined), given by the derivative of the energy with respect to all variations in the density \( n \) (see, e.g., ref. 24 and 52)

As usual, we may write
\[ v_s(r) = v_{\text{ext}}(r) + v_{\text{Hxc}}(r) \quad (13) \]
where
\[ v_{\text{Hxc}}(r) = \frac{\delta \epsilon_{\text{Hxc}}[n]}{\delta n(r)} \quad (14) \]
Crucially, however, in computing the exchange–correlation potential we have to take the functional derivative of \( \epsilon_{\text{Hxc}}[n] \) with respect to all possible variations of \( n \), namely to account for variations of the density at constant electron number, but also variation of the electron number itself, i.e., we regard \( v_{\text{Hxc}}(r) \) as an explicit functional of both \( N \) and \( n(r) \). Then, we mathematically express the Hxc potential as,
\[ v_{\text{Hxc}}(r) = \tilde{v}_{\text{Hxc}}(r) + v_{\text{Hxc}}^0(r) = \frac{\delta \epsilon_{\text{Hxc}}[n]}{\delta n(r)} \bigg|_N + \frac{\delta \epsilon_{\text{Hxc}}[n]}{\delta N} \bigg|_n \delta N \quad (15) \]
In the above expression we distinguish between: (a) \( \tilde{v}_{\text{Hxc}}(r) \), which is the functional derivative of the Hxc energy at fixed electron number \( N \), and (b) \( v_{\text{Hxc}}^0(r) \), which equals the partial derivative of the Hxc energy with respect to \( N \), at fixed density (we note that \( \delta N/\delta n(r) = 1 \), since \( N = \int n(r) \text{d}r \)). By fixed density, we mean that only \( N \) is allowed to explicitly vary in eqn (3) and in any related functionals [e.g., \( n^M \) and \( n^{M-1} \) are held fixed in eqn (5)].

The potential \( \tilde{v}_{\text{Hxc}}(r) \) is by itself defined up to an arbitrary constant shift and thus is synonymous to the “naïve” xc-potential, i.e., the potential obtained without considering the effect of changing electron number. The term \( v_{\text{Hxc}}^0(r) \) requires some further discussion. First, from eqn (15) we realize that this term is actually spatially uniform. Second, we note that for \( N \) approaching an integer, the value of \( \tilde{v}_{\text{Hxc}} \) is generally different when approaching an integer \( N \) from the left (\( N \to M^- \)) or from the right (\( N \to M^+ \)), due to the possible discontinuity in the derivative of the energy as a function of \( N \) (for non-integral \( N \), left and right limits are the same). As our objective in this work is not directly related to the computation of fundamental gaps, we shall investigate the long-range behavior of the potentials by approaching any given number of electrons always from the left.

With this in mind, we follow ref. 24 (See Section III in the Supplementary Material of that work) to derive an expression for \( v_{\text{Hxc}}^0 \). We account for the fact that, despite \( \epsilon_{\text{Hxc}} \) being formally a functional of \( n \), in practice \( \epsilon_{\text{Hxc}} \) is nearly uniform.
component $\varepsilon_{\text{Hx}}$ (see Section 3.2 below) are implicit functionals of $n$, being explicit functionals of the KS orbitals $\{\phi_i(r)\}$. Therefore, whereas $\frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i}$ is difficult to obtain, $\frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} = n_i \phi_i(r)$. Hence, 

$$
\frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} = \frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} + \int |d\varepsilon_{\text{Hx}}[n]|_{\phi_i} \frac{\partial n_i(r)}{\partial N} |_{\phi_i}. 
$$

(16)

Under the integral of the above expression we recognize two terms: the first one is $\psi_{\text{Hx}}(r)$. The second term represents the change in the total density that occurs due to the variation of the electron number, while all orbitals are fixed. Consequently, we obtain

$$
\psi_{\text{Hx}} = \frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} = \frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} - \int |d\varepsilon_{\text{Hx}}[n]|_{\phi_i} \frac{\partial n_i(r)}{\partial N} |_{\phi_i}. 
$$

(17)

Recalling that $n(r) = \sum_i f_i |\phi_i(r)|^2$, we readily understand that $\frac{\partial n_i(r)}{\partial N} |_{\phi_i} = \sum_i f_i |\phi_i(r)|^2$. Due to the aufbau principle, only the occupation factor(s) $f_i$ of the highest occupied molecular orbitals (HOMO, $h$) vary (linearly) with $N$. Therefore, in the absence of degeneracy, $\frac{\partial n_i(r)}{\partial N} |_{\phi_i} = |\phi_h(r)|^2$. Our case is more complex, however, as the HOMO is degenerate. Nevertheless, we can obtain

$$
\bar{n}_h(r) = \frac{\partial n_i(r)}{\partial N} |_{\phi_i} = \frac{1}{N_h} \sum_h |\phi_h(r)|^2, 
$$

(18)

as the average density of the $N_h$-fold degenerate HOMOs, which follows from equi-occupancy of the degenerate HOMOs (by construction), giving $\sum |\phi_h(r)|^2 = 1/N_h$ for $N_h$ degenerate orbitals (furthermore, $N_h$ does not change when taking left derivatives). Note that a similar term has been reported in spin-DFT of ensembles.40 Therefore, we finally conclude that

$$
\psi_{\text{Hx}} = \frac{\partial \varepsilon_{\text{Hx}}[n]}{\partial N} |_{\phi_i} - \int |d\varepsilon_{\text{Hx}}[n]|_{\phi_i} \bar{n}_h(r). 
$$

(19)

The term $\psi_{\text{Hx}}$ is a spatial constant. Moreover, it serves to ensure that $\psi_{\text{Hx}}$ is independent of any additive constant gauge we choose for $\bar{n}_{\text{Hx}}$ and is thus unique. Consider two choices: $\bar{n}_{\text{Hx}}(r)$ and $\bar{n}_{\text{Hx}}(r) + C$. Neither choice changes the orbitals, density or energy. In the second case, however, eqn (19) has a term $-C \int |d\bar{n}_h(r)| = -C$, in addition to the value found using $\bar{n}_{\text{Hx}}(r)$. Thus, we get $\bar{n}_{\text{Hx}}(r) + \psi_{\text{Hx}}(r) + [\psi_{\text{Hx}}(r) + C] + [\psi_{\text{Hx}}(r) - C] = \bar{n}_{\text{Hx}}(r) + \psi_{\text{Hx}}(r)$ so that the total Hx potential is independent of our gauge.

We can therefore choose, without loss of generality for the atomic systems we study here, the gauge in which $\bar{n}_{\text{Hx}}(r) = 0$ for $|r| \to \infty$. Then, it may be useful to express

$$
\psi_{\text{v}}(r) = \psi_{\text{Hx}}(r) + \psi_{\text{Hx}}(r). 
$$

(20)

where

$$
\psi_{\text{v}}(r) = \nu_{\text{ext}}(r) + \psi_{\text{Hx}}(r), 
$$

(21)

which also obeys $\psi_{\text{v}}(r) \to 0$ for $|r| \to \infty$. Based on this alone, we cannot say if $\psi_{\text{Hx}} = 0$, however.

To continue the analysis, we seek to find $\psi_{\text{Hx}}$. For non-integer $N$, the density is given by eqn (5), which follows from the convexity conjecture. Thus, the density eventually follows the weaker decaying density of $M + 1$ electrons, giving $n(r) \sim - (N - M)H_{N}^{M+1}(r)$ and $\psi_{\text{Hx}}(r) \propto \sqrt{N^{M+1}(r)}$ as $r \to \infty$. But $n^{M+1}(r)$ must itself decay with the ionization potential $I_N = E_M - E_{M+1}$ as $n^{M+1}(r) \sim e^{-2/\sqrt{I_N}}$, and thus we have $-1/2 \psi_{\text{Hx}}(r) \sim -I_N \psi_{\text{Hx}}(r)$ as $r \to \infty$. Since $1/2 \psi_{\text{Hx}}(r) = \{\psi_{\text{Hx}}(r)\}$ and $\lim_{r \to \infty} \bar{n}_{\text{Hx}}(r) = 0$, we thus see that $\{\psi_{\text{Hx}}(r) = -I_N\}$. Note, this also holds for integer $N = M$.

We can then use Janak’s theorem 53 on the frontier orbital to obtain $\bar{n}_{\text{Hx}} = -I_N$, which yields

$$
\psi_{\text{Hx}} = 0, 
$$

(22)

and therefore $\lim_{r \to \infty} \bar{n}_{\text{Hx}}(r) = 0$. Note that this is an exact behaviour of the Hx potential.5,64 It does not necessarily hold true for approximations, which can certainly have a non-zero constant.5,64

Furthermore, adding this constant can improve the calculation of ionisation potentials and fundamental gaps.65

Before proceeding further, it is useful to recall that the KS spatial orbitals in spherical atoms can be written as $\phi_l(r) = R_{lm}(\theta) Y_{lm}(\phi)$, where $R_{lm}$ is a real function and $Y_{lm}$ are the real spherical harmonics. Similarly, the corresponding KS orbital energies $\epsilon_l = \omega_l$ depend only on the quantum numbers $n$ and $l$.

Another consequence of the spherical symmetry is that the potential cannot reflect any nodal plane structure of the orbitals, which can cause problems in some cases,64 including systems with 2p orbitals. The reason these nodal planes are not a problem can be shown by noting that any property of the potential cannot depend on the angle. The nodal planes can only occur along the $x$, $y$, and $z$ axes, for the 2p orbitals. Furthermore, these axes can be rotated without changing the problem. Therefore, the only way the spherical symmetry can be maintained with the nodal structure is if the nodes do not make any impact on the potential.

The asymptotic behavior of $\psi_{\text{v}}(r)$ is $\psi_{\text{v}}(r) \sim -Z_{\infty,s}r/l$ to leading order. Here $Z_{\infty,s}$ is an asymptotic effective charge determined by the asymptotic form of the density. For the exact KS effective potential of integer $M$ electron atomic systems in the ground-state equi-ensemble, we have $Z_{\infty,s} = Z - M + 1$. This follows from the screening of the nuclear potential $\nu_{\text{ext}}(r) = -Z/r$ by the Hx potential. From the same convexity condition reasoning given above, it follows that for a fractional $N$ we have $\nu_{\text{ext}}[n^{M+1}(r)] \sim \nu_{\text{ext}}[N^{M+1}(r)]$ as $r \to \infty$ and thus $Z_{\infty,s} = Z - (M + 1) + 1$. Subtracting the external potential term similarly gives $Z_{\infty,s} = Z - Z - (M + 1) = -M$. In summary, we thus have

$$
\psi_{\text{v}}(r) \sim -Z_{\infty,s} r/l 
$$

(23)
\[
\begin{align*}
\nu_{\text{Hxc}}(r) & \sim -\frac{Z_{\infty} \nu_{\text{Hxc}}}{r} ,
\end{align*}
\]  
(24)

where

\[
\begin{align*}
Z_{\infty, s} & = Z + 1 - \left\lfloor \frac{N}{s} \right\rfloor ,
\end{align*}
\]  
(25)

\[
\begin{align*}
Z_{\infty, \text{Hxc}} & = 1 - \left\lfloor \frac{N}{2} \right\rfloor .
\end{align*}
\]  
(26)

We remind the reader that \(\left\lfloor \frac{N}{s} \right\rfloor = M\) for \(N\) integer, or \(M + 1\) otherwise.

To avoid risk of confusion, we recall that the well-known derivative discontinuity of the potential emerges only by considering the order of limits in which we start with the total electron number \(N\) approaching an integer from above.\(^{42,59}\)

That is to say that \(\lim_{N \to M, r \to \infty} \nu_s(n^N)(r) \neq \lim_{N \to M, r \to \infty} \nu_v(n^N)(r)\). Here, we are considering the order of limits where \(N\) is fixed and, then, the total electron number \(N\) approaches an integer from above.\(^{42,59}\)

3.2 Derivation for the ‘Hx’ and ‘c’ ensemble potentials: non-trivial asymptotics

Let us decompose the \(\nu_{\text{Hxc}}(r)\) potential into its ‘Hx’ and ‘c’ components, \(\nu_{\text{Hxc}}(r) = \nu_{\text{Hx}}(r) + \nu_{\text{c}}(r)\). Similarly to eqn (15), we start with

\[
\nu_{\text{Hx}}(r) = \nu_{\text{Hx}}(r) + \nu_{\text{Hx}}^0
\]  
(27)

where \(\nu_{\text{Hx}}(r) = \delta \nu_{\text{Hx}}[n]/\delta n(r)\) and

\[
\nu_{\text{Hx}}^0 = \frac{\partial \delta \nu_{\text{Hx}}[n]}{\partial n} \bigg|_{\{0\}} - \int \text{d}r \nu_{\text{Hx}}(r) \phi_0(r).
\]  
(28)

We shall proceed to investigate both these terms, first analytically, and later numerically, to show that both are non-trivial in ensemble calculations.

It is useful to note that eqn (11) can be conveniently broken down into its individual Hartree-like and Fock-like contributions as follows\(^{23}\)

\[
\delta_{\text{Hx}} = \frac{1}{2} \sum_{ij} \left\{ F^S_{ij} + F^D_{ij} \right\} (i|j) + \text{D}\left(\uparrow \uparrow + \downarrow \downarrow \right).
\]  
(29)

where

\[
(i|j) = \int \frac{\text{d}r \text{d}r'}{|r - r'|} \phi_i^*(r) \phi_j(r) \phi_i^*(r') \phi_j(r').
\]  
(30)

are the usual two-electron repulsion integrals, here evaluated on KS orbitals from EDFT. Note that all the information about the ensemble is encoded in the coefficients \(F^S_{ij}\) and \(F^D_{ij}\) – superscript \(S\) denotes same-spin terms \(\uparrow \uparrow + \downarrow \downarrow\) and \(D\) denotes different-spin terms \(\uparrow \downarrow + \downarrow \uparrow\). After expanding on the orbital occupancy factors,\(^{24}\) we find

\[
\begin{align*}
F^S_{ij} & = \sum_{\alpha} f^{(2)}_{\alpha, ij} ,
F^D_{ij} & = \sum_{\alpha} f^{(2)}_{\alpha, ij},
\end{align*}
\]  
(31)

here \(\sigma\) means the opposite spin to \(\sigma\) i.e., \(\sigma / \bar{\sigma} = \uparrow / \downarrow\) or \(\downarrow / \uparrow\); and, the expressions involve the average pair-occupation factors

\[
f^{(2)}_{\alpha, ij} = \sum_{x} w_x^{\alpha} \phi_x^{\alpha} \phi_{\bar{x}}^{\alpha}.
\]  
(32)

The quantities defined in eqn (31) are the pair-density equivalent of \(f_i = \sum_{x} w_x \phi_x^{\alpha}\). Thus the energy depends on the statistical probability (across the ensemble) of finding orbitals \(i\) or \(j\) occupied simultaneously. Note that for closed-shell systems with non-degenerate ground states \(|\omega_0 = 1\rangle\), we recover the ‘Hx’ energy expressed in terms of the usual Hartree and exchange energies of regular DFT.

From eqn (29), we get

\[
\nu_{\text{Hx}}(r) = \frac{1}{2} \sum_{ij} \left[ (F^S_{ij} + F^D_{ij}) \nu_{ij}(r) - F^S_{ij} \nu_{ij}(r) \right].
\]  
(33)

where

\[
\nu_{ij}(r) = \frac{\delta (i|j)}{\delta n(r)} |_N ,
\]  
(34)

from where these potentials can be determined by numerically solving the optimised-effective-potential (OEP) equations,\(^{60}\)

\[
\int \text{d}r' \nu_{ij}(r') \frac{\delta n(r')}{\delta \nu_{ij}(r)} = \frac{1}{2} \sum_{h} \int \text{d}r' \frac{\delta (i|j)}{\delta \phi_h(r')} \phi_h(r') \frac{\delta \phi_h(r')}{\delta \phi_h(r)} ,
\]  
(35)

where we have assumed real-valued orbitals.

Unlike its general values, the \(r \to \infty\) asymptotic behaviour of \(\nu_{\text{Hx}}(r)\) can be found analytically in finite systems. Following Kreibich et al.\(^{61}\) and Della Sala and Görлин,\(^{56}\) we obtain

\[
\sum_{h} f_h \phi_h(r)^2 \nu_{\text{Hx}}(r) \sim \frac{1}{r} \sum_{h} \phi_h(r) \frac{\delta \nu_{\text{Hx}}}{\delta \phi_h(r)} ,
\]  
(36)

Note that both sides depend only on \(r = |r|\) after summation over the degenerate HOMOs \(h\). Here, we have exploited again the fact that we have systems with spherical symmetry. Thus the density must be independent of both angle and choice of HOMO, with the latter leading to the sum over \(h\). For the same reason we do not need to worry about nodal planes.

To obtain the asymptote of \(\nu_{\text{Hx}}(r)\) through eqn (36), we use eqn (29) for \(\delta_{\text{Hx}}\), noting that we can easily take derivatives with respect to orbitals. To begin, it is straightforward to show that

\[
\frac{\delta (i|j)}{\delta \phi_h(r)} = \delta_{i|j} \phi_h(r) \int \text{d}r' |r - r'| \phi_h(r') \phi_j(r') + \{i \leftrightarrow j\} ,
\]  
(37)

\(|i \leftrightarrow j\} \text{ means swap labels } i \text{ and } j \text{ in the previous expression}\) and

\[
\frac{\delta (i|j)}{\delta \phi_h(r)} = \delta_{i|j} \phi_h(r) \int \text{d}r' |r - r'| \phi_h(r') \phi_i(r') + \{i \leftrightarrow j\} .
\]  
(38)

For large \(r\), we can write \(1/|r - r'| \approx 1/r\) and exploit the orthonormality of the orbitals to get

\[
\frac{\delta (i|j)}{\delta \phi_h(r)} \sim \frac{\delta_{i|j}}{r} ,
\]  
(39)

Paper
\[
\frac{\delta (ij)}{\delta \phi_h (r)} \sim \frac{\delta (\delta_{ij} + \delta_{jk}) \phi_h (r)}{r} \quad (40)
\]

Then, we can use eqn (39) and (40) on the right-hand side of eqn (36) to obtain

\[
\sum_h \phi_h (r) \frac{\delta \phi_h (r)}{\delta \phi_h (r)} = \frac{1}{2} \sum_h \phi_h (r)^2 \sum_{ij} \frac{\delta (\delta_{ij} + \delta_{jk}) \phi_h (r)}{r} \times \left\{ \left( F_{ij}^S + F_{ij}^D \right) \frac{\delta (\delta_{ij} + \delta_{jk})}{r} - F_{ij}^S \frac{\delta (\delta_{ij} + \delta_{jk})}{r} \right\}
= \frac{1}{2} \sum_h \phi_h (r)^2 \sum_{j} \left( F_{jj}^S + F_{jj}^D \right) - F_{hh}^S = \frac{1}{2} \sum_{h} \phi_h (r)^2 \left[ \sum_{j} \left( F_{jj}^S + F_{jj}^D \right) - F_{hh}^S \right]. \quad (41)
\]

Finally, we conclude that

\[
v_{Hx} (r) \sim \frac{Z_{\infty,Hx}}{r} \quad (42)
\]

with the effective charge

\[
Z_{\infty,Hx} = \frac{\sum_{h} F_{hh}^S - \sum_{j} \left( F_{jj}^S + F_{jj}^D \right)}{\sum_{h} \phi_h (r)^2} \leq 0 \quad (43)
\]

where we have accounted for symmetries.\(^\dagger\) It is easily shown, as done explicitly later, that for an integer number of electrons \(N = M\), this gives \(Z_{\infty,Hx} = 1 - M\), as expected. Not so in general. Similarly, the correlation potential can be decomposed as

\[
v_c (r) = v_{Hx} (r) + v_0 (r),
\]

and the asymptotic behaviour of \(v_c (r)\) is found from eqn (22) and (24) by simply using \(v_c (r) = v_{Hx} (r) - v_{Hx} (r)\). We readily arrive at

\[
Z_{\infty,c} = 1 - \left[ N \right] - Z_{\infty,Hx}, \quad v_c (r) = -v_{Hx} (r). \quad (45)
\]

The above analysis does not tell us whether or not \(v_0 (r) = 0\), however. In the next section we will be able to determine numerically that, in general, the exact \(v_{Hx}\) can be a non-vanishing constant, especially when \(N\) is non-integer.

Let us study the effective charge in more detail. First consider a closed-shell system with an even integer \(M\) number of electrons, which has only one state with \(w_{s0} = 1\). For this state, \(\theta_{\alpha_0} = 1\) for \(i \leq h = M/2\) and zero otherwise. Therefore, \(f_i = \sum_{\alpha} \theta_{\alpha} = 2\) for all occupied states \(i \leq h\). Similarly, \(F_{ii}^S = F_{ii}^D = 2\).

Then, from (43) we obtain

\[
Z_{\infty,Hx}^M (\text{pure}) = 1 - \frac{M/2 - 4}{2} = 1 - M. \quad (46)
\]

for the potential. This is the usual result,\(^6\) \(i.e., v_{cel} (r) + v_{Hx} (r) \sim -[Z + 1 - M]/r\) up to a constant. This means that the outermost electron feels an attractive potential from the \(Z\) nuclear charges, balanced by a repulsive force from the remaining \(M - 1\) electrons. In such systems we get the "typical" result \(Z_{\infty,Hx}^M (\text{pure}) = 0\).

Extending our result to ensembles by using eqn (31) lets us rewrite eqn (43) as

\[
Z_{\infty,Hx} = 1 - \frac{\sum_{j} w_{k} \theta_{\alpha_0} \theta_{\beta_0}}{\sum_{j} \theta_{\alpha_0}} = 1 - \frac{1}{\sum_{j} \theta_{\alpha_0}} \quad (47)
\]

where we used \(\theta_{\alpha_0} \theta_{\beta_0} = \theta_{\alpha_0}, \sum_{\alpha} \theta_{\alpha} = f_h\), and defined \(N^c = \sum_{\alpha} \theta_{\alpha}\) to be the number of electrons in state \(\alpha\). Eqn (47) then lets us obtain results for the various cases considered in this work.

Let us continue our analysis by considering the case when all ensemble members have the same number of electrons; \(i.e.,\) when the electron number is integer, but the ground state is degenerate. In the integer case \(N = M\) in all members, and we get the simple expression

\[
Z_{\infty,Hx}^M (\text{ensemble}) = 1 - \frac{\sum_{j} w_{k} \theta_{\alpha_0} M}{\sum_{j} \theta_{\alpha_0}} = 1 - M \equiv 1 - N. \quad (48)
\]

and \(Z_{\infty,c}^M (\text{ensemble}) = 0\).

Next, consider a fractional Li cation with \(N = 2 + c\) electrons. Here we have the states \(\kappa \in \{1s^2,1s^22s^1,1s^22s^1\}\) with the weights \(w_{\kappa} \in \{1 - c/2,c/2\}\). After some work we can show that

\[
Z_{\infty,Hx}^N (2 < N \leq 3) = 1 - \frac{1}{(N+1)} \equiv 1 - \left[ N \right], \quad (49)
\]

which is the same as for \(Z_{\infty,c}^N\), making \(Z_{\infty,c}^N (2 < N \leq 3) = 0\).

It may be tempting to think that the result \(Z_{\infty,Hx}^N = 1 - \left[ N \right]\) holds in general. However, let us now consider a system with \(N = 3 + c\) electrons. This has states \(\kappa \in \{1s^22s^1,1s^22s^1,1s^22s^1\}\) with weights \(w_{\kappa} \in \{(1 - c)/2,(1 - c)/2\}\) which leads, after some work, to

\[
Z_{\infty,Hx} (3 \leq N \leq 4) = \frac{2(2N - 5) - 2}{N - 2}. \quad (50)
\]

Here, \(Z_{\infty,Hx} = 1 - \left[ N \right]\) only for \(N = 3\) and 4, \(i.e.,\) the integers which we previously showed had the expected behaviour. It otherwise has a non-trivial and non-linear dependence on \(N\).

Similar arguments for the open p-shell systems considered here give

\[
Z_{\infty,Hx}^N (5 \leq N \leq 6) = \frac{2(3N - 13) - 2}{N - 4}, \quad (51)
\]

\[
Z_{\infty,Hx}^N (6 \leq N \leq 7) = \frac{2(4N - 19) - 2}{N - 4}, \quad (52)
\]

for fractional ions of C, and

\[
Z_{\infty,Hx}^N (8 \leq N \leq 9) = \frac{4(3N - 17) - 4}{N - 4}, \quad (53)
\]

\[
Z_{\infty,Hx}^N (9 \leq N \leq 10) = \frac{4(7N - 43) - 4}{N - 4}. \quad (54)
\]

\(^\dagger\) Here, we use that \(\phi_h (r) = R_h (r)Y_{\alpha_0} (\hat{r})\) where only the magnetic quantum number \(m_\alpha\) varies with \(h\), \(i.e.,\) the radial term is the same across the degenerate states. By construction, each orbital is occupied equally, giving \(\sum_h \phi_h^2 (r)F (r) = R_\alpha^2 (r)F (r)\) for an arbitrary radial function \(F (r)\). This holds for all potential-like properties by symmetry and thus leads to the left and right hand sides of eqn (36).
for fractional ions of F. They thus show that this non-trivial screening is common, rather than an exceptional case for Li anions. Note that in these cases the denominator is $N - 4$. This reflects the fact that only the outermost $2p$ shell plays a role in the asymptotics, with the four core electrons excluded. A similar result can be seen above for Li$^-$, where the denominator is $N - 2$ reflecting the exclusion of two core electrons.

Finally, we observe that eqn (49)–(54) all have the same form, namely $Z\_x(H_x) = \frac{AN - B}{N - N\_core}$, where $A$ and $B$ are constants. This result is not a coincidence. Rather, it follows directly from the fact that all terms in the numerator and denominator of eqn (47) depend linearly on the ensemble weights $w_s$, and thus linearly on $N$. The denominator comes from $\sum f_i = N - N\_core$. As discussed above, $N\_core$ is the number of core electrons (e.g., two for 1s electrons in Li, or four for 1s and 2s electrons in C or F). Thus, given $M < N \leq M + 1$ for $M$ integer and $M \geq N\_core$ electrons in a degenerate equi-ensemble ground-state, one obtains,

$$Z\_x(H_x)(N) = \frac{(N - 1)N\_core + (M + 1 - 2N)M}{N - N\_core},$$

(55)

by ensuring that limiting cases are satisfied, i.e., $Z\_x(H_x)(M) = 1 - M$ and $Z\_x(H_x)(M + 1) = -M$ for $M > N\_core$, or $Z\_x(H_x)(M + 1) = -M$ and $\partial Z\_x(H_x)/\partial N = 0$ for $M = N\_core$. It is easily seen by substitution that eqn (55) covers all previous expressions.

The values for $Z\_x(H_x)$ and $Z\_x(Hxc)$ are shown in Fig. 1 for the systems considered here. Note that $Z\_x(H_x)$ is continuous at most (but not all) integer electron numbers. It always takes the “typical” value for $N$ integer. By contrast, $\partial Z\_x(Hxc)/\partial N$ is discontinuous at integer electron numbers. As the combined contributions of the $H_x$ and $c$ potentials give $Z\_x(Hxc) = 1 - \lfloor N \rfloor$, the non piecewise constant behavior of $Z\_x(H_x)$ points, in turn, to a strong non-local functional dependence on the density in the remainder correlation potential. This leads to $Z\_x \neq 0$ for some non-integer $N$.

These asymptotic constants are closely related to the idea of freedom from self-interaction in DFT. Thus, prior to concluding this section, let us briefly consider this relation. The result that $Z\_x = Z + 1 - \lfloor N \rfloor$ can be interpreted as the outermost orbital feeling a nuclear potential that is screened by electrostatic repulsion from the remaining $\lfloor N \rfloor - 1$ electrons, i.e., all electrons not in the outermost orbital. This is known as freedom from self-interaction, and is an important quality of the KS potential, albeit one that is rarely met by approximations. The effect of their absence is known as a self-interaction error. In contrast, the correct asymptotic decay of a potential is not always equivalent to freedom from self-interaction, as discussed in detail by Schmidt et al.63

Typically, we expect the $H_x$ potential to be self-interaction free, meaning it is responsible for the $1 - \lfloor N \rfloor$ contribution to the screening. This is indeed the case for integer electron number and for Li cations, as shown above. However, this freedom from self interaction is manifestly absent from $H_x$ in the other fractional cases mentioned. It must therefore be compensated for by the $c$ potential.

We conclude that, in general, $Z\_x(H_x) \neq Z\_x(Hxc)$ and the ensemble $H_x$ potential has a different long-range behavior compared to the one of the total $Hxc$ potential. Attempts to ensure a correct asymptotic behavior in exchange potential alone based on what is known about the pure-state $H_x$ potential requires a careful revisiting in EDFT.

4 Numerical results

In this section, we complete our analysis with numerical results obtained for the exact $v_{Hxc}(r)$, $v_{Hx}(r)$, and $v_i(r)$. The exact KS potentials $v_i(r)$ (and thus their components) were calculated using the densities and methods described by Gould and Toulouse.32

All our calculations were carried out on logarithmic radial grids with $N_r = 256$ abscissae arranged to accurately capture both core ($r \rightarrow 0$) and asymptotic ($r \rightarrow \infty$) behaviours. The same grid is used for radial quadrature, derivatives, orbitals, and Green functions (which are used directly and in $Z_0$).

Orbitals $\{\phi_i\}$ are calculated by direct diagonalisation of the KS Hamiltonian expressed as an $N_r \times N_r$ matrix. Greens functions are evaluated by summing over all available solutions of the KS equations, i.e., $N_r$ orbitals in total from $N_r$ radial points. Spatial symmetries allow us to further break the ground state and response problems up via spherical harmonic expansions, in the fashion described in ref. 23 and 64.

4.1 Outline of the procedure

In order to calculate the potential $v_{Hxc}(r)$ [and thus, by difference, $v_i(r)$], we need to solve eqn (35). This equation involves the KS linear-response function

$$Z_0(r, r') = \frac{\delta v_i(r)}{\delta v_i(r')}$$

(56)

and the associated Greens functions

$$G_i(r, r') = \sum_{j, \neq i} \rho_j(r, r') \epsilon_j - \epsilon_i$$

(57)

where $\rho_j(r, r') = \phi_j(r)\phi_j(r')$, such that $Z_0(r, r') = 2 \sum_j G_i(r', r) \rho_j(r, r')$.

Therefore, we can rewrite eqn (35) as follows

$$\int dr' Z_0(r, r') \tilde{v}_x(r') = d_{tx}(r)$$

(58)
where

\[
d_{\text{KLI}}(r) = \sum_k \int \text{d}r' G_k(r, r') \phi_k(r') \frac{\delta \epsilon_{\text{KLI}}}{\delta \phi_k(r)}. \tag{59}
\]

Normally, when one seeks an OEP for exchange, one has access to various minimization procedures. Then, one can use variational techniques or virial theorems to efficiently compute \( v_{\text{Hx}} \).\(^5\) Our case, however, is complicated by two features. Firstly, we have a non-integer number of electrons which may or may not cause problems for exact theorems obtained assuming integers. Secondly, rather than obtaining an OEP self-consistently, we instead need to find the functional derivative after “reading” in the potential \( v_{\text{c}} \) that correspond to some given KS orbitals and orbital energies – those which are obtained from the KS inversion on exact QMC densities.\(^3\)

Instead, we approach the problem by basis set expansion, using a good starting guess and additional functions for remaining terms. As our starting guess, we use a KLI approximation, which is treated with semi-local DFAs.\(^6\) Moreover, they clearly demonstrate self-interaction errors when treated with semi-local DFAs.\(^7\)

In Fig. 2 we present components of the potentials for atoms, anions, and cations, at \( N \in \{Z - 1, Z = 0.6, Z, Z + 0.4, Z + 1\} \), to illustrate the asymptotics of each term. Values for \( v_{\text{Hx}}^0 \) and related quantities, are reported in Table 1.

The numerical results also confirm that, for non-integer electron numbers (\( \varepsilon \neq 0 \)), the potential from the ensemble Hx energy functional defined here does not follow the asymptotic behavior of the Hxc potential given in eqn (26), except in limited cases (e.g., Li\(^{3-}\)). Thus, at the Hx level, the outermost orbital spuriously “feels” its own field since \( Z_{\infty, \text{Hx}} \neq 1 - [N] \), e.g., \( Z_{\infty, \text{Hx}} = -2(2N - 3)/[N(2N - 3)] \neq 3 \) for Li\(^{3-}\) with \( 0 < \varepsilon < 1 \) and \( N = 3 + \). This means that the Hx potential cannot be regarded as self-interaction free. Its effect is manifested in the asymptotic behaviour of \( v_{\text{c}} \), which decays more rapidly than \( 1/r \) when \( v_{\text{Hx}} \) is self-interaction free, and as \( -Z_{\infty, \text{KLI}}/r \) otherwise.

We see that the asymptotic constant \( v_{\text{Hx}}^0 \) is zero for both Li and C at integer electron numbers. But for F – surprisingly – it is zero only in the closed-shell case \( N = 10 (\text{F}^-) \). \( v_{\text{Hx}}^0 \) is also quite significant in most partial ions, but this is less surprising given the asymptotic self-interaction contribution in those systems.

\[
X_b = \int 4\pi r^2 d\xi_b(r) \Delta d_{\text{Hx}}(r), \tag{63}
\]

and \( \Delta d_{\text{Hx}}(r) = d_{\text{Hx}}(r) - \int 4\pi r^2 d\xi_0(r, r') \Delta v_{\text{Hx,KLI}}(r') \). Again, we take advantage of spherical symmetry.

It remains to describe the basis functions, and how to avoid a spurious numerical constant in the determined potential that appears in some cases. Details are in the appendices.

4.2 Results

We report results for the exact KS potential and its components for Li, C, and F with fractional numbers of electrons. The neutral atoms are important examples of an electron donor (Li), an electron acceptor (F), and an atom with flexible bonding (C). Moreover, they clearly demonstrate self-interaction errors when treated with semi-local DFAs.\(^7\)

Fig. 2 Hxc (orange solid line), Hx (navy dashed line), and c (magenta dash-dot line) potentials (with the electron number derivative contribution) for selected ions of Li (left), C (centre), and F (right). The Hx and Hxc potentials are shown as \( v + Z'/r \equiv v + (1 - [N])/r \) to allow direct comparison with the c potential. These plots illustrate, most obviously, the effect of the asymptotic constant on the different potentials. Less obviously they reveal the effect of differing effective charges, since they are constructed to approach zero (or a constant) faster than \( 1/r \) for integer electron number cases, but not necessarily for non-integer cases.
The non-zero values in F likely reflect the fact that the upper “channel” of a shell (i.e., the second electron in an s-shell or 4th–6th electron in a p-shell) is more sensitive to ensemble effects than the lower channel, owing to the need to treat electrons of opposite spin within the same ensemble members [meaning $F_{kl}^{D}$ = 0 in the lower channel but $F_{kl}^{D}$ ≠ 0 in the upper channel, e.g., in eqn (29), where $h$ and $h'$ indicate electrons in the frontier orbital]. For this reason, partial anions of Li have a non-zero value and unusual asymptotic potentials but partial cations do not. Consequently, e.g., we expect neutral and fully anionic O (not studied here because high-quality reference data on its ions are not available) to have a non-zero constant, whereas fully cationic O likely will not.

It is also notable how unvarying the correlation potentials are for cations, even in cases where $v_c(r)$ has a long-range coulombic asymptotic behaviour. This is not entirely surprising, given the dominance of exchange in cations. But it nonetheless bodes well for the ability to approximate $v_c(r)$ in such systems. Anions paint a different story. There, correlation is known to be more important, due to the weak binding of the outermost electrons. This is reflected in the greater role played by $v_c(r)$ in governing the behaviour of the KS orbitals.

Finally, we note that the findings of this manuscript are also likely to be valid for molecules with degenerate ground-states.

A detailed analysis of molecular cases is rather challenging numerically, however, due to the difficulty of obtaining sufficiently accurate reference electron densities. It is therefore outside the scope of this work.

5 Conclusions

In this work, we analytically and numerically investigated exact DFT properties of the ‘Hx’ and ‘c’ potentials, for Li, C, and F atoms and fractional ions. Of primary theoretical interest, we revealed two important facts: (1) the exact Hx and c potentials can have equal and opposite asymptotic constants in some cases [eqn (22) and eqn (28)]; and (2) the effective charge “felt” by the outermost electron can imply an exchange self-interaction for the frontier orbitals [eqn (43)], at a fractional number of electrons. This conclusion is contrary to the common wisdom that exact exchange is always one-electron interaction free.

The Hx and c potentials of neutral atoms and cations are reasonably well-behaved, with the notable exception (in our tests) of F, which attains asymptotic constants in the Hx and c potentials in its atomic and cationic form, but not in its anion form. The role of the correlation potential in anions is, as might be expected, more complex both for integer and non-integer electron number cases.

Our findings also call for new considerations of how self interaction in the ensemble KS framework may be interpreted. For example, as mentioned above the division into Hx and c we employ here is not the only one. Understanding how similar effects manifest in other definitions may assist further functional development efforts. Similar effects to those found here may also be expected to appear in excited-state EDFT, and this should be investigated.

Conflicts of interest

There are no conflicts to declare.

Appendix A: basis functions for the potential

For the potential basis functions $\{\zeta_{k}(r)\}$ we begin with the orbital-derived functions

$$\begin{cases} n_{k}(r) \\ n(r) \end{cases}_{b < b'}$$

$$\left(\frac{d\rho_{bb'}}{dr}\right)_{b,b'}. \quad (64)$$

that comprise terms that enter into the KLI potential. Here $n_{k}(r) = \sum_{m} |\phi_{nk}(r)|^2$ and $\rho_{bb'}(r) = \delta_{bb'} \sum_{m} \phi_{nk}(r)\phi_{nm}(r)$ are shell averaged densities and mixed densities, respectively. We expect terms of these forms to contribute significantly to the potential. Thus, e.g., we get

$$\zeta_3(r) = n_{3d}(r)/n_{3s}(r), \quad \zeta_3 = \left(\frac{d\rho_{1010'}}{dr}/|r - r'| \right), \quad \zeta_3 = \left(\frac{d\rho_{1010'}}{dr}/|r - r'| \right).$$

In our calculations we use 16 augmenting functions. Thus, e.g., $\zeta_3(r) = e^{-\xi x^2}, \ldots, \zeta_6(r) = e^{-\xi s^2}$ for Li and its ions. During testing, we varied these functions to investigate the stability of various integrated quantities to changes in the basis – these tests revealed the issue discussed in the next section.

All together, these basis functions let us capture the important properties of the potential, including manifestations of shell structure. Results near the nuclei \(r \ll Z^{1/3}\) are imperfect, however. Fortunately they are also unimportant given the dominance of the nuclear potential $\sim 2\pi r^2$ over $v_{Hx}(r)$ for small $r$. We thus exclude them from most of our plots in Section 4.
Appendix B: avoiding spurious numerical constant terms

In addition to the general numerical considerations given above, we highlight an important detail in our analysis of the potentials $v_{\text{H}}(r)$, namely how to avoid a spurious numerical constant.

To begin with, let us consider the mathematical details of the problem. It is clear from the form of the KS Hamiltonian that the electron density of any quantum system is unchanged by a constant shift in its effective potential. Thus the density linear-response function has an eigenfunction with eigenvalue 0. Its inverse is thus ill-defined in general, and constant terms must thus be excluded from $\chi_0^{-1}$ for meaningful numerical results.

In the case of an exact inversion, this is not a problem. However, in our calculations we expand $\chi_0^{-1}$ on a finite basis.

In some cases this basis truncation leads to an effective pseudo-step function $\tilde{v}(r)$ obeying $\tilde{v}(r < r_c) \approx 1$ and $\tilde{v}(r > r_c) \approx 0$. When this error is present, the density at the cutoff radius $r_c$ is difficult in cases where we require $\nabla v$ in reasonable results for all systems we thus add a correction for all $\nabla v$.

An uncontrolled (and physically meaningless) “gauge”. To ensure a constant shift in the potential, when compared to the asymptotically correct $\nabla v$, we introduce $\Delta v_{\text{H}}(r)$ (65),

$$\nabla v_{\text{H}}(r) = \nabla v_{\text{H},\text{KLI}}(r) + \Delta v_{\text{H}}(r) + Ch(r)$$

where $\Delta v_{\text{H}}(r)$ is the true difference between the potentials, that decays to zero faster than $1/r$.

The additional term involves a constant $C$ and pseudo-step function $\tilde{h}(r)$ obeying $\tilde{h}(r < r_c) \approx 1$ and $\tilde{h}(r > r_c) \approx 0$. When this error is present, the density at the cutoff radius $r_c$ is typically $n(r_c) \approx 10^{-12}$, meaning that $|d\tilde{r}(r)\tilde{h}(r)| \approx N$ and $|d\tilde{r}(r)h(r)| \approx 1$ for all $i$. This contribution $Ch(r)$ to the potential is almost certainly an artifact of numerics rather than a real effect. This is made especially apparent by varying the basis set, which leads to large changes to $\langle \tilde{v}_{\text{H}} \rangle$ in the anomalous cases, and virtually no changes to $\langle \tilde{v}_{\text{H}} \rangle$ in cases when it is close in value to $\langle \tilde{v}_{\text{H},\text{KLI}} \rangle$.

Unfortunately, the presence of $Ch(r)$ makes analysis difficult in cases where we require $\nabla v_{\text{H}}$, since it introduces an uncontrolled (and physically meaningless) “gauge”. To ensure reasonable results for all systems we thus add a correction $C'$,

$$C' = \left[ d\tilde{r}(r) (\tilde{v}_{\text{H},\text{KLI}}(r) - \tilde{v}_{\text{H}}(r)) \right] \approx -C$$

and to our potentials to avoid the spurious pseudo-constant, i.e.,

$$C' \approx \left[ d\tilde{r}(r) (\tilde{v}_{\text{H},\text{KLI}}(r) - \tilde{v}_{\text{H}}(r)) \right]$$

The effect of the correction $C'$ can be tested on “good” cases where no shift is apparent. These case suggest that $\langle \tilde{v}_{\text{H}} \rangle$ differs from $\langle \tilde{v}_{\text{H},\text{KLI}} \rangle$ by at most a few mHa, more than an order of magnitude less than correlation energies. We further note that in calculations where we use $v_{\text{H}}(r) = \tilde{v}_{\text{H}}(r) + v_0$ the pseudo-constant does not make any difference at all to final results as $C$ it is cancelled out through the term $-d\tilde{r}(r)\tilde{v}_{\text{H}}(r)$ in $v_{\text{H}}$ (at least in the region $r < r_c$ of interest).

We note that it might be possible to obtain $v_{\text{H}}$ more directly, by using relationships between Kohn–Sham and Hartree–Fock quantities. However, this requires further scrutiny in the case of using the exact (as done here), rather than OEP (as done previously), orbitals in $v_{\text{H}}$ and a proper ensemble generalization of Hartree–Fock quantities in several cases. Due to these outstanding theoretical issues, this strategy is not pursued in this work.

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