

## Spurious Interactions, and Their Correction, in the Ensemble-Kohn-Sham Scheme for Excited States

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We observe that the direct Coulomb (Hartree) term appearing in the ensemble-density-functional theory for excited states contains an unphysical ("ghost") interaction which has to be corrected by the ensemble exchange and correlation functional. We propose a simple additive correction to the conventional ensemble exchange energy in the form of an orbital functional. By treating this corrected exchange energy functional self-consistently within the optimized effective potential method one finds a significant improvement of atomic excitation energies.

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Modern density functional theory (DFT) [1–3] is often the method of choice to calculate the electronic structure of atoms, molecules, and solids in the ground state. However, there is no unique generalization of DFT for excited states. Many different DF schemes dealing with excited states have been proposed, some focusing on a single excited state [4–9], some focusing on ensembles [10–19], and some relying on time-dependent DFT [20]. In the latter approach, excitation energies are determined from the poles of the frequency-dependent linear density response [21–23]. In spite of its tremendous success, the time-dependent DFT scheme has the computational disadvantage of requiring, in one way or another, the calculation of the linear density response near the poles, or, alternatively, the time propagation of the time-dependent Kohn-Sham equations [24].

In this Letter, we shall focus on the DFT for ensembles which is computationally simpler and conceptually closer to the ground state formalism. The ensemble DFT, first proposed by Theophilou [10,11], derives from a generalization of the Rayleigh-Ritz principle [10,14,25]: Consider, for simplicity, a two-state ensemble consisting of the ground state  $\Psi_0$  and the first excited state  $\Psi_1$  of the  $N$ -electron Hamiltonian [26]

$$H = T + V_{\text{ext}} + W_{\text{ee}}, \quad (1)$$

where the operators on the right-hand side represent the kinetic energy, the external potential, and the mutual Coulomb repulsion of the electrons. Then, the variational principle states that the functional

$$E^{(\omega)}[\Psi, \Psi'] = (1 - \omega)\langle\Psi|H|\Psi\rangle + \omega\langle\Psi'|H|\Psi'\rangle, \quad (2)$$

with orthonormal functions  $\Psi$  and  $\Psi'$  and  $0 < \omega \leq 1/2$ , attains its minimum value when  $\Psi = \Psi_0$  and  $\Psi' = \Psi_1$ . This statement holds true for any value of  $\omega$  in the interval  $(0, 1/2)$ . For  $\omega = 1/2$ , any two orthonormal functions lying in the space spanned by  $\Psi_0$  and  $\Psi_1$  minimize the functional (2). On one hand, one can use this ensemble

variational principle directly by inserting trial wave functions for  $\Psi$  and  $\Psi'$ . If  $\Psi$  and  $\Psi'$  are chosen to be Slater determinants  $\Phi_0$ ,  $\Phi_1$  one obtains the ensemble-Hartree-Fock (eHF) scheme by varying the ensemble energy

$$E_{\text{eHF}}^{(\omega)}[\Phi_0, \Phi_1] = (1 - \omega)\langle\Phi_0|H|\Phi_0\rangle + \omega\langle\Phi_1|H|\Phi_1\rangle \quad (3)$$

with respect to the orbitals contained in  $\Phi_0$ ,  $\Phi_1$  [27,28].

On the basis of the ensemble variational principle, Hohenberg-Kohn (HK) and Kohn-Sham (KS) type theorems have been formulated, where the ensemble spin densities

$$\rho^\sigma(\mathbf{r}) = (1 - \omega)\rho_{\Psi_0}^\sigma(\mathbf{r}) + \omega\rho_{\Psi_1}^\sigma(\mathbf{r}), \quad \sigma = \uparrow, \downarrow \quad (4)$$

serve as the basic variables.  $\rho_{\Psi_0}^\sigma(\mathbf{r})$  and  $\rho_{\Psi_1}^\sigma(\mathbf{r})$  are the spin densities associated with the ground state  $\Psi_0$  and the excited state  $\Psi_1$  of the interacting system.

In the KS scheme, the interacting ensemble is mapped onto an ensemble of noninteracting particles whose ensemble spin densities

$$\rho^\sigma(\mathbf{r}) = (1 - \omega)\rho_{\Phi_0}^\sigma(\mathbf{r}) + \omega\rho_{\Phi_1}^\sigma(\mathbf{r}), \quad \sigma = \uparrow, \downarrow \quad (5)$$

reproduce the ensemble spin densities (4) of the interacting system.  $\rho_{\Phi_0}^\sigma(\mathbf{r})$  and  $\rho_{\Phi_1}^\sigma(\mathbf{r})$  are the spin densities of the ground and first excited states,  $\Phi_0$  and  $\Phi_1$ , of the noninteracting system. Taking the case where  $\Phi_1$  differs from  $\Phi_0$  by a single-particle excitation of a spin-up electron,  $\Phi_0$  and  $\Phi_1$  will have the form  $\Phi_0 = (1/\sqrt{N!})\det[\varphi_1^\uparrow, \dots, \varphi_{N!}^\uparrow, \varphi_1^\downarrow, \dots, \varphi_{N!}^\downarrow]$  and  $\Phi_1 = (1/\sqrt{N!})\det[\varphi_1^\uparrow, \dots, \varphi_{N!-1}^\uparrow, \varphi_{N!+1}^\uparrow, \varphi_1^\downarrow, \dots, \varphi_{N!}^\downarrow]$ , where  $N^\uparrow$  ( $N^\downarrow$ ) is the number of spin-up (spin-down) electrons and  $N = N^\uparrow + N^\downarrow$ . The orbitals satisfy the ensemble KS equations

$$\left\{-\frac{\nabla^2}{2} + v_s^\sigma[\rho^\uparrow, \rho^\downarrow](\mathbf{r})\right\}\varphi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \varphi_i^\sigma(\mathbf{r}). \quad (6)$$

These equations have to be solved self-consistently with the ensemble spin densities (5) which, for the above

determinants  $\Phi_0$  and  $\Phi_1$ , take the explicit form

$$\rho^\uparrow(\mathbf{r}) = \sum_{j=1}^{N^\uparrow-1} n_j^\uparrow(\mathbf{r}) + (1 - \omega)n_{N^\uparrow}^\uparrow(\mathbf{r}) + \omega n_{N^\uparrow+1}^\uparrow(\mathbf{r}), \quad (7)$$

$$\rho^\downarrow(\mathbf{r}) = \sum_{j=1}^{N^\downarrow} n_j^\downarrow(\mathbf{r}), \quad (8)$$

with

$$n_j^\sigma(\mathbf{r}) = |\varphi_j^\sigma(\mathbf{r})|^2, \quad \sigma = \uparrow, \downarrow. \quad (9)$$

For notational simplicity we have omitted the obvious dependence of  $\varphi_j^\sigma(\mathbf{r})$  on the ensemble parameter  $\omega$ . The total energy of the interacting ensemble is given by

$$\begin{aligned} E^{(\omega)}[\rho^\uparrow, \rho^\downarrow] &= T_s^{(\omega)}[\rho^\uparrow, \rho^\downarrow] + \sum_{\sigma} \int d^3r v_{\text{ext}}^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) \\ &+ \frac{1}{2} \iint d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ E_{\text{xc}}^{(\omega)}[\rho^\uparrow, \rho^\downarrow], \end{aligned} \quad (10)$$

where  $T_s^{(\omega)}$  denotes the kinetic energy functional of the noninteracting ensemble and  $E_{\text{xc}}^{(\omega)}$  is the ensemble exchange and correlation (xc) energy.  $\rho(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r})$  is the total density. Minimization of the total energy (10) with respect to  $\rho^\sigma$  yields the explicit representation

$$\begin{aligned} E_{\text{Nagy}}^{(\omega)}[\rho^\uparrow, \rho^\downarrow] &= T_s^{(\omega)}[\rho^\uparrow, \rho^\downarrow] + \sum_{\sigma} \int d^3r v_{\text{ext}}^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) + \frac{1}{2} \iint d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &- \frac{1}{2} \sum_{\sigma} \iint d^3r d^3r' \frac{|\rho^\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \end{aligned} \quad (12)$$

where

$$\begin{aligned} \rho^\uparrow(\mathbf{r}, \mathbf{r}') &= \sum_{j=1}^{N^\uparrow-1} n_j^\uparrow(\mathbf{r}, \mathbf{r}') + (1 - \omega)n_{N^\uparrow}^\uparrow(\mathbf{r}, \mathbf{r}') \\ &+ \omega n_{N^\uparrow+1}^\uparrow(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (13)$$

$$\rho^\downarrow(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N^\downarrow} n_j^\downarrow(\mathbf{r}, \mathbf{r}') \quad (14)$$

with

$$n_j^\sigma(\mathbf{r}, \mathbf{r}') = \varphi_j^\sigma(\mathbf{r})\varphi_j^\sigma(\mathbf{r}')^*, \quad \sigma = \uparrow, \downarrow. \quad (15)$$

In this energy functional, the usual self-interaction terms contained in the ensemble Hartree energy [the third term on the right-hand side of Eq. (12)] are canceled by the corresponding self-exchange terms, similar to the ground state.

In this Letter, we propose a new orbital functional, to be used in the ensemble OEP formalism. It arises from the central observation that the same ensemble Hartree term contains an *additional* spurious (self-like) interaction

$$\begin{aligned} v_s^\sigma[\rho^\uparrow, \rho^\downarrow](\mathbf{r}) &= v_{\text{ext}}^\sigma(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \frac{\delta E_{\text{xc}}^{(\omega)}[\rho^\uparrow, \rho^\downarrow]}{\delta \rho^\sigma(\mathbf{r})} \end{aligned} \quad (11)$$

of the ensemble KS potential.

The success of any DFT crucially depends on the availability of good approximations for the xc energy functional. The standard functionals of ground-state DFT are the local density approximation (LDA) and the generalized gradient approximations (GGAs). Despite their impressive success, LDA and GGAs have one deficiency in common: They are not free from spurious self-interactions. Self-interaction corrections are most efficiently taken into account by explicitly orbital-dependent functionals. By virtue of the HK theorem, orbital functionals are implicit functionals of the spin densities and the functional derivatives of the latter can be calculated by the so-called optimized effective potential (OEP) method [29–31]. With self-interaction free functionals, especially with the exact exchange energy, the KS orbital energies are significantly improved over the LDA and GGAs: The KS band gaps are in close agreement with experiment [32], and in finite systems the Rydberg series is obtained [30]. Likewise, in the ensemble formulation, the first successful implementation [15] used an LDA-type functional [13] derived from a uniform electron gas at finite temperature. A crucial step forward was made by Nagy who introduced the OEP idea in the ensemble formalism [16] and applied it successfully to the Hartree-Fock-like functional

$$G_{\text{H}}^{(\omega)}[\rho^\uparrow, \rho^\downarrow] = \omega(1 - \omega) \iint d^3r d^3r' \frac{n_{N^\uparrow}^\uparrow(\mathbf{r})n_{N^\uparrow+1}^\uparrow(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (16)$$

not present in ordinary ground-state DFT. This term will be called *ghost interaction*. It is easily found by inserting the ensemble spin densities (7) and (8) in the Hartree energy functional. The ensemble exchange energy term [the last term on the right-hand side of Eq. (12)] contains a similar ghost interaction

$$\begin{aligned} G_{\text{x}}^{(\omega)}[\rho^\uparrow, \rho^\downarrow] &= -\omega(1 - \omega) \iint d^3r d^3r' \\ &\times \frac{n_{N^\uparrow}^\uparrow(\mathbf{r}, \mathbf{r}')n_{N^\uparrow+1}^\uparrow(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (17)$$

Unlike ordinary self-interaction terms, the ghost-Hartree and the ghost-exchange terms do not cancel each other. They correspond to the direct and exchange interaction of the orbital  $\varphi_{N^\uparrow}^\uparrow$  with the orbital  $\varphi_{N^\uparrow+1}^\uparrow$ .  $G_{\text{H}}^{(\omega)}$  and  $G_{\text{x}}^{(\omega)}$  are

unphysical because  $\varphi_{N^1}^\dagger$  and  $\varphi_{N^1+1}^\dagger$  are never occupied in one and the same determinant. We propose to employ the exchange-energy functional

$$E_x^{(\omega)}[\rho^\uparrow, \rho^\downarrow] = -\frac{1}{2} \sum_{\sigma} \iint d^3r d^3r' \times \frac{|\rho^\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - G^{(\omega)}[\rho^\uparrow, \rho^\downarrow], \quad (18)$$

where

$$\rho^\downarrow(\mathbf{x})v_x^\downarrow(\mathbf{x}) = \sum_{j=1}^{N^1+1} n_j^\downarrow(\mathbf{x}) \int d^3r n_j^\downarrow(\mathbf{r})v_x^\downarrow(\mathbf{r}) - \int \frac{d^3r |\rho^\downarrow(\mathbf{x}, \mathbf{r})|^2}{|\mathbf{x} - \mathbf{r}|} + \sum_{j=1}^{N^1+1} n_j^\downarrow(\mathbf{x}) \iint \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} n_j^\downarrow(\mathbf{r}, \mathbf{r}')\rho^\downarrow(\mathbf{r}', \mathbf{r}) \quad (20)$$

and

$$\begin{aligned} \rho^\uparrow(\mathbf{x})v_x^\uparrow(\mathbf{x}) &= \sum_{j=1}^{N^1+1} \alpha_j n_j^\uparrow(\mathbf{x}) \int d^3r n_j^\uparrow(\mathbf{r})v_x^\uparrow(\mathbf{r}) - \int \frac{d^3r |\rho^\uparrow(\mathbf{x}, \mathbf{r})|^2}{|\mathbf{x} - \mathbf{r}|} + \sum_{j=1}^{N^1+1} \alpha_j n_j^\uparrow(\mathbf{x}) \iint \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} n_j^\uparrow(\mathbf{r}, \mathbf{r}')\rho^\uparrow(\mathbf{r}', \mathbf{r}) \\ &- \omega(1 - \omega)[n_{N^1}(\mathbf{x}) + n_{N^1+1}(\mathbf{x})] \iint \frac{d^3r d^3r'}{|\mathbf{r} - \mathbf{r}'|} [n_{N^1}(\mathbf{r})n_{N^1+1}(\mathbf{r}') - n_{N^1}(\mathbf{r}, \mathbf{r}')n_{N^1+1}(\mathbf{r}', \mathbf{r})] \\ &+ \omega(1 - \omega) \int \frac{d^3r}{|\mathbf{r} - \mathbf{x}|} [n_{N^1}(\mathbf{x})n_{N^1+1}(\mathbf{r}) + n_{N^1}(\mathbf{r})n_{N^1+1}(\mathbf{x}) \\ &- n_{N^1}(\mathbf{r}, \mathbf{x})n_{N^1+1}(\mathbf{x}, \mathbf{r}) - n_{N^1}(\mathbf{x}, \mathbf{r})n_{N^1+1}(\mathbf{r}, \mathbf{x})], \end{aligned} \quad (21)$$

where  $\alpha_j = 1$ ,  $1 \leq j \leq N^1 - 1$ ,  $\alpha_{N^1} = 1 - \omega$ , and  $\alpha_{N^1+1} = \omega$ .

We have calculated the total ensemble energies of various atoms with and without the ghost-interaction correction ( $G^{(\omega)} \neq 0$ , or  $= 0$ ). In Table I, we present the results, exchange only (x only) as well as correlated (CS), through the ground-state Colle-Salvetti [38] approximation for the

$$G^{(\omega)}[\rho^\uparrow, \rho^\downarrow] = G_H^{(\omega)}[\rho^\uparrow, \rho^\downarrow] + G_x^{(\omega)}[\rho^\uparrow, \rho^\downarrow]. \quad (19)$$

With this exchange-energy functional, the total ensemble-energy functional  $E^{(\omega)}[\rho^\uparrow, \rho^\downarrow]$  is rendered ghost-interaction free. Naturally, the eHF energy  $E_{\text{eHF}}^{(\omega)}[\Phi_0, \Phi_1]$ , in (3), is also ghost-interaction free. The full OEP scheme [16], applied to the exchange functional (18), leads to an integral equation for the local ensemble exchange potential  $v_x^\sigma(\mathbf{r})$ . We solve this equation within the popular approximation by Krieger, Li, and Iafrate (KLI) [33–37], leading to

correlation energy, which is also an orbital functional. An equiensemble ( $\omega = 1/2$ ) has always been chosen. An OEP calculation (within the KLI approximation) is employed in all cases, also when we set  $G^{(\omega)} = 0$ . The states in each ensemble are proper eigenfunctions of the total spin [39] and consequently we had to use a different potential

TABLE I. Equiensemble total energies for various atoms in eV units. The ensemble configuration and dimensionality are shown in the second and third columns.

Atom	Ensemble	No. of states in ensemble	x only $G^{(\omega)} = 0$	x only $G^{(\omega)}$	CS $G^{(\omega)} = 0$	CS $G^{(\omega)}$	Experiment <sup>a</sup>
He	$\{1s^2\}^1S$ ; $\{1s2s\}^1S$	2	-66.531	-67.456	-67.565	-68.463	-68.705
He	$\{1s2s\}^3S$ ; $\{1s3s\}^3S$	2 <sup>b</sup>	-57.143	-57.606	-57.143	-57.606	-57.744
He	$\{1s2s\}^3S$ ; $\{1s2p\}^3P$	2 <sup>b,c</sup>	-58.096	-58.613	-58.096	-58.613	-58.621
He	$\{1s2s\}^3S$ ; $\{1s2p\}^3P$	4 <sup>b</sup>	-57.932	-58.313	-57.932	-58.313	-58.335
Li	$\{1s^22s\}^2S$ ; $\{1s^22p\}^2P$	4	-200.463	-200.953	-201.797	-202.287	-202.100
Li	$\{1s^22s\}^2S$ ; $\{1s^23s\}^2S$	2	-199.946	-200.382	-201.253	-201.661	-201.799
C <sup>2+</sup>	$\{1s^22s^2\}^1S$ ; $\{1s^22s2p\}^3P$	4	-985.392	-986.616	-988.113	-989.310	-989.278

<sup>a</sup>The total energy of the subspace or equiensemble is shown. In the case of an  $n$ -dimensional subspace with  $E_i$ ,  $1 \leq i \leq n$ , the  $n$  lowest eigenvalues, the total energy is equal to  $\frac{1}{n} \sum_{i=1}^n E_i$ .

<sup>b</sup>We ignore the threefold degeneracy due to the triplet spin part of the wave function.

<sup>c</sup>We have chosen one out of the three degenerate  $2p$  orbitals.

for each ensemble. These potentials were derived in a similar way to Eqs. (20) and (21). The experimental data in the eighth column are taken from the NIST database for atomic spectroscopy [40] and Ref. [41].

Comparing the results in columns 4 and 5, 6 and 7, without and with the ghost-interaction correction, we observe that the correction always lowers the energy as expected. Note that the x-only results give upper bounds to the experimental values, since they are actually upper bounds of the eHF energy (3). Comparison with experiment shows that in all cases incorporating the correction  $G^{(\omega)}$  significantly reduces the error.

When not properly subtracted, the ghost interaction terms (19) lead, in the ensemble KS equations (6), to a (direct and exchange) potential of orbital  $\varphi_{N^{\uparrow}+1}^{\uparrow}$  which acts on orbital  $\varphi_{N^{\uparrow}}^{\uparrow}$  and, likewise, to a (direct and exchange) potential of orbital  $\varphi_{N^{\downarrow}}^{\downarrow}$  acting on orbital  $\varphi_{N^{\downarrow}+1}^{\downarrow}$ . Terms similar to the latter (but not to the former) also appear in ground-state HF theory if one associates the unoccupied HF orbitals with excited electrons. It is the appearance of these terms which causes the virtual orbitals of ground-state HF theory to be too diffuse. Various remedies to cure this problem within the context of ground-state HF theory have been suggested [42–44]. In contrast to the ground-state HF case, the ghost interactions identified in this Letter contribute to the total (ensemble) energy to be minimized. The elusive *exact* ensemble KS potential should, of course, be free from the spurious ghost interactions. The central message of this Letter is that, in the necessary construction of *approximate* ensemble KS potentials, it is essential to properly subtract the spurious ghost interactions to improve the excitation energies obtained from ensemble DFT.

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