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Energy differences between density-functional-theory functional values for the near-exact and the Hartree-Fock densities by the line-integral method

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The line-integral method developed by van Leeuwen and Baerends [Phys. Rev. A **51**, 170 (1995)] is applied to the calculation of the differences of correlation energy functional values $\Delta E_c^{\mathrm{DFT}} = E_c^{\mathrm{DFT}}[\rho_{\mathrm{HF}}] - E_c^{\mathrm{DFT}}[\rho_{\mathrm{exact}}]$, where ρ_{HF} is the Hartree-Fock density and ρ_{exact} is the near-exact one (DFT is density-functional theory). From the Kohn-Sham wave functions yielding Hartree-Fock and the near-exact densities, the corresponding noninteracting kinetic energies and the exchange energies are calculated. An approximate relation between $E_c^{\mathrm{DFT}}[\rho_{\mathrm{HF}}]$ and the conventional quantum chemistry correlation energy is presented, accurate to $\leqslant 4\mu$ hartree for the isoelectronic series of He, and Li, and for the Be atom. [S1050-2947(98)12309-0]

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I. INTRODUCTION

A fundamental component of the total electronic energy functional in density-functional theory (DFT) is the exchange-correlation energy functional $E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho]$. Recently van Leeuwen and Baerends [1] advanced energy expressions in DFT using the line-integral method. The exchange-correlation energy differences for example, can be expressed as

$$\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_2,\rho_1] \equiv E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_2] - E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_1] = \int_0^1 dt \int d\mathbf{r}\, v_{\mathrm{xc}}([\gamma(t)],\mathbf{r}) \frac{d\gamma(t)}{dt}, \quad (1)$$

where $\gamma(0)=\rho_1(\mathbf{r})$, $\gamma(1)=\rho_2(\mathbf{r})$, and $v_{\mathrm{xc}}([\gamma(t)],\mathbf{r})$ is the exchange-correlation potential corresponding to the intermediate density $\gamma(t)$. The main difficulty for a direct application of Eq. (1) is to obtain the exchange-correlation potential $v_{\mathrm{xc}}([\gamma(t)],\mathbf{r})$ for $t\epsilon[0,1]$.

Various methods for the construction of the effective Kohn-Sham (KS) potential $\hat{v}_s$, necessary to obtain a KS wave function yielding a given density, have been developed in recent years [2–10]. The exchange-correlation potential can be extracted from the effective KS potential, and Eq. (1) can be applied to calculate the difference $\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_2,\rho_1]$.

In the present work the differences $\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_2,\rho_1]$ and $\Delta E_c^{\mathrm{DFT}}[\rho_2,\rho_1] = E_c^{\mathrm{DFT}}[\rho_2] - E_c^{\mathrm{DFT}}[\rho_1]$ are calculated for the two densities $\rho_1=\rho_{\mathrm{exact}}$ and $\rho_2=\rho_{\mathrm{HF}}$ for the He isoelectronic series ($Z=2,\ 3,\ 4,\ 5$, and 10), for the Li isoelectronic series ($Z=3,\ 4,\ 5,\ 6$, and 8) and for the Be atom. Correlation or exchange-correlation energy differences are important in fitting the parameters of any approximated correlation and exchange-correlation functionals, and in assessing the quality of these functionals when Hartree-Fock (HF) ground-state densities instead of exact ones are used to evaluate the energy values. If the differences $\Delta E_c^{\mathrm{DFT}}$ and $\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}$ are found to be small, then the common use of the Hartree-Fock densities in fitting procedures will be justified.

The same differences for the noninteracting kinetic energy $T_s[\rho_{\mathrm{HF}}] - T_s[\rho_{\mathrm{exact}}]$ can be calculated in two ways: by the line-integral method (see Sec. II), and directly from the KS wave functions yielding Hartree-Fock and near-exact densities. The availability of accurate values for this difference will provide a means for estimating the accuracy of the numerical procedure. In Sec. IV, the numerical results are discussed, and the differences $\Delta E_c^{\mathrm{DFT}}$ for the He isoelectronic series are compared with the nondynamical correlation energy [11] and with the magnitude Δ introduced recently Ref. [12].

II. BASIC FORMALISM

In all systems considered in this paper no degeneracies occur. Let $\hat{H}_v$ denote the N-electron Hamiltonian which describes the systems

$$\hat{H}_v = \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{v}, \quad (2)$$

where $\hat{T}$ is the kinetic-energy operator

$$\hat{T} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 \right), \quad (3)$$

$\hat{V}_{\mathrm{ee}}$ is the electron-electron interaction operator

$$\hat{V}_{\mathrm{ee}} = \frac{1}{2}\sum_{i\neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4)$$

and $\hat{v}$ is an one-particle local external potential

$$\hat{v} = \sum_{i=1}^{N} v(\mathbf{r}_i). \quad (5)$$

A basic quantity in DFT is the noninteracting kinetic-energy functional [13,14]

$$T_s[\rho]=\inf_{\Phi_D\to\rho}\langle\Phi_D|\hat{T}|\Phi_D\rangle=\langle\Phi_D^{\mathrm{KS}}[\rho]|\hat{T}|\Phi_D^{\mathrm{KS}}[\rho]\rangle, \tag{6}$$

where Φ_D is a single-Slater determinant that yields the one-particle density ρ. Lieb [15] showed that the infimum occurs at a minimum and, thus, that there exists a wave function $\Phi_D^{\mathrm{KS}}[\rho]$. $\Phi_D^{\mathrm{KS}}[\rho]$ is the KS wave function for a given density ρ, and it is the ground-state wave function of a noninteracting Schrödinger equation with an effective local potential $\hat{v}_s=\Sigma_{i=1}^{N}v_s([\rho],\mathbf{r}_i)$,

$$\{\hat{T}+\hat{v}_s\}\Phi_D^{\mathrm{KS}}[\rho]=E_s\Phi_D^{\mathrm{KS}}[\rho]. \tag{7}$$

The noninteracting total-energy functional is the expectation value of the interacting Hamiltonian [Eq. (2)] with respect to the KS determinant $\Phi_D^{\mathrm{KS}}[\rho]$,

$$E_v^{\mathrm{KS}}[\rho]=\langle\Phi_D^{\mathrm{KS}}[\rho]|\hat{H}_v|\Phi_D^{\mathrm{KS}}[\rho]\rangle=F^{\mathrm{KS}}[\rho]+E_{\mathrm{ext}}[\rho], \tag{8}$$

where $F^{\mathrm{KS}}[\rho]$ is the KS energy functional and $E_{\mathrm{ext}}[\rho]$ is an external potential-energy functional. Introducing the Hohenberg-Kohn (HK) functional [16]

$$F^{\mathrm{HK}}[\rho]=\min_{\Psi\to\rho}\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi\rangle=\langle\Psi^{\mathrm{HK}}[\rho]|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi^{\mathrm{HK}}[\rho]\rangle, \tag{9}$$

where the variational wave function Ψ associates with a given one-electron density ρ, one can define the DFT correlation energy [16] as

$$E_c^{\mathrm{DFT}}[\rho]=F^{\mathrm{HK}}[\rho]-F^{\mathrm{KS}}[\rho]. \tag{10}$$

Next, we introduce the difference of energy functionals calculated for two densities ρ_1 and ρ_2. The energy difference $\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}$ of the exchange-correlation functional

$$E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho]=\langle\Phi_D^{\mathrm{KS}}[\rho]|\hat{V}_{\mathrm{ee}}|\Phi_D^{\mathrm{KS}}[\rho]\rangle-\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+E_c^{\mathrm{DFT}}[\rho] \tag{11}$$

is expressed through Eq. (1), where $\gamma(t)$ is a path between the two densities ρ_1 and ρ_2

$$\gamma(t)=\rho_1(\mathbf{r})+t(\rho_2(\mathbf{r})-\rho_1(\mathbf{r})), \tag{12}$$

and $v_{\mathrm{xc}}([\gamma(t)],\mathbf{r})$ is an exchange-correlation potential

$$v_{\mathrm{xc}}([\rho],\mathbf{r})=v_s([\rho],\mathbf{r})-\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'-v(\mathbf{r}), \tag{13}$$

with $\rho=\gamma(t)$.

For the noninteracting kinetic-energy difference, the equation

$$\Delta T_s[\rho_2,\rho_1]\equiv T_s[\rho_2]-T_s[\rho_1]=-\int_0^1 dt\int d\mathbf{r}\,v_s([\gamma(t)],\mathbf{r})\frac{d\gamma(t)}{dt} \tag{14}$$

also holds. The proof of Eq. (14) is straightforward from the Euler equation

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}+v_s([\rho],\mathbf{r})=\mu. \tag{15}$$

From the additivity of the exchange-correlation functional Eq. (11), i.e., $E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho]=E_x[\rho]+E_c^{\mathrm{DFT}}[\rho]$, it follows that

$$\Delta E_c^{\mathrm{DFT}}[\rho_2,\rho_1]=\Delta E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho_2,\rho_1]-\Delta E_x[\rho_2,\rho_1], \tag{16}$$

where $\Delta E_x[\rho_2,\rho_1]$ is the difference of the exchange energy, which can be calculated directly from the KS wave functions

$$\Delta E_x[\rho_2,\rho_1]\equiv E_x[\rho_2]-E_x[\rho_1]=\langle\Phi_D^{\mathrm{KS}}[\rho_2]|\hat{V}_{\mathrm{ee}}|\Phi_D^{\mathrm{KS}}[\rho_2]\rangle-\langle\Phi_D^{\mathrm{KS}}[\rho_1]|\hat{V}_{\mathrm{ee}}|\Phi_D^{\mathrm{KS}}[\rho_1]\rangle-\frac{1}{2}\int\int\frac{(\rho_2(\mathbf{r})+\rho_1(\mathbf{r}))(\rho_2(\mathbf{r}')-\rho_1(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'. \tag{17}$$

III. CALCULATIONS AND RESULTS

The differences given by Eqs. (1), (14), (16), and (17) between near-exact and HF densities have been calculated. The near-exact densities for the He isoelectronic series were taken from Ref. [17]; these densities were obtained from 204-term Hylleraas-type wave functions leading to variational energies no more than 16 nhartree above the exact ones [17]. The densities for the Li isoelectronic series were taken from Ref. [18]. These densities were obtained from 164–233-term Hylleraas-type wave functions that take into account 99.13%–99.88% of the correlation energy. The accurate density of Be atom employed in this work is that of the ‘‘exact’’ 650-term nonrelativistic wave function of

TABLE I. Noninteracting kinetic-energy functional values (hartree).

Species	$T_s[\rho_{\rm exact}]$	$-\Delta T_s = T_s[\rho_{\rm exact}] - T_s[\rho_{\rm HF}]$	$-\Delta T_s^{\rm LIM}$ [Eq. (14)]	$\dfrac{\lvert\Delta T_s - \Delta T_s^{\rm LIM}\rvert}{\Delta T_s}\times 100\%$
H^-	0.500003	0.012073	0.012071	0.017
He	2.867259	0.005579	0.005579	$\leqslant 0.02$
Li^+	7.240085	0.003670	0.003670	$\leqslant 0.03$
Be^{+2}	13.614083	0.002784	0.002784	$\leqslant 0.04$
B^{+3}	21.988478	0.002244	0.002244	$\leqslant 0.04$
Ne^{+8}	93.862252	0.001139	0.001139	$\leqslant 0.09$
Li	7.436127	0.003722	0.003722	$\leqslant 0.03$
Be^{+1}	14.279995	0.003029	0.003029	$\leqslant 0.03$
B^{+2}	23.377965	0.002439	0.002441	0.082
C^{+3}	34.727641	0.002063	0.002071	0.39
O^{+5}	64.179125	0.001584	0.001588	0.25
Be	14.593123	0.020652	0.020656	0.019

Bunge [19], which reproduces 99.55% of the correlation energy. The HF densities are of the numerical type, and were calculated with the program of Froese Fischer [20]. The scheme of our calculations consists of the following steps.

(i) Path parametrization $\gamma(t)=\rho_{\rm exact}+t(\rho_{\rm HF}-\rho_{\rm exact})$.

(ii) Kinetic-energy minimization [Eq. (6)] and determination of wave functions $\Phi_D^{\rm KS}[\gamma(t)]$ for mesh points of $t=0,0.1,\dots,1$.

(iii) Definition of the effective KS potential $v_s([\gamma(t)],\mathbf{r})$ [Eq. (7)] and the exchange-correlation potential $v_{\rm xc}([\gamma(t)],\mathbf{r})$ [Eq. (13)].

(iv) Calculation of the differences $\Delta E_{\rm xc}^{\rm DFT}$ [Eq. (1)], ΔE_x [Eq. (17)], $\Delta E_c^{\rm DFT}$ [Eq. (16)], and ΔT_s [Eq. (14)].

Steps (ii) and (iii) are performed by a modified version of the method based on local-scaling transformations (LST's) [3,4] described in the Appendix. The existence of an effective KS potential and, consequently, of an exchange-correlation potential corresponding to a density $\rho=\gamma(t)$, would be guaranteed by the noninteracting v representability [16] of the density ρ. In the present work we leave aside a comparison between KS results obtained by the LST-based method and other methods [2–7,9,10].

The noninteracting kinetic-energy differences were calculated both directly from the formula $\Delta T_s=T_s[\rho_{\rm HF}]-T_s[\rho_{\rm exact}]$ and by the line-integral method [Eq. (14)] (which allows us to obtain the $\Delta T_s^{\rm LIM}$ values). The values of $T_s[\rho_{\rm exact}]$ and the differences ΔT_s and $\Delta T_s^{\rm LIM}$ are reported in Table I. It is seen in the last column of Table I that the error of the line integral method numerical procedure is small. This error is due to the inaccuracy in the $v_s([\gamma(t)],\mathbf{r})$ definition. Because the potential $v_{\rm xc}$ has the same inaccuracy as the potential v_s, it follows that the line-integral method numerical procedure for the exchange-correlation differences [Eq. (1)] should have the same order of precision as $\Delta T_s^{\rm LIM}$, i.e., an order of 0.5 % (see Table I).

The differences $\Delta E_{\rm xc}^{\rm DFT}$ calculated by the line-integral method [Eq. (1)], and the differences ΔE_x and $\Delta E_c^{\rm DFT}$ calculated by Eqs. (17) and (16), are reported in Table II. The values of the nondynamical correlation energy $E_c^{\rm nd(II)}$ [11] and of the magnitude $\Delta=E_{c,\rm exact}^{\rm QC}-E_{c,\rm exact}^{\rm DFT}$ (introduced Ref. [12]) for the He isoelectronic series are presented for comparison. It is seen that the three last columns of Table II have the same values within a few μhartree. Using the quantity $\Delta E_c^{\text{HF-KS}}$ (introduced by Görling and Ernzerhof [21]), we can write

$$\Delta E_c^{\rm DFT}=E_c^{\rm DFT}[\rho_{\rm HF}]-E_c^{\rm DFT}[\rho_{\rm exact}]\simeq\Delta+\Delta E_c^{\text{HF-KS}}[\rho_{\rm HF}]. \tag{18}$$

Equation (18) is an approximate expression that follows from Eq. (14) of Ref. [11] and the approximate relation $\Delta E_c^{\rm DFT}\simeq E_c^{\rm nd(II)}$.

Rearranging terms in Eq. (18), one obtains an approximate equation for the conventional quantum chemistry (QC) correlation energy

$$E_{c,\rm approx}^{\rm QC}=E_c^{\rm DFT}[\rho_{\rm HF}]-\Delta E_c^{\text{HF-KS}}[\rho_{\rm HF}], \tag{19}$$

where $\Delta E_c^{\text{HF-KS}}[\rho_{\rm HF}]$ is [21]

$$\begin{aligned}\Delta E^{\text{HF-KS}}[\rho_{\rm HF}]=\{&\langle\Phi^{\rm HF}[\rho_{\rm HF}]|T+V_{\rm ee}|\Phi^{\rm HF}[\rho_{\rm HF}]\rangle\\ &-\langle\Phi^{\rm KS}[\rho_{\rm HF}]|T+V_{\rm ee}|\Phi^{\rm KS}[\rho_{\rm HF}]\rangle\}.\end{aligned} \tag{20}$$

Equation (19) corresponds to the zeroth-order term of the functional Taylor-series expansion of the functional minimized in Eq. (9) [22].

Functional $E_{c,\rm approx}^{\rm QC}$ Eq. (20) is the functional of the HF density, and it approximates the exact quantum chemistry correlation energy. In Table III, we compare the values of quantum chemistry correlation energy calculated by Eq. (19) with those calculated directly,

$$E_{c,\rm exact}^{\rm QC}=E_{\rm exact}-E_{\rm HF}, \tag{21}$$

TABLE II. The ΔE_x and $\Delta E_c^{\mathrm{DFT}}$ differences (μhartree) and comparison of $\Delta E_c^{\mathrm{DFT}}$ with $E_c^{\mathrm{nd(II)}}$ and Δ.

Species	ΔE_x	$\Delta E_c^{\mathrm{DFT}}$	$E_c^{\mathrm{nd(II)}}$ [a]	$\Delta^b = E^{\mathrm{QC}}_{c,\mathrm{exact}} - E^{\mathrm{DFT}}_{c,\mathrm{exact}}$
H^{-1}	−14502	2168		2174
He	−1183.7	63.6	63.2	63
Li^{+}	−623.7	17.0	17.2	
Be^{+2}	−440.7	7.6	7.7	7
B^{+3}	−346.5	4.3	4.4	
Ne^{+8}	−173.5	0.8		-1
Li	−90.6	57.6		
Be^{+}	−95.9	31.1		
B^{+2}	−134.8	28.2		
C^{+3}	−142.4	28.3		
O^{+5}	−129.9	15.5		
Be	7821	1224		

[a] Reference [11].

[b] Reference [12].

where E_{exact} are the total-energy values reported in Refs. [17–19], and E_{HF} are the Hartree-Fock total energy values [23]. It is seen that Eq. (19) is exact with a precision $\leqslant 4\mu$hartree for the systems calculated. This means that the term which is omitted in Eq. (19) is of the order of 4μhartree.

IV. DISCUSSION

Near-exact densities of atoms and molecules are difficult to obtain. Extensive efforts to construct them are necessary [17–19]. On the other hand, the HF densities are known for atoms and many more complex systems. For this reason it is important to calculate the exact total energy through a ''single-shot'' correlation energy calculation, adding the correlation energy to a HF calculation, i.e., using just the HF density [24]. Levy [24] formulated the existence theorem for exact quantum-chemical correlation energies from HF and exchange-only densities, i.e., there exists the appropriate universal quantum chemistry correlation energy functional of ρ_{HF} or $\rho_{x\ \mathrm{only}}$ density (see also Harris and Pratt [25]). The numerical results of Table III show that $E^{\mathrm{QC}}_{c,\mathrm{approx}}$ [Eq. (19)] is a very close approximation to this functional.

TABLE III. Approximate and exact values of the quantum chemistry correlation energy (in μhartree).

Species	$-E^{\mathrm{QC}}_{c,\mathrm{approx}}$	$-E^{\mathrm{QC}}_{c,\mathrm{exact}}$
H^{-}	39827.4	39821.4
He	42044.4	42044.4
Li^{+}	43498.2	43498.2
Be^{+2}	44266.8	44266.8
B^{+3}	44737.1	44737.1
Ne^{+8}	45692.9	45693.0
Li	4532.4	4532.4
Be^{+}	4735.7	4735.6
B^{+2}	4860.5	4860.6
C^{+3}	4943.7	4944.4
O^{+5}	5048.5	5049.0
Be	93875.1	93878.8

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APPENDIX: DETERMINATION OF KOHN-SHAM ORBITALS AND POTENTIAL BY MEANS OF LOCAL-SCALING TRANSFORMATIONS

In the constrained variation [Eq. (6)], the condition that requires the one-particle density ρ for the noninteracting system to remain fixed during minimization procedure is imposed through the use of local scaling transformations [3]. These transformations, carrying a vector $\mathbf{r} \in \mathbb{R}^3$ into another vector $\mathbf{f}(\mathbf{r}) \in \mathbb{R}^3$, connect a trial density ρ_0,

$$\rho_0(\mathbf{r}) = \sum_{i=1}^{N} |\psi_{0i}(\mathbf{r})|^2, \tag{A1}$$

to another given density ρ by means of the relation

$$\rho(\mathbf{r}) = J(\mathbf{f}(\mathbf{r});\mathbf{r})\rho_0(\mathbf{f}(\mathbf{r})) \tag{A2}$$

where $J(\mathbf{f}(\mathbf{r});\mathbf{r})$ is the Jacobian of the transformations. Introducing into Eq. (A2) the explicit form of the Jacobian, one obtains a first-order differential equation for the function $\mathbf{f}(\mathbf{r})$. For spherically symmetric one-particle densities, this equation is written explicitly as

$$\frac{df(r)}{dr} = \frac{r^2}{f^2(r)} \frac{\rho(r)}{\rho_0(f(r))}, \tag{A3}$$

and the transformed orbitals are given by

$$\psi_i([\rho];\mathbf{r})=\sqrt{\frac{\rho(r)}{\rho_0(f(r))}}\,\psi_{0i}(\mathbf{f}(\mathbf{r})), \tag{A4}$$

where $\mathbf{f}(\mathbf{r})\equiv(f(r),\theta,\phi)$ and $\mathbf{r}\equiv(r,\theta,\phi)$.

Clearly, the single-Slater determinant

$$\Phi_D[\rho]=\frac{1}{\sqrt{N!}}\det\{\psi_i([\rho];\mathbf{r}_j)\} \tag{A5}$$

yields the density ρ independently of the trial density ρ_0 [Eq. (A1)].

The orbitals [Eq. (A4)] which minimize the noninteracting kinetic energy [Eq. (6)] are the noncanonical Kohn-Sham orbitals; they satisfy the noncanonical Kohn-Sham equations

$$\{-\tfrac{1}{2}\nabla^2+v_s([\rho],\mathbf{r})\}\psi_i^{\mathrm{KS}}([\rho];\mathbf{r})=\sum_j \epsilon_{ij}^{\mathrm{KS}}\psi_j^{\mathrm{KS}}([\rho];\mathbf{r}), \tag{A6}$$

where $v_s([\rho],\mathbf{r})$ is the effective Kohn-Sham potential. Multiplying Eq. (A6) by $\overline{\psi}_i^{\mathrm{KS}}([\rho];\mathbf{r})$ and summing equations, we obtain the following expression for the potential:

$$v_s([\rho],\mathbf{r})\equiv v_s([\rho],\mathbf{r};\epsilon_{ij}^{\mathrm{KS}})=\frac{\sum_{ij}\epsilon_{ij}^{\mathrm{KS}}\overline{\psi}_i^{\mathrm{KS}}([\rho];\mathbf{r})\psi_j^{\mathrm{KS}}([\rho];\mathbf{r})+\frac{1}{2}\nabla^2\sum_i|\psi_i^{\mathrm{KS}}([\rho];\mathbf{r})|^2}{\sum_i|\psi_i^{\mathrm{KS}}([\rho];\mathbf{r})|^2}. \tag{A7}$$

In Eq. (A7), we emphasize the dependence of the effective potential expression on the eigenvalues, because we must determine them. In Ref. [4] the effective potential was calculated by an iterative procedure, and the highest occupied molecular-orbit eigenvalue was taken from experiment, i.e., as the ionization energy. In the present work the eigenvalues $\epsilon_{ij}^{\mathrm{KS}}$ were calculated from the minimization of the absolute value difference integral of the density ρ, and the ground-state density coming from the solutions of the noninteracting Schrödinger one-particle equations with the effective potential $v_s([\rho],\mathbf{r};\epsilon_{ij})$ [Eq. (A7)]

$$\begin{aligned}\delta&=\min_{\epsilon_{ij}}\int\left|\sum_k\left|\psi_k^{\mathrm{KS}}(\mathbf{r})\right|^2-\sum_k\left|\psi_k^{v(\epsilon_{ij})}(\mathbf{r})\right|^2\right|d\mathbf{r}\\&=\int\left|\sum_k\left|\psi_k^{\mathrm{KS}}(\mathbf{r})\right|^2-\sum_k\left|\psi_k^{v(\epsilon_{ij}^{\mathrm{KS}})}(\mathbf{r})\right|^2\right|d\mathbf{r},\end{aligned} \tag{A8}$$

where $\psi_k^{v(\epsilon_{ij})}(\mathbf{r})$ are the eigenfunctions of the Hamiltonian

$$\hat{h}_v=-\tfrac{1}{2}\nabla^2+v_s([\rho],\mathbf{r};\epsilon_{ij}). \tag{A9}$$

We repeat the main steps of our numerical procedure.

(i) Noninteracting kinetic-energy minimization and determination of noncanonical KS orbitals [Eqs. (6) and (A1–A5)].

(ii) Determination of the KS eigenvalues $\epsilon_{ij}^{\mathrm{KS}}$ [Eqs. (A8)–(A9)].

(iii) Calculation of the effective KS potential [Eq. (A7)].

We have expanded the trial orbitals ψ_{0i} [Eq. (A1)] in terms of the 12-term exponential-type even-tempered atomic orbitals [26]. The typical value of the δ value in Eq. (A8) is 10^{-8} for the He isoelectronic series, and is 10^{-3} for the Li isoelectronic series and for the Be atom.

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