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A new method for extracting ensemble Kohn-Sham potentials from accurate excited state densities is applied to a variety of two-electron systems, exploring the behavior of exact ensemble density functional theory. The issue of separating the Hartree energy and the choice of degenerate eigenstates is explored. A new approximation, spin eigenstate Hartree-exchange, is derived. Exact conditions that are proven include the signs of the correlation energy components and the asymptotic behavior of the potential for small weights of the excited states. Many energy components are given as a function of the weights for two electrons in a one-dimensional flat box, in a box with a large barrier to create charge transfer excitations, in a three-dimensional harmonic well (Hooke's atom), and for the He atom singlet-triplet ensemble, singlet-triplet-singlet ensemble, and triplet bi-ensemble. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4872255]

## I. INTRODUCTION AND ILLUSTRATION

Ground-state density functional theory[1,2] (DFT) is a popular choice for finding the ground-state energy of electronic systems,[3] and excitations can now easily be extracted using time-dependent DFT[4–7] (TDDFT). Despite its popularity, TDDFT calculations have many well-known difficulties,[8–11] such as double excitations[12] and charge-transfer (CT) excitations.[13,14] Alternative DFT treatments of excitations[15–17] are always of interest.

Ensemble DFT (EDFT)[18–21] is one such alternative approach. Unlike TDDFT, it is based on an energy variational principle.[19,22] An ensemble of monotonically decreasing weights is constructed from the $M + 1$ lowest levels of the system, and the expectation value of the Hamiltonian over orthogonal trial wavefunctions is minimized by the $M + 1$ exact lowest eigenfunctions.[19] A one-to-one correspondence can be established between ensemble densities and potentials for a given set of weights, providing a Hohenberg-Kohn (HK) theorem, and application to non-interacting electrons of the same ensemble density yields a Kohn-Sham (KS) scheme with corresponding equations.[20] In principle, this yields the exact ensemble energy, from which individual excitations may be extracted.

But to make a practical scheme, approximations must be used.[23–27] These have been less successful for EDFT than those of ground-state DFT[28–32] and TDDFT,[6,33] and their accuracy is not yet competitive with TDDFT transition frequencies from standard approximations. Some progress has been made in identifying some major sources of error.[34–36]

To help speed up that progress, we have developed a numerical algorithm to calculate ensemble KS quantities (orbital energies, energy components, potentials, etc.) essentially exactly,[37] from highly accurate excited-state densities. In the present paper, we provide reference KS calculations and results for two-electron systems under a variety of conditions. The potentials we find differ in significant ways from the approximations suggested so far, hopefully leading to new and better approximations.

To illustrate the essential idea, we perform calculations on simple model systems. For example, Sec. VI A presents two "electrons" in a one-dimensional (1D) box, repelling one another via a (slightly softened) Coulomb repulsion. In Fig. 1, we show their ground- and excited-state densities, with $I$ indicating the specific ground or excited state. We also plot the ensemble exchange-correlation (XC) potentials for equally weighted mixtures of the ground and excited states, which result from our inversion scheme. In this lower plot, $I = 1$ denotes the ground-state exchange-correlation potential, and $I > 1$ indicates the potential corresponding to an equal mixture of the ground state and all multiplets up to and including the $I$th state. Excitation energies for all these states are extracted using the EDFT methods described below.

The paper is laid out as follows. In Sec. II, we briefly review the state-of-the-art for EDFT, introducing our notation. Then, in Sec. III, we give some formal considerations about how to define the Hartree energy. The naïve definition, taken directly from ground-state DFT, introduces spurious unphysical contributions (which then must be corrected-for) called "ghost" corrections.[34] We also consider how to make choices among KS eigenstates when they are degenerate, and show that such choices matter to the accuracy of the approximations. We close that section by showing how to construct symmetry-projected ensembles.

In Sec. IV, we prove a variety of exact conditions within EDFT. Such conditions have been vital in constructing useful approximations in ground-state DFT.[31,38] Following that, in Sec. V we describe our numerical methods in some detail.
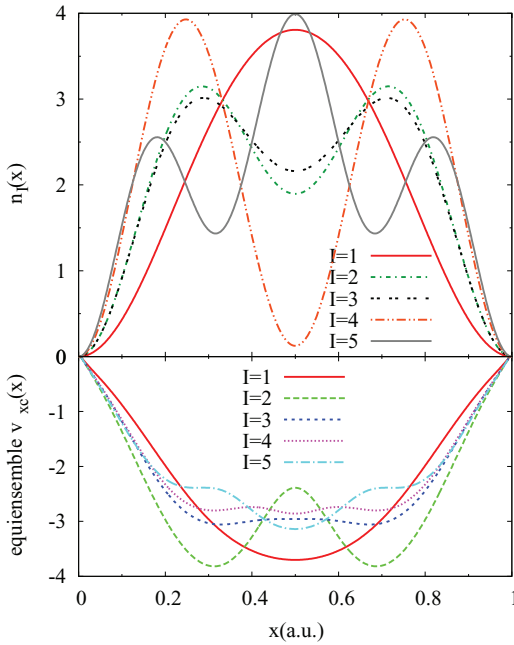
FIG. 1.  Exact densities and equiensemble exchange-correlation potentials of the 1D box with two electrons. The third excited state ($I = 4$) is a double excitation. See Sec. VI A.

Section VI consists of calculations for quite distinct systems, but all with just two electrons. The one-dimensional flat box was used for the illustration here, which also gives rise to double excitations. A box with a high, asymmetric barrier produces charge-transfer excitations. Hooke's atom is a three-dimensional (3D) system, containing two Coulomb-repelling electrons in a harmonic oscillator external potential.[39] It has proven useful in the past to test ideas and approximations in both ground-state and TDDFT calculations.[40] We close the section reporting several new results for the He atom, using ensembles that include low-lying triplet states. Atomic units [$e = \hbar = m_e = 1/(4\pi\epsilon_0) = 1$] are used throughout unless otherwise specified.

## II. BACKGROUND

### A. Basic theory

The ensemble variational principle[19] states that, for an ensemble of the lowest $M + 1$ eigenstates $\Psi_0, \ldots, \Psi_M$ of the Hamiltonian $\hat{H}$ and a set of orthonormal trial functions $\tilde{\Psi}_0, \ldots, \tilde{\Psi}_M$,

$$\sum_{m=0}^{M} \mathrm{w}_m \langle \tilde{\Psi}_m | \hat{H} | \tilde{\Psi}_m \rangle \geq \sum_{m=0}^{M} \mathrm{w}_m E_m, \qquad (1)$$

when the set of weights $\mathrm{w}_m$ satisfies

$$\mathrm{w}_0 \geq \mathrm{w}_1 \geq \ldots \geq \mathrm{w}_m \geq \ldots \geq 0, \qquad (2)$$

and $E_m$ is the eigenvalue of the $m$th eigenstate of $\hat{H}$. Equality holds only for $\tilde{\Psi}_m = \Psi_m$. The density matrix of such an ensemble is defined by

$$\hat{D}_w = \sum_{m=0}^{M} \mathrm{w}_m | \Psi_m \rangle \langle \Psi_m |, \qquad (3)$$

where $w$ denotes the entire set of weight parameters. Properties of the ensemble are then defined as traces of the corresponding operators with the density matrix. The ensemble density $n_w(\mathbf{r})$ is

$$n_w(\mathbf{r}) = \mathrm{tr}\{\hat{D}_w \hat{n}(\mathbf{r})\} = \sum_{m=0}^{M} \mathrm{w}_m n_m(\mathbf{r}), \qquad (4)$$

and the ensemble energy $E_w$ is

$$E_w = \mathrm{tr}\{\hat{D}_w \hat{H}\} = \sum_{m=0}^{M} \mathrm{w}_m E_m. \qquad (5)$$

$n_w(\mathbf{r})$ is normalized to the number of electrons, implying $\sum_{m=0}^{M} \mathrm{w}_m = 1$.

A HK[1] type theorem for the one-to-one correspondence between $n_w(\mathbf{r})$ and the potential in $\hat{H}$ has been proven,[18,20] so all ensemble properties are functionals of $n_w(\mathbf{r})$, including $\hat{D}_w$. The ensemble HK theorem allows the definition of a non-interacting KS system, which reproduces the exact $n_w(\mathbf{r})$. The existence of an ensemble KS system assumes ensemble $v$-representability. EDFT itself, however, only requires ensemble non-interacting $N$-representability, since a constrained-search formalism is available.[20,41] Ensemble $N$- and $v$-representability are not yet proven, only assumed.

As in the ground-state case, only the ensemble energy functional is formally known, which is

$$E_w[n] = F_w[n] + \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}), \qquad (6)$$

where $v(\mathbf{r})$ is the external potential. The ensemble universal functional $F_w$ is defined as

$$F_w[n] = \mathrm{tr}\{\hat{D}_w[n](\hat{T} + \hat{V}_{\mathrm{ee}})\}, \qquad (7)$$

where $\hat{T}$ and $\hat{V}_{\mathrm{ee}}$ are the kinetic and electron-electron interaction potential operators, respectively. The ensemble variational principle ensures that the ensemble energy functional evaluated at the exact ensemble density associated with $v(\mathbf{r})$ is the minimum of this functional, Eq. (5).

The ensemble KS system is defined as the non-interacting system that reproduces $n_w(\mathbf{r})$ and satisfies the following non-interacting Schrödinger equation:

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{s},w}[n_w](\mathbf{r}) \right\} \phi_{j,w}(\mathbf{r}) = \epsilon_{j,w}\phi_{j,w}(\mathbf{r}). \qquad (8)$$

The ensemble KS system has the same set of $\mathrm{w}_m$ as the interacting system. This consistency has non-trivial implications even for simple systems. This will be explored more in Sec. II B.

The KS density matrix $\hat{D}_{\mathrm{s},w}$ is

$$\hat{D}_{\mathrm{s},w} = \sum_{m=0}^{M} \mathrm{w}_m | \Phi_m \rangle \langle \Phi_m |, \qquad (9)$$

where $\Phi_m$ are non-interacting $N$-particle wavefunctions, usually assumed to be single Slater determinants formed by KS orbitals $\phi_{j,w}$. We find that this choice can be problematic, and it will be discussed in Sec. III A. The ensemble density $n_w(\mathbf{r})$

is reproduced by the KS system, meaning

$$n_w(\mathbf{r}) = \sum_{m=0}^{M} w_m n_m(\mathbf{r}) = \sum_{m=0}^{M} w_m n_{\mathrm{s,m}}(\mathbf{r}), \qquad (10)$$

where $n_m(\mathbf{r}) = \langle \Psi_m | \hat{n}(\mathbf{r}) | \Psi_m \rangle$, and $n_{\mathrm{s,m}}(\mathbf{r}) = \langle \Phi_m | \hat{n}(\mathbf{r}) | \Phi_m \rangle$. The KS densities of the individual states are generally not related to those of the interacting system; only their weighted sums are equal, as in Eq. (10).

$E_w[n]$ is decomposed as in ground-state DFT,

$$E_w[n] = T_{\mathrm{s},w}[n] + V[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc},w}[n]$$

$$= \mathrm{tr}\{\hat{D}_{\mathrm{s},w}\hat{T}\} + \int \mathrm{d}^3 r \; n(\mathbf{r})v(\mathbf{r})$$

$$+ E_{\mathrm{H}}[n] + E_{\mathrm{xc},w}[n], \qquad (11)$$

where only the ensemble XC energy $E_{\mathrm{xc},w}$ is unknown. The form of $v_{\mathrm{s},w}(\mathbf{r})$ is then determined according to the variational principle by requiring $\delta E_w[n_w]/\delta n_w(\mathbf{r}) = 0$, resulting in

$$v_{\mathrm{s},w}[n_w](\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{H}}[n_w](\mathbf{r}) + v_{\mathrm{xc},w}[n_w](\mathbf{r}), \qquad (12)$$

where $v_{\mathrm{H}}[n](\mathbf{r}) = \delta E_{\mathrm{H}}[n]/\delta n(\mathbf{r})$, and $v_{\mathrm{xc},w}[n](\mathbf{r}) = \delta E_{\mathrm{xc},w}[n]/\delta n(\mathbf{r})$. $E_{\mathrm{H}}$ is generally defined to have the same form as the ground-state Hartree energy functional. Although this choice is reasonable, we find that it is more consistent to consider $E_{\mathrm{HX}}$, the combined Hartree and exchange energy. This point will be discussed in Sec. III A.

The ensemble universal functional $F_w[n]$ depends on the set of weights $w_m$. Reference 20 introduced the following set of weights, so that only one parameter w is needed:

$$w_m = \begin{cases} \frac{1 - w g_I}{M_I - g_I} & m \le M_I - g_I, \\ w & m > M_I - g_I, \end{cases} \qquad (13)$$

where $w \in [0, 1/M_I]$. In this ensemble, here called GOK for the authors Gross, Oliveira, and Kohn,[34] $I$ denotes the set of degenerate states (or "multiplet") with the highest energy in the ensemble, $g_I$ is the multiplicity of the $I$th multiplet, and $M_I$ is the total number of states up to the $I$th multiplet. GOK ensembles must contain full sets of degenerate states to be well-defined. The weight parameter w interpolates between two ensembles: the equiensemble up to the $I$th multiplet ($w = 1/M_I$) and the equiensemble up to the $(I - 1)$th multiplet ($w = 0$). All previous studies of EDFT have been based on this type of ensemble.

The purpose of EDFT is to calculate excited-state properties, not ensemble properties. With the GOK ensemble, the excitation energy of multiplet $I$ from the ground state, $\omega_I$, is obtained using ensembles up to the $I$th multiplet as

$$\omega_I = \frac{1}{g_I} \left. \frac{\partial E_{I,\mathrm{w}}}{\partial \mathrm{w}} \right|_{\mathrm{w}=w_I} + \sum_{i=0}^{I-1} \frac{1}{M_i} \left. \frac{\partial E_{i,\mathrm{w}}}{\partial \mathrm{w}} \right|_{\mathrm{w}=w_i}, \qquad (14)$$

which simplifies to

$$\omega_1 = \omega_{\mathrm{s},1,w} + \left. \frac{\partial E_{\mathrm{xc},w}[n]}{\partial \mathrm{w}} \right|_{n=n_w} \qquad (15)$$

for the first excitation energy. Equation (14) holds for any valid $w_i$'s if the ensemble KS systems are exact, despite every term in Eq. (14) being w-dependent. No existing $E_{\mathrm{xc},w}$ approximations satisfy this condition.[21,24]

Levy[42] pointed out that there is a special case for $w \to 0$ of bi-ensembles ($I = 2$, with all degenerate states within a multiplet having the same density),

$$\Delta v_{\mathrm{xc}} = \lim_{\mathrm{w} \to 0} \left. \frac{\partial E_{\mathrm{xc},w}[n]}{\partial \mathrm{w}} \right|_{n=n_w}$$

$$= \left[ \lim_{\mathrm{w} \to 0} v_{\mathrm{xc},w}[n_w](\mathbf{r}) \right] - v_{\mathrm{xc},w=0}[n_{w=0}](\mathbf{r}) \qquad (16)$$

for finite $r$, where $\Delta v_{\mathrm{xc}}$ is the change in the KS highest-occupied-molecular-orbital (HOMO) energy between $w = 0$ (ground state) and $w \to 0_+$.[43] $\Delta v_{\mathrm{xc}}$ is a property of electron-number-neutral excitations, and should not be confused with the ground-state derivative discontinuity $\Delta_{\mathrm{xc}}$, which is related to ionization energies and electron affinities.[44]

## B. Degeneracies in the Kohn-Sham system

Taking the He atom as our example, the interacting system has a non-degenerate ground state, triply degenerate first excited state, and a non-degenerate second excited state. However, the KS system has a fourfold degenerate first excited state (corresponding to four Slater determinants), due to the KS singlet and triplet being degenerate (Fig. 2). Consider an ensemble of these states with arbitrary, decreasing weights, in order to work with the most general case. Represent the ensemble energy functional Eq. (5) as the KS ensemble energy, $E_{\mathrm{s},w}$, plus a correction, $G_w$. This correction then must encode the switch from depending only on the sum of the weights of the excited states as a whole in the KS case to depending on the sum of triplet weights and the singlet weight separately.

For the interacting system, the ensemble energy and density take the forms

$$E_w = E_0 + w_{\mathrm{T}}\omega_1 + w_{\mathrm{s}}\omega_2,$$
$$n_w(\mathbf{r}) = n_0(\mathbf{r}) + w_{\mathrm{T}}\Delta n_1(\mathbf{r}) + w_{\mathrm{s}}\Delta n_2(\mathbf{r}), \qquad (17)$$

where $\omega_i = E_i - E_0$, and so on, $w_{\mathrm{T}}$ is the sum of the triplet weights, and $w_{\mathrm{s}}$ is the singlet weight. On the other hand, for the KS system we have

$$E_{\mathrm{s},w} = E_{\mathrm{s},0} + (w_{\mathrm{T}} + w_{\mathrm{s}}) \Delta \epsilon_{1,w},$$
$$n_w(\mathbf{r}) = 2|\phi_{1s}|^2 + (w_{\mathrm{T}} + w_{\mathrm{s}})(|\phi_{2s}|^2 - |\phi_{1s}|^2). \qquad (18)$$
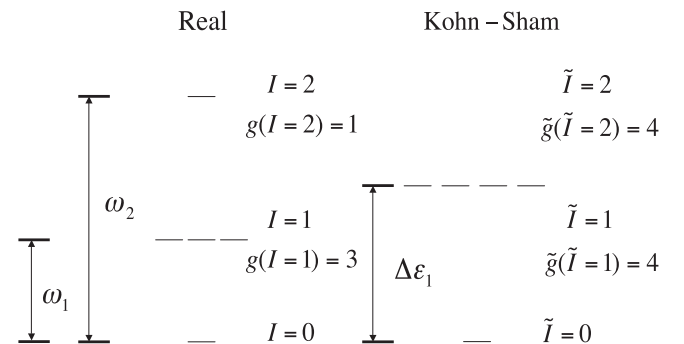


FIG. 2. Diagram of the interacting and KS multiplicity structure for He. Degeneracy of the $I$th multiplet is $g(I)$; tildes denote KS values. For instance, $\tilde{I} = 2$ refers to the KS multiplet used to construct the second (singlet) multiplet of the real system ($I = 2$), as is described in Sec. III B.

Each of the weights must be the same for the non- interacting and interacting systems, in order to define an adiabatic connection, but $w_T$ may differ from $w_S$. If they are equal as in some ensemble treatments, variational principles for ensembles may be connected to statistical mechanics and one another more readily.[45]

The functional $G_w = E_w - E_{s,w}$ in this case is

$$G_w[n_w] = E_0 - E_{s,0} + w_T (\omega_1 - \Delta\epsilon_1) + w_S (\omega_2 - \Delta\epsilon_1),$$

showing that, in its most general form, the exact ensemble energy functional (which can also be decomposed as in Eq. (11)) has to encode the change in the multiplet structure between non-interacting and interacting systems, even for a simple system like the He atom. Such information is unknown *a priori* for general systems, and can be very difficult to incorporate into approximations. In light of this difficulty, some researchers opt to use single-Slater-determinant states and equal weights for degenerate states.[45] However, we show that this problem can be alleviated if the degeneracies are the result of symmetry. This will be discussed in Sec. III C.

## C. Approximations

Available approximations to the ensemble $E_{XC}$ include the quasi-local-density approximation (qLDA) functional[21,46] and the "ghost"-corrected exact exchange (EXX) functional.[24,34] The qLDA functional is based on the equiensemble qLDA,[46] and it interpolates between two consecutive equiensembles[21]

$$E_{XC,I,w}^{qLDA}[n] = (1 - M_I w) E_{XC,I-1}^{eqLDA}[n]$$
$$+ M_I w E_{XC,I}^{eqLDA}[n], \quad (20)$$

where $E_{XC}^{eqLDA}$ is the equiensemble qLDA functional defined in terms of finite-temperature LDA in Ref. 46.

The ensemble Hartree energy is defined analogously to the ground-state Hartree energy as shown in Eq. (11). Similarly, Nagy[24] provides a definition of the exchange energy for bi-ensembles

$$E_{X,w}^{Nagy}[n_\uparrow, n_\downarrow] = -\frac{1}{2} \sum_\sigma \int d^3r d^3r' \frac{|n_\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (21)$$

where $n_\sigma(\mathbf{r}, \mathbf{r}')$ is the reduced density matrix defined analogously to its ground-state counterpart, assuming a spin-up electron is excited in the first excited state

$$n_{\sigma,w}(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N_\sigma} n_{j,\sigma}(\mathbf{r}, \mathbf{r}') + \delta_{\sigma,\uparrow} w \left( n_{L\uparrow}(\mathbf{r}, \mathbf{r}') - n_{H\uparrow}(\mathbf{r}, \mathbf{r}') \right), \quad (22)$$

with $n_{j,\sigma}(\mathbf{r}, \mathbf{r}') = \phi_{j,\sigma}(\mathbf{r})\phi_{j,\sigma}^*(\mathbf{r}')$, $L\uparrow = N_\uparrow + 1$, and $H\uparrow = N_\uparrow$, the spin-up lowest-unoccupied-molecular-orbital (LUMO) and HOMO, respectively. Both $E_H$ in Eqs. (11) and (21) contain "ghost" terms,[34] which are cross-terms between different states in the ensemble due to the summation form of $n_w(\mathbf{r})$ in Eq. (4) and $n_w(\mathbf{r}, \mathbf{r}')$ in Eq. (22). An EXX functional is obtained after such spurious terms are corrected. As an example of the GPG X energy functional[34] (named for its creators Gidopoulos, Papaconstantinou, and Gross), take two-

TABLE I. First non-triplet excitation energies (in eV) of various atoms and ions calculated with qLDA, EXX, GPG, and SEHX functionals. qLDA calculations were performed upon LDA (PW92)[58] ground states; EXX[24] ground states were used for the rest. Asterisks indicate use of spin-restricted ground states. qLDA relies on ground-state LDA orbital energy differences; it cannot be used with the single bound orbital of LDA He. GPG is used with single-determinant states and performs well, though GPG allows the choice of multi-determinant states.

| | He | Li | Li$^+$ | Be | Be$^+$ | Mg | Ca | Ne | Ar |
|---|---|---|---|---|---|---|---|---|---|
| Exp. | 20.62 | 1.85 | 60.76 | 5.28 | 3.96 | 4.34 | 2.94 | 16.7 | 11.6 |
| qLDA | ... | 1.93 | 53.85 | 3.71 | 4.30 | 3.58 | 1.79 | 14.2 | 10.7 |
| EXX | 27.30 | 6.34 | 72.26 | 10.22 | 12.38 | 8.25 | 9.89 | 26.0 | 18.2 |
| GPG | 20.67 | 1.84 | 60.40 | 3.53 | 4.00 | 3.25 | 3.25 | 18.2 | 12.1 |
| SEHX | 21.29 | 2.08* | 61.64 | 5.25 | 4.06* | 4.39 | 3.55 | 18.4 | 12.2 |

state ensembles constructed as in the Nagy example above. For this simplified case, the GPG X energy functional is

$$E_{X,w}^{GPG}[n_\uparrow, n_\downarrow] = \int \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} \left\{ -\frac{1}{2}(n_\sigma(\mathbf{r}, \mathbf{r}'))^2 \right.$$
$$\left. + w\overline{w}[n_{H\uparrow}(\mathbf{r}, \mathbf{r}')n_{L\uparrow}(\mathbf{r}, \mathbf{r}') - n_{H\uparrow}(\mathbf{r}')n_{H\uparrow}(\mathbf{r}')] \right\}, \quad (23)$$

where $\overline{w} = 1 - w$. These "ghost" corrections are small compared to the Hartree and exchange energies. However, they are large corrections to the excitation energies, as Eq. (14) contains energy derivatives instead of energies. Table I shows a few examples.

With the help of the exact ensemble KS systems to be presented in this paper, we construct a new approximation, the motivation and justification of which will be explained in Secs. III A and III B.

## III. THEORETICAL CONSIDERATIONS

In this section, we review important definitions and extend EDFT to improve the consistency and generality of the theory.

## A. Choice of Hartree energy

The energy decomposition in Eq. (11) is analogous to its ground-state counterpart. However, unlike $T_s$ and $V$, the choices for $E_H$ and $E_X$ and $E_C$ are ambiguous; only their sum is uniquely determined. As shown in Eqs. (11) and (21), definitions for $E_H$ and $E_X$ can introduce "ghost" terms. Corrections can be considered either a part of $E_H$ and $E_X$ or a part of $E_C$. Such correction terms also take a complicated form when generalized to multi-state ensembles.

A more natural way of defining $E_H$ and $E_{XC}$ for ensembles can be achieved by considering the purpose of this otherwise arbitrary energy decomposition. In the ground-state case, the electron-electron repulsion reduces[47] to the Hartree energy for large $Z$, which is a simple functional of the density. The remaining unknown, $E_{XC}$ (and its components $E_X$ and $E_C$), is a small portion of the total energy, so errors introduced by approximations to it are small.

For ensembles, we review a slightly different energy decomposition proposed by Nagy.[26,48] Instead of defining $E_\text{H}$ and $E_\text{x}$ in analogy to their ground-state counterparts, first define the combined Hartree-exchange energy $E_\text{HX}$, which is the more fundamental object in EDFT. $E_\text{HX}$ can be explicitly represented as the trace of the KS density matrix

$$E_{\text{HX},w} = \text{tr}\{\hat{D}_{s,w}\hat{V}_\text{ee}\} = \sum_{m=0}^{M} w_m \langle \Phi_m | \hat{V}_\text{ee} | \Phi_m \rangle. \quad (24)$$

For the ground state, both Hartree and exchange contributions are first-order in the adiabatic coupling constant, while correlation consists of all higher-order terms. According to the definition above, this property in the ensemble is retained. Equation (24) contains no "ghost" terms by definition, eliminating the need to correct them.[48] As a consequence, the correlation energy, $E_\text{c}$, is defined and decomposed as

$$E_{\text{c},w} = E_{\text{HXC},w} - E_{\text{HX},w} = T_{\text{c},w} + U_{\text{c},w}, \quad (25)$$

where $E_{\text{HXC},w} = E_w - T_{s,w} - V$, $T_{\text{c},w} = T_w - T_{s,w}$ and $U_{\text{c},w} = E_{\text{c},w} - T_{\text{c},w}$.

This form of $E_\text{HX}$ reveals a deeper problem in EDFT. As demonstrated in Sec. II B, the multiplet structure of real and KS He atoms is different. Real He has a triplet state and a singlet state as the first and second excited states, but KS He has four degenerate single Slater determinants as the first excited states. Worse, the KS single Slater determinants are not eigenstates of the total spin operator $\hat{S}^2$, so their ordering is completely arbitrary. The KS system is constructed to yield only the real spin densities, not other quantities. KS wavefunctions that are not eigenstates of $\hat{S}^2$ do not generally affect commonly calculated ground-state DFT properties,[49] but things are clearly different in EDFT. Consider the bi-ensemble of the ground state and the triplet excited state of He. Then $E_{\text{HX},w}[n_w]$ depends on which three of the four KS excited-state Slater determinants are chosen, though it must be uniquely defined. Therefore, we choose the KS wavefunctions in EDFT to be linear combinations of the degenerate KS Slater determinants, preserving spatial and spin symmetries and eliminating ambiguity in $E_\text{HX}$. We note here that GPG allows use of spin eigenstates[34] as in their own atomic calculations, but we *require* it from our approximation. Such multi-determinant, spin eigenstates are also required for construction of symmetry-projected ensembles, as described in Sec. III C.

With $E_\text{HX}$ fixed, the definitions of $E_\text{H}$ and $E_\text{x}$ depend on one another, but $E_\text{c}$ does not. Defining a Hartree functional in the same form as the ground-state

$$U[n] = \frac{1}{2} \int \text{d}^3 r \int \text{d}^3 r' \frac{n(\mathbf{r})n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (26)$$

we can examine different definitions for the GOK ensemble. A "ghost"-free ensemble Hartree, $E_\text{H}^\text{ens}$, can be defined as

$$E_{\text{H},w}^\text{ens} = \sum_{m=0}^{M} w_m U[n_m], \quad (27)$$

i.e., the ensemble sum of the Hartree energies of the interacting densities, or as the slightly different

$$E_{\text{H},w}^{\text{KS ens}} = \sum_{m=0}^{M} w_m U[n_{s,m}], \quad (28)$$

i.e., the ensemble sum of the Hartree energies of the KS densities. The traditional Hartree definition,

$$E_{\text{H},w}^\text{trad} = U[n_w], \quad (29)$$

introduces "ghost" terms through the fictitious interaction of ground- and excited-state densities. Traditional and ensemble definitions differ in their production of "ghosts," as well as in their w-dependence. The "ghost"-corrected $E_\text{H}$ in Ref. 34

$$E_{\text{H},w}^\text{GPG} = \sum_{m=0}^{M} w_m^2 U[n_{s,m}] \quad (30)$$

has a different form from Eq. (28), which is also "ghost"-free. Each of these definitions of $E_\text{H}$ reduces to the ground-state $E_\text{H}$ when $w_0 = 1$ and satisfies simple inequalities such as $E_\text{H} > 0$ and $E_\text{x} < 0$. However, this ambiguity in the definition of $E_\text{H}$ requires that an approximated ensemble $E_\text{xc}$ be explicit about its compatible $E_\text{H}$ definition.

The different flavors of $E_{\text{H},w}$ are compared for the He singlet ensemble[37] in Fig. 3. Even though $E_{\text{H},w}^\text{ens}$ and $E_{\text{H},w}^{\text{KS ens}}$ do not contain "ghost" terms by definition, their magnitude is slightly bigger than that of $E_\text{H}^\text{trad}$, which is not "ghost"-free. This apparent contradiction stems from $E_{\text{H},w}^\text{ens}$ and $E_{\text{H},w}^{\text{KS ens}}$ depending linearly on w, while $E_{\text{H},w}^\text{trad}$ depends on w quadratically. The quadratic dependence on w is made explicit with the "ghost"-corrected $E_{\text{H},w}^\text{GPG}$ of Ref. 34. Comparing with the "ghost"-free $E_{\text{H},w}^\text{ens}$ and $E_{\text{H},w}^{\text{KS ens}}$, it is clear that $E_\text{H}^\text{GPG}$ overcorrects in a sense, and is compensated by an over-correction of the opposite direction in $E_\text{x}^\text{GPG}$.

The traditional definition of Eq. (29) has the advantage that $v_\text{H}(\mathbf{r})$ is a simple functional derivative with respect to the ensemble density. Any other definition requires solving an optimized effective potential (OEP)[50,51]-type equation to obtain $v_\text{H}$. On the other hand, an approximated $E_\text{xc}$ compatible with $E_\text{H}^\text{trad}$ requires users to approximate the corresponding "ghost" correction as part of $E_\text{xc}$. Since the ghost correction is usually non-negligible, this is a major source of error for the qLDA functional.
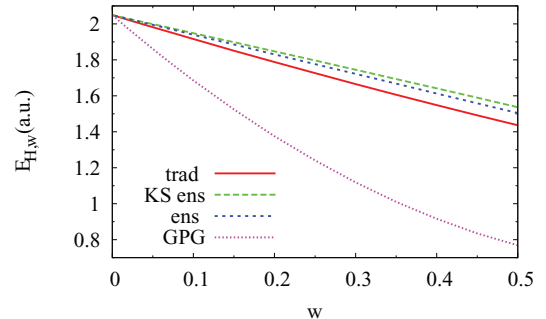


FIG. 3. Behaviors of the different ensemble Hartree energy definitions for the singlet ensemble of He.

## B. Symmetry-eigenstate Hartree-exchange (SEHX)

We have now identified $E_{HX}$ as being more consistent with the EDFT formalism than $E_H$ and $E_x$. Having also justified multi-determinant ensemble KS wavefunctions, we now derive a spin-consistent EXX potential, the SEHX. Define the two-electron repulsion integral

$$(\mu\nu \mid \kappa\lambda) = \int \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} \phi_\mu^*(\mathbf{r})\phi_\nu^*(\mathbf{r}')\phi_\kappa(\mathbf{r})\phi_\lambda(\mathbf{r}') \qquad (31)$$

and

$$L_{\mu\nu\kappa\lambda} = (\mu\nu \mid \kappa\lambda)\delta_{\sigma_\mu,\sigma_\kappa}\delta_{\sigma_\nu,\sigma_\lambda}. \qquad (32)$$

$\phi_\mu(\mathbf{r})$ denotes the $\mu$th KS orbital and $\sigma_\mu$ its spin state. If the occupation of the $p$th Slater determinant of the $\mu$th KS orbital of the $\tilde{i}$th multiplet of the KS system is $f_{p\mu}^{(\tilde{i})}$, define

$$\alpha_{\mu,\nu,\kappa,\lambda}^{(i,k)} = \sum_{p=1}^{\tilde{g}(\tilde{i})} C_p^{(i,k)} f_{p,\mu}^{(\tilde{i})} f_{p,\nu}^{(\tilde{i})} \prod_{\eta\neq\mu,\nu,\kappa,\lambda}^{\tilde{g}(\tilde{i})} \delta_{f_{p,\eta}^{\tilde{i}},f_{q,\eta}^{\tilde{i}}} \qquad (33)$$

for the $q$-dependent $k$th state of the $i$th multiplet of the exact system. $\tilde{g}(\tilde{i})$ is the KS multiplicity of the $i$th multiplet, and $C$'s are the coefficients of the multi-determinant wavefunctions defined by

$$\Psi_s^{(i,k)}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{p=1}^{\tilde{g}(\tilde{i})} C_p^{(i,k)} \tilde{\Psi}_{s,p}^{\tilde{i}}(\mathbf{r}_1, \ldots, \mathbf{r}_N). \qquad (34)$$

$\tilde{\Psi}_s$ is a KS single Slater determinant. Note the numbering of the KS multiplets, $\tilde{i}$, depends on $i$, the numbering of the exact multiplet structure. The $C$ coefficients are chosen according to the spatial and spin symmetries of the exact state. Now, with $p$ and $q$ KS single Slater determinants of the KS multiplet, define

$$h_{\mu\nu\kappa\lambda}^{(i,k)} = \sum_{q=1}^{\tilde{g}(\tilde{i})} \left( \alpha_{\mu,\nu,\kappa,\lambda}^{(i,k)} \alpha_{\kappa,\lambda,\mu,\nu}^{(i,k)} - \left(C_q^{(i,k)}\right)^2 f_{q,\mu}^{(\tilde{i})} f_{q,\nu}^{(\tilde{i})} f_{q,\kappa}^{(\tilde{i})} f_{q,\lambda}^{(\tilde{i})} \right), \qquad (35)$$

in order to write

$$H^{(i,k)} = \sum_{\substack{\mu,\ \nu > \mu \\ \kappa,\ \lambda > \kappa}} (L_{\mu\nu\kappa\lambda} - L_{\mu\nu\lambda\kappa}) h_{\mu\nu\kappa\lambda}^{(i,k)}. \qquad (36)$$

Then, if

$$G^{(i,k)} = \sum_{\mu,\nu > \mu} (L_{\mu\mu\nu\nu} - \Re L_{\mu\nu\mu\nu}) \sum_{p=1}^{\tilde{g}(\tilde{i})} \left| C_p^{(i,k)} \right|^2 f_{p,\mu}^{\tilde{i}} f_{p,\nu}^{\tilde{i}}, \qquad (37)$$

the Hartree-exchange energy for up to the $I$th multiplet is

$$E_{HX,w}^{SEHX} = \sum_{i=1}^{I} \sum_{k=1}^{g(i)} w^{(i,k)} \{G^{(i,k)} + H^{(i,k)}\}, \qquad (38)$$

where $g(i)$ is the exact multiplicity of the $i$th multiplet. The $v_{HX,w}$ potential is then

$$v_{HX,w,\sigma}^{SEHX}(\mathbf{r}) = \frac{\delta E_{HX,w}}{\delta n_{w,\sigma}(\mathbf{r})}$$

$$= \int d^3r' \sum_j \frac{\delta E_{HX,w}}{\delta \phi_{j,\sigma}(\mathbf{r}')} \frac{\delta \phi_{j,\sigma}(\mathbf{r}')}{\delta n_{w,\sigma}(\mathbf{r})} + c.c., \qquad (39)$$

which yields an OEP-type equation for $v_{HX,w}(\mathbf{r})$.

The $v_{HX,w}(\mathbf{r})$ of Eq. (39) produces no "ghost" terms. For closed-shell systems, Eq. (39) yields $v_{HX,w,\uparrow}(\mathbf{r}) = v_{HX,w,\downarrow}(\mathbf{r})$. An explicit $v_{HX,w}(\mathbf{r})$ can be obtained by applying the usual Krieger-Li-Iafrate (KLI)[52] approximation. Here, we provide the example of the singlet bi-ensemble studied in our previous paper.[37] $E_{HX}$ for a closed-shell, singlet ensemble is

$$E_{HX,w}^{SEHX} = \int \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} \{n_1^{orb}(\mathbf{r})n_1^{orb}(\mathbf{r}')$$
$$+ w[n_1^{orb}(\mathbf{r})\left(n_2^{orb}(\mathbf{r}') - n_1^{orb}(\mathbf{r}')\right)$$
$$+ \phi_1^*(\mathbf{r})\phi_2^*(\mathbf{r}')\phi_1(\mathbf{r}')\phi_2(\mathbf{r})]\}, \qquad (40)$$

where $n_j^{orb}(\mathbf{r}) = |\phi_j(\mathbf{r})|^2$ is the KS orbital density. Spin is not explicitly written out because the system is closed-shell. After applying the KLI approximation, we obtain

$$v_{HX,w}(\mathbf{r}) = \frac{1}{2n_w(\mathbf{r})} \{ (2 - w)n_1^{orb}(\mathbf{r})[v_1(\mathbf{r}) + \bar{v}_{HX1} - \bar{v}_1$$
$$+ wn_2^{orb}(\mathbf{r})[v_2(\mathbf{r}) + \bar{v}_{HX2} - \bar{v}_2] \}, \qquad (41)$$

with

$$v_1(\mathbf{r}) = \frac{1}{(2 - w)} \int \frac{d^3r'}{|\mathbf{r} - \mathbf{r}'|} \left[ 2(1 - w)n_1^{orb}(\mathbf{r}') + w\left(n_2^{orb}(\mathbf{r}') + \phi_1^*(\mathbf{r}')\phi_2^*(\mathbf{r})\phi_2(\mathbf{r}')/\phi_1^*(\mathbf{r})\right) \right], \qquad (42)$$

$$v_2(\mathbf{r}) = \int \frac{d^3r'}{|\mathbf{r} - \mathbf{r}'|} \left[ n_1^{orb}(\mathbf{r}') + \frac{\phi_1^*(\mathbf{r})\phi_2^*(\mathbf{r}')\phi_1(\mathbf{r}')}{\phi_2^*(\mathbf{r})} \right], \qquad (43)$$

and

$$\bar{v}_j = \int d^3r \ v_j(\mathbf{r})n_j^{orb}(\mathbf{r}). \qquad (44)$$

Equation (41) is an integral equation for $v_{HX}(\mathbf{r})$ that can be easily solved.

To fully understand the performance of $v_{HX}(\mathbf{r})$, self-consistent EDFT calculations would be needed at different values of w, which is beyond the scope of this paper. Ideally, these self-consistent calculations would be compared to the symmetry-eigenstate form of GPG used in Table I of Ref. 34. In this work, we demonstrate the performance of SEHX at w = 0 in Sec. IV C.

## C. Symmetry-projected Hamiltonian

The ensemble variational principle holds for any Hamiltonian. If the Hamiltonian $\hat{H}$ commutes with another operator $\hat{O}$, one can apply to $\hat{H}$ a projection operator formed by the eigenvectors of $\hat{O}$. One obtains a new Hamiltonian, and the

ensemble variational principle holds for this subspace of $\hat{H}$, allowing an EDFT to be formulated.

An example would be the total spin operator $\hat{S}^2$, where

$$S^2 = \sum_{S=0}^{\infty} (2S+1)|S\rangle\langle S| \tag{45}$$

and $|S\rangle$ are its eigenvectors. Define a new Hamiltonian $\hat{H}_1$ as

$$\hat{H}_1 = |S\rangle\langle S|\hat{H}. \tag{46}$$

$\hat{H}_1$ has the same set of eigenvectors as $\hat{H}$, but the eigenvalues are 0 for the eigenvectors not having spin $S$. Since one can change the additive constant in $\hat{H}$ arbitrarily, it is always possible to make the eigenvalues of any set of spin-$S$ eigenvectors negative and thus ensure that they are the lowest energy states of $\hat{H}_1$. The ensemble variational principle holds for ensembles of spin-$S$ states. We have employed this symmetry argument in our previous paper[37] for a purely singlet two-state ensemble of the He atom.

A similar statement is available in ground-state DFT, allowing direct calculation of the lowest state of a certain symmetry.[53,54] The differences between the subspace and full treatments are encoded in the differences in their corresponding $E_{xc}$. Thus, the lowest two states within each spatial and spin symmetry category can be treated in EDFT in a two-state-ensemble fashion, which is vastly simpler than the multi-state formalism.

Since the multiplet structures of the interacting system and the KS system must be compatible, a symmetry-projected ensemble also requires a symmetry-projected KS system, which is impossible if KS wavefunctions are single Slater determinants, as discussed in Sec. III A.

## IV. EXACT CONDITIONS

Here, we prove some basic relations for the signs of various components of the KS scheme and construct an energy density from the virial. We describe a feature of the ensemble derivative discontinuity and extraction of excited properties from the ground state.

### A. Inequalities and energy densities

Simple exact inequalities of the energy components (such as $E_c < 0$) have been proven in ground-state DFT.[44] If these are true in EDFT, experiences designing approximated $E_{xc}$ in ground-state DFT may be transferrable to EDFT. Here, we show that inequalities related to the correlation energy are still valid in EDFT.

Due to the variational principle,[19] the wavefunctions that minimize the ensemble energy Eq. (5) are the interacting wavefunctions $\Psi_m$. Thus,

$$E_{c,w} = \text{tr}\{\hat{D}_w\hat{H}\} - \text{tr}\{\hat{D}_{s,w}\hat{H}\} \leq 0. \tag{47}$$

The existence of a non-interacting KS system[20] means $T_{s,w}$ is the smallest possible kinetic energy for a given density $n_w(\mathbf{r})$, resulting in

$$T_{c,w} = T_w - T_{s,w} \geq 0. \tag{48}$$

From Eqs. (47) and (48), we immediately obtain

$$U_{c,w} = E_{c,w} - T_{c,w} \leq 0, \tag{49}$$

and

$$|U_{c,w}| \geq |T_{c,w}|. \tag{50}$$

These inequalities are later verified with exact ensemble KS calculations.

Since EDFT is a variational method, one expects that the virial theorem holds. This was first proven by Nagy[48,55] and later extended to excited states.[56] Here, we use the theorem to construct energy densities, which have been important interpretation tools in ground-state DFT. The virial theorem provides an expression for kinetic correlation in terms of HXC,

$$T_{c,w}[n] = -E_{\text{HXC},w}[n] - \int d^3r \, n(\mathbf{r})\mathbf{r} \cdot \nabla v_{\text{HXC},w}(\mathbf{r}), \tag{51}$$

for Hartree-exchange in terms of its potential,

$$E_{\text{HX},w}[n] = -\int d^3r \, n(\mathbf{r})\mathbf{r} \cdot \nabla v_{\text{HX},w}(\mathbf{r}), \tag{52}$$

and one relating correlation energies through the correlation potential

$$T_{c,w}[n] = -E_{c,w}[n] - \int d^3r \, n(\mathbf{r})\mathbf{r} \cdot \nabla v_{c,w}(\mathbf{r}). \tag{53}$$

The integrand of Eq. (51) can be interpreted as an energy density, since integrating over all space gives

$$E_{\text{HXC},w} + T_{c,w} = \int d^3r (e_{\text{HXC},w} + t_{c,w})$$
$$= -\int d^3r n(\mathbf{r})\mathbf{r} \cdot \nabla v_{\text{HXC},w}(\mathbf{r}), \tag{54}$$

which can easily be converted to an "unambiguous" energy density.[57]

### B. Asymptotic behavior

Reference 42 derived the ensemble derivative discontinuity of Eq. (16) for bi-ensembles, in the limit of $w \to 0$. For finite $w$ of an atomic system, as shown in our previous paper,[37] $\Delta v_{xc}$ is close to a finite constant for small $r$, and jumps to 0 at some position denoted by $r_c$. We provide the derivation of the location of $r_c$ as a function of $w$ here.

For atoms, the HOMO wavefunction and LUMO wavefunctions have the following behavior:

$$\phi_{\text{HOMO}}(\mathbf{r}) \sim Ar^{\beta}e^{-\alpha r},$$
$$\phi_{\text{LUMO}}(\mathbf{r}) \sim A'r^{\beta'}e^{-\alpha' r}, \tag{55}$$

with $\alpha \geq \alpha'$. For the bi-ensemble of the ground state and the first excited state, the ensemble density is

$$n_w(\mathbf{r}) \sim 2\sum_{n=1}^{\text{HOMO}} |\phi_n(\mathbf{r})|^2$$
$$+ w(A'^2 r^{2\beta'}e^{-2\alpha' r} - A^2 r^{2\beta}e^{-2\alpha r}), \quad r \to \infty, \tag{56}$$

assuming that the HOMO is doubly occupied. The behavior of the density at large $r$ is dominated by the density of the doubly occupied HOMO and the second term. In order to see where the density decay switches from that of the HOMO to the LUMO, we find the $r$-value at which the two differently decaying contributions are equal

$$(2 - w) A^2 r^{2\beta} e^{-2\alpha r} = w A'^2 r^{2\beta'} e^{-2\alpha r}. \tag{57}$$

As $w \to 0$, $r_c$ is then

$$r_c \to -\frac{\ln w}{2\Delta\alpha}, \tag{58}$$

with $\Delta\alpha = \alpha - \alpha'$.

The ionization energies are available for the He ground state and singlet excited state. Since

$$n(\mathbf{r}) \sim e^{-2\alpha r} \approx e^{-2\sqrt{2I}r}, \tag{59}$$

we obtain

$$r_c \to -0.621 \ln w, \quad w \to 0 \tag{60}$$

for the He singlet bi-ensemble with $w$ close to 0.

## C. Connection to ground-state DFT

With weights as in Eq. (13), calculation of the excitation energies is done recursively: for the $M$th excited state, one needs to perform an EDFT calculation with the $M$th state highest in the ensemble, and another EDFT calculation with the $(M-1)$th as the highest state, and so on. Thus, for the $M$th state, one needs to perform $M$ separate EDFT calculations for its excitation energy.

For bi-ensembles, however, the calculation of the excitation energy can be greatly simplified. Equation (14) holds for $w = 0$, so one can work with ground-state data only and obtain the first-excited state energy, without the need for an explicit EDFT calculation of the two-state ensemble.

We calculate the first excitation energies of various atoms and ions with Eq. (14) at $w = 0$ with both qLDA[21,46] (based on LDA ground states), EXX,[24] GPG,[34] and SEHX, with the last three based on OEP-EXX (KLI) ground states.[52] In order to ensure the correct symmetry in the end result, SEHX must be performed on spin-restricted ground states. However, for closed-shell systems, these results coincide with those of spin-unrestricted calculations. We use these readily available results when possible in this paper. The $w$-derivatives of the $E_{xc}$'s for qLDA and GPG required in Eq. (14) are (considering Eq. (65))

$$\lim_{w\to 0} \frac{\partial E_{xc,w}^{qLDA}[n]}{\partial w}\bigg|_{n=n_w} = M_I \left( E_{xc}^{eqLDA}[I=2,n] - E_{xc}^{LDA}[n] \right), \tag{61}$$

where $E_{xc}^{LDA}$ is the ground-state LDA functional, and

$$\lim_{w\to 0} \frac{\partial E_{X,w}^{GPG}[n]}{\partial w}\bigg|_{n=n_w}$$

$$= \iint \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} \left\{ \left[ \sum_{j=1}^{N_H} n_j(\mathbf{r}, \mathbf{r}') \right] [n_H(\mathbf{r}, \mathbf{r}') - n_L(\mathbf{r}, \mathbf{r}')] \right.$$

$$\left. - n_H(\mathbf{r})n_L(\mathbf{r}') + n_H(\mathbf{r}, \mathbf{r}')n_L(\mathbf{r}, \mathbf{r}') \right\}$$

$$+ \int d^3r \, v_{xc}(\mathbf{r})[n_H(\mathbf{r}) - n_L(\mathbf{r})], \tag{62}$$

where $j$ sums over the spin-up densities. Only ground state properties are needed to evaluate Eq. (62). The results are listed in Table I. Note that the single-determinant form of GPG performs well here, despite not being designed for this method. SEHX improves calculated excitation energies for systems where single-determinant GPG has large errors with this method, such as Be and Mg atoms.

## V. NUMERICAL PROCEDURE

We invert the ensemble KS equation with exact densities to obtain the exact KS potential. We describe the numerical inversion procedure in Ref. 37. For ease in obtaining the Hartree potential, $E_H$ is always chosen to be $E_H^{trad}$. The resulting KS potential, being exact, does not depend on the choice of $E_H$, but $E_{xc}$ and $v_{xc}(\mathbf{r})$ reported in later sections are those compatible with $E_H^{trad}$ and $v_H^{trad}(\mathbf{r})$, respectively. For simplicity, only GOK-type ensembles [Eq. (13)] are considered, though there is no difficulty adapting the method to other types of ensembles. With this numerical procedure, $v_{xc,w}(\mathbf{r})$ is determined up to an additive constant.

We implemented the numerical procedure on a real-space grid. The ensemble KS equation (8) is solved by direct diagonalization of the discrete Hamiltonian. The grid is in general nonuniform, which complicates the discretization of the KS kinetic energy operator. We tested two discretization schemes, details of which are available in the supplementary material.[66] Based on these tests, all results presented in this paper have been obtained using the finite-difference representation

$$-\frac{1}{2}\frac{d^2\phi(x)}{dx^2} \approx \frac{\phi(x_i)}{(x_i - x_{i-1})(x_{i+1} - x_i)}$$
$$- \frac{\phi(x_{i-1})}{(x_i - x_{i-1})(x_{i+1} - x_{i-1})}$$
$$- \frac{\phi(x_{i+1})}{(x_{i+1} - x_i)(x_{i+1} - x_{i-1})}. \tag{63}$$

### A. Derivative corrections

Exactness of the inversion process can be verified by calculating the excitation energies with Eq. (14) at different $w$ values. Equation (14) requires calculating $E_{xc,w}$ of the exact

ensemble KS system,

$$E_{\text{XC,w}}[n_{\text{w}}] = E_{\text{w}} - E_{\text{s,w}}$$
$$+ \int d^3r \, n_{\text{w}}(\mathbf{r}) \left[ \frac{v_{\text{H}}[n_{\text{w}}](\mathbf{r})}{2} + v_{\text{XC,w}}[n_{\text{w}}](\mathbf{r}) \right]. \quad (64)$$

Since we do not have a closed-form expression for the exact $E_{\text{XC}}$, its derivative can only be calculated numerically. However, the numerical derivative of $E_{\text{XC}}$, $\partial E_{\text{XC,w}}[n_{\text{w}}]/\partial \text{w}$, is not the quantity required in Eq. (14). It is related to the true derivative through

$$\left. \frac{\partial E_{\text{XC,w}}[n]}{\partial \text{w}} \right|_{n=n_{\text{w}}} = \frac{\partial E_{\text{XC,w}}[n_{\text{w}}]}{\partial \text{w}}$$
$$- \int d^3r \, v_{\text{XC,w}}[n_{\text{w}}](\mathbf{r}) \frac{\partial n_{\text{w}}(\mathbf{r})}{\partial \text{w}}. \quad (65)$$

The correction to the numerical derivative of $E_{\text{XC,w}}$ adjusts for the w-dependence of the ensemble density, which is not inherent to $E_{\text{XC,w}}$. All our calculations show that the two terms on the right hand side of Eq. (65) are of the same order of magnitude. This shows that the exact $E_{\text{XC,w}}[n]$ changes more slowly than $n_{\text{w}}(\mathbf{r})$ as w changes. Though the calculations of $E_{\text{XC,w}}$ and $\partial E_{\text{XC,w}}[n]/\partial \text{w}|_{n=n_{\text{w}}}$ both involve integrations containing $v_{\text{XC,w}}(\mathbf{r})$, they are independent of the additive constant.

## VI. RESULTS

We apply the numerical procedure described in Sec. V to both 1D and 3D model systems in order to further demonstrate our method for inverting ensemble densities.

### A. 1D flat box

The external potential of the 1D flat box is

$$v(x) = \begin{cases} 0, & 0 < x < L, \\ \infty, & x \leq 0 \text{ or } x \geq L. \end{cases} \quad (66)$$

The exact wavefunctions can be solved numerically for two electrons with the following soft-Coulomb interaction:

$$v_{\text{sc}}(x, x') = \frac{1}{\sqrt{(x - x')^2 + a^2}}, \quad (67)$$

where we choose $a = 0.1$.

Table II shows the total and kinetic energies of the exact ground state and first four excited states for $L = 1$ a.u., calculated on a 2D uniform grid with 1000 points for each position

TABLE II. Total and kinetic energies in a.u. for a unit-width box, including a doubly excited state ($I = 3$).

| $I$ | $E$ | $T$ |
|---|---|---|
| 0 (singlet) | 15.1226 | 10.0274 |
| 1 (triplet) | 27.5626 | 24.7045 |
| 2 (singlet) | 30.7427 | 24.7696 |
| 3 (singlet) | 43.9787 | 39.6153 |
| 4 (triplet) | 52.8253 | 49.3746 |

TABLE III. Excitation energies of the 1D box calculated at different w values using the exact ensemble KS systems and Eq. (14). The double excitation (4-multiplet) shows accuracy comparable to that of the single excitation (2-multiplet). All energies are in Hartree. See the supplementary material[66] for the full table.

| 2-multiplet: $\omega_1 = 12.4399$ hartree | | | |
|---|---|---|---|
| w2 | 0.25 | 0.125 | 0.03125 |
| $E_{1,\text{w}_2}^{\text{KS}} - E_{0,\text{w}_2}^{\text{KS}}$ | 13.9402 | 13.9201 | 13.8932 |
| $\partial E_{\text{xc,w}_2}[I = 2, n]/\partial \text{w}_2\vert_{n=n_{\text{w}_2}}$ | $-4.5010$ | $-4.4407$ | $-4.3598$ |
| $(E_1 - E_0)_{\text{w}_2}$ | 12.4399 | 12.4399 | 12.4399 |

| 3-multiplet: $\omega_2 = 15.6202$ hartree | | | |
|---|---|---|---|
| w3 | 0.2 | 0.1 | 0.025 |
| $E_{2,\text{w}_3}^{\text{KS}} - E_{0,\text{w}_3}^{\text{KS}}$ | 14.2179 | 14.0757 | 13.9735 |
| $\partial E_{\text{xc,w}_3}[I = 3, n]/\partial \text{w}_3\vert_{n=n_{\text{w}_3}}$ | 2.7358 | 2.7713 | 2.7969 |
| $(E_2 - E_0)_{\text{w}_2,\text{w}_3}$ | 15.6202 | 15.6201 | 15.6202 |

| 4-multiplet: $\omega_3 = 28.8561$ hartree (double) | | | |
|---|---|---|---|
| w4 | 0.166666 | 0.083333 | 0.020833 |
| $E_{3,\text{w}_4}^{\text{KS}} - E_{0,\text{w}_4}^{\text{KS}}$ | 28.7534 | 28.5826 | 28.4706 |
| $\partial E_{\text{xc,w}_4}[I = 4, n]/\partial \text{w}_4\vert_{n=n_{\text{w}_4}}$ | 1.1061 | 1.1186 | 1.1858 |
| $(E_3 - E_0)_{\text{w}_2,\text{w}_3,\text{w}_4}$ | 28.8561 | 28.8561 | 28.8561 |

| 5-multiplet: $\omega_4 = 37.7028$ hartree | | | |
|---|---|---|---|
| w5 | 0.111111 | 0.055555 | 0.013888 |
| $E_{4,\text{w}_5}^{\text{KS}} - E_{0,\text{w}_5}^{\text{KS}}$ | 38.8375 | 38.8602 | 38.8746 |
| $\partial E_{\text{xc,w}_5}[I = 5, n]/\partial \text{w}_5\vert_{n=n_{\text{w}_5}}$ | $-1.1279$ | $-1.2205$ | $-1.2787$ |
| $(E_4 - E_0)_{\text{w}_2,\text{w}_3,\text{w}_4,\text{w}_5}$ | 37.7028 | 37.7027 | 37.7028 |

variable. The third excited state is a doubly excited state corresponding to both electrons occupying the second orbital of the box. Fig. 1 shows the exact densities of the ground state and first four excited states, together with the XC potential of equiensembles containing 1–5 multiplets. Table III lists calculated excitation energies, showing that the excitation energy is independent of w, no matter how many states are included in the ensemble. This is a non-trivial exact condition for the ensemble $E_{\text{XC}}$.

Double excitations are generally difficult to calculate. It has been shown that adiabatic TDDFT cannot treat double or multiple excitations.[12] Table III shows that there is no fundamental difficulty in treating double excitations with EDFT. Fig. 1 shows that $v_{\text{XC,w}}(\mathbf{r})$ for the 4-multiplet equiensemble resembles the potentials of other ensembles. The exact two-multiplet ensemble XC potentials at different w are plotted in Fig. 4. The bump up near the center of the box in these
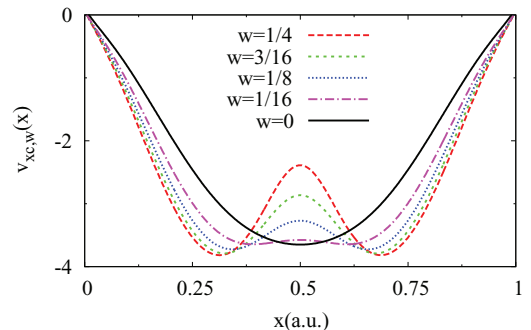


FIG. 4. Exact ensemble XC potentials of the 1D box with two electrons. The ensemble contains the ground state and the first (triplet) excited state.

potentials ensures that the ensemble KS density matches that of the real ensemble density. Increasing the proportion of the excited state density (see Fig. 1) included in the ensemble density requires a corresponding increase in the height of this bump (see the supplementary material[66]). With no asymptotic region, there is no derivative discontinuity for the box, and $v_{xc,w\to 0}(\mathbf{r})$ is equal to the ground-state $v_{xc}(\mathbf{r})$. Energy components for the bi-ensemble of the 1D box satisfy the inequalities shown in Sec. IV A and are reported in the supplementary material.[66]

## B. Charge-transfer excitation with 1D box

Charge-transfer excitations are difficult to treat with approximate TDDFT, due to the lack of overlap between orbitals.[59] With common approximations, the excitation energy calculated by TDDFT is much smaller than experimental values.[7] Here, we provide a 1D example of an excited state with CT character, showing that there is no fundamental difficulty in treating CT excitations with EDFT. Since EDFT calculations do not involve transition densities, they do not suffer from the lack-of-orbital-overlap problem in TDDFT.

The external potential for the CT box is

$$v(x) = \begin{cases} 0 & x \in [0,1] \cup [2,4] \\ 20 & x \in (1,2) \\ \infty & x < 0 \text{ or } x > 4, \end{cases} \quad (68)$$

with the barrier dimensions chosen for numerical stability of the inversion process. The lowest two eigenstate densities are given in the top of Fig. 5. The ground-state and first-excited-state total and kinetic energies of the CT system described are

$$\begin{aligned} E_0 &= 138.254 \text{ eV}, \quad T_0 = 63.4617 \text{ eV (singlet)}, \\ E_1 &= 140.652 \text{ eV}, \quad T_1 = 112.141 \text{ eV (triplet)}. \end{aligned} \quad (69)$$

This significant increase in kinetic energy together with a small total energy change designate the CT character of the first excited state. The electrons become distributed between the two wells of the potential, instead of being confined in one well.

The ground- and first-excited-state densities and ensemble XC potentials are plotted in Fig. 5. The potentials show the characteristic step-like structures of charge-transfer excitations, which align the chemical potentials of the two wells.[60,61] Table IV lists the ensemble energies of the CT box. Excitation energies have larger errors than those for the 1D flat box due to greater numerical instability, but they are still accurate to within 0.01 eV.

## C. Hooke's atom

Hooke's atom is a popular model system[39,62] with the following external potential:

$$v(\mathbf{r}) = \frac{k}{2}|\mathbf{r}|^2. \quad (70)$$

For our calculation, $k = 1/4$. Though the first excited state has cylindrical symmetry, we use a spherical grid, as it has been
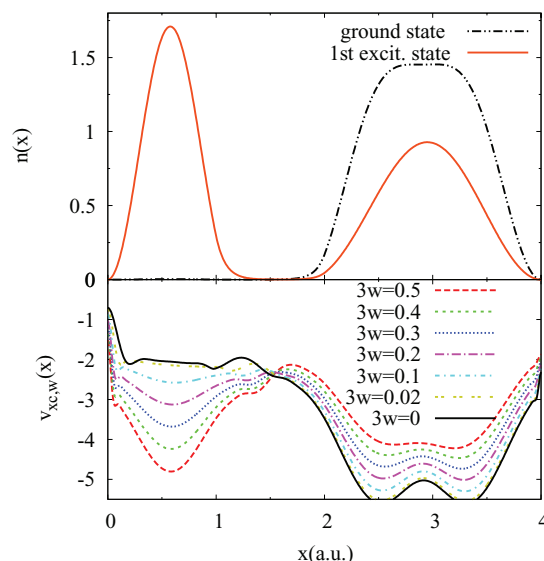


FIG. 5. Exact densities and ensemble xc potentials of the 1D charge-transfer box.

shown that the error due to spherical averaging is small.[63] As a closed-shell system, the spatial parts, and therefore the densities, of the spin-up and spin-down ensemble KS orbitals have to be the same, so we treat this system as a bi-ensemble.

The magnitude of the external potential of the Hooke's atom is smallest at $r = 0$, and becomes larger as $r$ increases. This is completely different from the Coulomb potential of real atoms. Since the electron-electron interaction is still coulombic, $v_{xc}(\mathbf{r})$ can be expected to have a $-1/r$ behavior as $r \to \infty$, which is negligibly small compared to $v(\mathbf{r})$. Combined with a density that decays faster than real atomic densities, $n(\mathbf{r}) \sim \exp(-ar^2)$ versus $n(\mathbf{r}) \sim \exp(-br)$, convergence of the Hooke's atom $v_{xc}(\mathbf{r})$ is difficult in the asymptotic region. Additionally, $v_{xc}(\mathbf{r}) \gg v(\mathbf{r})$ for small $r$, so larger discretization errors in this region also contribute to poorer inversion performance. Despite these challenges, we still obtain highly accurate excitation energies.

A logarithmic grid with 550 points ranging from $r = 10^{-5}$ a.u. to 10 a.u. is used for all the Hooke's atom calculations. On this grid, the exact ground- and first excited-state energies are

$$E_1 = 54.42 \text{ eV}, \quad E_2 = 64.19 \text{ eV}. \quad (71)$$

Calculated $\omega_2$ was 9.786 eV for all values of w tested (see the supplementary material[66]). Unlike the He atom and the 1D flat box, the $n_w(\mathbf{r})$ and $v_{xc,w}(\mathbf{r})$ show little variation with

TABLE IV. First excitation energy and energy decomposition of the two-multiplet ensemble of the 1D charge-transfer box at different w values, calculated using Eq. (14). All energies are in eV. The exact first excitation energy is $E_1 - E_0 = 2.3983$ eV. See the supplementary material[66] for additional data.

| 3w | 0.5 | 0.1 | 0.02 |
|---|---|---|---|
| $E_{1,w}^{\text{KS}} - E_{0,w}^{\text{KS}}$ | 2.2048 | 2.4092 | 2.4317 |
| $\partial E_{XC,w}[n]/\partial n\|_{n=n_w}/3$ | 0.1993 | −0.0108 | −0.0334 |
| $\omega_{1,w}$ | 2.4042 | 2.3983 | 2.3983 |

TABLE V. He atom excitation energies, calculated using Eq. (14) and various ensemble types: singlet-triplet (2-multiplet), singlet-triplet-singlet (3-multiplet), and strictly triplet. All energies are in eV. $w_2$ dependency of the 3-multiplet excitation energies is noted explicitly, though $w_2 = (1 - w_3)/4$ for the GOK ensemble. See the supplementary material[66] for additional data and figures.

| 2-multiplet ensemble: $\omega_1 = 19.8231$ eV | | | |
|---|---|---|---|
| $w_2$ | 0.25 | 0.125 | 0.03125 |
| $E_{1,w_2}^{KS} - E_{0,w_2}^{KS}$ | 25.1035 | 22.4676 | 21.6502 |
| $\partial E_{xc,w_2}[n]/\partial w_2\|_{n=n_{w_2}}$ | −15.8099 | −7.9358 | −5.4351 |
| $(E_1 - E_0)_{w_2}$ | 19.8336 | 19.8224 | 19.8385 |
| 3-multiplet ensemble: $\omega_2 = 20.6191$ eV | | | |
| $w_3$ | 0.2 | 0.1 | 0.025 |
| $E_{2,w_3}^{KS} - E_{0,w_3}^{KS}$ | 26.8457 | 25.8895 | 25.2853 |
| $\partial E_{xc,w_3}[n]/\partial w_3\|_{n=n_{w_3}}$ | −0.9596 | −0.7207 | −0.5696 |
| $(E_2 - E_0)_{w_2,w_3}$ | 20.6270 | 20.6184 | 20.6306 |
| Triplet ensemble: $\omega_1 = 2.8991$ eV | | | |
| $w$ | 0.16667 | 0.08333 | 0.02083 |
| $E_1^{KS} - E_0^{KS}$ | 2.8928 | 2.8956 | 2.8967 |
| $\partial E_{XC,w}[n]/\partial w\|_{n=n_w}$ | 0.0187 | 0.0104 | 0.0074 |
| $(E_1 - E_0)_w$ | 2.8990 | 2.8990 | 2.8992 |

w (see the supplementary material[66]). The second KS orbital of the Hooke's atom is a *p*-type orbital, which has no radial node and a radial shape similar to that of the first KS orbital. Consequently, the changes in the KS and xc potentials are also smaller.

### D. He

Using the methods in Ref. 37, we employ a Hylleraas expansion of the many-body wavefunction[64] to calculate highly accurate densities of the first few states of the He atom. We report the exact ensemble XC potentials for He singlet ensemble in that paper. Table V shows accurate excitation energies calculated from mixed symmetry, three-multiplet, and strictly triplet ensembles, demonstrating the versatility of EDFT.

Fig. 6 compares $v_{xc,w}(\mathbf{r})$ for four types of He equiensembles, highlighting their different features. The characteristic bump up in these potentials is shifted left in the 2-multiplet case, relative to the others shown. This shift has little impact on the first "shell" of the ensemble density's shell-like struc-
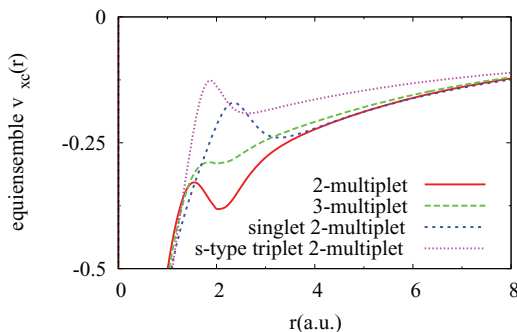


FIG. 6. Ensemble XC potentials of the singlet-triplet, singlet-triplet-singlet, strictly singlet, and strictly triplet He equiensembles.
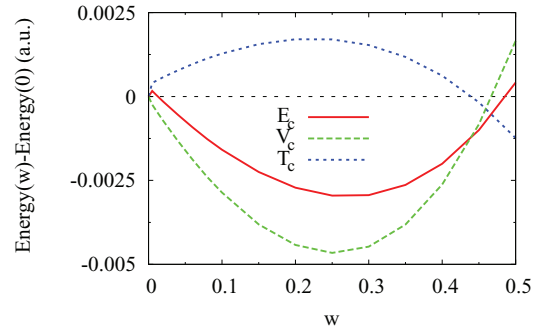


FIG. 7. Behaviors of the various energy components for the singlet ensemble of He. The ground state ($w = 0$) values are taken from Ref. 65. The small kinks near $w = 0$ are due to the difference in the numerical approaches of this work and Ref. 65.

ture, but the second is shifted left and has sharper decay, noticeably different from that of the singlet ensemble.[37]

The inequalities shown in Sec. IV A and the virial theorem Eq. (53) are verified by the exact results. Behaviors of the energy components for the singlet ensemble versus w are plotted in Fig. 7. Correlation energies show strong nonlinear behavior in w. According to Eq. (14), the excitation energies are related to the derivative of $E_{xc}$ versus w. Therefore, $E_c$ is crucial for accurate excitation energies, even though its absolute magnitude is small.

### VII. CONCLUSION

This paper is an in-depth exploration of ensemble DFT, an alternative to TDDFT for extracting excitations from DFT methodology. Unlike TDDFT, EDFT is based on a variational principle, and so one can expect that the failures and successes of approximate functionals should occur in different systems than those of TDDFT.

Apart from exploring the formalism and showing several new results, the main result of this work is to apply a new algorithm to highly accurate densities of eigenstates to explore the exact EDFT XC potential. We find intriguing characteristic features of the exact potentials that can be compared against the performance of old and new approximations. We also extract the weight-dependence of the KS eigenvalues, which are needed to extract accurate transition frequencies, and find that a large cancellation of weight-dependence occurs in the exact ensemble. Many details of these calculations are reported in the supplementary material.[66]

From the original works of Gross, Oliveira, and Kohn,[34] ensemble DFT has been slowly developed over three decades by a few brave pioneering groups, most prominently that of Nagy.[24] We hope that the insight these exact results bring will lead to a plethora of new ensemble approximations and calculations and, just possibly, a competitive method to treating excitations within DFT.

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[66]See supplementary material at http://dx.doi.org/10.1063/1.4872255 for discretization details, additional figures, and extended data tables.