

Energy functional of the axial marginal density in linear molecules

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The axial marginal density is defined as a projection of the three-dimensional electron density onto the symmetry axis in a linear molecule, and represents essential features of the bonding characteristics of that system. Based on the local scaling method, a theory is presented for the direct and variational determination of the axial marginal density. Illustrative applications are presented for the ground $1s\sigma_g$ state of the H_2^+ molecule, and simple yet sufficiently accurate marginal densities are reported.

1. Introduction

Using the method of the local scaling transformation [1], we have recently developed (see [2,3] for review) a theory for the energy density functional $E[\rho]$, which enables a direct and variational determination of the electron density $\rho(\mathbf{r})$. For the N -electron system under consideration, according to this theory, we first choose an appropriate (i.e., simple yet physically acceptable) reference wave function $\Psi_0(\{\mathbf{r}_i\})$ which is associated with the electron density $\rho_0(\mathbf{r})$. (Spin variables are suppressed, since they play no direct role in the present study.) We then construct a local scaling function $s = s(\mathbf{r})$ between the reference density $\rho_0(\mathbf{r})$ and the given density $\rho(\mathbf{r})$, and apply it to $\Psi_0(\{\mathbf{r}_i\})$ in order to generate a wave function $\Psi_\rho(\{\mathbf{r}_i\})$ corresponding to the given density $\rho(\mathbf{r})$. Since the generated wave function $\Psi_\rho(\{\mathbf{r}_i\})$ has the density exactly the same as the given density $\rho(\mathbf{r})$, 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 value over the wave function $\Psi_\rho(\{\mathbf{r}_i\})$. The momentum-space version [4] and the spin-polarized version [5] of the theory have also been developed. Generalizations to the electron-pair (or intracuclear) density [6] and to the excited-state electron density [7,8] have been proposed very recently.

The method has been actually applied to the helium and heliumlike atoms [9,10], the Li atom [5,11], and the Be atom [11]. Simple position and momentum

densities have been variationally determined that compare well with the near Hartree–Fock densities. A few calculations beyond the Hartree–Fock approximation have been given [9,10] for the helium and heliumlike atoms. An application of the method to mapping between the position and momentum densities has also been found to be very successful for all the first- and second-row atoms [12,13].

Up to now, however, these applications of the method have been limited only to atoms. In the present paper, we develop an energy functional theory for the axial marginal density of diatomic and linear polyatomic molecules using the local scaling technique. The present study is the first application of the local scaling method to the molecular density problem. The axial marginal density $\rho_z(z)$ is a condensation of the three-dimensional electron density $\rho(\mathbf{r}) = \rho(x, y, z)$ onto the internuclear z -axis yet still contains the essential feature of the density (re)distribution in linear polyatomic systems [14,15]. In section 2, a property of the axial marginal density is first outlined. A local scaling transformation is then introduced for the reference and given marginal densities, and an energy functional is defined in terms of the axial marginal density. In section 3, illustrative applications are presented for the ground $1\sigma_g$ state of the H_2^+ system. Several simple marginal densities resulting from the energy density variation are reported. Atomic units are used throughout this paper.

2. Energy functional of marginal density

2.1. MARGINAL DENSITY

The electron density function $\rho(\mathbf{r})$ defined by

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (1)$$

is a joint probability function with three variables symbolically expressed by the spatial vector \mathbf{r} . When we use the Cartesian coordinates $\mathbf{r} = (x, y, z)$, the one-dimensional marginal density function $\rho_z(z)$ with respect to the variable z is given by

$$\rho_z(z) = \int \rho(x, y, z) dx dy. \quad (2)$$

If the z -axis is taken to be the symmetry axis of a diatomic or linear polyatomic system, $\rho_z(z)$ is referred to as the “axial” marginal density, and the “equatorial” densities $\rho_x(x)$ and $\rho_y(y)$ are analogously defined.

The axial marginal density $\rho_z(z)$ is a projection of $\rho(\mathbf{r})$ onto the symmetry axis, and is the Fourier transform of the form factor $F(\mathbf{s}) = F(s_x, s_y, s_z)$ on the corresponding s_z -axis [14]. It should be noted that since $\rho_z(z)$ represents a “condensation” of the three-dimensional density $\rho(\mathbf{r})$ onto a line, the number of electrons is conserved:

$$\int_{-\infty}^{+\infty} \rho_z(z) dz = N. \quad (3)$$

A recent study [14] has shown that the axial marginal density $\rho_z(z)$ is a convenient quantity to grasp the essential feature of the bonding\antibonding density reorganization in diatomic systems. The marginal density $\rho_z(z)$ has also been used to analyze [15] the density distributions in different electronic states and to define [16–19] “atomic regions” and the resultant atomic charges in a molecule.

2.2. AN ENERGY FUNCTIONAL

For the N -electron diatomic or linear polyatomic system under consideration, we assume the presence of an appropriate reference wave function $\Psi_0(\{\mathbf{r}_i\})$. It is associated with the three-dimensional electron density $\rho_0(\mathbf{r})$ and the axial marginal density $\rho_{0z}(z)$ through the definitions (1) and (2), respectively. In order to generate a parent wave function $\Psi_z(\{\mathbf{r}_i\})$ of a given marginal density $\rho_z(z)$, we first introduce a local scaling $z' = z'(z)$ between the two marginal densities $\rho_z(z)$ and $\rho_{0z}(z)$:

$$\rho_z(z) = J(z'/z)\rho_{0z}(z'), \quad (4)$$

where $J(z'/z)$ is the Jacobian for the transformation $z' = z'(z)$ and satisfies the relation

$$J(z'/z) dz = dz', \quad (5a)$$

or

$$J(z'/z) d\mathbf{r} = d\mathbf{r}', \quad (5b)$$

in which $d\mathbf{r} = dx dy dz$ and $d\mathbf{r}' = dx dy dz'$. The explicit functional form of $z' = z'(z)$ is determined by the solution of either the differential equation

$$dz'/dz = \rho_z(z)/\rho_{0z}(z') \quad (6a)$$

or the integral equation

$$\int_{-\infty}^z \rho_z(t) dt = \int_{-\infty}^{z'(z)} \rho_{0z}(t) dt. \quad (6b)$$

Applying the local scaling $z' = z'(z)$ thus determined, we generate a new wave function $\Psi_z(\{\mathbf{r}_i\})$ as follows:

$$\Psi_z(\{\mathbf{r}_i\}) = \left\{ \prod_{k=1}^N [J(z'_k/z_k)]^{1/2} \right\} \Psi_0(\{\mathbf{r}'_i\}), \quad (7a)$$

where

$$\mathbf{r}'_i = (x_i, y_i, z'_i) \quad \text{and} \quad z'_i = z'(z_i). \quad (7b)$$

The generated wave function $\Psi_z(\{\mathbf{r}_i\})$ is associated with the following axial marginal density:

$$\begin{aligned}
 & N \int |\Psi_z(x, y, z, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N dx dy \\
 &= NJ(z'/z) \int \left[\prod_{k=2}^N J(z'_k/z_k) \right] |\Psi_0(x, y, z', \mathbf{r}'_2, \dots, \mathbf{r}'_N)|^2 \\
 &\quad \times d\mathbf{r}_2 \dots d\mathbf{r}_N dx dy \\
 &= J(z'/z) \int \rho_0(x, y, z') dx dy \\
 &= J(z'/z) \rho_{0z}(z') \\
 &= \rho_z(z). \tag{8}
 \end{aligned}$$

The first equality in eq. (8) follows from eq. (7a), the second from eqs. (5b) and (1), the third from eq. (2), and the last from eq. (4). Equation (8) means that the generated wave function $\Psi_z(\{\mathbf{r}_i\})$ has an axial marginal density exactly the same as the given density $\rho_z(z)$, and hence the function Ψ_z is a candidate for the parent wave function of the marginal density $\rho_z(z)$.

We assign the wave function Ψ_z to the parent wave function of the given axial marginal density $\rho_z(z)$. Then the energy E associated with the density $\rho_z(z)$ is defined as the Hamiltonian expectation value over the function Ψ_z :

$$\begin{aligned}
 E[\Psi_z] &= \langle \Psi_z | H | \Psi_z \rangle / \langle \Psi_z | \Psi_z \rangle \\
 &= E[\rho_z, \Psi_0], \tag{9}
 \end{aligned}$$

where H is the Hamiltonian of the system. Notice that the energy E is *not* a true functional of the auxiliary function Ψ_z but a functional of the given marginal density $\rho_z(z)$ and the reference wave function Ψ_0 , since Ψ_z is totally specified by ρ_z and Ψ_0 . In other words, the energy E is now a well-defined functional of the axial marginal density $\rho_z(z)$ within the framework of the reference function Ψ_0 initially chosen and fixed. Since the function Ψ_z is generated through a simple variable-transformation of Ψ_0 (see eq. (7a)), we suppose that Ψ_z is physically acceptable so long as Ψ_0 is acceptable. Then the energy functional (9) is an upper bound to the exact energy. For a chosen Ψ_0 , we can then determine the axial marginal density $\rho_z(z)$ so as to minimize the energy E . The procedure constitutes a direct and variational determination of the axial marginal density of diatomic and linear polyatomic systems. Since the auxiliary wave function Ψ_z has an increased variational freedom compared to Ψ_0 through the scaling function $z' = z'(z)$, we expect that the minimum energy $E_{\min} = E[\rho_{z,\text{opt}}, \Psi_0]$ will be lower than the reference energy $E_0 = E[\rho_{0z}, \Psi_0]$.

3. Application to H_2^+ molecule

For the special case of one-electron systems, we can bypass the explicit determination of the scaling function $z' = z'(z)$. In this case, eq. (7a) combined with eq. (4) reads

$$\Psi_z(x, y, z) = [\rho_z(z)/\rho_{0z}(z')]^{1/2}\Psi_0(x, y, z'). \quad (10a)$$

If we introduce new reference quantities,

$$\Psi'_0(x, y, z) = \Psi_0(x, y, z'(z)), \quad (11a)$$

$$\rho'_{0z}(z) = \rho_{0z}(z'(z)), \quad (11b)$$

we can rewrite eq. (10a) as

$$\Psi_z(x, y, z) = [\rho_z(z)/\rho'_{0z}(z)]^{1/2}\Psi'_0(x, y, z). \quad (10b)$$

Since the wave function Ψ'_0 is associated with the marginal density ρ'_{0z} , we can easily verify that Ψ_z defined by eq. (10b) has the marginal density $\rho_z(z)$ irrespective of the reference function Ψ'_0 . Choosing an appropriate Ψ'_0 , we can then straightforwardly generate a parent wave function Ψ_z of the given marginal density $\rho_z(z)$ by eq. (10b). Such a simplification is also possible for the Hartree–Fock treatment of two-electron systems in their singlet spin states. However, this is not true for many-electron systems, since in those cases there is no direct correspondence between the quantities Ψ'_0 and ρ'_{0z} .

For the ground $1s\sigma_g$ state of the H_2^+ molecule (the internuclear distance R is kept fixed at 2), we use a linear combination of M symmetrized $1s$ Gaussian functions as the reference wave function:

$$\psi_M(\mathbf{r}) = \sum_{i=1}^M C_i G(\mathbf{r}; A_i, D_i), \quad (12a)$$

$$G(\mathbf{r}; A, D) = \exp\{-A[x^2 + y^2 + (z + D/2)^2]\} \\ + \exp\{-A[x^2 + y^2 + (z - D/2)^2]\}, \quad (12b)$$

where the origin is taken to be the midpoint of the two nuclei. The parameters $\{C_i, A_i, D_i\}$ have been determined by the ordinary variational method. The reference function (12a) has the axial marginal density

$$\rho_{0z}(z) = \pi \sum_{i,j=1}^M [C_i C_j / (A_i + A_j)] g(z; A_i, D_i) g(z; A_j, D_j), \quad (13a)$$

where

$$g(z; A, D) = \exp[-A(z + D/2)^2] + \exp[-A(z - D/2)^2] \\ = 2 \exp[-A(z^2 + D^2/4)] \cosh(ADz). \quad (13b)$$

For the sake of comparison later, we note that the right-hand side of eq. (13a) is

quadratic with respect to the function g , and the density is composed of $M(M+1)/2$ different terms.

As a trial density $\rho_z(z)$, we use a *linear* combination of the Gaussian functions defined by eq. (13b):

$$F_K(z) = \sum_{i=1}^K c_i g(z; a_i, d_i), \quad (14)$$

which contains adjustable parameters $\{c_i, a_i, d_i\}$. Since the analysis of the diatomic marginal density has shown [14] that the axial marginal density does not have any cusps, eq. (14) can be considered as a reasonable approximation. In fig. 1, the near exact $\rho_z(z)$ of the H_2^+ molecule, which is dealt with in the present study, is depicted for reference (see below for details).

Since we have fixed a functional form of the trial marginal density $\rho_z(z)$, the energy functional (9) now reduces to an energy function of the parameters embedded in F_K :

$$E[\rho_z] = E(\{c_i, a_i, d_i\}), \quad (15)$$

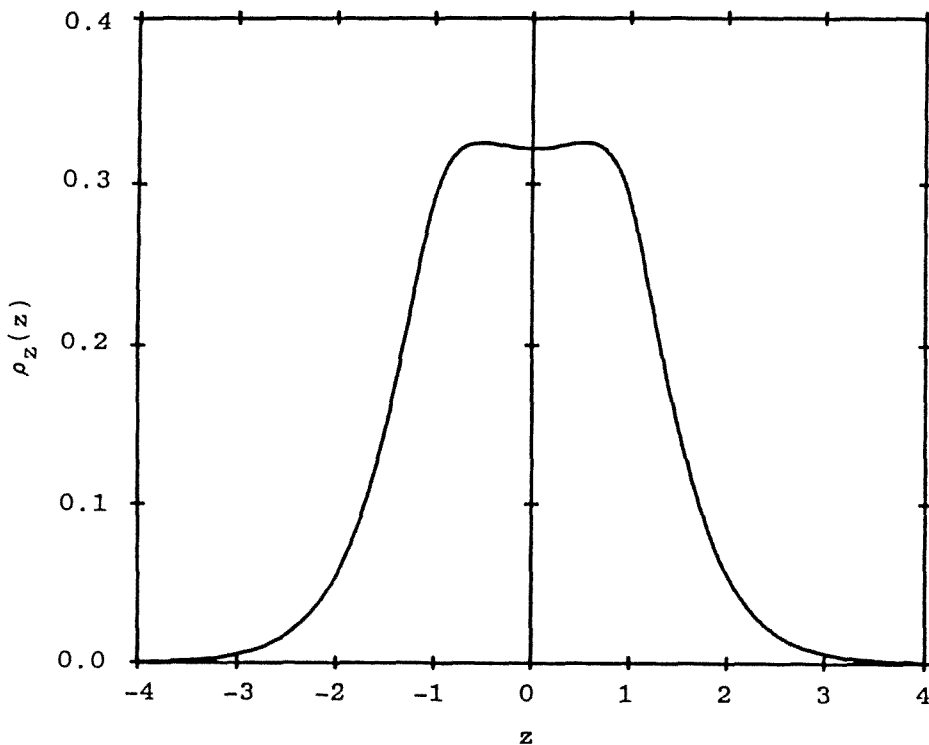


Fig. 1. The near exact marginal density $\rho_{z,nc}(z)$ of the H_2^+ molecule. All the $F_2(z) - F_5(z)$ densities obtained by referring to either $\psi_3(r)$ or $\psi_6(r)$ (summarized in tables 2 and 3) are superimposable on $\rho_{z,nc}(z)$ in the present scale of figure.

for a chosen reference function ψ_M . In the following computations, the integrations involved in the evaluation of the energy expectation value have been performed analytically with respect to x and y , and numerically with respect to z using the double exponential method [20]. Sufficient accuracy of the numerical integration has been verified. The optimization of the parameters $\{c_i, a_i, d_i\}$ has been carried out using the Powell method of conjugate directions [21].

We have first employed the simplest function ψ_1 (i.e., $M = 1$ in eq. (12a)) as the references for the density functional calculations. The results for the five trial marginal densities $F_K(z)$ are summarized in table 1 together with the associated electronic energies $E[F_K]$. Since the reference function ψ_1 has an energy of $-1.037\ 411\ 11$, all the densities in table 1 are superior to the reference density in the variational sense. However, the best energy of $-1.043\ 875\ 11$, obtained with $F_5(z)$, is still far from the known [22] exact value of $-1.102\ 634\ 21$. The analysis of the density functions themselves has shown that the overall behavior is acceptable, but in quantitative sense the distribution in the internuclear region is poor compared to the near exact density (see below for detailed discussion). Not much improvement in the energy and the density distribution is observed, with an increase in the number of terms in the trial density. The function ψ_1 composed only of a single Gaussian appears to be too crude and not appropriate as a reference of the system.

Table 1

Variationally-determined axial marginal densities for the H_2^+ molecule, when $\psi_1(r)$ is employed as the reference.

Density	Optimum parameters	Energy
$F_1(z)$	$c_1 = 0.27193, a_1 = 0.92924, d_1 = 1.39722$	$-1.039\ 591\ 88$
$F_2(z)$	$c_1 = 0.15884, a_1 = 0.46608, d_1 = 0.00481;$ $c_2 = 0.07968, a_2 = 2.59902, d_2 = 1.85017$	$-1.043\ 677\ 25$
$F_3(z)$	$c_1 = 0.08510, a_1 = 0.40195, d_1 = 0.01146;$ $c_2 = 0.15568, a_2 = 1.24734, d_2 = 1.42611;$ $c_3 = 0.02116, a_3 = 6.23628, d_3 = 1.91520$	$-1.043\ 852\ 37$
$F_4(z)$	$c_1 = 0.03246, a_1 = 0.33738, d_1 = 0.02202;$ $c_2 = 0.16408, a_2 = 0.79270, d_2 = 1.15400;$ $c_3 = 0.06093, a_3 = 2.40969, d_3 = 1.78162;$ $c_4 = 0.00879, a_4 = 10.9301, d_4 = 1.94274$	$-1.043\ 872\ 41$
$F_5(z)$	$c_1 = 0.01505, a_1 = 0.30166, d_1 = 0.06786;$ $c_2 = 0.13629, a_2 = 0.61814, d_2 = 0.93515;$ $c_3 = 0.08913, a_3 = 1.54133, d_3 = 1.59987;$ $c_4 = 0.02041, a_4 = 5.06876, d_4 = 1.90305;$ $c_5 = 0.00240, a_5 = 25.1838, d_5 = 1.97279$	$-1.043\ 875\ 11$

We have then carried out the density functional calculations using ψ_3 and ψ_6 functions as the reference. (The functions ψ_3 and ψ_6 have energies of $-1.100\ 218\ 33$ and $-1.102\ 524\ 17$, respectively.) The results are summarized in tables 2 and 3 for the trial functions $F_1(z)$ through $F_5(z)$. Compared to the values in table 1, we find that the energies $E[F_K]$ are greatly improved by the adoption of the better reference functions. In particular, the energy $-1.102\ 553\ 12$ associated with the $F_5(z)$ density in table 3 is reasonably accurate, when we consider the slow convergence [23] of Gaussian approximations in the ordinary variational calculations.

The accuracies of the 15 axial marginal densities determined in the present density functional calculations (and tabulated in tables 1–3) are compared in table 4. The characteristics examined are the value at the midpoint of the nuclei $\rho_z(0)$, the values at the nuclear positions $\rho_z(\pm 1)$, the peak height $\rho_{z,\max}$, and the peak locations z_{\max} . In order to assess the overall accuracy, we have also examined the deviation Δ defined by

$$\Delta = \left\{ \int_{-\infty}^{\infty} [\rho_z(z) - \rho_{z,\text{ne}}(z)]^2 dz \right\}^{1/2}, \quad (16)$$

and the similarity index S defined [24] by

$$S = \int_{-\infty}^{\infty} \rho_z(z) \rho_{z,\text{ne}}(z) dz / \left\{ \int_{-\infty}^{\infty} [\rho_z(z)]^2 dz \int_{-\infty}^{\infty} [\rho_{z,\text{ne}}(z)]^2 dz \right\}^{1/2}, \quad (17)$$

Table 2

Variationally-determined axial marginal densities for the H_2^+ molecule, when $\psi_3(r)$ is employed as the reference.

Density	Optimum parameters	Energy
$F_1(z)$	$c_1 = 0.27914, a_1 = 0.97919, d_1 = 1.45274$	$-1.093\ 362\ 53$
$F_2(z)$	$c_1 = 0.15566, a_1 = 0.44836, d_1 = 0.00213;$ $c_2 = 0.08852, a_2 = 3.18103, d_2 = 1.88525$	$-1.099\ 919\ 24$
$F_3(z)$	$c_1 = 0.08621, a_1 = 0.38415, d_1 = 0.00866;$ $c_2 = 0.15638, a_2 = 1.36430, d_2 = 1.47666;$ $c_3 = 0.02641, a_3 = 8.38213, d_3 = 1.95298$	$-1.100\ 279\ 44$
$F_4(z)$	$c_1 = 0.04208, a_1 = 0.33160, d_1 = 0.00459;$ $c_2 = 0.15991, a_2 = 0.87415, d_2 = 1.24741;$ $c_3 = 0.06203, a_3 = 3.08752, d_3 = 1.83422;$ $c_4 = 0.01068, a_4 = 15.7573, d_4 = 1.96570$	$-1.100\ 316\ 33$
$F_5(z)$	$c_1 = 0.01846, a_1 = 0.28980, d_1 = 0.03107;$ $c_2 = 0.13737, a_2 = 0.62452, d_2 = 0.96715;$ $c_3 = 0.08600, a_3 = 1.81467, d_3 = 1.69575;$ $c_4 = 0.02439, a_4 = 6.61304, d_4 = 1.93126;$ $c_5 = 0.00362, a_5 = 31.7025, d_5 = 1.98224$	$-1.100\ 322\ 46$

Table 3

Variationally-determined axial marginal densities for the H_2^+ molecule, when $\psi_6(r)$ is employed as the reference.

Density	Optimum parameters	Energy
$F_1(z)$	$c_1 = 0.27933, a_1 = 0.98050, d_1 = 1.45362$	-1.095 349 93
$F_2(z)$	$c_1 = 0.15566, a_1 = 0.44713, d_1 = 0.00412;$ $c_2 = 0.08860, a_2 = 3.22939, d_2 = 1.88668$	-1.102 121 19
$F_3(z)$	$c_1 = 0.08168, a_1 = 0.37719, d_1 = 0.13906;$ $c_2 = 0.16182, a_2 = 1.34289, d_2 = 1.46381;$ $c_3 = 0.02728, a_3 = 8.30504, d_3 = 1.95314$	-1.102 500 30
$F_4(z)$	$c_1 = 0.03828, a_1 = 0.32032, d_1 = 0.05915;$ $c_2 = 0.16541, a_2 = 0.86953, d_2 = 1.24653;$ $c_3 = 0.06239, a_3 = 3.22435, d_3 = 1.84196;$ $c_4 = 0.00973, a_4 = 17.3693, d_4 = 1.97026$	-1.102 545 72
$F_5(z)$	$c_1 = 0.01711, a_1 = 0.27914, d_1 = 0.09396;$ $c_2 = 0.13910, a_2 = 0.62427, d_2 = 0.96918;$ $c_3 = 0.08489, a_3 = 1.81544, d_3 = 1.69525;$ $c_4 = 0.02564, a_4 = 6.52699, d_4 = 1.93228;$ $c_5 = 0.00360, a_5 = 34.6892, d_5 = 1.98428$	-1.102 553 12

Table 4

Characteristics of the axial marginal densities for the H_2^+ molecule obtained from the present density functional calculations.

Reference function	Marginal density	$\rho_z(0)$	$\rho_z(\pm 1)$	$\rho_{z,max}$	$ z_{max} $	Δ	S
$\psi_1(r)$	$F_1(z)$	0.3456	0.2685	0.3456	0.0000	0.028020	0.998583
	$F_2(z)$	0.3349	0.2279	0.3351	0.2563	0.015979	0.999548
	$F_3(z)$	0.3355	0.2793	0.3355	0.0000	0.015278	0.999583
	$F_4(z)$	0.3350	0.2795	0.3351	0.1989	0.015243	0.999585
	$F_5(z)$	0.3351	0.2796	0.3351	0.0613	0.015248	0.999586
$\psi_3(r)$	$F_1(z)$	0.3330	0.2745	0.3330	0.2228	0.020043	0.999263
	$F_2(z)$	0.3218	0.2864	0.3261	0.5535	0.002784	0.999984
	$F_3(z)$	0.3211	0.2887	0.3246	0.5022	0.000741	0.999999
	$F_4(z)$	0.3210	0.2890	0.3249	0.5054	0.000555	0.999999
	$F_5(z)$	0.3211	0.2891	0.3248	0.5227	0.000553	0.999999
$\psi_6(r)$	$F_1(z)$	0.3328	0.2746	0.3331	0.2311	0.019923	0.999272
	$F_2(z)$	0.3213	0.2868	0.3258	0.5621	0.002533	0.999986
	$F_3(z)$	0.3207	0.2889	0.3242	0.5130	0.000536	0.999999
	$F_4(z)$	0.3206	0.2893	0.3246	0.5164	0.000279	1.000000
	$F_5(z)$	0.3207	0.2895	0.3245	0.5327	0.000237	1.000000
Near exact		0.3207	0.2897	0.3246	0.5288	0	1

where $\rho_z(z)$ is an approximate density and $\rho_{z,ne}(z)$ is the near exact density. In the present study, the function ψ_{15} (see eq. (12a)) with an energy of $-1.102\ 634\ 05$ has been regarded as giving the density $\rho_{z,ne}(z)$ to avoid undue numerical complexity. The profile of $\rho_{z,ne}(z)$ is shown in fig. 1.

In table 4, we see that the first five densities obtained by referring to ψ_1 have larger $\rho_z(0)$ and $\rho_{z,max}$ and smaller $\rho_z(\pm 1)$ values compared to the near exact values. The peak locations z_{max} are particularly poor. The measures Δ and S also indicate that these densities are rather inaccurate. This is due to the insufficient accuracy of the reference ψ_1 function as mentioned before.

When ψ_3 is employed as the reference function, however, the accuracy is remarkably improved for all $F_K(z)$ except for $F_1(z)$. The four characteristics of the marginal densities compare well with the exact values, and the overall measures Δ and S also guarantee the closeness of the present densities $F_2(z) - F_5(z)$ to the near exact density $\rho_{z,ne}(z)$. In fact, when these densities are plotted, they are all superimposed with $\rho_{z,ne}(z)$ shown in fig. 1. The accuracy of the marginal density is further improved by the use of the ψ_6 function as the reference. The smaller values of the measure Δ well reflect the improvement. Figure 2, which depicts the density deviations

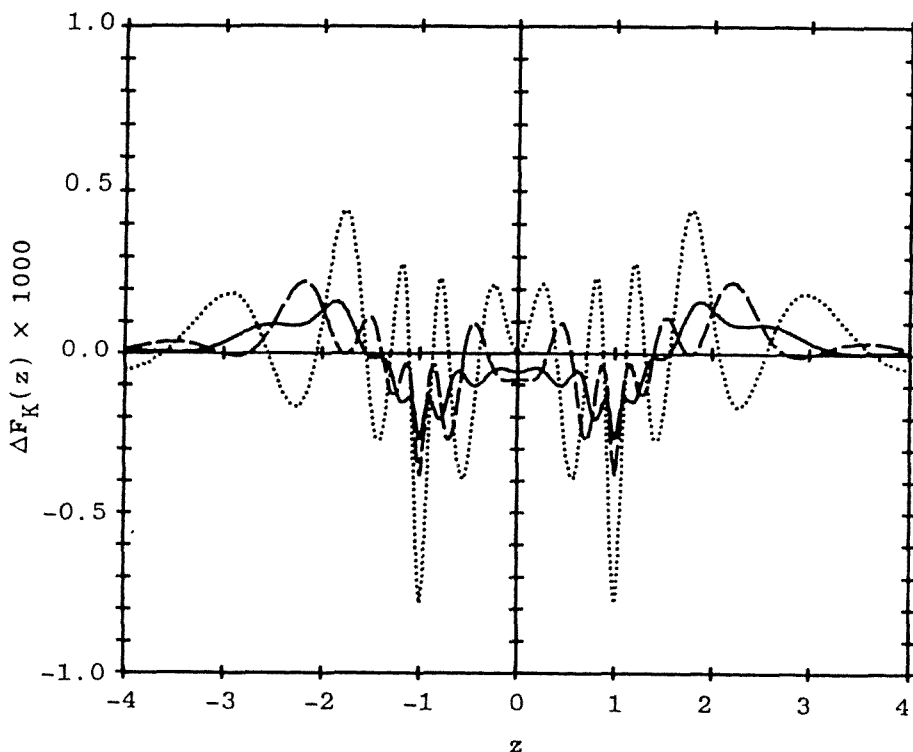


Fig. 2. The deviations $\Delta F_K(z)$ [$K = 3, 4, 5$] for the marginal densities obtained by referring to $\psi_6(r)$. Dotted line: $\Delta F_3(z)$; dashed line: $\Delta F_4(z)$; solid line: $\Delta F_5(z)$.

$$\Delta F_K(z) = F_K(z) - \rho_{z,nc}(z) \quad (18)$$

as a function of z , clearly demonstrates the high accuracy of the present marginal densities. In addition to their accuracy, the simplicity of these densities should be noted; for example, $F_5(z)$ consists of 5 terms, whereas $\rho_{z,nc}(z)$ consists of 120 terms (see eqs. (14) and (13a)).

In summary, we have developed an energy functional theory which enables a variational determination of the marginal electron density of a molecular system. The method has been actually applied to the H_2^+ molecule in its ground state, and several axial marginal densities have been determined. In spite of their simplicity, the densities $F_2(z) - F_5(z)$ obtained by referring to ψ_3 or ψ_6 are shown to have sufficient accuracy. The present study is the first, exploratory application of the local scaling method to the molecular electron density problem, and extensions to larger systems are being planned. We expect the method will be useful for the direct density analysis of the covalency, polarity, charge transfer, etc., in a molecule, and of the density reorganizations resulting from interatomic interactions in a linear system.

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