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An energy functional of electron-pair density

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The electron-pair (or intracule) density is the probability density function for an interelectronic vector and is intimately related to the electron correlation in many-electron systems. Based on the local scaling method, a theory is presented for the direct variational determination of the electron-pair density. Illustrative applications are given for the ground state of the helium atom. Simple electron-pair density functions are reported which compare quantitatively with the exact density.

I. INTRODUCTION

Using the method of local scaling,[1-7] we have recently developed[8,9] a practical theory for the energy density functional $E[\rho]$, which enables us a *direct variational* determination of the electron density (i.e., diagonal 1 matrix) $\rho(\mathbf{r})$. For the N-electron system under consideration, we first assume the presence of an appropriate (i.e., simple yet physically acceptable) reference wave function $\Psi_0(\{\mathbf{r}_i\})$ which associates the electron density $\rho_0(\mathbf{r})$. We then construct a local scaling transformation $\mathbf{s} = \mathbf{s}(\mathbf{r})$ between the reference $\rho_0(\mathbf{r})$ and the given $\rho(\mathbf{r})$ densities, and apply it to $\Psi_0(\{\mathbf{r}_i\})$ to *generate* a wave function $\Psi_\rho(\{\mathbf{r}_i\})$ corresponding to the given density $\rho(\mathbf{r})$. The generated wave function $\Psi_\rho(\{\mathbf{r}_i\})$ has the density exactly the same as the given density $\rho(\mathbf{r})$ and hence we regard $\Psi_\rho(\{\mathbf{r}_i\})$ as a parent wave function of the density $\rho(\mathbf{r})$. The energy density functional $E[\rho]$ is then defined as the Hamiltonian expectation over the wave function $\Psi_\rho(\{\mathbf{r}_i\})$.

The approach has been actually applied[8] to the ground-state helium atom and its analogs both in position and momentum spaces. Simple position and momentum densities have been reported that well reproduce the Hartree–Fock limit energy. The applications to the Li and Be atoms,[9] which have two different electronic shells, have also been successful. Using the single-zeta wave function as a reference, we have also constructed the simple density functions whose electronic energies are lower than the reference single-zeta energies by 0.013 188 a.u. for Li and 0.012 904 a.u. for Be. A few calculations beyond the Hartree–Fock approximation have also been given[8] for the helium and helium-like atoms.

In the present paper, we develop an energy density functional theory for the electron-pair density based on the method of local scaling transformation. The electron-pair (or intracule) density $I(\mathbf{u})$ represents the probability density for the interelectronic vector $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ (see Ref. 10 for a review). Naturally, the electron-pair density $I(\mathbf{u})$ is closely connected with the electron correlation problem. Coulson and Neilson,[11] e.g., defined the Coulomb hole in terms of the difference of the Hartree–Fock and exact electron-pair densities. In Sec. II, the property of the electron-pair density is first outlined. A local scaling transformation is then introduced for the reference and given electron-pair densities, and an energy functional is defined in terms of the electron-pair density. In Sec. III, illustrative applications are presented for the helium atom. Several simple electron-pair densities are reported which well compare with that from the Hylleraas six-term wave function. Atomic units are used throughout this paper.

II. ENERGY FUNCTIONAL OF ELECTRON-PAIR DENSITY

A. Definition of electron-pair or intracule density

For the calculation of the nonrelativistic energy of an N-electron atom or molecule, the three types of density matrices are required;[12] the off-diagonal 1 matrix $\gamma(\mathbf{r};\mathbf{r}')$ for the kinetic energy T,

$$T = T[\gamma] = (-1/2)\int [\Delta_r \gamma(\mathbf{r}|\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}\, d\mathbf{r}, \tag{1a}$$

the diagonal 1 matrix $\rho(\mathbf{r})$ for the electron–nucleus attraction potential U,

$$U = U[\rho] = -\int \left[\sum_a Z_a/|\mathbf{r} - \mathbf{R}_a|\right]\rho(\mathbf{r})d\mathbf{r}, \tag{1b}$$

and the diagonal 2 matrix $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ for the electron–electron repulsion potential W,

$$W = W[\Gamma] = \int [1/|\mathbf{r}_1 - \mathbf{r}_2|]\Gamma(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1\, d\mathbf{r}_2. \tag{1c}$$

These density matrices are all derived[12] from the spinless 2 matrix $\Gamma(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2')$:

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2) = \Gamma(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2), \tag{2a}$$

$$\gamma(\mathbf{r}|\mathbf{r}') = [2/(N-1)]\int \Gamma(\mathbf{r},\mathbf{r}_2|\mathbf{r}',\mathbf{r}_2)d\mathbf{r}_2, \tag{2b}$$

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}|\mathbf{r}). \tag{2c}$$

Therefore, the 2 matrix Γ can be considered as the parent quantity for the energy. Introducing the extracular and intracular variables

$$\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \text{ and } \mathbf{R}' = (\mathbf{r}_1' + \mathbf{r}_2')/2, \tag{3a}$$

$$\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2 \text{ and } \mathbf{u}' = \mathbf{r}_1' - \mathbf{r}_2', \tag{3b}$$

we have the intracular–extracular representation of the 2 matrix:

$$\Gamma'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = \Gamma(\mathbf{R} + \mathbf{u}/2,\mathbf{R} - \mathbf{u}/2|\mathbf{R}' + \mathbf{u}'/2,\mathbf{R}' - \mathbf{u}'/2), \tag{4a}$$

whose inverse transformation is

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$$\Gamma(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2') = \Gamma'((\mathbf{r}_1+\mathbf{r}_2)/2,\mathbf{r}_1-\mathbf{r}_2|(\mathbf{r}_1'+\mathbf{r}_2')/2,\mathbf{r}_1'-\mathbf{r}_2'). \quad (4b)$$

Then the electron-pair or intracular density $I(\mathbf{u})$ is defined by

$$I(\mathbf{u}) \equiv \int \Gamma'(\mathbf{R},\mathbf{u}|\mathbf{R},\mathbf{u})d\mathbf{R}, \quad (5a)$$

$$\int I(\mathbf{u})d\mathbf{u} = N(N-1)/2, \quad (5b)$$

which is the probability density function for an interelectronic vector $\mathbf{u}$. The radial electron-pair density $f(u)$ is also defined by

$$f(u) = u^2 \int I(\mathbf{u})d\Omega, \quad (6a)$$

$$\int_0^\infty f(u)du = N(N-1)/2, \quad (6b)$$

where (u,Ω) is the spherical polar coordinates of the vector $\mathbf{u}$.

B. Generation of the 2 matrix from electron-pair density by local scaling

For the system under consideration, we assume the presence of a prototypical 2 matrix $\Gamma_0'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}')$ and the associated radial electron-pair density $f_0(u)$ as a reference. To generate a 2 matrix $\Gamma_f'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}')$ corresponding to a given radial electron-pair density $f(u)$, we first establish a local scaling between the two densities $f(u)$ and $f_0(u)$:

$$f(u) = J(v/u)f_0(v), \quad (7a)$$

where $J(v/u)$ is the Jacobian for the variable transformation $v=v(u)$ and guarantees the relation

$$J(v/u)du = dv. \quad (7b)$$

Combining Eqs. (7a) and (7b), we can determine the explicit functional form of $v=v(u)$ by the solution of either the differential equation

$$\frac{dv}{du} = f(u)/f_0(v), \quad (8a)$$

or the integral equation

$$\int_0^u f(x)dx = \int_0^{v(u)} f_0(y)dy. \quad (8b)$$

The function $v(u)$ is a monotonically increasing function of u, and $v(0)=0$ and $v(\infty)=\infty$.

Applying the local scaling $v=v(u)$ thus determined, we define a new 2 matrix $\Gamma_f'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}')$ as follows:

$$\Gamma_f'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = [J(v/u)J(v'/u')]^{1/2}\Gamma_0'(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}'), \quad (9a)$$

where

$$\mathbf{v} = [v(u),\Omega] \text{ and } \mathbf{v}' = [v(u'),\Omega'] \quad (9b)$$

in the spherical polar coordinates. In Eq. (9a), we modify only the radial variable and the angular part remains unchanged. Then it can be proved that the 2 matrix Γ_f' associates the radial electron-pair density exactly the same as the given density $f(u)$, and hence the generated 2 matrix Γ_f' can be a candidate of the parent 2 matrix of $f(u)$.

C. An energy functional

We assign the 2 matrix Γ_f' defined by Eq. (9a) to the parent 2 matrix of the given electron-pair density $f(u)$. Then the 2 matrix $\Gamma_f(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2')$ is obtained through the inverse transformation (4b), and the three density matrices $\gamma_f(\mathbf{r}|\mathbf{r}')$, $\rho_f(\mathbf{r})$, and $\Gamma_f(\mathbf{r}_1,\mathbf{r}_2)$ follow straightforwardly [Eqs. (2a)–(2c)], all of which *are* consistent with the initially given density $f(u)$. Consequently, we find that the energy E of the system is a functional of the given electron-pair density $f(u)$ and the reference 2 matrix $\Gamma_0'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = \Gamma_0(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2')$,

$$E = T[\gamma_f] + U[\rho_f] + W[\Gamma_f] = E[f,\Gamma_0']. \quad (10a)$$

Since Eq. (9a) represents a simple modification of the reference 2 matrix Γ_0', we suppose that the generated matrix Γ_f' is physically acceptable so long as Γ_0' is physically acceptable. Then the energy functional (10a) is an upper bound to the exact energy,

$$E[f,\Gamma_0'] \geqslant E_{\text{exact}}. \quad (10b)$$

For a chosen Γ_0', we can then determine the electron-pair function $f(u)$ so as to minimize the energy E. This is a direct variational determination of the radial electron-pair density.

To generate a parent 2 matrix Γ_f' of a given density $f(u)$, we have to explicitly know the local scaling transformation $v=v(u)$ by solving either Eq. (8a) or (8b). This is not a simple task. When we vary the function $f(u)$, as is the case of the present study, we can avoid this procedure.

Combining Eqs. (7a) and (9a), we have

$$\Gamma_f'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = \{[f(u)/f_0(v)][f(u')/f_0(v')]\}^{1/2} \times\Gamma_0'(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}'). \quad (11a)$$

We define the transformation $u=u(v)$ as the inverse transformation of the local scaling $v=v(u)$. Then Eq. (11a) is rewritten as

$$\Gamma_f'[\mathbf{R},\mathbf{u}(\mathbf{v})|\mathbf{R}',\mathbf{u}(\mathbf{v}')] = (\{f[u(v)]/f_0(v)\}\{f[u(v')]/f_0(v')\})^{1/2} \times\Gamma_0'(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}'), \quad (11b)$$

which can be rearranged as

$$\Gamma_f''(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}') = \{[f'(v)/f_0(v)][f'(v')/f_0(v')]\}^{1/2} \times\Gamma_0'(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}'), \quad (11c)$$

where

$$\Gamma_f''(\mathbf{R},\mathbf{v}|\mathbf{R}',\mathbf{v}') = \Gamma_f'[\mathbf{R},\mathbf{u}(\mathbf{v})|\mathbf{R}',\mathbf{u}(\mathbf{v}')], \quad (12a)$$

$$f'(v) = f[u(v)]. \quad (12b)$$

It is clear that the new 2 matrix $\Gamma_f''(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}')$ associates the radial electron-pair density $f'(u)$. The density function $f'(u)$ is specified by the given density $f(u)$ and the resultant local scaling $v=v(u)$ or $u=u(v)$ [see Eq. (12b)]. When we optimize the function $f(u)$ so as to minimize the energy functional $E[f,\Gamma_0']$, however, it is very convenient to treat the function $f'(u)$ as an independent quantity, since we can bypass the explicit determination of the scaling function.

Renaming the function $f'(u)$ as $f(u)$, we may summarize the procedure of a variational determination of the electron-pair density $f(u)$ as follows:

(i) Choose a reference 2 matrix $\Gamma_0'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}')$ which associates $f_0(u)$.

(ii) For a trial density $f(u)$, construct a 2 matrix:

$$\Gamma_f''(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = \{[f(u)/f_0(u)][f(u')/f_0(u')]\}^{1/2} \times\Gamma_0'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}'), \tag{13}$$

where $f(u)$ should satisfy the normalization condition [Eq. (6b)].

(iii) Using the densities γ_f,ρ_f, and Γ_f resulting from Eq. (13), optimize the function $f(u)$ so as to minimize the energy functional [Eq. (10a)].

III. APPLICATION TO HELIUM ATOM

A characteristic of the two-electron system is that the 2 matrix is a simple product of the wave function with its complex conjugate, i.e.,

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2') = \Psi^*(\mathbf{r}_1',\mathbf{r}_2')\Psi(\mathbf{r}_1,\mathbf{r}_2), \tag{14a}$$

$$\Gamma'(\mathbf{R},\mathbf{u}|\mathbf{R}',\mathbf{u}') = \Psi'^*(\mathbf{R}',\mathbf{u}')\Psi'(\mathbf{R},\mathbf{u}). \tag{14b}$$

Since the information contents in Γ (or Γ') and Ψ (or Ψ') are equivalent, the proposed method for the two-electron system can be rewritten in terms of the wave function. For a trial pair density $f(u)$ and a reference wave function $\Psi_0'(\mathbf{R},\mathbf{u})$, Eq. (13) reads

$$\Psi_f''(\mathbf{R},\mathbf{u}) = [f(u)/f_0(u)]^{1/2}\Psi_0'(\mathbf{R},\mathbf{u}), \tag{15a}$$

where

$$f_0(u) = u^2\int d\Omega_u \int d\mathbf{R}|\Psi_0'(\mathbf{R},\mathbf{u})|^2. \tag{15b}$$

Furthermore, it was proved[13] for the helium atom in its ground state that the exact wave function is expressible by the three basic variables $r_1\equiv|\mathbf{r}_1|$, $r_2\equiv|\mathbf{r}_2|$, and $r_{12}\equiv|\mathbf{r}_1-\mathbf{r}_2|$. In the present study, it is then convenient to use the Hylleraas variables defined by[13]

$$s\equiv r_1+r_2,\quad t\equiv r_1-r_2,\quad \text{and } u\equiv r_{12}. \tag{16}$$

In the Hylleraas coordinates, Eqs. (15a) and (15b) are rewritten as

$$\psi_f(s,t,u) = [f(u)/f_0(u)]^{1/2}\psi_0(s,t,u), \tag{17a}$$

$$f_0(u) = 2\pi^2 u\int_0^u dt\int_u^\infty ds(s^2-t^2)|\psi_0(s,t,u)|^2. \tag{17b}$$

For any $\psi_0(s,t,u)$, we can verify that the generated wave function $\psi_f(s,t,u)$ associates the electron-pair density exactly the same as the given density $f(u)$:

$$\begin{aligned}2\pi^2 u&\int_0^u dt\int_u^\infty ds(s^2-t^2)|\psi_f(s,t,u)|^2\\ &= [f(u)/f_0(u)]\left[2\pi^2 u\int_0^u dt \times\int_u^\infty ds(s^2-t^2)|\psi_0(s,t,u)|^2\right]\\ &= [f(u)/f_0(u)]f_0(u) = f(u).\end{aligned} \tag{18}$$

Now the energy functional E takes the form

$$E = E[\psi_f] = E[f;\psi_0], \tag{19}$$

which means that the energy E is a functional of the pair density $f(u)$ for a given reference function $\psi_0(s,t,u)$. In the actual calculation, we assume a density function $f(u;a,b,c...)$ which has adjustable parameters $a,b,c,...$. An appropriate reference function $\psi_0(s,t,u;\alpha,\beta...)$ with parameters $\alpha,\beta,...$ is also chosen. Then the energy functional reduces to an energy

TABLE I. Several electron-pair densities examined for the helium atom with the reference function $\psi_0 = (\alpha^3/\pi)\exp(-\alpha s)$.

Total No. of parameters	Normalized electron-pair density (optimum parameters)[a]	Energy
1	$f_0(u)$ $(\alpha = 1.687\,50)$	$-2.847\,656$
3	$N^2u^a\exp(-bu)$ $(a = 2.734\,21, b = 2.650\,78; \alpha = 1.851\,61; N = 2.962\,58)$	$-2.874\,526$
3	$N^2(u^2+au^3)\exp(-bu)$ $(a = 8.875\,43, b = 2.798\,03; \alpha = 1.854\,27; N = 1.020\,55)$	$-2.885\,799$
4	$N^2u^a\exp(-bu^c)$ $(a = 2.213\,12, b = 1.446\,06, c = 1.366\,42; \alpha = 1.848\,24; N = 1.643\,55)$	$-2.889\,324$
4	$N^2(u^2+au^3+bu^4)\exp(-cu)$ $(a = 3.930\,70, b = 7.234\,58, c = 3.315\,38; \alpha = 1.848\,48; N = 1.209\,52)$	$-2.891\,234$
5	$N^2(u^2+au^3+bu^4+cu^5)\exp(-du)$ $(a = 4.391\,38, b = 7.437\,47, c = 1.797\,93, d = 3.482\,31; \alpha = 1.848\,33; N = 1.198\,56)$	$-2.891\,254$
5	$N^2(u^2+au^3+bu^4)\exp(-cu^d)$ $(a = 3.949\,50, b = 5.908\,74, c = 3.180\,29, d = 1.021\,41; \alpha = 1.848\,33; N = 1.196\,17)$	$-2.891\,254$
...	Exact[b]	$-2.903\,724$

[a] N stands for the normalization constant.

[b] Reference 16.

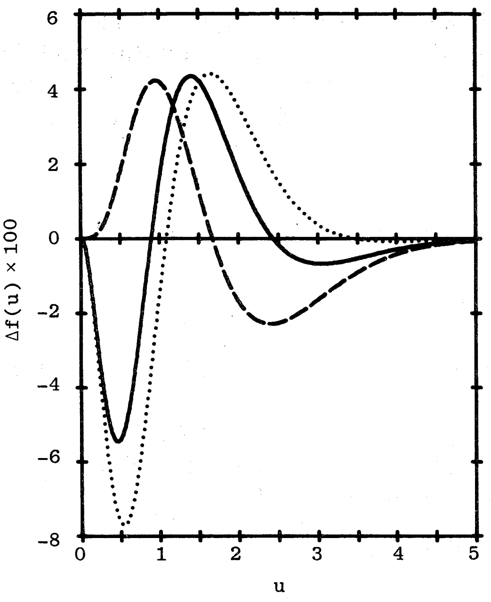

FIG. 1. Comparison of the helium Coulomb hole functions $\Delta f(u)$ when the reference function (21a) is employed. Dashed, solid, and dotted lines mean the reference, generated, and exact hole functions, respectively.

function with respect to the parameters embedded in f and ψ_0:

$$E[f;\psi_0] = E(a,b,c,...;\alpha,\beta,...), \tag{20}$$

and hence the variational problem is simplified to the optimization problem.

As a reference function, we have first employed the Kellner (or single-zeta) function,[14]

$$\psi_0(s,t,u) = (\alpha^3/\pi)\exp(-\alpha s), \tag{21a}$$

which associates the electron-pair density

$$f_0(u) = (1/6)\alpha^3u^2(3 + 6\alpha u + 4\alpha^2u^2)\exp(-2\alpha u). \tag{21b}$$

For a given $f(u)$ the wave function ψ_f has been generated through Eq. (17). The integrations involved in the evaluation of the associated energy have been performed analytically with respect to s and t, and numerically with respect to u using the double exponential method.[15]

After the examination of various functions for $f(u)$, we have found that functions simply constructed from a polynomial and an exponential give sufficiently good results. Table I summarizes several of such functions. The energy improvement is almost "saturated" when we cast four adjustable parameters in $f(u)$. For the reference function (21), the present best energy is obtained to be $-2.891\,254$ with the density,

$$f(u) = N^2(u^2 + au^3 + bu^4)\exp(-cu^d). \tag{22}$$

The energy is lower than the energy of ψ_0 by 0.043 598. Since the energy difference between the reference and exact wave functions is 0.056 068, the present method recovers 77.8% of this difference. The energy improvement is really remarkable.

The behavior of the generated electron-pair density $f(u)$ is shown in Fig. 1 using the Coulomb hole function[11] defined by

$$\Delta f(u) = f(u) - f_{\rm HF}(u), \tag{23a}$$

$$\int_0^\infty \Delta f(u)du = 0, \tag{23b}$$

where $f_{\rm HF}(u)$ is the Hartree–Fock electron-pair density which we have obtained from the Clementi–Roetti wave

TABLE II. Several electron-pair densities examined for the helium atom with the reference function $\psi_0 = N_0\exp(-\alpha s)(1 + \beta t^2)$.

Total No. of parameters	Normalized electron-pair density (optimum parameters)[a]	Energy
2	$f_0(u)$ $(\alpha = 1.685\,60, \beta = 0.140\,10)$	$-2.876\,675$
4	$N^2u^a\exp(-bu)$ $a = 2.697\,54, b = 2.535\,58; \alpha = 1.805\,41, \beta = 0.095\,11;$ $N = 2.738\,85)$	$-2.888\,817$
4	$N^2(u^2 + au^3)\exp(-bu)$ $(a = 8.090\,56, b = 2.708\,06; \alpha = 1.809\,86, \beta = 0.090\,79;$ $N = 0.998\,35)$	$-2.898\,800$
5	$N^2u^a\exp(-bu^c)$ $(a = 2.228\,32, b = 1.454\,75, c = 1.331\,62; \alpha = 1.809\,30,$ $\beta = 0.084\,14; N = 1.617\,87)$	$-2.900\,109$
5	$N^2(u^2 + au^3 + bu^4)\exp(-cu)$ $(a = 4.275\,99, b = 6.052\,80, c = 3.182\,51; \alpha = 1.809\,08,$ $\beta = 0.084\,63; N = 1.149\,27)$	$-2.902\,253$
6	$N^2(u^2 + au^3 + bu^4)\exp(-cu^d)$ $(a = 4.253\,72, b = 7.540\,87, c = 3.327\,99, d = 0.977\,70;$ $\alpha = 1.809\,05, \beta = 0.084\,90; N = 1.163\,51)$	$-2.902\,273$
7	$N^2(u^2 + au^3 + bu^4 + cu^5)\exp(-du^e)$ $(a = 6.761\,66, b = 13.392\,55, c = 13.340\,33, d = 4.323\,58,$ $e = 0.895\,53; \alpha = 1.809\,02, \beta = 0.084\,93; N = 1.166\,18)$	$-2.902\,280$
...	Exact[b]	$-2.903\,724$

[a] N stands for the normalization constant.

[b] Reference 16.

function.[17] Also plotted in Fig. 1 are the Coulomb hole functions associated with the reference wave function (21) and the exact wave function. The Hylleraas six-term wave function[13,18] has been regarded as giving the exact $f(u)$ to avoid undue numerical complexity. It is clear in the figure that the reference density $f_0(u)$ exhibits an incorrect behavior; the exact $\Delta f(u)$ shows a decrease/increase in a small/large u region, while the reference $\Delta f(u)$ shows the opposite change. On the other hand, the generated pair density has a qualitatively correct character.

The second wave function we have employed as a reference function is

$$\psi_0(s,t,u) = N_0 \exp(-\alpha s)(1+\beta t^2), \tag{24a}$$

which includes two adjustable parameters. N_0 is the normalization constant

$$N_0^{-2} = (\pi^2/\alpha^{10})(\alpha^4 + 3\alpha^2\beta + 9\beta^2), \tag{24b}$$

and the associated electron-pair density is

$$\begin{aligned} f_0(u) = N_0^2(\pi^2u^2/210\alpha^3)[&3\beta^2(4w^2+14w+7)u^4 \\ &+ 14\beta(4w^2+10w+5)u^2 \\ &+ 35(4w^2+6w+3)]\exp(-2w), \end{aligned} \tag{24c}$$

where $w = \alpha u$. The results of the density functional calculations are summarized in Table II. To obtain a "saturated energy," a five-parameter function has been required in the present case. The lowest energy ($-2.902\,280$) has been obtained with the density function,

$$f(u) = N^2(u^2 + au^3 + bu^4 + cu^5)\exp(-du^e). \tag{25}$$

The energy is lower than that of the reference function (24a) by 0.025 605 and covers 94.7% of the energy gap between the reference and exact wave functions. The generated pair density is compared in Fig. 2 with the reference and exact ones using the Coulomb hole function $\Delta f(u)$. The reference density $f_0(u)$ [Eq. (24c)] already reveals correct qualitative features, but it is clear that the generated density has a Coulomb hole which compares quantitatively with the exact Coulomb hole. The simplicity of the function (25) is noticeable.

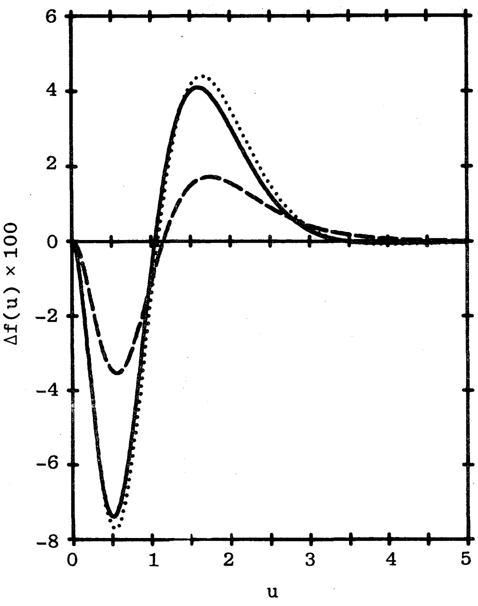

FIG. 2. Comparison of the helium Coulomb hole functions $\Delta f(u)$ when the reference function (24a) is employed. See the caption to Fig. 1.

TABLE III. Several electron-pair densities examined for the helium atom with the reference function $\psi_0 = N_0\exp(-\alpha s)(1+\beta t^2+\gamma u)$.

Total No. of parameters	Normalized electron-pair density (optimum parameters)[a]	Energy
3	$f_0(u)$ ($\alpha = 1.816\,07, \beta = 0.130\,81, \gamma = 0.291\,79$)	$-2.902\,432$
5	$N^2u^a\exp(-bu)$ ($a = 2.701\,84, b = 2.538\,43; \alpha = 1.805\,09, \beta = 0.129\,72,$ $\gamma = 0.181\,59; N = 2.743\,15$)	$-2.888\,998$
5	$N^2(u^2+au^3)\exp(-bu)$ ($a = 8.157\,81, b = 2.707\,62; \alpha = 1.809\,45, \beta = 0.141\,39,$ $\gamma = 0.283\,21; N = 0.994\,32$)	$-2.899\,094$
6	$N^2u^a\exp(-bu^c)$ ($a = 2.218\,82, b = 1.421\,64, c = 1.348\,01; \alpha = 1.808\,03,$ $\beta = 0.248\,75, \gamma = 1.058\,33; N = 1.591\,80$)	$-2.901\,116$
6	$N^2(u^2+au^3+bu^4)\exp(-cu)$ ($a = 4.090\,36, b = 6.308\,10, c = 3.195\,02; \alpha = 1.808\,11,$ $\beta = 0.214\,76, \gamma = 0.826\,27; N = 1.153\,50$)	$-2.903\,002$
7	$N^2(u^2+au^3+bu^4+cu^5)\exp(-du)$ ($a = 4.147\,85, b = 6.456\,09, c = 0.292\,97, d = 3.236\,88;$ $\alpha = 1.808\,11, \beta = 0.215\,20, \gamma = 0.829\,42; N = 1.152\,92$)	$-2.903\,002$
7	$N^2(u^2+au^3+bu^4)\exp(-cu^d)$ ($a = 4.090\,79, b = 6.194\,49, c = 3.183\,20, d = 1.001\,86;$ $\alpha = 1.808\,11, \beta = 0.215\,33, \gamma = 0.830\,32; N = 1.152\,41$)	$-2.903\,002$
...	Exact[b]	$-2.903\,724$

[a] N stands for the normalization constant.
[b] Reference 16.

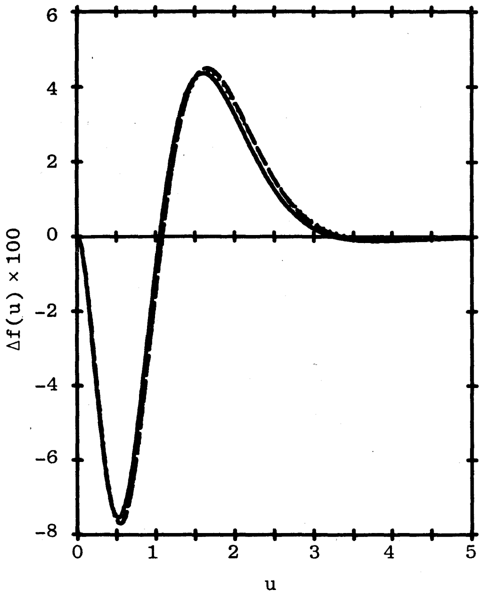

FIG. 3. Comparison of the helium Coulomb hole functions $\Delta f(u)$ when the reference function (26a) is employed. See the caption to Fig. 1.

The third (and last) example of the present approach uses the three-parameter reference function

$$\psi_0(s,t,u) = N_0 \exp(-\alpha s)(1+\beta t^2+\gamma u), \tag{26a}$$

$$N_0^{-2} = (\pi^2/8\alpha^{10})(8\alpha^4+35\alpha^3\gamma + 24\alpha^2\beta+48\alpha^2\gamma^2+77\alpha\beta\gamma+72\beta^2), \tag{26b}$$

$$f_0(u) = N_0^2(\pi^2u^2/210\alpha^3)[3\beta^2(4w^2+14w+7)u^4 + 14\beta(\gamma u+1)(4w^2+10w+5)u^2 + 35(\gamma u+1)^2(4w^2+6w+3)]\exp(-2w), \tag{26c}$$

where $w=\alpha u$. The results for several simple pair density functions are summarized in Table III. Since the reference function (26a) is considerably accurate by itself, the first three density functions in the table cannot give an energy better than the reference energy ($-2.902\,432$). The three- and four-parameter electron-pair densities improve the energy, but its amount is small (0.000 570). Inclusion of additional parameters has not given essential improvement and the energy lowering has seemed to be saturated with these functions. As a result, all the Coulomb hole functions derived from the reference, exact, and present best electron-pair densities are almost superimposable (as seen in Fig. 3).

In summary, we have developed an energy functional theory for the electron-pair density based on the local scaling method. The method has been applied to the helium atom in its ground state and simple electron-pair densities have been determined which quantitatively compare with the exact density. The approach has been found to be effective particularly when the reference function is not sufficiently accurate.

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