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The flexible nature of exchange, correlation, and Hartree physics: Resolving “delocalization” errors in a “correlation free” density functional

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By exploiting freedoms in the definitions of “correlation,” “exchange,” and “Hartree” physics in ensemble systems, we better generalise the notion of “exact exchange” (EXX) to systems with fractional occupations of the frontier orbitals, arising in the dissociation limit of some molecules. We introduce the linear EXX (“LEXX”) theory whose pair distribution and energy are explicitly *piecewise linear* in the occupations f_i^σ . We provide explicit expressions for these functions for frontier s and p shells. Used in an optimised effective potential (OEP) approach the LEXX yields energies bounded by the piecewise linear “ensemble EXX” (EEXX) energy and standard fractional optimised EXX energy: $E^{\text{EEXX}} \leq E^{\text{LEXX}} \leq E^{\text{EXX}}$. Analysis of the LEXX explains the success of standard OEP methods for diatoms at large spacing, and why they can fail when both spins are allowed to be non-integer so that “ghost” Hartree interactions appear between *opposite* spin electrons in the usual formula. The energy E^{LEXX} contains a cancellation term for the spin ghost case. It is evaluated for H, Li, and Na fractional ions with clear derivative discontinuities for all cases. The p -shell form reproduces accurate correlation-free energies of B-F and Al-Cl. We further test LEXX plus correlation energy calculations on fractional ions of C and F and again we find both derivative discontinuities and good agreement with exact results. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773284>]

I. INTRODUCTION

Following initial work by Yang and co-workers¹⁻⁴ on non-interacting ensembles⁵ with spin-resolved fractional occupancy, much consideration has been given to the behaviour of density functional theory (DFT) under the Kohn-Sham (KS) prescription,⁶ and its various common approximations (e.g., local-density approximation,⁶ generalized gradient approximations,⁷ Becke-like,⁸ optimised effective potential (OEP)⁹) in such ensembles. Many attempts have been made to understand and deal with the issues that arise in ensembles (see, e.g., Refs. 10–12), with variable success. We will show that, in such systems, the notion of “correlation” physics becomes intertwined with “exchange” and “Hartree” physics in the usual prescription, with (improvable) consequences for common approximations.

Let us begin by considering, quite generally, the nature of “electron correlation” and “electron exchange” in a non-ensemble system. The usual expression for the groundstate correlation energy can be written as

$$E_c = \langle \Psi | \hat{H} | \Psi \rangle - \langle \Psi^T | \hat{H} | \Psi^T \rangle, \quad (1)$$

where \hat{H} is the Hamiltonian of a many-electron system, $|\Psi\rangle$ is its groundstate wavefunction, and $|\Psi^T\rangle$ is some approximation to the wavefunction (by the variational principle, correlation, energy is never positive). Thus correlation is not an intrinsic property of the system, but a property of the chosen trial wavefunction. In standard OEP approaches,⁹ including KS DFT, $|\Psi^T\rangle$ takes the form of a single Hartree-Fock (HF) like Slater determinant which is constructed from one-particle orbitals $|\sigma\rangle$ evaluated in a *common* one-particle Hamiltonian $\hat{h} = \hat{t} + \hat{V}^{13}$ where $\hat{t} \equiv -\frac{1}{2}\nabla^2$

and $\hat{V} \equiv V_\sigma(\mathbf{r})$. We can now define the exchange energy $E_x = \langle \Psi^T | \hat{H} | \Psi^T \rangle - \bar{E}$ and the “naive Hartree” energy of the system¹⁴ $\bar{E} = \sum_{i\sigma} \langle i\sigma | \hat{t} + \hat{V}_{\text{Ext}} | i\sigma \rangle + \frac{1}{2} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r})n(\mathbf{r}')$. Here, $n(\mathbf{r}) = \langle \Psi^T | \hat{n}(\mathbf{r}) | \Psi^T \rangle = \sum_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2$ [where $\hat{n}(\mathbf{r})$ is the electron number density operator and $\phi_{i\sigma}(\mathbf{r}) = \langle \mathbf{r} | i\sigma \rangle$] and $\hat{V}_{\text{Ext}} \equiv V_{\text{Ext}}(\mathbf{r})$ is the external potential. The groundstate energy is thus $E = \bar{E} + E_x + E_c$ where the partitioning depends on both the choice of \bar{E} and $|\Psi^T\rangle$.

This can be extended into ensembles by replacing projections on wavefunctions $O = \langle \Psi | \hat{O} | \Psi \rangle$ by traces on density matrices $O = \text{Tr}[\hat{\rho} \hat{O}]$ (where operators act appropriately for any number of electrons) and by summing \bar{E} over ensemble members. The density matrix $\hat{\rho}$ is defined as

$$\hat{\rho} = \sum_{\mathcal{E}} w_{\mathcal{E}} |\Phi_{\mathcal{E}}\rangle \langle \Phi_{\mathcal{E}}|, \quad (2)$$

where $0 \leq w_{\mathcal{E}} \leq 1$ is the weight of member \mathcal{E} with wavefunction $|\Phi_{\mathcal{E}}\rangle$ and $\sum_{\mathcal{E}} w_{\mathcal{E}} = 1$. Minimisations can then be carried out over $\hat{\rho}$ rather than $|\Phi\rangle$.

II. EXACT EXCHANGE APPROACHES

We can now succinctly define the standard “exact exchange” (EXX) functional approach. Here we consider only $E^{\text{EXX}} = \bar{E} + E_x$ with E_c assumed to be zero. Investigations into EXX in fractionally occupied ensemble systems^{2,15-17} show both successes and shortcomings (discussed in more detail later). In all these works, the Hartree and exchange energy takes the “standard” form, *bilinear* in the occupations f_i^σ ,

$$E_{\text{Hx}}^S = \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} \sum_{i\sigma j\sigma'} f_i^\sigma f_j^{\sigma'} [P_{i\sigma j\sigma'} - \delta_{\sigma\sigma'} Q_{i\sigma j\sigma'}], \quad (3)$$

where $P_{i\sigma j\sigma'} = |\phi_{i\sigma}(\mathbf{r})|^2 |\phi_{j\sigma'}(\mathbf{r}')|^2$ and $Q_{i\sigma j\sigma'} = \phi_{i\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}') \phi_{j\sigma'}^*(\mathbf{r}) \phi_{j\sigma'}(\mathbf{r}')$. Here, the negative exchange term cancels the unphysical positive Hartree interaction of each spin orbital $|i\sigma\rangle$ with itself. However, if two different orbitals of the same spin are partly occupied ($0 < f_i^\sigma, f_j^\sigma < 1$ with $i \neq j$), or if there is partial occupation of both spins in the same orbital ($0 < f_i^\uparrow, f_i^\downarrow < 1$), there is a corresponding cross-term in (3) that is not cancelled.

In a slightly different context Gidopoulos *et al.*¹⁸ call this spurious term the “ghost interaction” as it represents an unphysical interaction between orbitals in different *non-interacting* ensemble members. In the regular EXX energy expression (3), the ghost interaction appears in the Hartree and exchange energy terms involving pairs of orbitals in the frontier orbital. In a Kohn-Sham interpretation of the equivalent diatom problem, these interactions would be suppressed in the total energy via orthogonality of the degenerate groundstate wavefunctions. However, when one does not have the exact exchange-correlation functional, or as here neglects correlation, it can reappear, particularly when one does not properly account for the ensemble nature of the system.

We will argue that, in the ensemble interpretation of partial occupation,¹⁻³ this cross term should not be present, and its explicit removal results in an improved linear exact exchange (LEXX) approach which is correctly piecewise *linear*, not *bilinear*, in the occupation factors f . Here, defining $\theta_{i\mathcal{E}}^\sigma$ to be one for orbital $|i\sigma\rangle$ occupied in ensemble member \mathcal{E} and zero otherwise, we exploit the fact that the “ensemble occupancy” factor $f_i^\sigma = \langle \theta_i^\sigma \rangle_{\mathcal{E}} \equiv \sum_{\mathcal{E}} w_{\mathcal{E}} \theta_{i\mathcal{E}}^\sigma$ requires weights $w_{\mathcal{E}}$ that are piecewise linear in f_i^σ , from which it follows that $\langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_{\mathcal{E}} \equiv \sum_{\mathcal{E}} w_{\mathcal{E}} \theta_{i\mathcal{E}}^\sigma \theta_{j\mathcal{E}}^{\sigma'}$ is similarly piecewise linear. All energy terms are proportional to $\langle \theta_i^\sigma \rangle_{\mathcal{E}}$ or $\langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_{\mathcal{E}}$ and are thus piecewise linear. As will be discussed in more detail later this is equivalent, under an exchange approach, to finding a non-interacting ensemble of Slater determinants formed from a *common* set of orbitals produced in a *common* potential.

This allows the creation of simple functionals that avoid much of the “localization and delocalization error” of Yang *et al.*,¹⁻⁴ and the “many electron self-interaction error” of Perdew *et al.*¹⁹ In the present work, we focus on two illustrative cases: (i) a single partially occupied “frontier” orbital denoted “ h ” with $0 \leq f_h^\uparrow \leq 1$ and $0 \leq f_h^\downarrow \leq 1$; and (ii) open p shells with $f_h^\uparrow = f_h^\downarrow$. However, the scheme itself has wider applicability, including the full dissociation problem of molecules. Reference 18 might be considered another specific example of this approach, while Ref. 20 outlines a similar approach via HF for the restricted case of fractional occupation of a single spin (their ISSO approach).

A. Non-interacting “exchange” ensembles

To illustrate the general approach we consider, as an example, ensembles with total and spin-resolved electron number $N_t = N + f$ and $N_{\sigma} = N/2 + f^\sigma$ (N is even). The ground-state ensemble members and weights can be found by minimizing over density matrices subject to various constraints. However, for simple cases where energy ordering is obvious,

one can construct the ensemble more intuitively, just by demanding that a given set of occupations f_i^σ be reproduced. For example if the frontier orbital is non-degenerate (e.g., in an s shell), then the ensemble will be composed of up to three components. For $f \leq 1$, the ensemble is formed from f^\uparrow parts an $N + 1$ electron system with extra electron in \uparrow (short-hand $N + \uparrow$), f^\downarrow parts $N + \downarrow$ and $(1 - f)$ parts N where, because N is even, both spins are filled equally. For $f \geq 1$ the ensemble comprises $(1 - f^\downarrow)$ parts $N + \uparrow$, $(1 - f^\uparrow)$ parts $N + \downarrow$, and $(f - 1)$ parts $N + 2$.

The density matrix is composed of many-electron wavefunctions $|\Phi_{\mathcal{E}}\rangle$ and is

$$\hat{\rho}^f = \sum_{\mathcal{E}} w_{\mathcal{E}} |\Phi_{\mathcal{E}}\rangle \langle \Phi_{\mathcal{E}}|. \quad (4)$$

For the present case of a non-degenerate frontier orbital $w_{\mathcal{E}} \in \{1 - f, f^\uparrow, f^\downarrow\}$ and $\Phi_{\mathcal{E}} \in \{\Phi_N, \Phi_{N+\uparrow}, \Phi_{N+\downarrow}\}$ for $f \leq 1$, while $w_{\mathcal{E}} \in \{1 - f^\downarrow, 1 - f^\uparrow, f - 1\}$ and $\Phi_{\mathcal{E}} \in \{\Phi_{N+\uparrow}, \Phi_{N+\downarrow}, \Phi_{N+2}\}$ for $f > 1$. This leads to a total energy $E(f) = \text{Tr}[\hat{\rho}^f \hat{H}] = \sum_{\mathcal{E}} w_{\mathcal{E}} E[\Phi_{\mathcal{E}}]$ that obeys

$$E(f) = \begin{cases} f E_{N+1} + (1 - f) E_N, & 0 \leq f \leq 1 \\ (f - 1) E_{N+2} + (2 - f) E_{N+1}, & 1 < f \leq 2, \end{cases} \quad (5)$$

where E_N is the energy of an N -electron system (note that $E_{N+\uparrow} = E_{N+\downarrow} \equiv E_{N+1}$).

The LEXX is defined, in general, by assuming that the trial density matrix $\hat{\rho}^{fT}$ of the ensemble obeys the same relationship (4) but with the component wavefunctions $|\Phi_{\mathcal{E}}\rangle$ replaced by Hartree-Fock like determinants $|\Phi_{\mathcal{E}}^T\rangle$ constructed from a *single* set of spin-dependent orbitals $\{|i\sigma\rangle\}$. This trial density matrix: (i) reduces to the regular EXX for integer occupation, (ii) gives correct energies for H with less than one electron, split arbitrarily between spins, and (iii) is constructed from a single set of orbitals $|i\sigma\rangle$ evaluated in a common Hamiltonian, a requirement that ensures that OEP or KS methods can be used. Here, the orbitals are eigen-solutions $\hat{h}|i\sigma\rangle = \epsilon_{i\sigma}|i\sigma\rangle$ of a one-body Hamiltonian $\hat{h} = \hat{t} + \hat{V}$. We sort the orbitals so that $\epsilon_{i\sigma} \leq \epsilon_{j\sigma}$ for $i < j$. Taking the spin-resolved density $n_{\sigma}(\mathbf{r}) = \text{Tr}[\hat{\rho}^{fT} \hat{n}_{\sigma}(\mathbf{r})]$, one now finds

$$n_{\sigma}(\mathbf{r}) = \sum_i \langle \theta_i^\sigma \rangle_{\mathcal{E}} |\phi_{i\sigma}(\mathbf{r})|^2 \equiv \sum_i f_i^\sigma |\phi_{i\sigma}(\mathbf{r})|^2, \quad (6)$$

where typically $f_i^\sigma = 1$ for the inner orbitals and $f_h^\sigma = f^\sigma$ where $|h\sigma\rangle$ is the frontier orbital in the spin-shell with highest energy: which may or may not be occupied in both spins.

The EXX approximation ($E_c = 0$) allows us to use only the Hartree and exchange (Hx) components of the pair-density $n_{2\text{Hx}\sigma\sigma'} \equiv \text{Tr}[\hat{\rho}^{fT} \hat{n}_{\sigma}(\mathbf{r}) \hat{n}_{\sigma'}(\mathbf{r}')]]$ to evaluate the electronic groundstate. From the properties of HF wavefunctions, the pair-density of an ensemble can be written as

$$\begin{aligned} n_{2\text{Hx}\sigma\sigma'} &\equiv n_{2\text{H}\sigma\sigma'} + n_{2\text{x}\sigma\sigma'} \\ &= \sum_{ij} \langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_{\mathcal{E}} [P_{i\sigma j\sigma'} - \delta_{\sigma\sigma'} Q_{i\sigma j\sigma'}]. \end{aligned} \quad (7)$$

Finally, we can use (7) to calculate the energy via

$$E^{\text{LEXX}} = \sum_{\sigma} \int d\mathbf{r} [t_{\sigma}(\mathbf{r}) + n_{\sigma}(\mathbf{r}) V^{\text{Ext}}(\mathbf{r})] + \frac{1}{2} \sum_{\sigma\sigma'} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} n_{2\text{Hx}\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \quad (8)$$

$$\equiv \sum_{i\sigma} \langle \theta_i^{\sigma} \rangle_{\mathcal{E}} e_{i\sigma}^{(1)} + \sum_{i\sigma j\sigma'} \langle \theta_i^{\sigma} \theta_j^{\sigma'} \rangle_{\mathcal{E}} e_{i\sigma j\sigma'}^{(2)}, \quad (9)$$

where $t_{\sigma}(\mathbf{r}) = \sum_i \frac{\langle \theta_i^{\sigma} \rangle_{\mathcal{E}}}{2} |\nabla \phi_{i\sigma}(\mathbf{r})|^2$ and

$$e_{i\sigma}^{(1)} = \int d\mathbf{r} \left[\frac{1}{2} |\nabla \phi_{i\sigma}|^2 + V^{\text{Ext}} |\phi_{i\sigma}|^2 \right], \quad (10)$$

$$e_{i\sigma j\sigma'}^{(2)} = \frac{1}{2} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} [P_{i\sigma j\sigma'} - \delta_{\sigma\sigma'} Q_{i\sigma j\sigma'}]. \quad (11)$$

These energy expressions are perhaps the most general, and most important in this work, highlighting the importance of ensemble averages in the evaluation of average occupation and pair-occupation factors for groundstate energy calculations.

B. Fractional s shells

For the fractionally occupied s shells discussed here, detailed calculation shows that $\langle \theta_i^{\sigma} \theta_j^{\sigma'} \rangle_{\mathcal{E}} = \min[f_i^{\sigma}, f_j^{\sigma'}] - \delta_{i\bar{h}, j\bar{h}} \delta_{\sigma\bar{\sigma}'} C_U^h$ ($\bar{\sigma}$ is the opposite spin to σ and C_U^h is defined below). The Hartree and exchange components can be compactly written as

$$n_{2\text{H}\sigma\sigma'} = \sum_{ij} \min[f_i^{\sigma}, f_j^{\sigma'}] P_{i\sigma j\sigma'} - \delta_{\sigma\bar{\sigma}'} C_U^h P_{h\sigma h\bar{\sigma}}, \quad (12)$$

$$n_{2\text{x}\sigma\sigma'} = -\delta_{\sigma\sigma'} \sum_{ij} \min[f_i^{\sigma}, f_j^{\sigma'}] Q_{i\sigma j\sigma'}, \quad (13)$$

where we have chosen to split Hartree and exchange terms via P and Q . The term

$$C_U^h = \min[f^{\uparrow}, f^{\downarrow}, (1 - f^{\uparrow}), (1 - f^{\downarrow})] \quad (14)$$

removes spurious ‘‘ghost interactions’’ between electrons of unlike spin. For a zero to two electron system, Eqs. (12)–(14) are equivalent (after integration) to Eq. (7) of Ref. 4 sans the correlation energy term. This desirable outcome is a direct result of the ensemble averaging.

When either f^{\uparrow} or f^{\downarrow} is integer, $C_U^h = 0$ and $n_{2\text{Hx}\sigma\sigma'} \equiv \sum_{ij} f_i^{\sigma} f_j^{\sigma'} [P_{i\sigma j\sigma'} - \delta_{\sigma\sigma'} Q_{i\sigma j\sigma'}]$ since $P_{i\sigma i\sigma} = Q_{i\sigma i\sigma}$. Clearly, this is the form used in (3) and thus energies derived from (12) to (13) will be identical. We can now proffer an explanation for the variable success of the EXX for fractionally occupied ensembles. By violating the aufbau principle and/or allowing spins to vary in an unrestricted fashion, good results have been obtained for atoms and diatoms^{15,16} and systems with fractional occupancy.² In these works, only one spin was allowed to be non-integer so that $\langle \theta_h^{\sigma} \theta_h^{\sigma'} \rangle_{\mathcal{E}} = f_h^{\sigma} f_h^{\sigma'}$ and the EXX and LEXX energies were equivalent. In systems where both spins were fractionally occupied (e.g., Refs. 15 and 17), the EXX failed to reproduce the correct derivative discontinuity. In these works $f^{\uparrow} = f^{\downarrow} = f/2$ and $\langle \theta_h^{\sigma} \theta_h^{\sigma'} \rangle_{\mathcal{E}} \neq f_h^{\sigma} f_h^{\sigma'}$. Thus

the EXX and LEXX energies differed. We show later that, in this case, the LEXX is guaranteed to produce a lower energy.

C. Fractional p shells

As a less trivial example, we also consider the case of degenerate frontier p orbitals with equal densities in each spin. Here, we must sum not only over ensemble members of different electron number but also over the degenerate combinations of p_x , p_y , and p_z orbitals. For example, in an isolated carbon atom each ensemble member has fully occupied $1s$ and $2s$ shells, but only two occupied $2p$ orbitals of the same spin σ which we denote $p_{\gamma\sigma}$ and $p_{\delta\sigma}$ where $\gamma \neq \delta$ and $\gamma, \delta \in \{x, y, z\}$. To find the equal-spin, spherically symmetric ensemble we weight each ensemble member equally so that $w_{p_{\gamma}p_{\delta}\sigma} = \frac{1}{6}$ for all six combinations of $\gamma \neq \delta$ and σ . In member $p_{\gamma}p_{\delta}\sigma$, we set $\theta_{2p, p_{\gamma}}^{\sigma} = \theta_{2p, p_{\delta}}^{\sigma} = 1$ while the remaining $2p$ orbital with spin σ , and all $2p$ orbitals with spin $\bar{\sigma}$ have zero occupation. Averaging over all cases gives $\langle \theta_{2p, p_{\gamma}}^{\sigma} \rangle_{\mathcal{E}} = \frac{1}{3}$ as expected, while $\langle \theta_{2p, p_{\gamma}}^{\sigma} \theta_{2p, p_{\delta}}^{\sigma} \rangle_{\mathcal{E}} = \frac{1}{3}$, $\langle \theta_{2p, p_{\gamma}}^{\sigma} \theta_{2p, p_{\delta}}^{\bar{\sigma}} \rangle_{\mathcal{E}} = \frac{1}{6}$ for $\gamma \neq \delta$ and $\langle \theta_{2p, p_{\gamma}}^{\sigma} \theta_{2p, p_{\delta}}^{\bar{\sigma}} \rangle_{\mathcal{E}} = 0$.

For general unfilled frontier p shells, this yields an additional like-spin correction of the form $-C_L^{h\sigma} [P - Q]$ to (12) and (13) so that

$$n_{2\text{H}\sigma\sigma'} = \sum_{ij} \min[f_i^{\sigma}, f_j^{\sigma'}] P_{i\sigma j\sigma'} - (\delta_{\sigma\sigma'} C_L^h - \delta_{\sigma\bar{\sigma}'} C_U^h) \sum_h P_{h\sigma h\sigma'}, \quad (15)$$

$$n_{2\text{x}\sigma\sigma'} = -\delta_{\sigma\sigma'} \sum_{ij} \min[f_i^{\sigma}, f_j^{\sigma'}] Q_{i\sigma j\sigma'} - \delta_{\sigma\sigma'} C_L^h \sum_h Q_{h\sigma h\bar{\sigma}}, \quad (16)$$

where we recognise the degeneracy in the outermost p orbitals by summing over the degenerate h_x , h_y , and h_z states with equal weights to yield a spherically symmetric groundstate. Let us restrict ourselves to the case $f^{\uparrow} = f^{\downarrow} = f/2$ where $0 \leq f < 2$ is the total occupation (over both spins) of each orbital in the shell. One can sum over the ensemble to show (after much work),

$$C_L^{h\sigma} = \frac{1}{2} \min[f, 2 - f, |1 - f|, 1/3] \quad (17)$$

for open p shells. We note that the total number of electrons in the shell is $N_p = 3f$ and (15)–(17) are valid for N_p integer or fractional.

The like-spin correction ensures that a bilinear approach would fail even for systems with one spin fully occupied. Indeed it is only true for the case $f^{\uparrow} = 1, f^{\downarrow} = 0$ (or vice versa) occurring for half-occupied shells in N and P. In general, one must not only allow the spin-symmetry to be broken, but also break the spherical symmetry to make the bilinear expression (3) correct.

The energy expression from the LEXX scheme with spin and spherical symmetry is equivalent to the regular EXX energy from a system with broken spin and/or space symmetry

(unrestricted EXX energy) and thus should be close to the unrestricted Hartree Fock energy. The LEXX is thus able to predict the energy of an open-shell system while maintaining appropriate symmetries, in contrast to regular EXX with symmetries imposed which is not expected to yield meaningful results.

D. General ensemble systems

While we have so far determined our ensembles using explicit knowledge of the degenerate groundstate, it is possible to carry out a more general ensemble minimisation to determine $w_\mathcal{E}$. Here, for a given potential, we allow ensemble members (determined by member occupancy factors θ_i^σ) to sample all combinations of ‘‘occupied’’ and ‘‘unoccupied’’ orbitals of the one-electron Hamiltonian, and minimise the energy with respect to $w_\mathcal{E}$. In practice, we would restrict the allowed ensemble members to limited combinations predicted to be low in energy. For example, in the p shell case given above, or indeed Be, we might search for the minimum over cases with full occupancy in $1s^2$ and varying occupancy in the near-degenerate $2p$ and $2s$ orbitals.

As shown in Eq. (9), the general LEXX energy $E^{\text{LEXX}}[\{w_\mathcal{E}\}]$ for a given ensemble can be written as a sum of the ensemble averaged occupations $\langle \theta_i^\sigma \rangle_\mathcal{E}$ and pair-occupations $\langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_\mathcal{E}$ with orbital dependent energy prefactors given in Eqs. (10) and (11). These averaged occupations depend piecewise linearly on $w_\mathcal{E}$ and thus $E^{\text{LEXX}}[\{w_\mathcal{E}\}]$ can be minimised under the constraints $0 \leq w_\mathcal{E} \leq 1$, $\sum_\mathcal{E} w_\mathcal{E} = 1$, and $\sum_\mathcal{E} w_\mathcal{E} N_\mathcal{E} = N$ (where $N_\mathcal{E}$ is the number of electrons in member \mathcal{E} and N is the desired, possibly non-integer, total number of electrons), as well as other desired constraints such as spin and spatial symmetries. That is, we look for the (constrained) set of weights minimising

$$E^{\text{LEXX}} = \sum_\mathcal{E} w_\mathcal{E} \left[\sum_{i\sigma} \theta_{i\mathcal{E}}^\sigma e_{i\sigma}^{(1)} + \sum_{i\sigma j\sigma'} \theta_{i\mathcal{E}}^\sigma \theta_{j\mathcal{E}}^{\sigma'} e_{i\sigma j\sigma'}^{(2)} \right], \quad (18)$$

which may have multiple solutions. We can thus find, for a given potential and orbitals, optimal weights $w_\mathcal{E}$, and through them $\langle \theta_i^\sigma \rangle_\mathcal{E}$ and $\langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_\mathcal{E}$. For the true KS potential, this should be equivalent to finding the temperature $\rightarrow 0^+$ limit of finite-temperature DFT. Such an approach might be useful for dealing with the difficult atomic dissociation problem.

III. OPTIMISED EFFECTIVE POTENTIALS

For a many-electron system the EXX (or LEXX) ground-state energy is composed of the orbital kinetic energy $T_s = \frac{1}{2} \int d\mathbf{r} \sum_{i\sigma} f_i^\sigma |\nabla \phi_{i\sigma}|^2$, the energy from the external potential $E_{\text{Ext}} = \int d\mathbf{r} V_{\text{Ext}} n$ and the Hartree plus exchange energy E_{Hx} . For an ensemble we calculate E_{Hx} via, for example, the expansion (12) and (13) of $n_{2\text{Hx}\sigma\sigma'}$ for s shells [or (15) and (16) for equi- p shells] to form the orbital dependent LEXX expression

$$E_{\text{Hx}} = \sum_{\sigma\sigma'} \int \frac{d\mathbf{r}d\mathbf{r}'}{2|\mathbf{r}-\mathbf{r}'|} n_{2\text{Hx}\sigma\sigma'}(\mathbf{r}, \mathbf{r}'), \quad (19)$$

while for ‘‘standard’’ EXX we instead use (3). The difference in energies between the LEXX and ‘‘standard’’ EXX for frontier s shells is thus the difference between (3) and (19). For example, for the s case

$$E^{\text{LEXX}} - E^{\text{EXX}} = E_{\text{Hx}} - E_{\text{Hx}}^S = -\tilde{C}_U^h e_h, \quad (20)$$

where E_{Hx}^S is given by (3) and $e_h = \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_{h\uparrow h\downarrow}$ and $\tilde{C}_U^h = C_U^h - \min[f^\uparrow, f^\downarrow] + f^\uparrow f^\downarrow = \min[f^\uparrow f^\downarrow, (1-f^\uparrow)(1-f^\downarrow)]$ governs the unlike-spin correction to the Hartree energy required when both f^\uparrow and f^\downarrow are non-integer. A similar expression can be derived for the like-spin correction to p -shells.

We can now define orbital dependent groundstate energies via $E^{\text{EXX}} = T_s + E_{\text{Ext}} + E_{\text{Hx}}^S$ for the EXX and $E^{\text{LEXX}} = E^{\text{EXX}} - \tilde{C}_U^h e_h$ for the LEXX. In an optimised-effective potential⁹ approach, we look for a potential $V \equiv V_{\sigma\sigma}(\mathbf{r})$ such that the orbitals satisfying $[\hat{t} + V_{\sigma\sigma}] \phi_{i\sigma} = \epsilon_{i\sigma} \phi_{i\sigma}$ minimise the energy. Here, we call this approach the $\overline{\text{EXX}}$ or $\overline{\text{LEXX}}$ (with an overline to denote use of an optimised effective potential) depending on the Hx functional used. Finding $V_{\sigma\sigma}$ involves, as input, the functional derivatives $D_{i\sigma}(\mathbf{r}) = \delta E_{\text{Hx}} / \delta \phi_{i\sigma}(\mathbf{r})$. Thus, the scheme for finding optimised LEXX solutions differs only from that for the regular EXX in that $\tilde{D}_{i\sigma}$ for the LEXX includes an extra term for $i = h$. Via \tilde{C}_U^h , the additional term vanishes whenever f^\uparrow or f^\downarrow is integer, as expected (at least for s shells).

Let us consider some of the formal implications of the LEXX. First, the total energy found in an optimised LEXX scheme must be bounded below by the EXX energy of the full ensemble. To prove this, we first note that the ensemble EXX energy E^{EXX} for an ensemble of positive weights $w_\mathcal{E}$ of elements \mathcal{E} can be written as $E^{\text{EXX}}(f) = \sum_\mathcal{E} w_\mathcal{E} E_\mathcal{E}^{\text{EXX}}[\{\phi_{i\sigma}^\mathcal{E}\}]$ where $[\hat{t} + V_{\sigma\sigma}^\mathcal{E}] \phi_{i\sigma}^\mathcal{E} = \epsilon_{i\sigma}^\mathcal{E} \phi_{i\sigma}^\mathcal{E}$ and $V_{\sigma\sigma}^\mathcal{E}$ is chosen to minimise $E_\mathcal{E}^{\text{EXX}}[\{\phi\}]$ and may vary between different ensemble members. From (6) to (19), it is clear that $E^{\text{LEXX}}[\{\phi_{i\sigma}\}] = \sum_\mathcal{E} w_\mathcal{E} E_\mathcal{E}^{\text{EXX}}[\{\phi_{i\sigma}\}]$ where $V_{\sigma\sigma}$ in $[\hat{t} + V_{\sigma\sigma}] \phi_{i\sigma} = \epsilon_{i\sigma} \phi_{i\sigma}$ can no longer vary separately for each part of the ensemble. Thus by the variational nature of an OEP, we find $E_\mathcal{E}^{\text{EXX}}[\{\phi_{i\sigma}^\mathcal{E}\}] \leq E_\mathcal{E}^{\text{EXX}}[\{\phi_{i\sigma}\}]$ and $E^{\text{EXX}}(f) \leq E^{\text{LEXX}}$. Second, we see that $E^{\text{LEXX}}[\{\phi\}] \leq E^{\text{EXX}}[\{\phi\}]$ for any set of orbitals $\{\phi\}$ and thus $E^{\text{LEXX}}[\text{LEXX}] \leq E^{\text{LEXX}}[\text{EXX}] \leq E^{\text{EXX}}[\text{EXX}]$ (where the term in the square brackets labels the OEP used to evaluate the orbitals) with the equality holding (for s shells) only when $\tilde{C}_U^h = 0$ (i.e., when each of the spins is integer occupied). The former inequality follows from (20) by noting that $\tilde{C}_U^h \geq 0$ and $e^h = \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_{h\uparrow h\downarrow} \geq 0$ as $P_{h\uparrow h\downarrow} \geq 0$ (similarly for the like spin term) and the latter follows from the minimisation principle of OEPs. Putting the OEP inequalities together, we find

$$E^{\text{EXX}} \leq E^{\overline{\text{LEXX}}} \leq E^{\overline{\text{EXX}}}, \quad (21)$$

where we include the overline (indicating an optimised potential was used) for clarity.

IV. CORRELATION ENERGIES

The consequences of the improved pair-densities also extend beyond exchange physics. Some beyond-direct

random-phase approximation (dRPA) correlation energy methods [see Ref. 21 for an overview] like the RPAx,²² RXH,²³ and PGG²⁴ kernels, ISTLS²⁵ and tdEXX²⁶ depend in some way on the groundstate pair-density. The difference between the EXX and LEXX expressions will therefore manifest in *correlation* energies too. Here, we can calculate the correlation energy via the “ACFD” functional (see, e.g., Ref. 21) involving the orbital-dependent linear response function χ_0 , and “xc kernel” f_{xc} . By way of example, the “PGG”²⁴ kernel directly uses the groundstate pair-density to approximate

$$f_{xc\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \approx \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left(\frac{n_{2Hx\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}{n_{\sigma}(\mathbf{r})n_{\sigma'}(\mathbf{r}')} - 1 \right). \quad (22)$$

It thus captures the ensemble physics at both the LEXX and correlation levels via n_{2Hx} .

V. RESULTS

In Figure 1, we show correlation-free energies for H, Li, and Na-like fractional ions calculated in the optimised EXX and LEXX schemes under the Krieger, Li, and Iafrate²⁷ (KLI)

approximation to the potential in a real space code for spherically symmetric systems. Results are presented for f^{\uparrow} and f^{\downarrow} ranging from zero to one such that f ranges from zero (e.g., Na^+) to two (e.g., Na^-). The true ensemble EXX energy E^{EXX} takes the same, piecewise linear form as (5) but with groundstate energies E_N of the ensemble members (for integer N) replaced by EXX energies E_N^{EXX} from the optimal Slater determinant. The sides of the surface plots show the case where one frontier spin orbital is integer occupied and the other fractionally occupied (or integer at the corners) and it is clear that the results for the optimised EXX and LEXX are identical as expected. In the interior, however, a different picture emerges, with the required derivative discontinuities at $f^{\uparrow} + f^{\downarrow} = 1$ being absent in the EXX but clearly present in the LEXX. The LEXX also varies minimally with $f = f^{\uparrow} + f^{\downarrow}$ fixed (along diagonals perpendicular to the projection), unlike the EXX. The slight remaining non-linearity must be explained via the implicit dependence of the orbitals on f as the energy formula is explicitly linear in f . We are unsure if this is a result of the optimised effective potential approach itself, or the KLI approximation thereto.

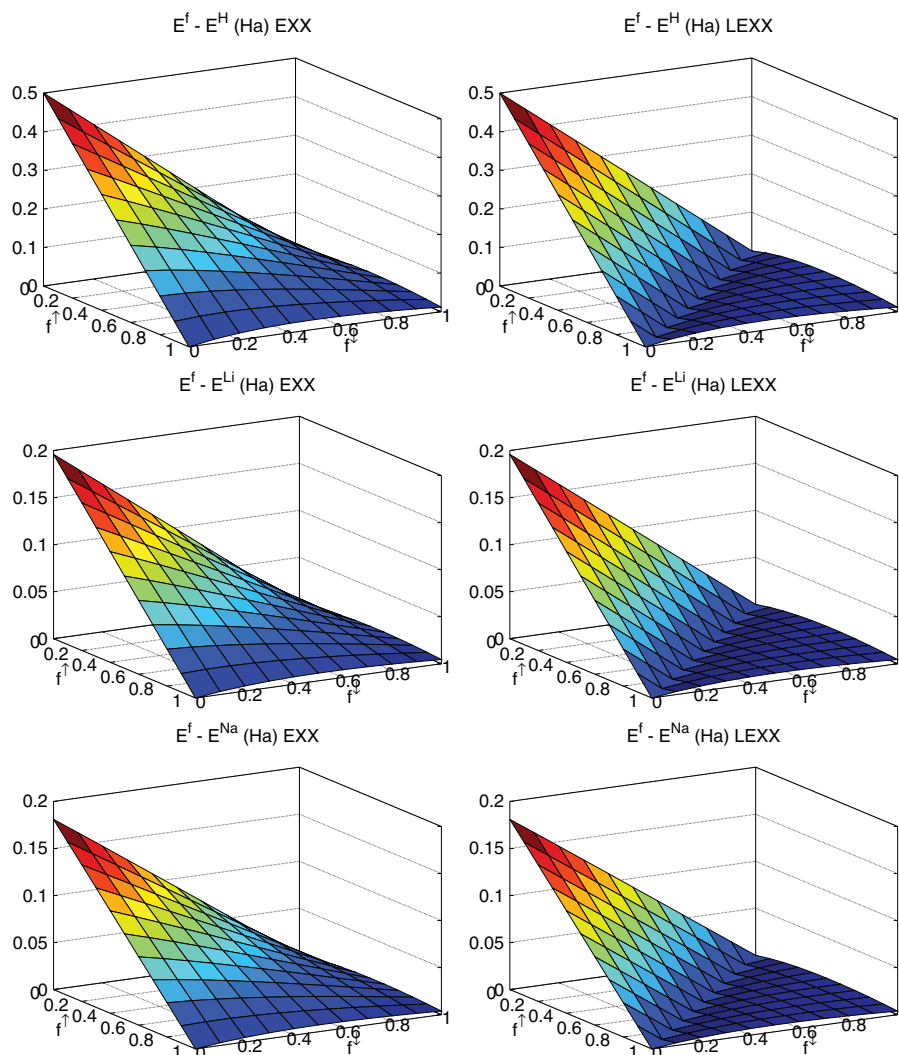


FIG. 1. Groundstate energy differences $E(f^{\uparrow}, f^{\downarrow}) - E^{\text{LEXX}}(\frac{1}{2}, \frac{1}{2})$ (Ha) of H, Li, and Na ions with fractional occupations under EXX (left) and LEXX (right).

The LEXX clearly offers dramatic improvements over the EEXX in energy calculations. For Li and Na it also makes a good approximation to the true EEXX energy without resorting to correlation physics. Here, the maximum variation from EEXX is at most 6 mHa for Li and Na, significantly smaller than the correlation energies of 45 mHa and 396 mHa, respectively,²⁸ for the neutral atoms. Only for H, where the orbitals of H and H⁻ differ significantly through space, is the difference significant, growing to almost 20 mHa for $f \approx 1.5$, comparable to the H⁻ correlation energy of 42 mHa.

The LEXX was previously used²³ to generate groundstates for correlation energy calculations. We are thus able to compare the correlation-free LEXX results from that work with benchmark HF energies calculated by Chakravorty *et al.*²⁸ To test the validity of the p shell LEXX expression (using Eqs. (15)–(17)), we compared the energies of the first and second row open p shell atoms B-F and Al-Cl as these have integer electron numbers, but *fractional* f . For these atoms the LEXX energy has a maximum error of <1.5mHa (for O) and a mean average error of just 0.6 mHa. To numerical accuracy in our calculations, this is close to exact agreement and justifies both the LEXX itself and the KLI approximation to the OEP, at least for integer electron number.

In Figure 2, we show the energy of carbon and fluorine ions with five/eight to seven/ten electrons. For illustrative purposes, we show results with (dRPA, PGG, exact) and without (LEXX, EEXX) correlation energies evaluated in the “ACFD” functional (see, e.g., Ref. 21). The LEXX is used for the kinetic, external, Hartree, and exchange energies in all calculations bar EEXX and exact. Correlation energies are evaluated using the dRPA and PGG kernel (see Ref. 23 for technical details). The exact groundstate energy of fractional ions

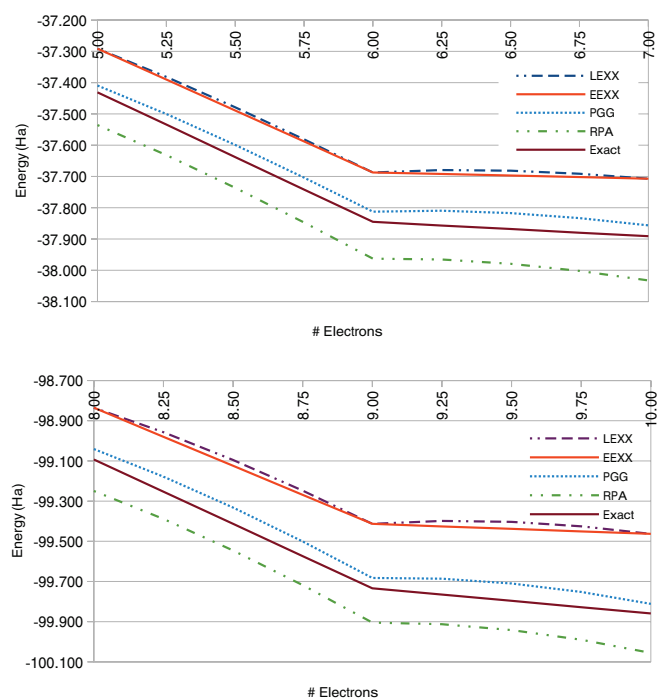


FIG. 2. Groundstate energy $E(N)$ of C and F ions under the LEXX approach with and without correlation energy included. Electrons are split equally between up and down spin $N_{\uparrow} = N_{\downarrow} = N/2$.

of C is given by the piecewise linear function $E(N) = E_0^C - (N - 6)I^C$ for $5 \leq N \leq 6$ and $E(N) = E_0^C - (N - 6)A^C$ for $6 < N \leq 7$ where E_0^C is the groundstate energy of carbon, I^C is its ionisation potential and A^C its electron affinity (with similar expression for F). Energies and ionisation potentials are taken from Ref. 28 and affinities from Refs. 29 and 30. The EEXX energy is defined in the same way but with E_0 , I and A replaced by correlation-free EEXX values. We note that, at integer electron number, our groundstate LEXX energies are within 1 mHa of those found via HF in Ref. 28. As such we reproduce the energy of the triplet state of carbon.

Clearly, the LEXX without correlation approximates the piecewise linear form, albeit incorrectly predicting negative fractional affinities for $N \lesssim 6.75$ for C and $N \lesssim 9.60$ for F. Including correlation improves things, although even here there is a small range with negative affinities, at $N \lesssim 6.25$ for C with the RPA and PGG kernels, and $N \lesssim 9.25$ for F with the PGG kernel. It is clear that the “LEXX-PGG” (PGG evaluated with an LEXX pair-density) is a fairly good approximation to the groundstate ensemble energy at all fractions in both cases, especially for the positive ions. The derivative discontinuity shown here comes entirely from our correct treatment of Hx in most cases, with a nonzero but very small extra contribution from correlation in the PGG case. We aim to further investigate correlation energies at fractional occupation in future work.

VI. CONCLUSIONS AND FURTHER WORK

While the discussion here has focused on Fermionic systems with non-degenerate frontier orbitals and ensembles constructed around varying electron number, the general approach holds true for any non-interacting ensemble system. For example, in Bosonic systems, orbital SI is not cancelled by exchange terms even for integer occupation, a situation which favours the present type of analysis of the “Hartree” and “exchange” terms. Other interesting cases include finite distance dissociation, where quantum superpositions of determinants are required as well as classical ensembles; and thermal ensembles.

LEXX physics is also useful beyond the OEP LEXX method discussed here. It should be possible to construct local density functionals (such as the LSDA) from pseudo-densities based on the modified exchange and/or Hartree pair-density via an approach like that of Ref. 31 or Ref. 32. This perhaps provides some further justification for the success of recent work by Johnson and Contreras-García.¹² The LEXX may also have potential uses in $\mathcal{O}(N)$ -scaling DFT approaches (see Ref. 33 for a recent review).

By constructing a density matrix with similar properties to the exact ensemble, we were able to develop a LEXX formalism yielding an orbital-dependent total energy (8) via a pair-density, piecewise *linear* in the occupation factors, and involving ensemble averages of the one $\langle \theta_i^\sigma \rangle_\mathcal{E}$ and two $\langle \theta_i^\sigma \theta_j^{\sigma'} \rangle_\mathcal{E}$ orbital pair factors [see (9)–(11)]. This is exemplified for doubly fractional s shells in (12) and (13) with ghost-interactions suppressed by the correction term (14) and with similar expressions for p shells discussed in (15) and (16) with

additional like-spin correction term (17). Using these energy expressions in the OEP LEXX functional proposed here gives clearly improved results (with $E^{\text{EEXX}} \leq E^{\text{LEXX}} \leq E^{\text{EXX}}$) when compared with the more common form of EXX, without resorting to correlation physics. This suggests that the very notion of electron correlation is imprecisely defined for OEP or KS systems with fractional occupancy. Using the properties of ensembles to create better trial wavefunctions and density matrices can be an excellent means of reducing the workload of the correlation functional in such systems.

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