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# Local-scaling density-functional theory for excited states

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The local-scaling density-functional method enables us to determine the ground-state electron density directly and variationally through the generation of a parent wave function of a given density. A generalization of the method to excited states is developed by the use of a configuration-interaction-type reference wave function. From a given density which approximates the  $n$ th-state density, all the  $m$ th-state wave functions ( $m \leq n$ ) are generated in such a manner that they satisfy the wave function and Hamiltonian orthogonalities. The  $n$ th-state electron density is determined so as to minimize the Hamiltonian expectation value over the generated  $n$ th-state wave function. An illustrative application is presented for the  $2^1S$  state of the helium atom, and simple electron-density functions which compare well with the near-exact density are reported.

## I. INTRODUCTION

The local scaling<sup>1,2</sup> modifies the spatial coordinates  $\{\mathbf{r}_i\}$  of electrons in the wave function in a locally different manner based on scaling functions  $\{s_i = s(\mathbf{r}_i)\}$ , where the subscript  $i$  enumerates the electrons in the system. The ordinary (or uniform) scaling method<sup>3</sup> corresponds to a special case of the local scaling method, where the scaling function is taken to be  $\{s_i = \eta r_i\}$  with  $\eta$  being a positive constant.

Recently, Kryachko and co-workers<sup>4</sup> proposed an application of the local-scaling method to the construction of the unknown parent wave function from a given one-electron density  $\rho(\mathbf{r})$ . For the  $N$ -electron system under consideration, they assume the presence of an appropriate reference electron density  $\rho_0(\mathbf{r})$  whose parent wave function  $\Psi_0(\{\mathbf{r}_k\})$  is known. (The symbol  $\{\mathbf{r}_k\}$  stands for the spatial coordinates of the  $N$  electrons collectively. Spin variables are suppressed, since they play no direct role in the present study.) They first construct a local-scaling transformation  $\mathbf{s} = \mathbf{s}(\mathbf{r})$  between the reference  $\rho_0(\mathbf{r})$  and given  $\rho(\mathbf{r})$  densities. The transformation is then applied to the reference wave function  $\Psi_0(\{\mathbf{r}_k\})$  to generate a new wave function  $\Psi_\rho(\{\mathbf{r}_k\})$  in such a manner that  $\Psi_\rho(\{\mathbf{r}_k\})$  has an electron density exactly the same as the given density  $\rho(\mathbf{r})$ . The generated function  $\Psi_\rho(\{\mathbf{r}_k\})$  is regarded as a parent wave function of  $\rho(\mathbf{r})$ , and the energy associated with the given density  $\rho(\mathbf{r})$  is defined by

$$E(\rho) = \langle \Psi_\rho | H | \Psi_\rho \rangle / \langle \Psi_\rho | \Psi_\rho \rangle,$$

where  $H$  is the Hamiltonian of the system. Within the framework of the chosen reference wave function  $\Psi_0(\{\mathbf{r}_k\})$ , the energy  $E$  is thus a functional of the electron density, and the density  $\rho(\mathbf{r})$  can be determined variationally so as to minimize the energy  $E(\rho)$ . An analogous procedure has been developed in momentum space.<sup>5</sup> The method may be called the local-scaling density-functional method.

The method has been actually applied<sup>6</sup> to the ground-state helium atom and its analogs both in position and momentum spaces. Simple position and momentum densities, which well reproduce the Hartree-Fock limit energy, have been reported. The applications to the Li and Be atoms have

also been successful.<sup>7</sup> Using the single- $\zeta$  wave function as a reference, we have been able to construct simple density functions which have a near double- $\zeta$  accuracy. A few calculations beyond the Hartree-Fock approximation have been also performed<sup>6</sup> for the helium and helium-like atoms.

However, the local-scaling density-functional method applies only to the ground state (i.e., the lowest-energy state of the same symmetry) of a system in its original form. In the present paper, we develop a generalized version of the local-scaling density-functional theory which works for excited states as well as for the ground state. In the next section, our formalism is presented. We use a configuration-interaction (CI) type reference wave function. From a given density  $\rho(\mathbf{r})$  which approximates the  $n$ th-state density, we generate all the  $m$ th-state wave functions  $\{\Psi_{m,\rho}\}$  ( $m \leq n$ ) in such a manner that they satisfy the wave function and Hamiltonian orthogonalities. The  $n$ th-state density  $\rho(\mathbf{r})$  is determined so as to minimize the energy density functional

$$E_n(\rho) = \langle \Psi_{n,\rho} | H | \Psi_{n,\rho} \rangle / \langle \Psi_{n,\rho} | \Psi_{n,\rho} \rangle$$

defined through the  $n$ th-state wave function  $\Psi_{n,\rho}$ , which is generated under the two orthogonality conditions. In Sec. III, numerical illustrations are given for the  $2^1S$  state of the helium atom. Simple density functions which compare well with the near-exact density due to Coolidge and James<sup>8</sup> are obtained. Atomic units are used throughout this paper.

## II. FORMALISM

In order to establish an energy functional  $E_n(\rho)$  of the electron density  $\rho(\mathbf{r})$  for the  $n$ th state following the local-scaling density-functional spirit, we have to generate a corresponding (normalized)  $n$ th-state wave function  $\Psi_{n,\rho}(\{\mathbf{r}_k\})$  from the given density  $\rho(\mathbf{r})$ . Moreover, the generated wave function  $\Psi_{n,\rho}$  is required to satisfy the wave function and Hamiltonian orthogonalities,

$$\langle \Psi_{n,\rho} | \Psi_{m,\rho} \rangle = \delta_{nm}, \quad (1a)$$

$$\langle \Psi_{n,\rho} | H | \Psi_{m,\rho} \rangle = E_n(\rho) \delta_{nm}. \quad (1b)$$

Equation (1) implies that from the given density  $\rho(\mathbf{r})$ , we

have to generate not only the  $n$ th-state function  $\Psi_{n,\rho}$  but also other (lower) state functions  $\{\Psi_{m,\rho}\}$  in such a manner that they satisfy Eq. (1).

For this purpose, we start from a reference function in the form of a CI function,

$$\Psi_{n,0}(\{\mathbf{r}_k\}) = B_0 C_n = \sum_{i=1}^M C_{in} \psi_{i,0}(\{\mathbf{r}_k\}), \quad (2)$$

where  $B_0$  is a row matrix of  $M$  basis configuration functions,

$$B_0 = (\psi_{1,0}, \psi_{2,0}, \dots, \psi_{M,0}), \quad (3a)$$

and  $C_n$  is a column matrix of expansion coefficients,

$$C_n = (C_{1n}, C_{2n}, \dots, C_{Mn}). \quad (3b)$$

Until the last stage of the present theory, we keep the explicit value of  $C_n$  unspecified except for the imposition of the normalization condition,

$$C_n^+ S_0 C_n = 1, \quad (4)$$

where  $S_0$  is the overlap matrix between the basis configurations,

$$S_0 = (S_{ij,0}), \quad (5a)$$

$$S_{ij,0} = \int \psi_{i,0}^*(\{\mathbf{r}_k\}) \psi_{j,0}(\{\mathbf{r}_k\}) d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (5b)$$

The electron density  $\rho_{n,0}(\mathbf{r})$  associated with the reference function (2) is defined by

$$\rho_{n,0}(\mathbf{r}) = N \int |\Psi_{n,0}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6)$$

Let a trial density  $\rho(\mathbf{r})$  (normalized to  $N$ ) be given as an approximation to the  $n$ th-state electron density. The two densities  $\rho_{n,0}(\mathbf{r})$  and  $\rho(\mathbf{r})$  can be related to each other through the local-scaling transformation,<sup>4</sup>

$$\rho(\mathbf{r}) = J(\mathbf{s}/\mathbf{r}) \rho_{n,0}(\mathbf{s}), \quad (7a)$$

where  $\mathbf{s} = \mathbf{s}(\mathbf{r})$  is a local-scaling function and  $J(\mathbf{s}/\mathbf{r})$  is the Jacobian for the variable transformation from  $\mathbf{r}$  to  $\mathbf{s}$ . The latter guarantees the relation

$$J(\mathbf{s}/\mathbf{r}) d\mathbf{r} = d\mathbf{s}. \quad (7b)$$

When the system under consideration has spherical symmetry, Eqs. (7a) and (7b) can be replaced with

$$\rho(r) = J(s/r) \rho_{n,0}(s), \quad s = s(r), \quad (8a)$$

$$J(s/r) r^2 dr = s^2 ds, \quad (8b)$$

and the explicit functional form of the radial transformation  $s = s(r)$  is determined either by the differential equation<sup>4</sup>

$$ds/dr = (r/s)^2 [\rho(r)/\rho_{n,0}(s)], \quad (9a)$$

or by the integral equation<sup>5</sup>

$$\int_0^r \rho(x) x^2 dx = \int_0^s \rho_{n,0}(y) y^2 dy. \quad (9b)$$

We note that Eqs. (7a) and (7b) are general and apply both to atoms and molecules in their arbitrary states and structures. On the other hand, Eqs. (8a)–(9b) are restricted to the electron density of  $S$ -state atoms and to the spherically averaged electron density.

For a given and fixed basis configurations  $B_0$ , the reference density  $\rho_{n,0}(\mathbf{r})$  is a function of the coefficient matrix

$C_n$ , and hence the local-scaling function  $\mathbf{s}$  defined above is a functional of the given density  $\rho(\mathbf{r})$  and the coefficient matrix  $C_n$ ,

$$\mathbf{s} = \mathbf{s}[\rho, C_n]. \quad (10)$$

Now using the local scaling  $\mathbf{s}$  involved in Eq. (7a), we define a new  $n$ th-state wave function  $\Psi_{n,\rho}(\{\mathbf{r}_k\})$ ,

$$\Psi_{n,\rho}(\{\mathbf{r}_k\}) = \left[ \prod_{j=1}^N J(\mathbf{s}_j/\mathbf{r}_j) \right]^{1/2} \Psi_{n,0}(\{\mathbf{s}_k\}), \quad (11a)$$

$$\mathbf{s}_k = \mathbf{s}(\mathbf{r}_k),$$

which is rewritten as

$$\Psi_{n,\rho} = B_\rho C_n \quad (11b)$$

in terms of the locally scaled basis configurations  $B_\rho$ ,

$$B_\rho = (\psi_{1,\rho}, \psi_{2,\rho}, \dots, \psi_{M,\rho}), \quad (12a)$$

$$\psi_{i,\rho}(\{\mathbf{r}_k\}) = \left[ \prod_{j=1}^N J(\mathbf{s}_j/\mathbf{r}_j) \right]^{1/2} \psi_{i,0}(\{\mathbf{s}_k\}). \quad (12b)$$

Note that the overlap matrix  $S_\rho$  between the generated configuration functions  $\{\psi_{i,\rho}\}$  is identical to the original overlap matrix  $S_0$ ,

$$S_\rho = S_0, \quad (13)$$

because of relation (7b). It is essential for the present theory to recognize that the generated wave function  $\Psi_{n,\rho}$  has an associated electron density exactly the same as the given density  $\rho(\mathbf{r})$ ,

$$N \int |\Psi_{n,\rho}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = J(\mathbf{s}/\mathbf{r}) \rho_{n,0}(\mathbf{s}) = \rho(\mathbf{r}), \quad (14)$$

and therefore we can regard  $\Psi_{n,\rho}$  as a parent wave function of the given density  $\rho(\mathbf{r})$ .

The energy expectation value  $E_n$  over the generated wave function  $\Psi_{n,\rho}$  is given by

$$E_n = C_n^+ H C_n / C_n^+ S_0 C_n, \quad (15)$$

where  $H$  is the Hamiltonian matrix,

$$H = (H_{ij}), \quad (16a)$$

$$H_{ij} = \int \psi_{i,\rho}^*(\{\mathbf{r}_k\}) H \psi_{j,\rho}(\{\mathbf{r}_k\}) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (16b)$$

and is a functional of  $\rho(\mathbf{r})$  and  $C_n$ ,

$$H = H[\rho, C_n]. \quad (16c)$$

The variation of the energy expression in the form of Eq. (15) with respect to the expansion coefficient results in a generalized eigenvalue equation,

$$H C = S_0 C E, \quad C = (C_1, \dots, C_n, \dots, C_M), \quad (17a)$$

$$E = (E_{ij}), \quad E_{ij} = E_i \delta_{ij}.$$

From the  $M$  eigenvectors, we obtain  $M$  wave functions  $\{\Psi_{m,\rho} = B_\rho C_m\}$  that satisfy the orthogonality requirements given by Eq. (1). However, we have a constraint to the solution of Eq. (17a). Taking relation (16c) into account, we rewrite Eq. (17a) explicitly as

$$H[\rho, C_n] C = S_0 C E. \quad (17b)$$

Since the Hamiltonian matrix  $H$  depends on the eigenvector

$C_n$ , Eq. (17a) must be iteratively solved with respect to  $C_n$  until the self-consistency is achieved. The convergent  $C_n$  defines the reference wave function (2) as well as a set of the  $M$  generated wave functions  $\{\Psi_{m,\rho} = B_\rho C_m\}$ . The resultant  $n$ th eigenvalue  $E_n$  is a functional of the given electron density  $\rho(\mathbf{r})$  within the framework of the basis configuration  $B_0$  initially chosen.

We have now established a route from a given electron density  $\rho(\mathbf{r})$  to the excited-state energy functional  $E_n = E_n(\rho)$ . According to the Hylleraas–Undheim–MacDonald theorem,<sup>9</sup> the  $n$ th eigenvalue from the solution of Eq. (17) is always an upper bound to the exact  $n$ th-state energy,

$$E_n(\rho) \geq E_{n,\text{exact}} \quad (18)$$

Therefore, we can variationally determine the excited-state electron density so as to minimize the  $n$ th eigenvalue of the pseudoeigenvalue equation (17b).

We emphasize that the present method enables us to determine an excited-state electron density directly and variationally. This should be compared with the ordinary indirect procedure where the integration over  $N - 1$  electron coordinates follows after the (variational) determination of the wave function. We also note that in the present approach we can obtain the electron density in a considerably simple functional form when compared with the density function resulting, in particular, from the basis-set-expansion wave function.

The present excited-state theory is completely different from that proposed very recently by Kryachko and Ludeña.<sup>10</sup> Based on Katriel's superparticle approach,<sup>11</sup> the latter authors developed a local-scaling density-functional theory for the determination of the *sum* of the first  $n$ -state densities (see also Ref. 12). On the other hand, here we have presented a theory which determines the *individual*  $n$ th-state density separately.

### III. ILLUSTRATIVE APPLICATION TO THE HELIUM 2 <sup>1</sup>S STATE

We have applied the proposed method to the 2 <sup>1</sup>S state of the helium atom. As a reference function, we have employed a CI wave function constructed from the orthogonalized hydrogenic 1s and 2s orbitals,<sup>13</sup>

$$\Psi_{2,0} = C_{12}(1s1s) + C_{22}(1s2s + 2s1s)/\sqrt{2} + C_{32}(2s2s), \quad (19)$$

where

$$1s = (\alpha^3/\pi)^{1/2} \exp(-\alpha r), \quad (20a)$$

$$2s = [\beta^3/\pi(3\lambda^2 - 3\lambda + 1)]^{1/2}(1 - \lambda\beta r) \exp(-\beta r), \quad (20b)$$

$$\lambda = (\alpha + \beta)/3\beta, \quad (20c)$$

and the relation  $\langle 1s|2s \rangle = 0$  is always fulfilled by condition (20c). (The two-electron singlet spin function is implicit.) The reference electron density  $\rho_{2,0}(r)$  associated with the wave function (19) is given by

$$\rho_{2,0}(r) = (2C_{12}^2 + C_{22}^2)(1s)^2 + 2\sqrt{2}C_{22}(C_{12} + C_{32}) \times (1s)(2s) + (C_{22}^2 + 2C_{32}^2)(2s)^2. \quad (21)$$

When the ordinary CI calculation is performed, the function (19) gives the best 2 <sup>1</sup>S energy (the second lowest eigenvalue)  $E_{2,0} = -2.143\,000\,6$  for the parameter values

$$\alpha = 1.991\,76, \quad \beta = 0.520\,58,$$

with the corresponding eigenvector

$$C_{12} = 0.120\,66, \quad C_{22} = 0.992\,56, \quad C_{32} = -0.016\,14.$$

For the 2 <sup>1</sup>S electron density  $\rho(r)$  to be determined, we assume its functional form as

$$F_K(r) = G \left[ \exp(-c_0 r) + \sum_{i=1}^K a_i r^{b_i} \exp(-c_i r) \right], \quad (22)$$

TABLE I. Results of the local-scaling density-functional calculations for the 2 <sup>1</sup>S state of the helium atom. For the explicit form of the density function  $F_K(r)$ , see Eq. (22) of the text.

Density	Optimum parameters	Energy
$\rho_{2,0}(r)$	$(\alpha = 1.991\,76, \beta = 0.520\,58)$	-2.143 000 6
$F_1(r)$	$c_0 = 4.028\,18$ $a_1 = 1.087\,33 \times 10^{-4}, b_1 = 5.538\,65, c_1 = 1.604\,01$ $G = 2.658\,71 (\alpha/\beta = 3.892\,95)$	-2.141 615 5
$F_2(r)$	$c_0 = 3.971\,37$ $a_1 = 2.436\,82 \times 10^{-3}, b_1 = 1.964\,75, c_1 = 1.061\,56$ $a_2 = -8.577\,05 \times 10^{-3}, b_2 = 2.703\,77, c_2 = 1.996\,82$ $G = 2.607\,26 (\alpha/\beta = 4.210\,40)$	-2.144 114 6
$F_3(r)$	$c_0 = 3.986\,95$ $a_1 = 2.483\,95 \times 10^{-3}, b_1 = 2.008\,25, c_1 = 1.073\,79$ $a_2 = -4.412\,21 \times 10^{-3}, b_2 = 2.969\,07, c_2 = 1.892\,35$ $a_3 = -1.540\,62 \times 10^{-2}, b_3 = 5.759\,27, c_3 = 4.026\,64$ $G = 2.618\,19 (\alpha/\beta = 4.216\,69)$	-2.144 140 3
Exact <sup>a</sup>	...	-2.145 974 0

<sup>a</sup>References 17 and 18.

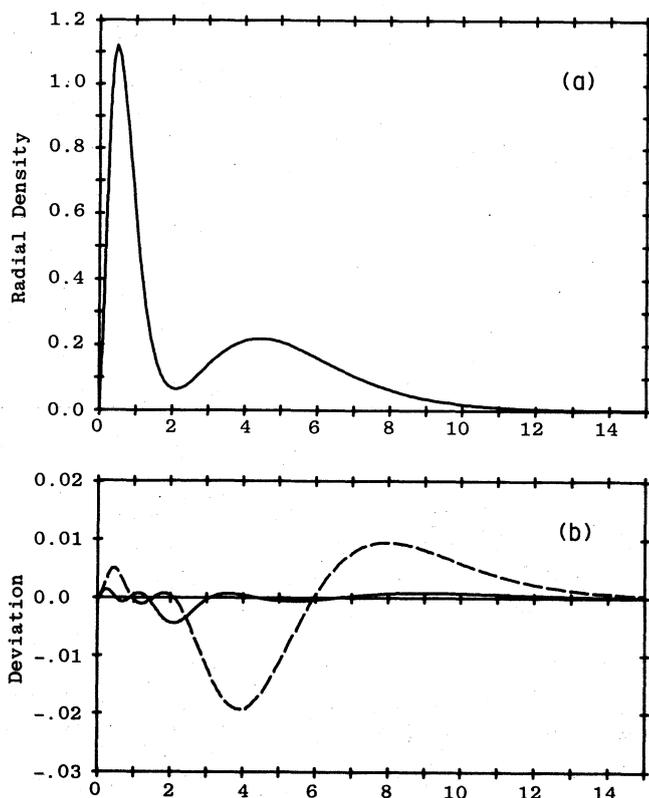


FIG. 1. (a) The near-exact radial density  $D_{CJ}(r)$  for the  $2^1S$  state of the helium atom. (b) Deviation in the radial density from  $D_{CJ}(r)$ . The solid and dashed lines show  $[4\pi r^2 F_1(r) - D_{CJ}(r)]$  and  $[4\pi r^2 \rho_{2,0}(r) - D_{CJ}(r)]$ , respectively.

which represents a linear combination of generalized Slater-type functions. The  $\{a_i, b_i, c_i\}$  are variational parameters and  $G$  is the normalization constant. The index  $K$  governs the number of basis functions in Eq. (22). By this choice of the functions  $\rho_{2,0}(r)$  and  $F_K(r)$ , the integrals appearing in Eq. (9b) are expressed<sup>14</sup> in terms of the incomplete gamma function  $\gamma(a, x)$ ,

$$\int_0^x t^b \exp(-ct) dt = c^{-(b+1)} \gamma(b+1, cx). \quad (23)$$

TABLE II. Position moments  $\langle r^n \rangle$  associated with the density function  $\rho(r) = F_3(r)$  for the  $2^1S$  state of the helium atom. The values in parentheses are errors in percent relative to the exact values.

Moment <sup>a</sup>	$\rho_{2,0}(r)$	$F_3(r)$	Exact
$\langle r^{-2} \rangle$	8.306 37 (0.15)	8.299 50 (0.07)	8.293 57 <sup>b</sup>
$\langle r^{-1} \rangle$	2.270 13 (-0.03)	2.270 54 (-0.01)	2.270 82 <sup>b</sup>
$\langle r \rangle$	6.145 65 (3.36)	5.974 11 (0.47)	5.946 12 <sup>c</sup>
$\langle r^2 \rangle$	34.934 1 (8.56)	32.478 8 (0.93)	32.178 2 <sup>c</sup>
$\langle r^3 \rangle$	247.134 (14.36)	218.969 (1.32)	216.107 <sup>b</sup>
$\langle r^4 \rangle$	1 992.10 (20.64)	1 679.95 (1.73)	1 651.3 <sup>b</sup>

<sup>a</sup> The parent densities are normalized to two.

<sup>b</sup> Reference 19.

<sup>c</sup> References 17 and 18.

For a given set of parameter values  $\alpha, \beta, \{C_{iz}\}$ , and  $\{a_i, b_i, c_i\}$ , Eq. (9b) is then solved numerically by the Newton method to determine the scaling function  $s = s(r)$ .

Since we have fixed the functional forms of  $\Psi_{2,0}$  and  $\rho$ , the energy density functional  $E_2(\rho)$  now reduces to a function of the parameters embedded in  $\rho$  and  $\Psi_{2,0}$ . The reference function  $\Psi_{2,0}$  includes the two adjustable exponents  $\alpha$  and  $\beta$ , but it has been already proven<sup>15</sup> that only the ratio  $\alpha/\beta$  is meaningful in the optimization of a reference wave function. Therefore, we have

$$E_2(\rho) = E_2(\{a_i, b_i, c_i\}; \alpha/\beta). \quad (24)$$

Using the Powell method of conjugate directions,<sup>16</sup> we have carried out the optimization of these parameters so as to minimize the energy  $E_2$ . In each energy evaluation, the mixing coefficients  $\{C_{iz}\}$  of the three configurations are iteratively determined based on Eq. (17b) under the convergence condition,

$$|C_{iz}^{(\text{input})} - C_{iz}^{(\text{output})}| < 1 \times 10^{-8} \quad \text{for all } i.$$

The results of the present local-scaling density-functional calculations are summarized in Table I. The near-exact radial density  $D_{CJ}(r)$  of Coolidge and James<sup>8</sup> is plotted in Fig. 1(a) for reference. When compared with this density, even the simplest function  $F_1(r)$  constructed from only two exponential functions has been found to give a distribution whose overall behavior is acceptable. However, it is not sufficiently accurate in a quantitative sense. When we define the error by

$$\Delta_K = \max |4\pi r^2 F_K(r) - D_{CJ}(r)|, \quad (25)$$

$\Delta_1$  is found to be 0.019 624 at  $r = 3.2$ . Since the reference density  $\rho_{2,0}(r)$  [Eq. (21)] has  $\Delta_{2,0} = 0.019 436$  (at  $r = 3.9$ ), the quality of  $F_1(r)$  is poorer than that of  $\rho_{2,0}(r)$ . The situation is also reflected in their associated energy values (the last column of Table I).

The addition of another exponential function, i.e., the  $F_2(r)$  function, remarkably improves both the density distribution and the associated energy: The maximum error obtained is  $\Delta_2 = 0.004 461$  (at  $r = 2.2$ ). The associated energy  $-2.144 114 6$  is lower than the reference energy  $E_{2,0} (= -2.143 000 6)$  by 0.001 114 0. The simplicity of the density function  $F_2(r)$  should be noted: The  $F_2(r)$  con-

sists of three terms, while the reference  $\rho_{2,0}(r)$  has six terms when Eq. (21) is expanded.

However, further addition of exponential terms does not seem to give an essential improvement. The  $F_3(r)$  function has the error  $\Delta_3 = 0.004\,425$  and the associated energy  $-2.144\,140\,3$ . In this sense, the improvement is approximately "saturated" with the  $F_3(r)$  function having four exponential terms. The energy difference between the reference and exact wave functions is  $0.002\,973\,4$ , and the present best density  $F_3(r)$  recovers 62% of this difference. The high accuracy of the  $F_3(r)$  density function is demonstrated in Fig. 1(b) as a function of  $r$ .

In Table II the position moments  $\langle r^n \rangle$  ( $-2 \leq n \leq 4$ ) resulting from the density  $F_3(r)$  are summarized and compared with the exact values.<sup>17-19</sup> The moments obtained from the reference density  $\rho_{2,0}(r)$  are also given there for comparison. The relative error remains 1.73% at most, and satisfactory accuracy of the density function  $F_3(r)$ , obtained by the local-scaling density-functional method, is again clear.

In summary, we have developed a density-functional method for excited states. In the application to the  $2^1S$  state of the helium atom, we have been able to determine a simple and yet accurate density function variationally. We anticipate that the proposed method would also work well for other states and systems.

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