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Local scaling transformations applied to density-functional calculations of Li and Be atoms

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The local scaling transformation is used to generate a wave function $\Psi_\rho(\{\mathbf{r}_k\})$ from a reference function $\Psi_0(\{\mathbf{r}_k\})$ in such a manner that the generated function $\Psi_\rho(\{\mathbf{r}_k\})$ has exactly the same one-electron density as a given density $\rho(\mathbf{r})$. The method enables us to perform a variational determination of the density $\rho(\mathbf{r})$ through the minimization of the energy $E[\rho]$ associated with the wave function $\Psi_\rho(\{\mathbf{r}_k\})$. Using the single-$\zeta$ wave function as a reference, we apply this procedure to the ground-state Li and Be atoms within the Hartree-Fock approximation. Comparison of the densities themselves as well as the associated position $\langle r^n \rangle$ and momentum $\langle p^n \rangle$ moments shows that the present density compares well with the near-Hartree-Fock density.

I. INTRODUCTION

In contrast to the usual scaling method,[1] which uniformly modifies the electron coordinates in the wave function by a constant factor, the local scaling method[2] modifies the electron coordinates by a function $\mathbf{s}=\mathbf{s}(\mathbf{r})$ to obtain a new wave function. About 30 years ago, Hall[2] applied the method to the Kellner approximation[3] of the He atom and obtained a nontrivial improvement, though he restricted the transformation function $\mathbf{s}(\mathbf{r})$ to a definite class of functions. A further generalization of Hall's approach has been studied by ten Hoor.[4-6]

Recently, Kryachko and co-workers[7-9] proposed an application of the local scaling method to the generation of the unknown parent wave function from a given one-electron density $\rho(\mathbf{r})$. For the N-electron system under consideration, they first chose an appropriate reference density $\rho_0(\mathbf{r})$ whose parent wave function $\Psi_0(\{\mathbf{r}_k\})$ was known, and then constructed a local scaling transformation between the reference $\rho_0(\mathbf{r})$ and given $\rho(\mathbf{r})$ densities. The transformation was then applied to $\Psi_0(\{\mathbf{r}_k\})$ to generate a wave function $\Psi_\rho(\{\mathbf{r}_k\})$ corresponding to the given density $\rho(\mathbf{r})$. Based on this procedure, they[7-9] discussed formally the density-functional theory. A numerical illustration of this method has been presented[10] very recently for the He atom, and the practical utility of the method has been shown; at least, for this simple case. The use of the same procedure for the investigation of the interrelation between the position $\rho(\mathbf{r})$ and momentum $\gamma(\mathbf{p})$ densities has also been reported.[11-13]

In the present paper, we apply the method of local scaling transformations to the density-functional calculation of the Li and Be atoms within the Hartree-Fock framework. Since these atoms have two electronic shells with different characters, the present study is the first crucial step of the proposed approach towards the general application to more complicated atoms and molecules. In Sec. II, we outline the procedure for the generation of a wave function $\Psi_\rho(\{\mathbf{r}_k\})$ from a given density $\rho(\mathbf{r})$, and define the energy $E[\rho]$ as a functional of the density. In Sec. III, the numerical results are presented and discussed for the Li and Be atoms in their ground states. The single-ζ wave function and the associated electron density are employed as a reference. Simple density functions are reported, which well reproduce the near-Hartree-Fock results. Atomic units are used throughout this paper.

II. AN ENERGY DENSITY FUNCTIONAL

For an N-electron atom in the S state, let a one-electron density $\rho(\mathbf{r})=\rho(r)$ be given, which is a function of the radius $r=|\mathbf{r}|$. If we could know the parent wave function $\Psi_\rho(\{\mathbf{r}_k\})$ of the given density $\rho(r)$ in some manner, the energy E of the system would be uniquely defined as a functional of $\rho(r)$ through the function $\Psi_\rho(\{\mathbf{r}_k\})$.

For this purpose, we assume the presence of a reference wave function $\Psi_0(\{\mathbf{r}_k\})$ and the associated density $\rho_0(r)$ for the system. We then introduce the *radial* local scaling transformation $s=s(r)$ between the two densities $\rho_0(r)$ and $\rho(r)$:[7-10]

$$\rho(r)=J(s/r)\rho_0(s) , \tag{1}$$

where $J(s/r)$ is the Jacobian of the transformation that ensures the relation

$$J(s/r)r^2dr=s^2ds . \tag{2}$$

The function $s=s(r)$ is a monotonically increasing function of r and is explicitly determined by the integral equation[11]

$$\int_0^r \rho(x)x^2dx=\int_0^s \rho_0(y)y^2dy . \tag{3}$$

For a small value of r, the asymptotic behavior of the transformation is given by

$$s(r)=[\rho(0)/\rho_0(0)]^{1/3}r+O(r^2) , \tag{4}$$

where we have assumed that $\rho_0(0)\neq 0$.

Using the local scaling transformation $s=s(r)$, we now construct[7-10] a wave function $\Psi_\rho(\{\mathbf{r}_k\})$ as

$$\Psi_\rho(\{\mathbf{r}_k\}) = \left[\prod_{k=1}^{N} J(s_k/r_k)^{1/2} \right] \Psi_0(\{\mathbf{s}_k\}) , \qquad (5)$$

where $\mathbf{r}_k = (r_k, \Omega_k)$ and $\mathbf{s}_k = (s_k, \Omega_k)$ in the spherical polar coordinates. By virtue of Eq. (2), we can easily verify that the wave function $\Psi_\rho(\{\mathbf{r}_k\})$ has the electron density exactly the same as the give density $\rho(r)$, that is,

$$\begin{aligned} N \int |\Psi_\rho(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N & \\ = NJ(s/r) \int |\Psi_0(\mathbf{s}, \mathbf{s}_2, \ldots, \mathbf{s}_N)|^2 d\mathbf{s}_2 \cdots d\mathbf{s}_N & \\ = J(s/r)\rho_0(s) = \rho(r) . & \qquad (6) \end{aligned}$$

Thus the generated wave function $\Psi_\rho(\{\mathbf{r}_k\})$ may be regarded as a possible parent wave function of the given density $\rho(r)$. When the reference wave function $\Psi_0(\{\mathbf{r}_k\})$ consists of a set of one-electron function (i.e., orbitals) $\{\psi_{0i}(\mathbf{r})\}$, as is the case of the present study, the N-electron transformation involved in Eq. (5) reduces to N single-electron transformations for the constituent orbitals.[13] Equation (5) is then replaced with

$$\psi_{\rho i}(\mathbf{r}) = [J(s/r)]^{1/2} \psi_{0i}(\mathbf{s}), \quad i = 1, 2, \ldots, N . \qquad (7)$$

If the reference orbitals $\{\psi_{0i}(\mathbf{r})\}$ are orthonormal, the same is true for the generated orbitals $\{\psi_{\rho i}(\mathbf{r})\}$, and the structure of the wave function $\Psi_\rho(\{\mathbf{r}_k\})$ remains unaltered from that of the reference function $\Psi_0(\{\mathbf{r}_k\})$.[13]

Assigning the wave function $\Psi_\rho(\{\mathbf{r}_k\})$ to the parent wave function of the given density $\rho(r)$, we may now define the energy E as a functional of the density:

$$E[\rho] \equiv E[\rho; \Psi_0] = \langle \Psi_\rho | H | \Psi_\rho \rangle / \langle \Psi_\rho | \Psi_\rho \rangle , \qquad (8)$$

where H is the Hamiltonian of the system. Clearly, the generated wave function $\Psi_\rho(\{\mathbf{r}_k\})$ depends on the reference function $\Psi_0(\{\mathbf{r}_k\})$ initially chosen, and therefore the energy E is also a functional of Ψ_0, except for some special cases.[10,12] In the following, however, we fix the reference function Ψ_0 to some appropriate (i.e., simple and yet physically acceptable) function and determine the electron density $\rho(r)$ variationally based on Eq. (8).

III. APPLICATIONS TO Li AND Be ATOMS

For the ground-state Li atom, we adopt the single-ζ wave function as the reference, which is specified by the two exponents ζ_1 and ζ_2. The optimized exponents were reported by Clementi and Roetti.[14,15] For the electron density function $\rho(r)$ to be determined, we assume its (unnormalized) functional form as

$$\rho_n(r) = \exp(-c_0 r) + \sum_{i=1}^{n} a_i r^{b_i} \exp(-c_i r) , \qquad (9)$$

which represents a linear combination of generalized Slater-type functions. $\{a_i, b_i, c_i\}$ are variational parameters where $\{b_i\}$ are restricted to be non-negative. The index n governs the number of basis functions in Eq. (9). By this choice of the functions for $\rho_0(r)$ and $\rho(r)$, the integrals appearing in Eq. (3), which determine the transformation function $s = s(r)$, can be analytically evaluated based on the formula[16]

$$\int_0^x t^b \exp(-ct) dt = c^{-(b+1)} \gamma(b+1, cx), \quad x \geq 0, \quad b > -1 \qquad (10)$$

where $\gamma(a,x)$ is the incomplete gamma function.

Since we have fixed the functional forms of $\Psi_0(\{\mathbf{r}_k\})$ and $\rho(r)$, the energy density functional $E[\rho]$ now reduces to a function of the parameters embedded in ρ and Ψ_0:

$$E[\rho] = E(\{a_i, b_i, c_i\}; \zeta_1, \zeta_2) . \qquad (11)$$

We have carried out the optimization of these parameters so as to minimize the energy E, which is defined as

TABLE I. Results of the density-functional calculation for the ground-state Li atom based on the local scaling method. For the explicit form of the density function $\rho_n(r)$, see Eq. (9) of the text.

Density	Optimum parameters	Energy
Single-ζ (reference)	$\zeta_1=2.690\,63$, $\zeta_2=0.639\,61$	$-7.418\,482$
$\rho_1(r)$	$c_0=5.451\,14$ $a_1=0.982\,49\times10^{-3}$, $b_1=2.010\,74$, $c_1=1.301\,30$ $\zeta_1=2.995\,69$, $\zeta_2=0.738\,77$	$-7.423\,251$
$\rho_2(r)$	$c_0=5.944\,58$ $a_1=0.920\,36$, $b_1=2.329\,14$, $c_1=6.326\,80$ $a_2=0.711\,18\times10^{-3}$, $b_2=2.745\,27$, $c_2=1.480\,45$ $\zeta_1=2.738\,36$, $\zeta_2=0.665\,49$	$-7.431\,530$
$\rho_3(r)$	$c_0=6.055\,00$ $a_1=0.637\,07$, $b_1=1.774\,84$, $c_1=5.786\,00$ $a_2=0.132\,63\times10^{-3}$, $b_2=3.663\,10$, $c_2=1.502\,50$ $a_3=0.801\,30\times10^{-3}$, $b_3=4.268\,90$, $c_3=2.287\,60$ $\zeta_1=2.565\,39$, $\zeta_2=0.621\,20$	$-7.431\,670$
Near-Hartree-Fock[a]		$-7.432\,727$

[a] References 17 and 18.

TABLE II. Position $\langle r^n \rangle$ and momentum $\langle p^n \rangle$ moments associated with the density function $\rho_3(r)$ for the ground-state Li atom. The values in parentheses are errors in percent relative to the near-Hartree-Fock values.

Moments[a]	Single-ζ (reference)	$\rho_3(r)$	Near-Hartree-Fock[b]
$\langle r^{-2} \rangle$	9.7731(−3.0)	10.070(−0.0)	10.072
$\langle r^{-1} \rangle$	1.9045(−0.0)	1.9045(−0.0)	1.9052
$\langle r \rangle$	1.6947(+1.3)	1.6837(+0.6)	1.6733
$\langle r^{2} \rangle$	6.5286(+5.1)	6.3067(+1.6)	6.2104
$\langle r^{3} \rangle$	34.564(+9.4)	32.296(+2.2)	31.586
$\langle r^{4} \rangle$	215.05(+13.8)	193.96(+2.6)	189.03
$\langle p^{-2} \rangle$	9.4157(+6.4)	8.9346(+0.9)	8.8520
$\langle p^{-1} \rangle$	1.7638(+2.0)	1.7369(+0.5)	1.7286
$\langle p \rangle$	1.6505(+0.9)	1.6348(−0.0)	1.6352
$\langle p^{2} \rangle$	4.9457(−0.2)	4.9544(−0.0)	4.9550
$\langle p^{3} \rangle$	22.403(−5.3)	23.659(−0.0)	23.665
$\langle p^{4} \rangle$	177.20(−14.8)	207.16(−0.4)	207.89

[a] The position and momentum densities are normalized to unity.

[b] The position moments are taken from Ref. 19, while the momentum moments from Ref. 20.

the Hamiltonian expectation over the wave function $\Psi_\rho(\{\mathbf{r}_k\})$ generated by the local scaling procedure [see Eq. (8)]. The results for the ground-state Li atom are summarized in Table I, where the index n is restricted to be 1, 2, or 3. We find that even the simplest function $\rho_1(r)$ constructed from two exponential functions associates the energy (−7.423 251) lower than the single-ζ energy (−7.418 482). Addition of another exponential function, i.e., the $\rho_2(r)$ function, noticeably improves the energy to −7.431 530. However, the energy improvement seems to be approximately "saturated" for the $\rho_3(r)$ function, having four exponential terms. The energy −7.431 670 of the density $\rho_3(r)$, which is the most flexible function in the present study, is lower than the single-ζ energy by 0.013 188. Since the energy difference between the single-ζ and near-Hartree-Fock wave functions is 0.014 245, the density function $\rho_3(r)$ recovers 93% of this difference.

In Table II, the one-electron position moments $\langle r^n \rangle$ $(-2 \leq n \leq 4)$ resulting from the density $\rho_3(r)$ for the Li atom are summarized and compared with those from the near-Hartree-Fock density.[19] The moments of the single-ζ wave function are also given there for reference. It is clear that the moments of $\rho_3(r)$ are much closer to the Hartree-Fock moments than the single-ζ ones. The same is true for the momentum moments $\langle p^n \rangle$ $(-2 \leq n \leq 4)$ summarized in the table, where the momentum moments of the $\rho_3(r)$ have been evaluated based on the density mapping procedure[11–13] developed recently.

Figure 1 examines directly the deviation of the radial density $4\pi r^2 \rho_3(r)$ from the near-Hartree-Fock density[19] as a function of r. When compared with the correspond-

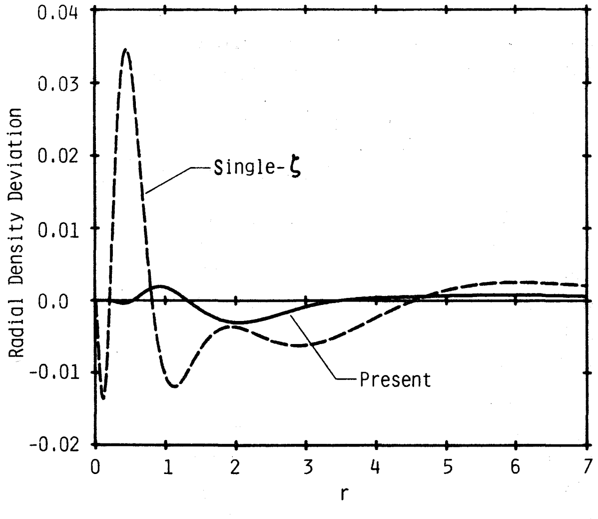

FIG. 1. Deviation in the radial density from the near-Hartree-Fock result for the Li atom. The parent densities are normalized to unity. The deviation and the radial distance r are in atomic units.

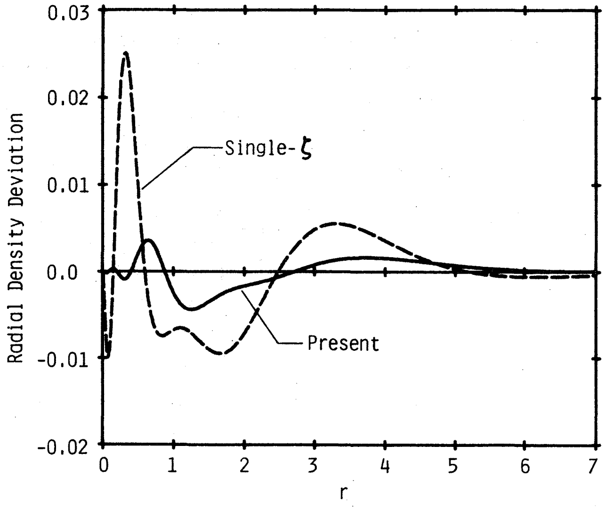

FIG. 2. Deviation in the radial density from the near-Hartree-Fock result for the Be atom. The parent densities are normalized to unity. The deviation and the radial distance r are in atomic units.

TABLE III. Results of the density-functional calculation for the ground-state Be atom based on the local scaling method. For the explicit form of the density function $\rho_n(r)$, see Eq. (9) of the text.

Density	Optimum parameters	Energy
Single-ζ (reference)	$\zeta_1=3.684\,78$, $\zeta_2=0.956\,03$	$-14.556\,740$
$\rho_1(r)$	$c_0=7.551\,14$ $a_1=5.198\,05\times10^{-3}$, $b_1=2.421\,09$, $c_1=2.060\,96$ $\zeta_1=3.603\,69$, $\zeta_2=0.958\,31$	$-14.563\,622$
$\rho_2(r)$	$c_0=7.796\,77$ $a_1=-0.220\,80$, $b_1=3.334\,52$, $c_1=4.988\,35$ $a_2=8.866\,46\times10^{-3}$, $b_2=0.000\,00$, $c_2=1.373\,72$ $\zeta_1=3.632\,93$, $\zeta_2=0.953\,95$	$-14.568\,511$
$\rho_3(r)$	$c_0=8.501\,32$ $a_1=-0.302\,66$, $b_1=2.005\,50$, $c_1=5.133\,55$ $a_2=0.168\,93$, $b_2=0.000\,00$, $c_2=4.649\,42$ $a_3=6.881\,32\times10^{-3}$, $b_3=1.218\,94$, $c_3=1.690\,38$ $\zeta_1=3.654\,24$, $\zeta_2=0.956\,93$	$-14.569\,644$
Near-Hartree-Fock[a]		$-14.573\,023$

[a] References 17 and 18.

ing single-ζ curve, the superiority of $\rho_3(r)$ is remarkable, particularly in the small-r region. It can be then said that the variationally determined density function $\rho_3(r)$ is quite a good approximation to the Hartree-Fock density.

Similar density-functional calculations have been done for the ground state of the Be atom. The results are summarized in Tables III and IV and Fig. 2. As has been the case of the Li atom (Table I), Table III shows that even the simplest function $\rho_1(r)$ gives an energy ($-14.563\,622$) much lower than the single-ζ energy ($-14.556\,740$), though the latter wave function has been employed as the reference to generate a parent wave function of the density $\rho_n(r)$. Addition of density basis functions further improves the energy, and the present best function $\rho_3(r)$ associates the energy $-14.569\,644$. This density function recovers 79% of the energy difference of the single-ζ and near-Hartree-Fock calculations. Figure 2 demonstrates how the present density $\rho_3(r)$ is closer to the near-Hartree-Fock density than the single-ζ one. However, there is a significant difference between the energies of $\rho_2(r)$ and $\rho_3(r)$ densities, and the present density-functional calculation for the Be atom appears to be subject to further improvement. This situation is different from that of the Li atom.

The position and momentum moments, $\langle r^n\rangle$ and $\langle p^n\rangle$ with $-2\le n\le 4$, associated with the density function $\rho_3(r)$ are tabulated in Table IV. For the position moments, we find that $\langle r^{-2}\rangle$ and $\langle r^4\rangle$ are improved, but $\langle r\rangle$ and $\langle r^2\rangle$ slightly change for the worse. Figure 2 shows, however, that the better agreement of the single-ζ

TABLE IV. Position $\langle r^n\rangle$ and momentum $\langle p^n\rangle$ moments associated with the density function $\rho_3(r)$ for the ground-state Be atom. Values in parentheses are errors in percent relative to the near-Hartree-Fock values.

Moments[a]	Single-ζ (reference)	$\rho_3(r)$	Near-Hartree-Fock[b]
$\langle r^{-2}\rangle$	14.105(-2.1)	14.390(-0.1)	14.406
$\langle r^{-1}\rangle$	2.1012(-0.0)	2.1012(-0.0)	2.1022
$\langle r\rangle$	1.5350($+0.2$)	1.5390($+0.4$)	1.5322
$\langle r^{2}\rangle$	4.3348($+0.1$)	4.3696($+0.9$)	4.3297
$\langle r^{3}\rangle$	15.609(-1.1)	15.967($+1.1$)	15.787
$\langle r^{4}\rangle$	65.165(-3.7)	68.327($+1.0$)	67.655
$\langle p^{-2}\rangle$	6.1744(-2.3)	6.3455($+0.4$)	6.3228
$\langle p^{-1}\rangle$	1.5688(-0.7)	1.5839($+0.3$)	1.5796
$\langle p\rangle$	1.8698($+0.6$)	1.8580(-0.0)	1.8586
$\langle p^{2}\rangle$	7.2784(-0.1)	7.2847(-0.0)	7.2865
$\langle p^{3}\rangle$	44.716(-3.6)	46.331(-0.1)	46.398
$\langle p^{4}\rangle$	482.99(-10.6)	535.92(-0.8)	540.23

[a] The position and momentum densities are normalized to unity.

[b] The position moments are taken from Ref. 19, while the momentum moments from Ref. 20.

moments with the near-Hartree-Fock ones is the result of an accidental cancellation of the contributions from the positive and negative deviations in the radial density. On the other hand, all the momentum moments show considerable improvement: The moments $\langle p^n \rangle$ generated from the position density $\rho_3(r)$ coincide with the near-Hartree-Fock results within 1% error.

In conclusion, the density-functional approach based on the local scaling method has been found to be quite successful for the Li and Be atoms. The present density $\rho_3(r)$ is a satisfactory approximation to the Hartree-Fock density. The most critical point of this approach is an accurate determination of the local scaling function $s = s(r)$ by the solution of the nonlinear equation, Eq. (3). Before we extend the present approach to heavier atoms and molecules, we would like to develop a modified theory which may simplify the determination of the scaling function.

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