Optimized Potential Method for Ensembles of Excited States

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ABSTRACT: The optimized potential method is derived for ensembles of excited states. The ensemble Hartree–Fock method is introduced and ensemble Hartree–Fock equations are derived. By posing the ensemble Hartree–Fock method as an ensemble density functional one, an ensemble exchange potential is derived. By approximating the ensemble Hartree–Fock orbitals with the ensemble Kohn–Sham ones, the generalized version of the Krieger–Li–Iafrate (KLI) approximation to the optimized effective potential (OPM) method is obtained.   © 1998 John Wiley & Sons, Inc. Int J Quant Chem 69: 247–254, 1998

Introduction

The ground-state density functional theory [1] can be applied to the lowest excited states with different symmetries [2]. To calculate excitation energies, Slater [3] introduced the so-called transition-state method. The density functional theory was first rigorously generalized for excited states by Theophilou [4]. Formalisms for excited states were also provided by Fritsche [5] and English et al. [6]. A more general treatment was given by Gross et al. [7]. The relativistic general-

ization of this formalism was also done [8]. Recently, Görling [9] presented a new density functional formalism for excited states generalizing a recent perturbation theory [10].

Gross et al. [7] calculated the excitation energies of the He atom using the quasi-local-density approximation of Kohn [11]. The first excitation energies of several atoms [12] were calculated with the parameter-free exchange potential of Gáspár [13]. Higher excitation energies were also studied [14]. Other ground-state local-density approximations were also tested [15]. The coordinate scaling for the density matrix of ensembles was explored [16]. The ground-state adiabatic connection formula was extended to the ensemble exchange–correlation energy. A simple local ensemble exchange potential was proposed [17]. Accurate ensemble exchange potentials were calculated as a function of the radial distance from the Hartree–Fock ensemble electron density [18, 19].

Unfortunately, the exchange–correlation part of the ensemble Kohn–Sham potential is not known exactly. In the ground-state theory, the exchange potential can be treated exactly using the optimized potential method [20–23].

In this article, the optimized potential is defined for ensembles of excited states. In a recent article [24], an alternative derivation of the Krieger–Li–Iafrate (KLI) [23] approximation to the optimized effective potential (OPM) method was presented for the ground state. This method can be generalized for ensembles, making use of the ensemble Hartree–Fock method that is also introduced here.

The outline of this article is as follows: In the next section, the ensemble theory of excited states is summarized. The optimized potential method for ensembles of excited states is presented in the third section, while ensemble Hartree–Fock equations are introduced in the fourth section. In the fifth and sixth sections, a transcription of the Hartree–Fock and the Kohn–Sham equations is provided. By approximating the ensemble Hartree–Fock orbitals with the ensemble Kohn–Sham ones, the ensemble generalization of the KLI approximation to the OPM method is presented in the seventh section. A discussion and an illustrative example are presented in the eighth and ninth sections.

Density Functional Theory for Ensembles

Here, only the most general treatment of Gross et al. [7] is outlined. (The subspace theory of Theophilou [4] can be considered as a special case of the former.) The density functional theory for ensembles is based on the generalized Rayleigh–Ritz variational principle [7]. The eigenvalue problem of the Hamiltonian $\hat{H}$ is given by

$$\hat{H}\Psi_k = E_k\Psi_k \qquad (k = 1, \ldots, M), \qquad (1)$$

where

$$E_1 \le E_2 \le \cdots \qquad (2)$$

are the energy eigenvalues. The generalized Rayleigh–Ritz variational principle [7] can be applied to the ensemble energy:

$$\mathcal{E} = \sum_{k=1}^{M} w_k E_k, \qquad (3)$$

where $w_1 \ge w_2 \ge \cdots \ge w_M \ge 0$. The weighting factors w_i are chosen as

$$w_1 = w_2 = \cdots = w_{M-g} = \frac{1 - wg}{M - g} \qquad (4)$$

$$w_{M-g+1} = w_{M-g+2} = \cdots = w_M = w, \qquad (5)$$

$$0 \le w \le \frac{1}{M}, \qquad (6)$$

and

$$1 \le g \le M - 1. \qquad (7)$$

The limit $w = 0$ corresponds to the eigenensemble of $M - g$ states ($w_1 = \cdots = w_{M-g} = 1/(M - g)$ and $w_{M-g+1} = \cdots = w_M = 0$). The case $w = 1/M$ leads to the eigenensemble of M states ($w_1 = w_2 = \cdots = w_M = 1/M$).

The generalized Hohenberg–Kohn theorems read as follows:

(i) The external potential $v(r)$ is determined within a trivial additive constant by the ensemble density n defined as

$$n = \sum_{k=1}^{M} w_k n_k. \qquad (8)$$

(ii) For a trial ensemble density $n'(r)$,

$$n'(r) \ge 0 \qquad (9)$$

and

$$\int n'(\mathbf{r}) \, d\mathbf{r} = N \qquad (10)$$

$$\mathcal{E}[n] \le \mathcal{E}[n']. \qquad (11)$$

The ensemble functional $\mathcal{E}$ takes its minimum at the correct ensemble density n.

Using the variational principle, the Euler equation can be obtained:

$$\frac{\delta \mathcal{E}}{\delta n} = \mu. \qquad (12)$$

Kohn–Sham equations for the ensemble can also be derived:

$$\left[-\frac{1}{2}\nabla^2 + v_{KS} \right] u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}). \qquad (13)$$

The ensemble Kohn–Sham potential,

$$v_{KS}(\mathbf{r}; n_w) = v(\mathbf{r}) + \int \frac{n_w(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} + v_{xc}(\mathbf{r}; w, n_w), \tag{14}$$

is a functional of the ensemble density:

$$n_w^I(\mathbf{r}) = \frac{1 - wg_I}{M_{I-1}} \sum_{m=1}^{M_I - g_I} \sum_j \lambda_{mj} |u_j(\mathbf{r})|^2$$
$$+ w \sum_{\substack{m = M_I - g_I \\ +1}}^{M_I} \sum_j \lambda_{mj} |u_j(\mathbf{r})|^2. \tag{15}$$

g_I is the degeneracy of the Ith multiplet,

$$M_I = \sum_{i=1}^I g_i \tag{16}$$

is the multiplicity of the ensemble, and

$$0 \le w \le 1/M_I. \tag{17}$$

λ_{mj} are the occupation numbers. The density matrix is defined as

$$\hat{D}^{M,g,w} = \sum_{m=1}^M w_m |\Psi_m\rangle\langle\Psi_m|. \tag{18}$$

The ensemble exchange–correlation potential v_{xc} is the functional derivative of the ensemble exchange–correlation energy functional E_{xc}:

$$v_{xc}(\mathbf{r}; w, n) = \frac{\delta E_{xc}[n, w]}{\delta n(r)}. \tag{19}$$

The excitation energies can be expressed with the one-electron energies ϵ_j as

$$\bar{E}^I = \frac{1}{g_I} \frac{d\mathcal{E}^I(w)}{dw}\bigg|_{w=w_I} + \sum_{i=2}^{I-1} \frac{1}{M_I} \frac{d\mathcal{E}^I(w)}{dw}\bigg|_{w=w_i}, \tag{20}$$

where

$$\frac{d\mathcal{E}^I(w)}{dw} = \sum_{j=N+M_{I-1}}^{N-1+M_I} \epsilon_j$$
$$- \frac{g_I}{M_{I-1}} \sum_{j=N}^{N-1+M_{I-1}} \epsilon_j + \frac{\partial E_{xc}^I}{\partial w}\bigg|_{n_w} \tag{21}$$

and

$$0 \le w_i \le 1/M_I. \tag{22}$$

It is emphasized that the excitation energy cannot generally be calculated as a difference of the one-electron energies. There is an extra term $(\partial E_{xc})/(\partial w)|_{n_w}$ to be determined.

Optimized Potential Method for Ensembles of Excited States

Although the Kohn–Sham approach is an exact scheme, unfortunately, the exchange–correlation part of this Kohn–Sham potential is not known exactly. In the ground-state theory, the exchange potential can be determined exactly by finding the optimized effective potential [20–24].

The optimized potential method can be applied when the total energy is given as a functional of the one-electron orbitals u_i. Here, we consider the total ensemble energy $\mathcal{E}$ as a functional of the ensemble Kohn–Sham orbitals:

$$\mathcal{E}^{M,g,w}[u_i] = T_s^{M,g,w}[u_i] + J^{M,g,w}[u_i]$$
$$+ E_{xc}^{M,g,w}[u_i] + \int d\mathbf{r} \, v(\mathbf{r})n(\mathbf{r}), \tag{23}$$

where $T_s^{M,g,w}[u_i]$, $J^{M,g,w}[u_i]$, and $E_{xc}^{M,g,w}[u_i]$ are the noninteracting kinetic, the Coulomb, and the exchange–correlation energies for the ensemble, respectively.

The one-electron orbitals u_i are eigenfunctions of a local effective potential $V^{M,g,w}$:

$$\hat{h}^{M,g,w} u_i = \left(-\frac{1}{2}\nabla^2 + V^{M,g,w}\right) u_i = \epsilon_i u_i, \tag{24}$$

with $V^{M,g,w}$ being determined by requiring that the ensemble energy $\mathcal{E}^{M,g,w}[u_i]$ is minimized for all u_i obtained from Eq. (24). This results in

$$\frac{\delta \mathcal{E}^{M,g,w}}{\delta V^{M,g,w}} = \sum_i \int \frac{\delta \mathcal{E}^{M,g,w}}{\delta u_i^*(\mathbf{r}')} \frac{\delta u_i^*(\mathbf{r}')}{\delta V^{M,g,w}(\mathbf{r})} \, d\mathbf{r}'$$
$$+ c.c. = 0. \tag{25}$$

The functional derivative of the one-electron orbitals u_i with respect to the local effective potential $V^{M,g,w}$ can be calculated with the help of the

Green's function:

$$\frac{\delta u_i^*(\mathbf{r}')}{\delta V^{M,g,w}(\mathbf{r})} = -G_i^{M,g,w}(\mathbf{r}',\mathbf{r})u_i(\mathbf{r}), \quad (26)$$

$$\left(\hat{h}^{M,g,w} - \varepsilon_i\right)G_i^{M,g,w}(\mathbf{r}',\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}')$$
$$- u_i(\mathbf{r})u_i^*(\mathbf{r}'). \quad (27)$$

Using Eqs. (24)–(27), an integral equation for the effective ensemble exchange–correlation potential V_{xc} follows:

$$\int H^{M,g,w}(\mathbf{r},\mathbf{r}')V_{xc}^{M,g,w}(\mathbf{r}')\,d\mathbf{r}' = Q^{M,g,w}(\mathbf{r}), \quad (28)$$

$$H^{M,g,w}(\mathbf{r},\mathbf{r}') = \sum_i \lambda_i u_i^*(\mathbf{r})G_i^{M,g,w}(\mathbf{r},\mathbf{r}')u_i(\mathbf{r}'), \quad (29)$$

$$Q^{M,g,w}(\mathbf{r})$$
$$= \sum_i \lambda_i \int d\mathbf{r}'\, u_i^*(\mathbf{r})G_i^{M,g,w}(\mathbf{r},\mathbf{r}')v_{xc}^i(\mathbf{r}')u_i(\mathbf{r}'). \quad (30)$$

The orbital-dependent potential $v_{xc}^i(\mathbf{r}; M, g, w)$ is given by

$$v_{xc}^i(\mathbf{r}; M, g, w) = \frac{1}{\lambda_i u_i}\frac{\delta E_{xc}^{M,g,w}[u_i]}{\delta u_i^*}. \quad (31)$$

The effective ensemble exchange–correlation potential $V_{xc}^{M,g,w}$ can be determined from the effective potential $V^{M,g,w}$:

$$v_{xc}^{M,g,w}(\mathbf{r}) = V^{M,g,w} - v - v_J^{M,g,w}. \quad (32)$$

If the total energy were known as a functional of the one-electron orbitals u_i, Eq. (31) would result in the exact ensemble exchange–correlation potential.

It is very difficult to calculate the effective potential $V^{M,g,w}$ because of multiple numerical problems. So, an approximation, the ensemble analog of the KLI [23] approach, is presented in the seventh section.

Ensemble Hartree–Fock Equations

The subspace generalization of the Hartree–Fock method was presented by Gidopoulis and Theophilou [25]. In this article, Hartree–Fock equations for ensembles of unequally weighted states are formulated.

In the ground-state theory, the Hartree–Fock two-particle density matrix can be expressed with the one-particle density matrix γ:

$$\Gamma(\mathbf{x}_1',\mathbf{x}_2';\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{2}[\gamma(\mathbf{x}_1',\mathbf{x}_1)\gamma(\mathbf{x}_2',\mathbf{x}_2)$$
$$- \gamma(\mathbf{x}_1',\mathbf{x}_2)\gamma(\mathbf{x}_2',\mathbf{x}_1)]. \quad (33)$$

The ground-state Hartree–Fock exchange energy has the form

$$E_x^{HF} = -\frac{1}{2}\int \frac{|\gamma(\mathbf{x},\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{x}\,d\mathbf{x}'. \quad (34)$$

The ground-state Hartree–Fock exchange potentials are given by the functional derivative of the exchange energy with respect to the Hartree–Fock one-electron orbitals ϕ_i:

$$v_{xi}^{HF}\phi_i = -\int d\mathbf{x}'\frac{\gamma(\mathbf{x},\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{x}'), \quad (35)$$

where the one-particle density matrix can be expressed in terms of the Hartree–Fock one-electron orbitals:

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_j \phi_j^*(\mathbf{x}')\phi_j(\mathbf{x}). \quad (36)$$

Analogously, the ensemble Hartree–Fock two-particle density matrix is defined as

$$\Gamma^{M,g,w}(\mathbf{x}_1',\mathbf{x}_2';\mathbf{x}_1,\mathbf{x}_2)$$
$$= \frac{1}{2}\big[\gamma^{M,g,w}(\mathbf{x}_1',\mathbf{x}_1)\gamma^{M,g,w}(\mathbf{x}_2',\mathbf{x}_2)$$
$$- \gamma^{M,g,w}(\mathbf{x}_1',\mathbf{x}_2)\gamma^{M,g,w}(\mathbf{x}_2',\mathbf{x}_1)\big], \quad (37)$$

where, following Eq. (18), the one-particle matrix has the form

$$\gamma^{M,g,w} = \sum_{m=1}^M w_m \gamma_m. \quad (38)$$

γ_m is the one-particle density matrix of the m-th excited state. If the eigenfunctions of Eq. (1) are approximated by Slater determinants, the one-particle matrix can be expressed in terms of one-electron orbitals as

$$\gamma^{M,g,w}(\mathbf{x},\mathbf{x}') = \sum_j \lambda_j \psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}), \quad (39)$$

where the sum in Eq. (39) goes through all the one-electron orbitals with the nonzero occupation number λ_j. Now, we define the ensemble

Hartree–Fock exchange energy as

$$E_x^{HF}(M, g, w) = -\frac{1}{2} \int \frac{|\gamma^{M, g, w}(\mathbf{x}, \mathbf{x}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{x} \, d\mathbf{x}'. \tag{40}$$

The total ensemble Hartree–Fock energy is given by

$$\mathscr{E}_{HF}^{M, g, w}[\psi_i]$$
$$= T_{HF}^{M, g, w}[\psi_i] + J_{HF}^{M, g, w}[\psi_i]$$
$$+ E_x^{HF}(M, g, w)[\psi_i] + \int d\mathbf{r} \, v(\mathbf{r}) n(\mathbf{r}). \tag{41}$$

For the ensemble energy Eq. (3), the generalized Rayleigh–Ritz variational principle holds. The variation of the total ensemble Hartree–Fock energy leads to the ensemble Hartree–Fock equations:

$$-\frac{1}{2}\nabla^2 \psi_i + (v + v_J)\psi_i - \int d\mathbf{x}' \, \frac{\gamma_{HF}^{M, g, w}(\mathbf{x}, \mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{x}')$$
$$= \varepsilon_i \psi_i, \tag{42}$$

where ψ_i and ε_i are the ensemble Hartree–Fock one-electron orbitals and energies, respectively.

In a recent article [24], an alternative derivation of the KLI approximation was presented for the ground state. In the following sections, that method is generalized for the ensembles.

Transcription of the Ensemble Hartree–Fock Equations

The ensemble Hartree–Fock equation can be written in another form: First, we introduce the functions K_i with the following definition:

$$\psi_i = n_{HF}^{1/2} K_i. \tag{43}$$

Substituting Eq. (43) into Eq. (42), we obtain

$$\frac{\delta T_{Weiz}}{\delta n}\bigg|_{n = n_{HF}} K_i - \frac{1}{2} \frac{\nabla n_{HF}}{n_{HF}} \nabla K_i$$
$$- \frac{1}{2}\nabla^2 K_i + (v + v_J) K_i$$
$$- \int d\mathbf{x}' \, W(\mathbf{x}, \mathbf{x}') K_i(\mathbf{x}') n_{HF}(\mathbf{r}') = \varepsilon_i K_i, \tag{44}$$

where

$$W(\mathbf{x}, \mathbf{x}') = \sum_j \lambda_j K_j^*(\mathbf{x}') K_j \mathbf{x})/|\mathbf{r} - \mathbf{r}'| \tag{45}$$

and $(\delta T_{Weiz})/(\delta n)$ is the functional derivative of the full Weizsacker kinetic energy functional:

$$T_{Weiz} = \frac{1}{8} \int d\mathbf{r} \, \frac{(\nabla n)^2}{n}, \tag{46}$$

with respect to the density n. As can be seen from definition (43), the functions K_i are not all independent:

$$1 = \sum_i \lambda_i |K_i|^2. \tag{47}$$

Taking the gradient of this equation, we obtain

$$0 = \sum_i \lambda_i (K_i^* \, \nabla K_i + \nabla K_i K_i^*). \tag{48}$$

Multiplying Eq. (44) with K_i, summing for all orbitals, and using Eq. (48), then adding the complex conjugate, we arrive at the following equation:

$$\frac{\delta T_{Weiz}}{\delta n}\bigg|_{n = n_{HF}} + \frac{1}{2}\sum_i \lambda_i |\nabla K_i|^2 + v + v_J + v_S$$
$$= \sum_i \lambda_i \varepsilon_i |K_i|^2, \tag{49}$$

where v_S is the ensemble Slater potential:

$$v_S(\mathbf{x}) = -\int d\mathbf{x}' \, n_{HF}(\mathbf{x}') \left| \sum_j \lambda_j K_j^*(\mathbf{x}') K_J(\mathbf{x}) \right|^2$$
$$/|\mathbf{r} - \mathbf{r}'|. \tag{50}$$

Transcription of the Ensemble Kohn–Sham Equations

Introducing new functions k_i with definition

$$u_i = n^{1/2} k_i, \tag{51}$$

the ensemble Kohn–Sham equations [Eq. (13)] take the form

$$\frac{\delta T_{Weiz}}{\delta n}\bigg| k_i - \frac{1}{2}\frac{\nabla n}{n}\nabla k_i - \frac{1}{2}\nabla^2 k_i + v_{KS} k_i = \epsilon_i k_i. \tag{52}$$

Here, again, the functions k_i are not all independent:

$$1 = \sum_i \lambda_i |k_i|^2. \qquad (53)$$

Taking the gradient of this equation, we obtain

$$0 = \sum_i \lambda_i (k_i^* \, \nabla k_i + \nabla k_i^* k_i). \qquad (54)$$

Multiplying Eq. (52) with k_i, summing for all orbitals and using Eq. (54), and adding the complex conjugate of the equation obtained, we arrive at the following equation:

$$\frac{\delta T_{Weiz}}{\delta n} + \frac{1}{2} \sum_i \lambda_i |\nabla k_i|^2 + v_{KS} = \sum_i \lambda_i \epsilon_i |k_i|^2. \qquad (55)$$

Generalized KLI Approximation to the OPM Potential

To derive the generalized KLI approximation to the OPM potential, we compare the ensemble Hartree−Fock- and ensemble Kohn−Sham-type equations (49) and (55). We treat the case when both equations provide the same Hartree−Fock ensemble density n_{HF}, i.e,. the ensemble Hartree−Fock method is posed as an ensemble density functional theory. From Eqs. (49) and (55) then follows

$$v_x = v_S + \sum_i \lambda_i (\epsilon_i - \varepsilon_i) |k_i|^2 - \sum_i \lambda_i \varepsilon_i \big(|K_i|^2 - |k_i|^2 \big)$$

$$- \frac{1}{2} \sum_i \lambda_i \big[|\nabla k_i|^2 - |\nabla K_i|^2 \big]. \qquad (56)$$

This is an exact expression for the ensemble exchange potential provided that the ensemble density equals the Hartree−Fock ensemble density n_{HF}, i.e., the Hartree−Fock method is posed as an ensemble density functional theory. Strictly speaking, v_x^{HF} is not the exact ensemble exchange potential v_x as the Hartree−Fock ensemble density is not exactly equal to the exchange-only density of the ensemble density functional theory (for details concerning the ground-state problem, see [9, 26]), but it is very close to the exact one. So, loosely, we can refer to it as the exchange potential.

In the ground-state theory, it was found that Hartree−Fock and the corresponding OPM orbitals are very similar. (The overlap integrals are very close to unity [23].) Analogously, supposing that the ensemble Hartree−Fock orbitals are close to the Kohn−Sham ones, the ensemble exchange potential has the form

$$v_x = v_S + \sum_i \lambda_i (\epsilon_i - \varepsilon_i) |k_i|^2. \qquad (57)$$

From Eqs. (13) and (42), we obtain

$$\epsilon_i - \varepsilon_i = (\bar{v}_{xi} - \bar{v}_{xi}^{HF}), \qquad (58)$$

where $\bar{v}_{xi}$ and $\bar{v}_{xi}^{HF}$ are the expectation values of the Kohn−Sham exchange potential v_x and the Hartree−Fock exchange potentials v_{xi}^{HF} with respect to orbital u_i. Equations (57) and (58) lead to the ensemble analog of the KLI [23] approximation to the optimized potential method:

$$v_x(r) = v_S + \sum_i \frac{|u_i|^2}{n_{HF}} (\bar{v}_{xi} - \bar{v}_{xi}^{HF}), \qquad (59)$$

Discussion

The ensemble exchange−correlation and exchange energy depends on the weighting factors w. In the following, the w-dependence of the first excitation energy is discussed within the OPM scheme. In this case, the ensemble one-particle density matrix $\gamma(\mathbf{x}, \mathbf{x}')$ can be expressed in terms of the one-particle density matrices of the ground (γ_1) and the first excited states (γ_2):

$$\gamma(\mathbf{x}, \mathbf{x}') = w_1 \gamma_1(\mathbf{x}, \mathbf{x}') + w_2 \gamma_2(\mathbf{x}, \mathbf{x}'). \qquad (60)$$

Denoting with g_2 the degeneracy of the first excited state and using Eqs. (4) and (6),

$$\gamma = \gamma_1 + w g_2 \, \Delta \gamma, \qquad (61)$$

where

$$\Delta \gamma = \gamma_2 - \gamma_1. \qquad (62)$$

Similarly, the ensemble density has the form

$$n = n_1 + w g_2 \, \Delta n, \qquad (63)$$

where

$$\Delta n = n_2 - n_1. \qquad (64)$$

Now, the first excitation energy can be given as

$$\Delta E \doteq E_2 - E_1 = \frac{\mathscr{E} - E_1}{wg_2}. \qquad (65)$$

Substituting the ensemble energy $\mathscr{E}$ and the ground-state energy E_1 into Eq. (65), we obtain

$$
\begin{aligned}
\Delta E &= \Delta T + \int v\, \Delta n\, d\mathbf{r} \\
&+ \int \left[n_1(\mathbf{r}_1) + \frac{1}{2} wg_2\, \Delta n(\mathbf{r}_1) \right] \frac{\Delta n(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 \\
&- \int \left[\gamma_1(\mathbf{r}_1, \mathbf{r}_2) + \frac{1}{2} wg_2\, \Delta\gamma(\mathbf{r}_1, \mathbf{r}_2) \right] \\
&\times \frac{\Delta\gamma(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2,
\end{aligned}
\qquad (66)
$$

where

$$\Delta T = -\frac{1}{2} \int \nabla^2 [\Delta\gamma(\mathbf{r}, \mathbf{r}')]|_{r'=r}\, d\mathbf{r} = T_2 - T_1. \quad (67)$$

Thus, we arrive at the result that there is an explicit linear dependence on the weighting factor w in the first excitation energy. This dependence is a consequence of the construction of the ensemble, i.e., the ensemble classical Coulomb energy is defined [7] as

$$J = \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2. \qquad (68)$$

Another possibility would be

$$J = J_1 + J_2. \qquad (69)$$

In this case, the exchange energy would also be additive and the excitation energy would not depend on w. The disadvantage of this definition is that the Kohn–Sham potential contains explicitly not only the ensemble density but also the densi-

ties of the ground and excited states. That is why the original definition of Gross et al. [7] is applied in this article. Finally, we mention that in this way the definition of the ensemble exchange energy Eq. (40) is consistent with the definition of the ensemble classical Coulomb energy Eq. (68), in the sense that the self-interaction terms cancel.

An Illustrative Example

As an illustration, the first excitation energy of the He atom is presented. Following Gross et al. [7], the average energy of the singlet and triplet levels was calculated. Table I contains the calculated excitation energies for a couple of weighting factors w. For comparison, the Hartree–Fock [27], the experimental [28] energies, and the value calculated by Gross et al. [7] are also shown. The latter was determined using the equiensemble exchange–correlation energy functional proposed by Kohn [13]. The OPM excitation energies were determined by total energy differences [Eq. (3)] and not the one-electron energy differences [Eq. 20]. The calculation of the Slater potential [Eq. (50)] was performed for average energy configuration (also called hyper-Hartree–Fock method) [3] because of the noninteger occupation numbers. Calculations were done for a couple of weighting factors w. It follows from the definition [Eq. (40)] that the exchange energy depends on the weighting factor w. Consequently, the excitation energy also depends on w. The best value was obtained for the maximum possible value of the weighting factor w. The large difference between the OPM and Hartree–Fock numbers arises from the difference of the definitions: In the traditional Hartree–Fock method, the first excitation energy is

$$\Delta E = \Delta T + \int v\, \Delta n\, d\mathbf{r} + \Delta J + \Delta E_x, \qquad (70)$$

TABLE I

First excitation energy (in Ry) of the He atom for several values of the weighting factor w.

w	Electron configuration	OPM	HF	OGK	Exp.
0.05	$1s^{1.8}2s^{0.2}$	0.918	1.377	1.418	1.471
0.10	$1s^{1.6}2s^{0.4}$	1.020			
0.15	$1s^{1.4}2s^{0.6}$	1.138			
0.20	$1s^{1.2}2s^{0.8}$	1.265			

where

$$\Delta J = J_2 - J_1 = \frac{1}{2} \int \frac{n_1(\mathbf{r}_1)n_1(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$- \frac{1}{2} \int \frac{n_2(\mathbf{r}_1)n_2(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (71)$$

and

$$\Delta E_x = E_{x2} - E_{x1} = -\frac{1}{2} \int \frac{|\gamma_2(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$+ \frac{1}{2} \int \frac{|\gamma_1(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2,$$
$$(72)$$

which is different from expression (66). The comparison with the experimental energy shows that exchange alone is not enough and it would be important to include correlation.

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