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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.

I. 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. Because this discontinuity must be reflected in the KS system, the KS potential can and usually does experience "jumps" by a uniform constant as the electron number passes through an integer.[3] These derivative discontinuities give rise to surprising yet important phenomena (e.g., Refs. [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., Refs. [5, 20–24]) Given the density of a system, one can also find the KS potential $v_s[n](\mathbf{r})$ through the numerical procedure of "density inversion", (e.g., Refs. [25–37]) and thus provide benchmarks for effective potentials, as well as energies.

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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.[29, 38–42] Only very recently[32] 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[32] 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 were 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 analytic 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 quantifying our analytical findings numerically, we describe the numerical method employed and provide results for fractional ions of Li, C, and F. Finally, we conclude.

II. 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, $\mathscr{E}_0[v_{\text{ext}}]$, for a given external potential, $v_{\text{ext}}(\mathbf{r})$, is found by minimizing an energy density functional over N-representable densities, $n(\mathbf{r})$:

$$\mathscr{E}_0[v_{\text{ext}}] = \min_{n\to N}\left\{\mathscr{F}[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n(\mathbf{r})\right\}\,, \tag{1}$$

where the universal, ensemble-generalised functional[3, 43–46] is

$$\mathscr{F}[n] := \min_{\hat{\Gamma}\to n}\text{Tr}[\hat{\Gamma}(\hat{T}+\hat{W})] \equiv \text{Tr}[\hat{\Gamma}_I(\hat{T}+\hat{W})]\,. \tag{2}$$

Here $\hat{T}$ is the usual kinetic-energy operator, and $\hat{W}$ is the Coulomb electron-electron repulsion operator. The minimisation in Eq. (2) is carried out over ensemble density matrices $\hat{\Gamma}$ formed out of a set of mutually orthonormal states, possibly with different number of electrons. We denote the minimizing ensemble as $\hat{\Gamma}_I$, where I 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 $\hat{\Gamma}$ considered in the minimisation yield the same density, $n(\mathbf{r})$, i.e. $\text{Tr}[\hat{\Gamma}\hat{n}(\mathbf{r})] = n(\mathbf{r})$ where $\hat{n}(\mathbf{r})$ is the density operator. The average electron number, $N = \int d\mathbf{r} n(\mathbf{r})$, may be either integer or fractional.

By the convexity conjecture [47], the minimising ensemble density matrix can be written as[3]

$$\hat{\Gamma}^N = (M+1-N)\hat{\Gamma}^M + (N-M)\hat{\Gamma}^{M+1} \tag{3}$$

$$\equiv (1-c)\hat{\Gamma}^M + c\hat{\Gamma}^{(M+1)}, \tag{4}$$

where $M = \lfloor N \rfloor$ is the largest integer less than N, and $c = N - M$ is the fractional part of the electron number. $\lceil N \rceil$ 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 $\lceil N \rceil$ when it matters. The density thus becomes,

$$n^N(\mathbf{r}) = \text{Tr}[\hat{\Gamma}^N\hat{n}(\mathbf{r})] = (M+1-N)n^M(\mathbf{r}) + (N-M)n^{M+1}(\mathbf{r})\,. \tag{5}$$

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,

$$\mathscr{T}_s[n] := \min_{\hat{\Gamma}\to n}\text{Tr}[\hat{\Gamma}\hat{T}] = \text{Tr}[\hat{\Gamma}_s\hat{T}] = \sum_{\kappa} w_\kappa \langle \kappa_s|\hat{T}|\kappa_s\rangle \tag{6}$$

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

$$\mathscr{E}_{\text{Hxc}}[n] := \mathscr{F}[n] - \mathscr{T}_s[n]\,. \tag{7}$$

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

$$\hat{\Gamma}_s = \sum_{\kappa} w_\kappa |\kappa_s\rangle\langle\kappa_s|, \tag{8}$$

where $|\kappa_s\rangle$ is the κth KS non-interacting state and w_κ is its associated ensemble weight.

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

The orbitals can be further separated, using $\varphi_{i\sigma}(\mathbf{r}) = \phi_i(\mathbf{r})\xi_\sigma$, into spin-independent spatial orbitals, $\phi_i(\mathbf{r})$, and spin-projectors, ξ_σ. The spatial components $\phi_i(\mathbf{r})$ obey the KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})\,. \tag{9}$$

The electron density is then obtained as

$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2, \tag{10}$$

where f_i are the ensemble averaged occupations of the KS orbitals, $f_i \equiv \sum_{\kappa\sigma} w_\kappa \theta^\kappa_{i\sigma}$. In the case of Li we get $f_{1s} = 2$ and $f_{2s} = 1$, as expected.

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

The next functional to consider is the Hartree-exchange (Hx) energy $\mathscr{E}_{\rm Hx}$. For closed-shell pure states, $\mathscr{E}_{\rm Hx}$ 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

$$\mathscr{E}_{\rm Hx}[n] := {\rm Tr}[\hat{\Gamma}_s \hat{W}] = \sum_\kappa w_\kappa \langle \kappa_s | \hat{W} | \kappa_s \rangle \ , \tag{11}$$

for the atomic cases we concern ourselves with here; and consistent with previous work.[23, 24, 32, 48] Eq. (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

$$\mathscr{E}_{\rm c}[n] := \mathscr{E}_{\rm Hxc}[n] - \mathscr{E}_{\rm Hx}[n] \equiv {\rm Tr}[(\hat{T} + \hat{W})(\hat{\Gamma}_I - \hat{\Gamma}_s)] \ . \tag{12}$$

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 $\mathscr{T}_s$, $\mathscr{E}_{\rm Hx}$, and $\mathscr{E}_{\rm c}$ 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 eqs. (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 surprising properties.

III. Hxc, 'Hx' and 'c' potential for ensembles

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

A. Behaviour of the Hxc potential: a brief review

In the traditional derivation of DFT, the KS potential $v_s(\mathbf{r})$ 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 $v_s(\mathbf{r})$ associated with a density $n(\mathbf{r})$ 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, 52])

As usual, we may write

$$v_s(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + v_{\rm Hxc}(\mathbf{r}) \tag{13}$$

where

$$v_{\rm Hxc}(\mathbf{r}) = \frac{\delta \mathscr{E}_{\rm Hxc}[n]}{\delta n(\mathbf{r})} \ . \tag{14}$$

Crucially, however, in computing the exchange-correlation potential we have to take the functional derivative of $\mathscr{E}_{\rm Hxc}[n]$ 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 $v_{\rm Hxc}(\mathbf{r})$ as an explicit functional of both N and $n(\mathbf{r})$. Then, we mathematically express the Hxc potential as,

$$v_{\rm Hxc}(\mathbf{r}) = \tilde{v}_{\rm Hxc}(\mathbf{r}) + v^0_{\rm Hxc}(\mathbf{r}) = \frac{\delta \mathscr{E}_{\rm Hxc}[n]}{\delta n(\mathbf{r})}\Big|_N + \frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\Big|_n \frac{\delta N}{\delta n(\mathbf{r})}. \tag{15}$$

In the above expression we distinguish between: a) $\tilde{v}_{\rm Hxc}(\mathbf{r})$, which is the functional derivative of the Hxc energy at fixed electron number N, and b) $v^0_{\rm Hxc}(\mathbf{r})$, which equals the partial derivative of the Hxc energy with respect to N, at fixed density (we note that $\frac{\delta N}{\delta n(\mathbf{r})} = 1$, since $N = \int n(\mathbf{r}) d\mathbf{r}$). By fixed density, we mean that only N is allowed to explicitly vary in Eq. (3) and in any related functionals [e.g., n^M and n^{M+1} are held fixed in Eq. (5)].

The potential $\tilde{v}_{\rm Hxc}(\mathbf{r})$ is by itself defined up to an *arbitrary* constant shift and thus is synonymous to the "naive" xc-potential, i.e. the potential obtained without considering the effect of changing electron number. The term $v^0_{\rm Hxc}(\mathbf{r})$ requires some further discussion. First, from Eq. (15) we realize that this term is actually *spatially uniform*. Second, we note that for N approaching an integer, the value of $\partial \mathscr{E}_{\rm Hxc}/\partial N$ 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-integer 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] (Supplemental Material, Sec. III) to derive an expression for $v^0_{\rm Hxc}$. We account for the fact that, despite $\mathscr{E}_{\rm Hxc}$ being formally a functional of n, in practice $\mathscr{E}_{\rm Hxc}$, and particularly its component $\mathscr{E}_{\rm Hx}$ (see Sec. B below) are *implicit* functionals of n, being explicit functionals of the KS orbitals $\{\phi_i(\mathbf{r})\}$. Therefore,

whereas $\frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_n$ is difficult to obtain, $\frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_{\{\phi_i\}}$ is available.

To relate the two aforementioned quantities and derive a relation for $v^0_{\rm Hxc}$, we express $\mathscr{E}_{\rm Hxc}$ as a functional of N and $n(\mathbf{r})$, which is in turn a functional of N and $\{\phi_i(\mathbf{r})\}$: $\mathscr{E}_{\rm Hxc} = \mathscr{E}_{\rm Hxc}[N, n[N, \{\phi_i(\mathbf{r})\}]$. Then,

$$\frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_{\{\phi_i\}} = \frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_n + \int d\mathbf{r} \frac{\delta \mathscr{E}_{\rm Hxc}}{\delta n(\mathbf{r})}\big|_N \frac{\partial n(\mathbf{r})}{\partial N}\big|_{\{\phi_i\}}. \quad (16)$$

Under the integral of the above expression we recognize two terms: the first one is $\tilde{v}_{\rm Hxc}(\mathbf{r})$. 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,

$$v^0_{\rm Hxc} = \frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_n = \frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_{\{\phi_i\}} - \int d\mathbf{r} \frac{\delta \mathscr{E}_{\rm Hxc}}{\delta n(\mathbf{r})}\big|_N \frac{\partial n(\mathbf{r})}{\partial N}\big|_{\{\phi_i\}} . \quad (17)$$

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

$$\bar{n}_h(\mathbf{r}) \equiv \frac{\partial n(\mathbf{r})}{\partial N}\big|_{\{\phi_i\}} = \frac{1}{N_h} \sum_h |\phi_h(\mathbf{r})|^2, \quad (18)$$

as the average density of the N_h-fold degenerate HOMOs, which follows from equi-occupancy of the degenerate HOMOs (by construction), giving $\partial f_h / \partial N = 1/N_h$ 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

$$v^0_{\rm Hxc} = \frac{\partial \mathscr{E}_{\rm Hxc}[n]}{\partial N}\big|_{\{\phi_i\}} - \int d\mathbf{r} \tilde{v}_{\rm Hxc}(\mathbf{r}) \bar{n}_h(\mathbf{r}). \quad (19)$$

The term $v^0_{\rm Hxc}$ is a spatial constant. Moreover, it serves to ensure that $v_{\rm Hxc}$ is independent of any additive constant gauge we choose for $\tilde{v}_{\rm Hxc}$ and is thus unique. Consider two choices: $\tilde{v}_{\rm Hxc}(\mathbf{r})$ and $\tilde{v}_{\rm Hxc}(\mathbf{r}) + C$. Neither choice changes the orbitals, density or energy. In the second case, however, Eq. (19) has a term $-C \int d\mathbf{r} \bar{n}_h(\mathbf{r}) = -C$, in addition to the value found using $\tilde{v}_{\rm Hxc}(\mathbf{r})$. Thus, we get $\tilde{v}_{\rm Hxc}(\mathbf{r}) + v^0_{\rm Hxc}$ or $[\tilde{v}_{\rm Hxc}(\mathbf{r}) + C] + [v^0_{\rm Hxc} - C] = \tilde{v}_{\rm Hxc}(\mathbf{r}) + v^0_{\rm Hxc}$, so that the total Hxc 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 $\tilde{v}_{\rm Hxc}(\mathbf{r}) \to 0$ for $|\mathbf{r}| \to \infty$. Then, it may be useful to express

$$v_s(\mathbf{r}) = \tilde{v}_s(\mathbf{r}) + v^0_{\rm Hxc} . \quad (20)$$

where

$$\tilde{v}_s(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + \tilde{v}_{\rm Hxc}(\mathbf{r}) , \quad (21)$$

which also obeys $\tilde{v}_s(\mathbf{r}) \to 0$ for $|\mathbf{r}| \to \infty$. Based on this alone, we cannot say if $v^0_{\rm Hxc} = 0$, however.

To continue the analysis, we seek to find $v^0_{\rm Hxc}$. For non-integer N, the density is given by Eq. (5), which follows from the convexity conjecture. Thus, the density eventually follows the weaker decaying density of $M+1$ electrons, giving $n^N(\mathbf{r}) \sim (N-M) n^{M+1}(\mathbf{r})$ and $\phi_h(\mathbf{r}) \propto \sqrt{n^{M+1}(\mathbf{r})}$ as $r = |\mathbf{r}| \to \infty$. But $n^{M+1}(\mathbf{r})$ must itself decay with the ionization potential $I_N = E_M - E_{M+1}$ as $n^{M+1}(\mathbf{r}) \sim e^{-2\sqrt{2I_N} r}$, and thus we have $-\frac{1}{2}\nabla^2 \phi_h(\mathbf{r}) \sim -I_N \phi_h(\mathbf{r})$ as $r \to \infty$. Since $-\frac{1}{2}\nabla^2 \phi_h(\mathbf{r}) = \{\varepsilon_h - v_s(\mathbf{r})\} \phi_h(\mathbf{r})$ and $\lim_{r\to\infty} \tilde{v}_s(\mathbf{r}) = 0$, we thus see that $(\varepsilon_h - v^0_{\rm Hxc}) = -I_N$. Note, this also holds for integer $N = M$.

We can then use Janak's theorem [53] on the frontier orbital to obtain $\varepsilon_h = -I_N$, which yields

$$v^0_{\rm Hxc} = 0 , \quad (22)$$

and therefore $\lim_{r\to\infty} v_s(\mathbf{r}) = 0$. Note that this is an exact behaviour of the Hxc potential[3, 54]. It does not necessarily hold true for approximations, which can certainly have a non-zero constant.[13, 24] Furthermore, adding this constant can improve the calculation of ionisation potentials and fundamental gaps [55].

Before proceeding further, it is useful to recall that the KS spatial orbitals in spherical atoms can be written as $\phi_i(\mathbf{r}) = R_{nl}(r) Y_{lm}(\hat{\mathbf{r}})$, where R_{nl} is a real function and Y_{lm} are the real spherical harmonics. Similarly, the corresponding KS orbital energies $\varepsilon_i = \varepsilon_{nl}$ 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,[56] 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 $v_s(\mathbf{r})$ is $v_s(\mathbf{r}) \sim -Z_{\infty,s}/r$ 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 $Z^M_{\infty,s} = Z - M + 1$. This follows[57, 58] from the screening of the nuclear potential $v_{\rm ext}(r) = -Z/r$ by the Hxc potential. From the same convexity condition reasoning given above, it follows that for a fractional N we have $v_s[n^N](\mathbf{r}) \sim v_s[n^{M+1}](\mathbf{r})$ as $r \to \infty$ and thus $Z_{\infty,s} = Z - (M+1) + 1$. Subtracting the external potential term similarly gives $Z_{\infty,\rm Hxc} = Z_{\infty,s} - Z =$

$1-(M+1)=-M$. In summary, we thus have

$$v_s(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{-Z_{\infty,s}}{r} \tag{23}$$

$$v_{\rm Hxc}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{-Z_{\infty,\rm Hxc}}{r} \ , \tag{24}$$

where

$$Z_{\infty,s} = Z+1-\lceil N\rceil \ , \tag{25}$$

$$Z_{\infty,\rm Hxc} = 1-\lceil N\rceil \ . \tag{26}$$

We remind the reader that $\lceil N\rceil = M$ 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 r is fixed and, then, the total electron number N approaches an integer from *above*.[42, 59] That is to say that $\lim_{N\to M}\lim_{r\to\infty} v_s[n^N](r) \neq \lim_{r\to\infty}\lim_{N\to M} v_s[n^N](r)$. Here, we are considering the order of limits where N is fixed as $r\to\infty$, at which $v_s[n^N]$ decays to zero. Moreover, we approach integer numbers of electrons always from *the left*.

B. Derivation for the 'Hx' and 'c' ensemble potentials: non-trivial asymptotics

Let us decompose the $v_{\rm Hxc}(\mathbf{r})$ potential into its 'Hx' and 'c' components, $v_{\rm Hxc}(\mathbf{r}) = v_{\rm Hx}(\mathbf{r}) + v_{\rm c}(\mathbf{r})$. Similarly to Eq. (15), we start with

$$v_{\rm Hx}(\mathbf{r}) = \tilde{v}_{\rm Hx}(\mathbf{r}) + v^0_{\rm Hx} \ , \tag{27}$$

where $\tilde{v}_{\rm Hx}(\mathbf{r}) = \delta\mathscr{E}_{\rm Hx}[n]/\delta n(\mathbf{r})|_N$ and

$$v^0_{\rm Hx} = \frac{\partial\mathscr{E}_{\rm Hx}[n]}{\partial N}\Big|_{\{\phi_i\}} - \int d\mathbf{r}\tilde{v}_{\rm Hx}(\mathbf{r})\bar{n}_h(\mathbf{r}). \tag{28}$$

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 Eq. (11) can be conveniently broken down into its individual Hartree-like and Fock-like contributions as follows [23]

$$\mathscr{E}_{\rm Hx} = \frac{1}{2}\sum_{ij}\left\{\left[F^S_{ij}+F^D_{ij}\right](ii|jj) - F^S_{ij}(ij|ji)\right\} \ , \tag{29}$$

where

$$(ij|kl) \equiv \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\phi^*_i(\mathbf{r})\phi_j(\mathbf{r})\phi^*_k(\mathbf{r}')\phi_l(\mathbf{r}') \ . \tag{30}$$

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,[23] we find

$$F^S_{ij} = \sum_\sigma f^{(2)}_{i\sigma,j\sigma}, \qquad F^D_{ij} = \sum_\sigma f^{(2)}_{i\sigma,j\bar{\sigma}}, \tag{31}$$

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

$$f^{(2)}_{i\sigma,j\sigma'} = \sum_\kappa w_\kappa \theta^\kappa_{i\sigma}\theta^\kappa_{j\sigma'} \ . \tag{32}$$

The quantities defined in Eq. (31) are the pair-density equivalent of $f_i = \sum_{\kappa\sigma} w_\kappa\theta^\kappa_{i\sigma}$. Thus the energy depends on the statistical probability (across the ensemble) of finding orbitals $i\sigma$ and $j\sigma'$ occupied simultaneously. Note that for closed-shell systems with non-degenerate ground states ($w_0=1$), we recover the 'Hx' energy expressed in terms of the usual Hartree and exchange energies of regular DFT.

From Eq. (29), we get

$$\tilde{v}_{\rm Hx}(\mathbf{r}) = \frac{1}{2}\sum_{ij}(F^S_{ij}+F^D_{ij})v_{(ii|jj)}(\mathbf{r}) - F^S_{ij}v_{(ij|ji)}(\mathbf{r}). \tag{33}$$

where

$$v_{(ik|jl)}(\mathbf{r}) = \frac{\delta(ik|jl)}{\delta n(\mathbf{r})}\Big|_N \ , \tag{34}$$

where these potentials can be determined by numerically solving the optimised-effective-potential (OEP) equations,[60]

$$\int d\mathbf{r}' v_{(ik|jl)}(\mathbf{r}')\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_I \int d\mathbf{r}' \frac{\delta(ik|jl)}{\delta\phi_I(\mathbf{r}')}\frac{\delta\phi_I(\mathbf{r}')}{\delta v_s(\mathbf{r})} \ , \tag{35}$$

where we have assumed real-valued orbitals.

Unlike its general values, the $r\to\infty$ asymptotic behaviour of $\tilde{v}_{\rm Hx}(\mathbf{r})$ can be found analytically in finite systems. Following Kreibich *et al.*[61] and Della Sala and Görling[56], we obtain

$$\sum_h f_h\phi_h(\mathbf{r})^2\tilde{v}_{\rm Hx}(\mathbf{r}) \underset{r\to\infty}{\sim} \sum_h \phi_h(\mathbf{r})\frac{\delta\mathscr{E}_{\rm Hx}}{\delta\phi_h(\mathbf{r})} \ . \tag{36}$$

Note that both sides depend only on $r=|\mathbf{r}|$ 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 $\tilde{v}_{\rm Hx}(\mathbf{r})$ through Eq. (36), we use Eq. (29) for $\mathscr{E}_{\rm Hx}$, noting that we can easily take derivatives with respect to orbitals. To begin, it is straightforward to show that

$$\frac{\delta(ii|jj)}{\delta\phi_h(\mathbf{r})} = \delta_{ih}\phi_i(\mathbf{r})\int\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r}')\phi_j(\mathbf{r}') + \{i\leftrightarrow j\} \tag{37}$$

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

$$\frac{\delta(ij|ji)}{\delta\phi_h(\mathbf{r})} = \delta_{ih}\phi_j(\mathbf{r})\int\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}')\phi_j(\mathbf{r}') + \{i\leftrightarrow j\}. \tag{38}$$

For large r, we can write $1/|\mathbf{r}-\mathbf{r}'| \approx 1/r$ and exploit the orthonormality of the orbitals to get

$$\frac{\delta(ii|jj)}{\delta\phi_h(\mathbf{r})} \underset{r\to\infty}{\sim} \frac{(\delta_{ih}+\delta_{jh})\phi_h(\mathbf{r})}{r}\,, \tag{39}$$

$$\frac{\delta(ij|ji)}{\delta\phi_h(\mathbf{r})} \underset{r\to\infty}{\sim} \frac{\delta_{ij}(\delta_{ih}+\delta_{jh})\phi_h(\mathbf{r})}{r}\,. \tag{40}$$

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

$$\begin{aligned}\sum_h \phi_h(\mathbf{r})\frac{\delta\mathscr{E}_{\rm Hx}}{\delta\phi_h(\mathbf{r})} =& \frac{1}{2}\sum_h \phi_h(\mathbf{r})^2 \sum_{ij} \\ &\times\left\{(F^S_{ij}+F^D_{ij})\frac{(\delta_{ih}+\delta_{jh})}{r} - F^S_{ij}\frac{\delta_{ij}(\delta_{ih}+\delta_{jh})}{r}\right\} \\ =& \frac{1}{r}\sum_h \phi_h(\mathbf{r})^2\left[\sum_j (F^S_{jh}+F^D_{jh}) - F^S_{hh}\right]\,. \end{aligned} \tag{41}$$

Finally, we conclude that

$$\tilde{v}_{\rm Hx}(\mathbf{r}) \underset{r\to\infty}{\sim} \frac{-Z_{\infty,{\rm Hx}}}{r} \tag{42}$$

with the effective charge

$$Z_{\infty,{\rm Hx}} = \frac{\sum_h F^S_{hh} - \sum_{jh}(F^S_{jh}+F^D_{jh})}{\sum_h f_h} \le 0 \tag{43}$$

where we have accounted for symmetries.[62] It is easily shown, as done explicitly later, that for an integer number of electrons $N=M$, this gives $Z_{\infty,{\rm Hx}} = 1-M$, as expected. Not so in general.

Similarly, the correlation potential can be decomposed as

$$v_{\rm c}(\mathbf{r}) = \tilde{v}_{\rm c}(\mathbf{r}) + v^0_{\rm c}\,, \tag{44}$$

and the asymptotic behaviour of $v_{\rm c}(\mathbf{r})$ is found from eqs (22) and (24) by simply using $v_{\rm c}(\mathbf{r}) = v_{\rm Hxc}(\mathbf{r}) - v_{\rm Hx}(\mathbf{r})$. We readily arrive at

$$Z_{\infty,{\rm c}} = 1 - \lceil N\rceil - Z_{\infty,{\rm Hx}}, \qquad v^0_{\rm c} = -v^0_{\rm Hx}. \tag{45}$$

The above analysis *does not tell us whether or not* $v^0_{Hx}=0$, however. In the next section we will be able to determine numerically that, in general, the *exact* $v^0_{\rm Hx}$ 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 $w_{\kappa=0}=1$. For this state, $\theta^{\kappa=0}_{i\sigma}=1$ for $i\le h = M/2$ and zero otherwise. Therefore, $f_i = \sum_\sigma \theta_{i\sigma} = 2$ for all occupied states $i\le h$. Similarly, $F^S_{ij} = F^D_{ij} = 2$. Then, from (43) we obtain

$$Z^M_{\infty,{\rm Hx}}({\rm pure}) = \frac{2-\sum_{j=1}^{M/2} 4}{2} = 1-M, \tag{46}$$

for the potential. This is the usual result[60], i.e. $v_{\rm ext}(\mathbf{r}) + v_{\rm Hx}(\mathbf{r}) \sim -(Z+1-M)/r$ 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 $Z^M_{\infty,{\rm c}}({\rm pure}) = 0$.

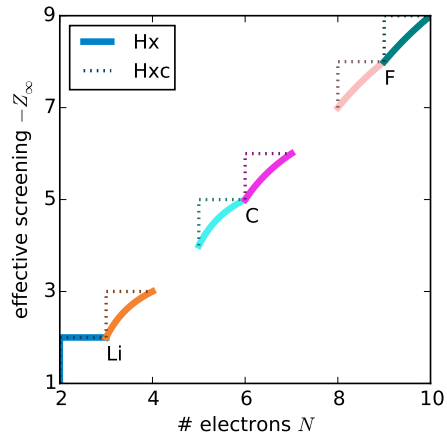

Figure 1 $Z_{\infty,{\rm Hx}}$ and $Z_{\infty,{\rm Hxc}}$ versus N for all the systems (Li, C, and F ions) considered in this work.

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

$$\begin{aligned} Z_{\infty,{\rm Hx}} =& \frac{\sum_{\kappa\sigma} w_\kappa \sum_h \theta^\kappa_{h\sigma}\theta^\kappa_{h\sigma} - \sum_{\kappa\sigma\sigma'} w_\kappa \sum_{hj} \theta^\kappa_{h\sigma}\theta^\kappa_{j\sigma'}}{\sum_h f_h} \\ =& 1 - \frac{\sum_{\kappa h\sigma} w_\kappa \theta^\kappa_{h\sigma} N^\kappa}{\sum_h f_h}, \end{aligned} \tag{47}$$

where we used $\theta^\kappa_{h\sigma}\theta^\kappa_{h\sigma} = \theta^\kappa_{h\sigma}$, $\sum_{\kappa\sigma} w_\kappa \theta^\kappa_{h\sigma} = f_h$, and defined $N^\kappa \equiv \sum_{j\sigma'} \theta^\kappa_{j\sigma'}$ to be the number of electrons in state κ. Eq. (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 $N^\kappa = M$ in all members, and we get the simple expression

$$Z^M_{\infty,{\rm Hx}}({\rm ensemble}) = 1 - \frac{\sum_{\kappa h\sigma} w_\kappa \theta^\kappa_{h\sigma} M}{\sum_h f_h} = 1 - M \equiv 1 - \lceil N\rceil, \tag{48}$$

and $Z^M_{\infty,{\rm c}}({\rm ensemble}) = 0$.

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

$$Z_{\infty,{\rm Hx}}(2 < N \le 3) = -2 = 1-(M+1) \equiv 1 - \lceil N\rceil, \tag{49}$$

which is the same as for $Z_{\infty,s}$, making $Z_{\infty,{\rm c}}(2<N\le 3) = 0$.

It may be tempting to think that the result $Z^N_{\infty,{\rm Hx}} = 1 - \lceil N\rceil$ holds in general. However, let us now consider a system with $N = 3+c$ electrons. This has states $\kappa \in$

$\{1s^2 2s^\uparrow, 1s^2 2s^\downarrow, 1s^2 2s^2\}$ with weights $w_\kappa \in \{(1-c)/2, (1-c)/2, c\}$ which leads, after some work, to

$$Z_{\infty,\mathrm{Hx}}(3 \leq N \leq 4) = \frac{-2(2N-5)}{N-2}. \tag{50}$$

Here, $Z_{\infty,\mathrm{Hx}} = 1 - \lceil N \rceil$ 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

$$Z_{\infty,\mathrm{Hx}}(5 \leq N \leq 6) = \frac{-2(3N-13)}{N-4}, \tag{51}$$

$$Z_{\infty,\mathrm{Hx}}(6 \leq N \leq 7) = \frac{-2(4N-19)}{N-4}, \tag{52}$$

for fractional ions of C, and

$$Z_{\infty,\mathrm{Hx}}(8 \leq N \leq 9) = \frac{-4(3N-17)}{N-4}, \tag{53}$$

$$Z_{\infty,\mathrm{Hx}}(9 \leq N \leq 10) = \frac{-4(7N-43)}{N-4}, \tag{54}$$

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^{-c}, where the denominator is $N-2$ reflecting the exclusion of two core electrons.

Finally, we observe that eqs. (49)-(54) all have the same form, namely $Z_{\infty,\mathrm{Hx}} = \frac{AN-B}{N-N_{\mathrm{core}}}$, 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 Eq. (47) depend linearly on the ensemble weights w_κ, and thus linearly on N. The denominator comes from $\sum_h f_h = N - N_{\mathrm{core}}$. 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 $M \geq N_{\mathrm{core}}$ electrons in a degenerate equi-ensemble ground-state, one obtains,

$$Z_{\infty,\mathrm{Hx}}(N) = \frac{(N-1)N_{\mathrm{core}} + (M+1-2N)M}{N - N_{\mathrm{core}}}, \tag{55}$$

by ensuring that limiting cases are satisfied, i.e., $Z_{\infty,\mathrm{Hx}}(M) = 1-M$ and $Z_{\infty,\mathrm{Hx}}(M+1) = -M$ for $M > N_{\mathrm{core}}$, or $Z_{\infty,\mathrm{Hx}}(M+1) = -M$ and $dZ_{\infty,\mathrm{Hx}}(M+1)/dN = 0$ for $M = N_{\mathrm{core}}$. It is easily seen by substitution that Eq. (55) covers all previous expressions.

The values for $Z_{\infty,\mathrm{Hx}}$ and $Z_{\infty,\mathrm{Hxc}}$ are shown in Figure 1 for the systems considered here. Note that $Z_{\infty,\mathrm{Hx}}$ is continuous at most (but not all) integer electron numbers. It always takes the "typical" value for N integer. By contrast, $\partial Z_{\infty,\mathrm{Hx}}/\partial N$ is discontinuous at integer electron numbers. As the *combined* contributions of the Hx and c potentials give $Z_{\infty,\mathrm{Hxc}} = 1 - \lceil N \rceil$, the non piecewise constant behavior of $Z_{\infty,\mathrm{Hx}}$ points, in turn, to a strong non-local functional dependence on the density in the remainder correlation potential. This leads to $Z_{\infty,\mathrm{c}} \neq 0$ 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 $Z_{\infty,s} = Z + 1 - \lceil N \rceil$ can be interpreted as the outermost orbital feeling a nuclear potential that is screened by electrostatic repulsion from the remaining $\lceil N \rceil - 1$ 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[63], 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.*[64]

Typically, we expect the Hx potential to be self-interaction free, meaning it is responsible for the $1 - \lceil N \rceil$ 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 Hx in the other fractional cases mentioned*. It must therefore be compensated for by the c potential.

We conclude that, in general, $Z_{\infty,\mathrm{Hx}} \neq Z_{\infty,\mathrm{Hxc}}$ and the ensemble Hx 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* Hx potential requires a careful revisiting in EDFT.

IV. Numerical results

In this section, we complete our analysis with numerical results obtained for the exact $v_{\mathrm{Hxc}}(\mathbf{r})$, $v_{\mathrm{Hx}}(\mathbf{r})$, and $v_{\mathrm{c}}(\mathbf{r})$. The exact KS potentials $v_s(\mathbf{r})$ (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 ($r \to 0$) and asymptotic ($r \to \infty$) behaviours. The same grid is used for radial quadrature, derivatives, orbitals, and Green functions (which are used directly and in χ_0).

Orbitals $\{\phi_k\}$ 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 Refs. [23, 65].

A. Outline of the procedure

In order to calculate the potential $v_{\mathrm{Hx}}(\mathbf{r})$ [and thus, by difference, $v_{\mathrm{c}}(\mathbf{r})$], we need to solve Eq. (35). This equation involves the KS linear-response function

$$\chi_0(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} \tag{56}$$

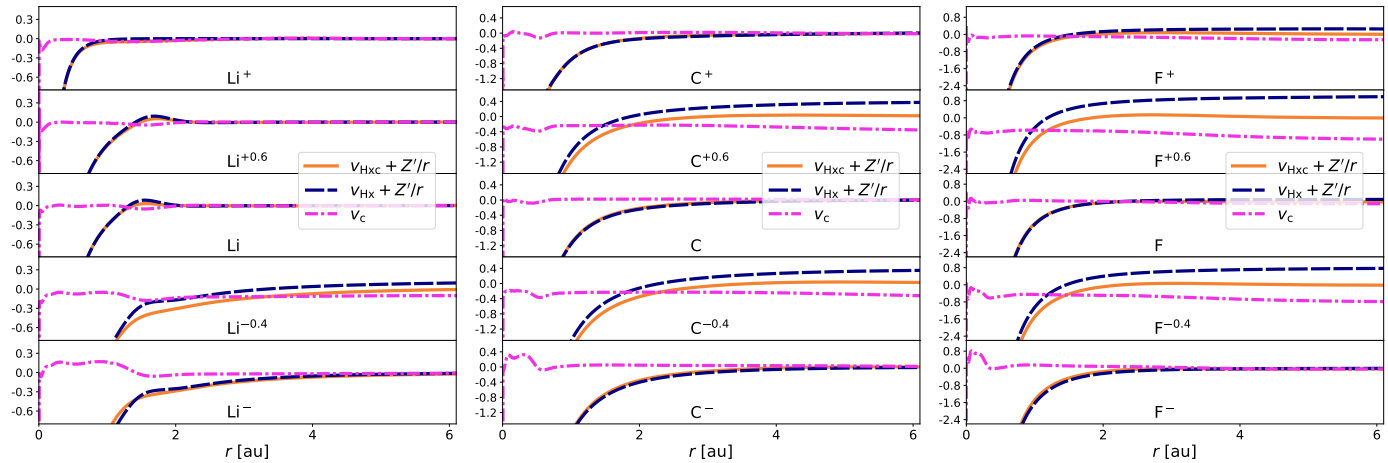

Figure 2 Hxc (orange solid line), Hx (navy dashed line), and c (magenta dash–dot line) potentials (with the electron number derivative contribution) for selected ions of Li (left), C (centre), and F (right). The Hx and Hxc potentials are shown as $v+Z'/r \equiv v+(1-\lceil N \rceil)/r$ to allow direct 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.

and the associated Greens functions

$$G_i(\mathbf{r},\mathbf{r}') = \sum_{j,\varepsilon_j \neq \varepsilon_i} \frac{\rho_j(\mathbf{r},\mathbf{r}')}{(\varepsilon_i - \varepsilon_j)} \tag{57}$$

where $\rho_i(\mathbf{r},\mathbf{r}') = \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$, such that $\chi_0(\mathbf{r},\mathbf{r}') = 2\sum_i f_i G_i(\mathbf{r}',\mathbf{r})\rho_i(\mathbf{r},\mathbf{r}')$. Therefore, we can rewrite Eq. (35), as follows

$$\int d\mathbf{r}' \chi_0(\mathbf{r},\mathbf{r}')\tilde{v}_{\mathrm{Hx}}(\mathbf{r}') = d_{\mathrm{Hx}}(\mathbf{r}) \tag{58}$$

where

$$d_{\mathrm{Hx}}(\mathbf{r}) = \sum_k \int d\mathbf{r}' G_k(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r}) \frac{\delta \mathscr{E}_{\mathrm{Hx}}}{\delta \phi_k(\mathbf{r})} \,. \tag{59}$$

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_{Hx}.[66] 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 $v_s(\mathbf{r})$ that correspond to some given KS orbitals and orbital energies – those which are obtained from the KS inversion on exact QMC densities.[32]

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 known to be correct in the asymptotic limit, and generally good elsewhere. We the follow Yang and Wu [67] and introduce a basis set to represent the difference between the real OEP, and the KLI one. That is, we seek to find values for $\{c_b\}$, in

$$\tilde{v}_{\mathrm{Hx}}(r) = \tilde{v}_{\mathrm{Hx,KLI}}(r) + \sum_b c_b \xi_b(r), \tag{60}$$

where $\xi_b(r)$ are a set of basis functions that depend only on $r = |\mathbf{r}|$ due to the spherical symmetry. To determine the coefficients $\{c_b\}$, we use Eq. (60) in Eqs (58) and (59), then integrate over $\{\xi_b\}$ to give the matrix equation:

$$c_b = \sum_{b'} [A^{-1}]_{bb'} X_{b'} \,, \tag{61}$$

where,

$$A_{bb'} = \int 4\pi r^2 dr \; 4\pi r'^2 dr' \; \xi_b(r)\chi_0(r,r')\xi_{b'}(r') \,, \tag{62}$$

$$X_b = \int 4\pi r^2 dr \; \xi_b(r)\Delta d_{\mathrm{Hx}}(r) \,, \tag{63}$$

and $\Delta d_{\mathrm{Hx}}(r) = d_{\mathrm{Hx}}(r) - \int 4\pi r'^2 dr' \chi_0(r,r')\tilde{v}_{\mathrm{Hx,KLI}}(r')$. Again, we take advanatge 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.

B. 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.[68]

In Figure 2 we present components of the potentials for atoms, anions, and cations, at $N \in \{Z-1, Z-0.6, Z, Z+$

Table I Asymptotic potential constant $v^0_{\rm Hx}$ in Ha, and its contributions $\partial\mathscr{E}_{\rm Hx}/\partial N$ and $\langle\tilde{v}_{\rm Hx,KLI}\rangle_h = \int d\mathbf{r}\tilde{v}_{\rm Hx,KLI}(\mathbf{r})\bar{n}_h(\mathbf{r})$ using Eq. (28). We use $\tilde{v}_{\rm Hx,KLI}$ as a proxy for $\tilde{v}_{\rm Hx}$ to avoid spurious constants (see Appendix B). Errors from the KLI approximation are expected to be just a few mHa.

System	N	$\partial\mathscr{E}_{\rm Hx}/\partial N$	$\langle\tilde{v}_{\rm Hx,KLI}\rangle_h$	$v^0_{\rm Hx}$
Li^+	2	1.650	1.650	0.000
$Li^{+0.6}$	2.4	0.645	0.645	0.000
Li	3	0.645	0.645	0.000
$Li^{-0.4}$	3.4	0.720	0.673	0.047
Li^-	4	0.669	0.669	0.000
C^+	5	2.837	2.837	0.000
$C^{+0.6}$	5.4	3.125	2.998	0.127
C	6	3.013	3.013	0.000
$C^{-0.4}$	6.4	3.110	2.981	0.129
C^-	7	2.938	2.938	0.000
F^+	8	7.214	7.086	0.129
$F^{+0.6}$	8.4	7.637	7.283	0.353
F	9	7.402	7.357	0.045
$F^{-0.4}$	9.4	7.589	7.320	0.269
F^-	10	7.270	7.270	0.000

$0.4, Z+1\}$, to illustrate the asymptotics of each term. Values for $v^0_{\rm Hx}$, and related quantities, are reported in Table I.

The numerical results also confirm that, for non-integer electron numbers ($c \neq 0$), the potential from the ensemble Hx energy functional defined here does not follow the asymptotic behavior of the Hxc potential given in Eq. (26), except in limited cases (e.g., $Li^{(1-c)+}$). Thus, at the Hx level, the outermost orbital spuriously "feels" its own field since $Z_{\infty,\rm Hx} \neq 1 - \lceil N \rceil$, e.g. $Z_{\infty,\rm Hx} = -2(2N-5)/(N-2) \neq 3$ for Li^{c-} with $0 < c < 1$ and $N = 3 + c$. This means that the Hx potential cannot be regarded as self-interaction free. Its effect is manifested in the asymptotic behaviour of $v_{\rm c}$, which decays more rapidly than $1/r$ when $v_{\rm Hx}$ is self-interaction free, and as $-Z_{\infty,\rm c}/r$ otherwise.

We see that the asymptotic constant $v^0_{\rm Hx}$ is zero for both Li and C at integer electron numbers. But for F – surprisingly – it is zero only in the closed-shell case $N = 10$ (F^-). $v^0_{\rm Hx}$ is also quite significant in most partial ions, but this is less surprising given the asymptotic self-interaction contribution in those systems. 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 $F^D_{hh'} = 0$ in the lower channel but $F^D_{hh'} \neq 0$ in the upper channel, e.g. in Eq. (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 netural and fully anionic O (not studied here because high-quality reference densities[32, 33] 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 $v_{\rm c}(\mathbf{r})$ 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 $v_{\rm c}(\mathbf{r})$ 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 $v_{\rm c}(\mathbf{r})$ 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[33]. It is therefore outside the scope of this work.

V. 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 [Eq. (22) and Eq. (28)]; and 2) the effective charge "felt" by the outermost electron can imply a self interaction for the frontier orbitals [Eq. (43)], at a fractional number of electrons. This conclusion is contrary to the common wisdom that exact exchange is always one-electron self-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.

Acknowledgements

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Appendix

A. Basis functions for the potential

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

$$\left\{\frac{n_k(r)}{n(r)}\right\}_{k<h}, \qquad \left\{\int \frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho_{kk'}(r')\right\}_{k,k'}, \tag{A1}$$

that comprise terms that enter into the KLI potential. Here $n_k(r) = \sum_m |\phi_{n_k l_k m}(\mathbf{r})|^2$ and $\rho_{kk'}(r) = \delta_{l_k l_{k'}} \sum_m \phi_{n_k l_k m}(r)\phi_{n_{k'} l_k m}(r)$ 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 $\xi_1(r) = n_{1s}(r)/n(r)$, $\xi_2(r) = \int d\mathbf{r}'\rho_{1s1s}(r')/|\mathbf{r}-\mathbf{r}'|$, $\xi_3(r) = \int d\mathbf{r}'\rho_{1s2s}(r')/|\mathbf{r}-\mathbf{r}'|$ and $\xi_4(r) = \int d\mathbf{r}'\rho_{2s2s}(r')/|\mathbf{r}-\mathbf{r}'|$ for Li and its ions.

The orbital-derived basis in Eq. (A1) is then augmented by a set of Gaussian functions $\{e^{-\zeta_k r^2}\}$ for $k \in \{1,\ldots,N_{\text{Aug}}\}$ to capture details missed by the orbital-derived functions. In our calculations we use 16 augmenting functions. Thus, e.g., $\xi_5(r) = e^{-\zeta_1 r^2},\ldots,\xi_{20}(r) = e^{-\zeta_{16} r^2}$ 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 nucleus ($r \ll Z^{-1/3}$) are imperfect, however. Fortunately they are also unimportant given the dominance of the nuclear potential $-Z/r$ over $v_{\text{Hxc}}(r)$ for small r. We thus exclude them from most of our plots in Sec. IV

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 $\tilde{v}_{\text{Hx}}(r)$, 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 χ_0^{-1} for meaningful numerical results.

In the case of an exact inversion, this is not a problem. However, in our calculations we expand χ_0^{-1} on a *finite basis*. In some cases this basis truncation leads to an effective pseudo-constant shift in the potential, when compared to the asymptotically decaying and otherwise similar KLI potential $v_{\text{Hx,KLI}}(r)$. That is, we find

$$v_{\text{Hx}}(r) = v_{\text{Hx,KLI}}(r) + \Delta v_{\text{Hx}}(r) + Ch(r) \tag{B1}$$

where $\Delta v_{\text{Hx}}(r)$ 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 $h(r)$ obeying $h(r < r_c) \approx 1$ and $h(r > r_c) \approx 0$. When this error is present, the density at the cutoff radius r_c is typically $n(r_c) \approx 10^{-12}$, meaning that $\int d\mathbf{r} n(r) h(r) \approx N$ and $\int d\mathbf{r} n_i(r) h(r) \approx 1$ 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 $\langle \tilde{v}_{\text{Hx}} \rangle_h$ in the anomalous cases, and virtually no changes to $\langle \tilde{v}_{\text{Hx}} \rangle_h$ in cases when it is close in value to $\langle \tilde{v}_{\text{Hx,KLI}} \rangle_h$.

Unfortunately, the presence of $Ch(r)$ can make analysis difficult in cases where we requires $\tilde{v}_{\text{Hx}}(r)$, since it introduces an uncontrolled (and physically meaningless) "gauge". To ensure reasonable results for all systems we thus add a correction

$$C' = \int d\mathbf{r} \bar{n}_h(r) [\tilde{v}_{\text{Hx,KLI}}(r) - \tilde{v}_{\text{Hx}}(r)] \approx -C \tag{B2}$$

to our potentials to avoid the spurious pseudo-constant, i.e. C' determined above cancels $Ch(r)$ in the region where it causes problems. In cases where we need $\langle \tilde{v}_{\text{Hx}} \rangle_h = \int d\mathbf{r} \bar{n}_h(r) \tilde{v}_{\text{Hx}}(r)$ this is equivalent to replacing $\tilde{v}_{\text{Hx}}(r)$ by $\tilde{v}_{\text{Hx,KLI}}(r)$ inside the average.

The effect of the correction C' can be tested on "good" cases where no shift is apparent. These case suggest that $\langle \tilde{v}_{\text{Hx}} \rangle_h$ differs from $\langle \tilde{v}_{\text{Hx,KLI}} \rangle_h$ 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 $v_{\text{Hx}}(r) = \tilde{v}_{\text{Hx}}(r) + v^0_{\text{Hx}}$, the pseudo-constant does not make any difference at all to final results as C it is cancelled out through the term $-\int d\mathbf{r} n_h(r) \tilde{v}_{\text{Hx}}(r)$ in v^0_{Hx} (at least in the region $r < r_c$ of interest).

We note that it might be possible to obtain v^0_{Hx} more directly, by using relationships between Kohn-Sham and Hartree-Fock quantities.[58, 69] However, this requires further scrutiny in the case of using the *exact* (as done here), rather than OEP (as done previously), orbitals in v_{Hx}; 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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