Local scaling transformation function and atomic shell structure in density functional theory

B M DEB* and BIJOY KR. DEY

Theoretical Chemistry Group, Department of Chemistry, Panjab University, Chandigarh
160014, India
*Also from the Jawaharlal Nehru Centre for Advanced Scientific Research, Indian Institute
of Science Campus, Bangalore 560012, India

Abstract. The method of local scaling transformation in density functional theory calculates a transformation function (TRF) in order to generate an optimized atomic N-electron wave function from a trial density and a reference density/wave function. The TRFs $f(r)$ for several atomic systems are studied and it is observed that the number of minima in $df(r)/dr$ equals the number of atomic shells, except when $\rho = \rho_0$ and $f = r$.

1. Introduction

Recently, the method of local scaling transformations (LST) in density functional theory (DFT) has attracted some attention [1–5]. Starting from a reference N-electron wave function $\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)$, corresponding to a reference one-electron density $\rho_0(\mathbf{r})$, the method generates an N-electron wave function $\Psi_\rho(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ from a given (trial) one-electron density $\rho(\mathbf{r})$ through a unique one-electron transformation T, where $\rho(\mathbf{r}) = T\rho_0(\mathbf{r})$. If $\rho(\mathbf{r})$ contains adjustable parameters then these would enter into Ψ_ρ, enabling one to variationally optimize the parameters. It has been shown [3–5] that even if one uses a trial density $\rho(\mathbf{r})$ which is considerably simpler than the Hartree-Fock (HF) density, the method can deliver atomic density and energy of near-HF accuracy. It is also interesting to note that for the ground states of two-electron atomic systems Ψ_ρ is independent of Ψ_0 [3]. Apart from numerical accuracy, a principal advantage of this method is the retention of the wave function concept within DFT (see also [6]). It has been opined [7] that discarding the wave function concept in DFT is the primary reason for the latter's discomfiture while being extended to excited and time-dependent states.

2. The method

The LST method has been described in detail by others [1–5]. Here we summarize the essential equations which are useful to us, for the ground states of spherically symmetric systems.

The transformation function (TRF) $f(r)$ which is of primary interest in this report

is defined and calculated through the following expressions:

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

$$J(f/r) = \frac{f^2}{r^2}\frac{df}{dr}, \tag{2}$$

$$\frac{df}{dr} = \frac{r^2\rho(r)}{f^2\rho_0(f)}, \tag{3}$$

$$\int_0^r \rho(x)x^2\,dx = \int_0^f \rho_0(y)y^2\,dy \tag{4}$$

$$f(r) = [\rho(0)/\rho_0(0)]^{1/3}r + O(r^2), \text{ for small } r \tag{5}$$

$$\Psi_\rho(r_1,\ldots,r_N) = \left[\prod_{i=1}^N J(f_i/r_i)^{1/2}\right]\Psi_0(f_1,\ldots,f_N). \tag{6}$$

Thus, Ψ_ρ yields the one electron-density $\rho(r)$. In case Ψ_0 is constructed from a set of orthonormal orbitals $\{\psi_{0i}(r)\}$, $i = 1,\ldots,N$, then one obtains the following set of transformed orthonormal orbitals $\{\phi_{\rho i}(r)\}$ for constructing Ψ_ρ:

$$\phi_{\rho i}(r) = J(f/r)^{1/2}\psi_{0i}(f) \tag{7}$$

Thus, the structures of Ψ_ρ and Ψ_0 are the same, and

$$E[\rho] = E[\rho; \Psi_0] = \langle\Psi_\rho|H|\Psi_\rho\rangle/\langle\Psi_\rho|\Psi_\rho\rangle \tag{8}$$

where H is the Hamiltonian of the system.

The TRF $f(r)$ can be ascribed the same physical meaning as that of the radial coordinate r, i.e., f is a distance quantity, $0 \leqslant f \leqslant \infty$. Thus, $\rho_0(f)$ is obtained by simply replacing r in $\rho_0(r)$ by f. The TRF in effect implies a mapping between r-space and f-space. The plots of $f^2\rho_0(f)$ as functions of $\sqrt{f}$ and $\sqrt{r}$ have been shown later.

Apart from the statement [4] that $f(r)$ is a monotonically increasing function of r, no attention seems to have been paid to the detailed structure of $f(r)$ which, as shown by (3), is dependent on ρ_0 and ρ. In particular, the number of minima in df/dr is observed by us to correspond to the number of shells and hence the number of maxima in atomic radial density.

Although the calculations reported in this paper correspond to the ground states of spherically symmetric systems, it is worthwhile to note that, in principle, the LST method is also applicable to excited states and to non-spherical systems, e.g., diatomic molecules. While no calculations seem to be reported for molecules, Koga [5] has reported LST calculations on the $2\,^1S$ excited state of the He atom, by taking a configuration-interaction wave function as Ψ_0 and satisfying both Hamiltonian and wave-function orthogonalities.

3. Results and discussion

In order to examine the structure of $f(r)$, we have repeated Koga's calculations, using his optimized electron densities for the ground states of H^-, He, Li^+, Be^{++}, Li and Be [3, 4]. The reference density ρ_0 and the wave function Ψ_0 for He, Li^+, Li and Be were taken from the single-zeta calculations of Clementi and Roetti [8] while those

Table 1. Calculated kinetic energies (a.u.) for atoms and ions containing 2–4 electrons by the local scaling transformation method. The electron density is normalized up to the fifteenth decimal place. In columns 3 and 4, the negative of total energy is taken as the kinetic energy (values from table 3 of Koga [3], tables 1 and 3 from Koga [4]).

	Kinetic energy		
Atom/Ion	Present value	Koga's value	Hartree-Fock value
H^-	0·4885550[a]	0·4879262	0·4879297
He	2·8615775[a]	2·8616799	2·8616800
Li^+	7·2349501[a]	7·2364148	7·2364152
Be^{++}	13·613227[a]	13·611299	13·611299
Li	7·4328695[b]	7·431530	7·432727
Be	14·565166[c]	14·568511	14·573023

[a]Using the optimized electron density from table 3 of Koga [3]; [b]Using the optimized $\rho_2(r)$ from table 1 of Koga [4]; [c]Using the optimized $\rho_2(r)$ from table 3 of Koga [4].

Table 2. Comparison of calculated position moments (a.u.) with the corresponding values from table 2 of Koga [3] for the He atom as well as with the Hartree-Fock values [3]. The present Ψ_ρ has been normalized to unity up to the fifteenth decimal place.

Position moment	Present value	Koga's value	Hartree-Fock value
$\langle r^{-2} \rangle$	5·9936	5·9959	5·996
$\langle r^{-1} \rangle$	1·6873	1·6873	1·6873
$\langle r \rangle$	0·9273	0·9273	0·9272
$\langle r^2 \rangle$	1·1847	1·1849	1·1846
$\langle r^3 \rangle$	1·9396	1·9407	1·9398
$\langle r^4 \rangle$	3·8810	3·8882	3·8838

for H^- and Be^{++} were taken from the single-zeta calculations of Roothaan and Soukup [9]. Table 1 compares our kinetic energy values with Koga's and HF values [3, 4]. We see that although our kinetic energy value has occasionally gone slightly above the HF value, our computed values are in excellent agreement with the HF and Koga's values. We also compare our calculated position moments, by using Ψ_ρ, for the He atom with those of Koga [3] in table 2. The agreement is again excellent and in fact our values generally show better agreement with the HF values than those of Koga [3]. All calculations were performed in double precision.

Figures 1 and 2 depict $f(r)$ and df/dr for H^- ion and Be atom respectively. The plots for the other two-electron systems, He, Li^+ and Be^{++}, are qualitatively similar to those for H^- while the plots for Li atom are qualitatively similar to those of Be.

Several remarks can be made regarding these plots:

1. $f(r)$ is depicted as a monotonically increasing function of r [4]; $f = 0, \infty$ corresponding to $r = 0, \infty$.

2. df/dr plots show the effects of both Z and N. As r increases, df/dr increases with Z from H^- to Be^{++}. The same is true from Li to Be.
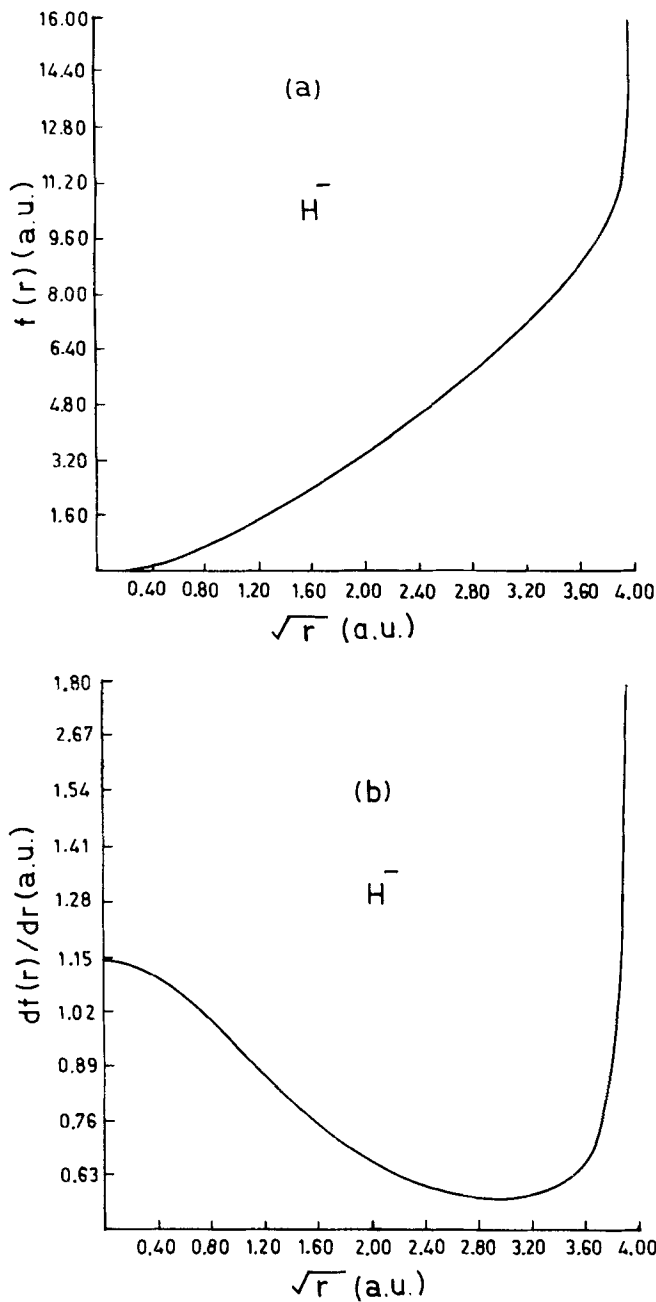
Figure 1. Plot of (a) $f(r)$ against $\sqrt{r}$ and (b) df/dr against $\sqrt{r}$, in a.u., for the H^- ion. The plots for other two-electron systems, He, Li^+ and Be^{++}, are similar. Normalized transformed orbital is employed.

3. $f(r)$ increases rapidly with r so that at an r-value where the electron density is very small f is quite large, leading to a rapid increase in df/dr which tends to ∞ as $r \to \infty$.

4. From (5), $[df/dr]_{r=0} \simeq 1$, since $\rho_0(0)$ and $\rho(0)$ are quite close to each other. This is always true in our calculations.
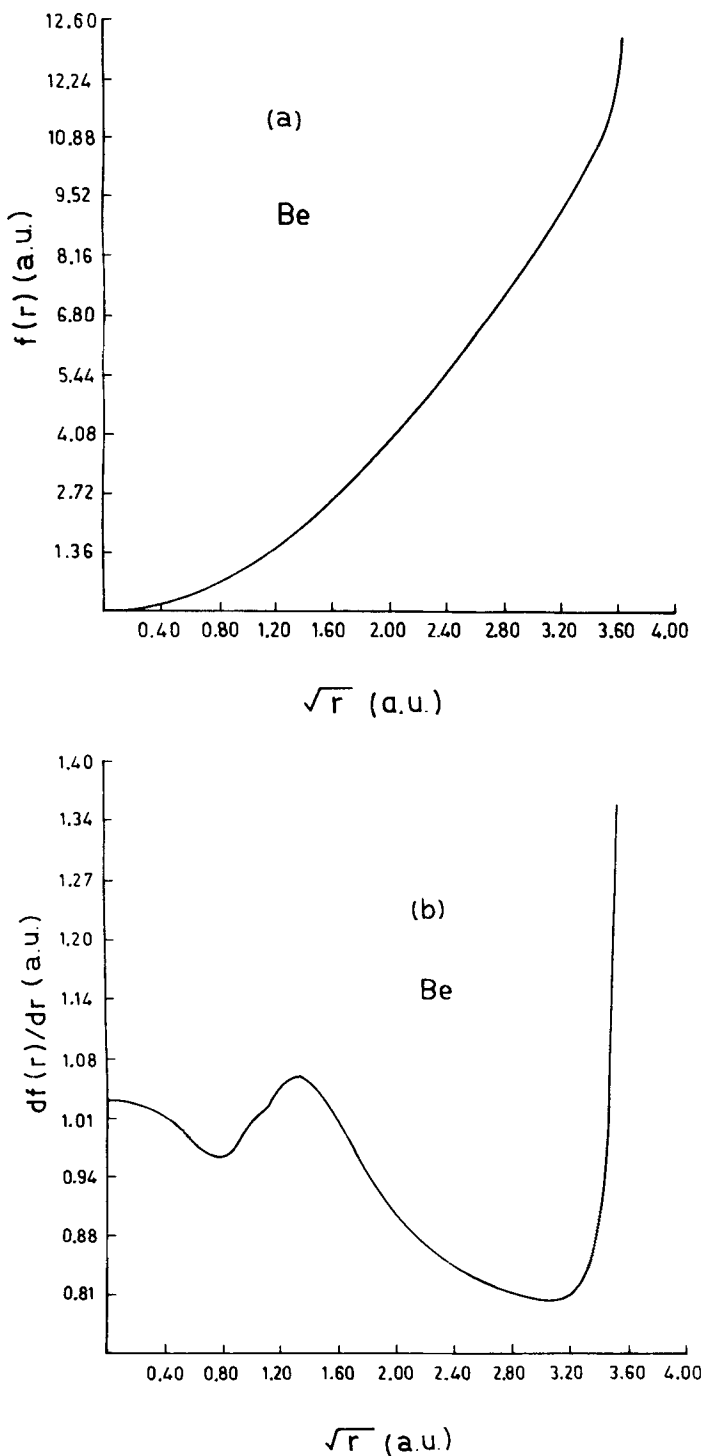
Figure 2. Plot of (a) $f(r)$ against $\sqrt{r}$ and (b) df/dr against $\sqrt{r}$, in a.u., for the Be atom. The plots for the Li atom are similar. Orthonormalized transformed orbitals are employed.

5. df/dr shows one minimum for H$^-$, He, Li$^+$ and Be^{++} and two minima for Li and Be, corresponding to the presence of one and two shells respectively. However, the locations of these minima do not coincide with the maxima or minima in the radial density. The first minimum occurs at 9·042 (H$^-$), 3·652 (He), 2·217 (Li$^+$), 2·350 (Be^{++}), 1·024 (Li), 0·575 (Be) a.u. while the second minimum occurs at 12·96 (Li) and 9·248 (Be) a.u. respectively.

6. Thus $f(r) = f(r, Z, N)$, as also df/dr.

Although no LST calculation has been reported so far on atomic systems containing three shells, we feel that our observation of the number of minima in df/dr being equal to the number of atomic shells should be of general validity. This observation is of interest for two reasons: (a) Observation of shell structure in a distance quantity, f. This is different from the familiar shell structure in density quantities. (b) Although (3) indicates that df/dr should contain information about shell structure since both $r^2\rho(r)$ and $f^2\rho_0(f)$ contain such information, it is not clear how such information is encoded in df/dr. Equation (3) gives

$$\frac{d^2 f}{dr^2} = \frac{1}{f^2\rho_0(f)}\left[\frac{d}{dr}\left\{r^2\rho(r)\right\} - \frac{r^4\rho^2(r)}{f^4\rho_0^2(f)}\frac{d}{df}\left\{f^2\rho_0(f)\right\}\right] \tag{9}$$
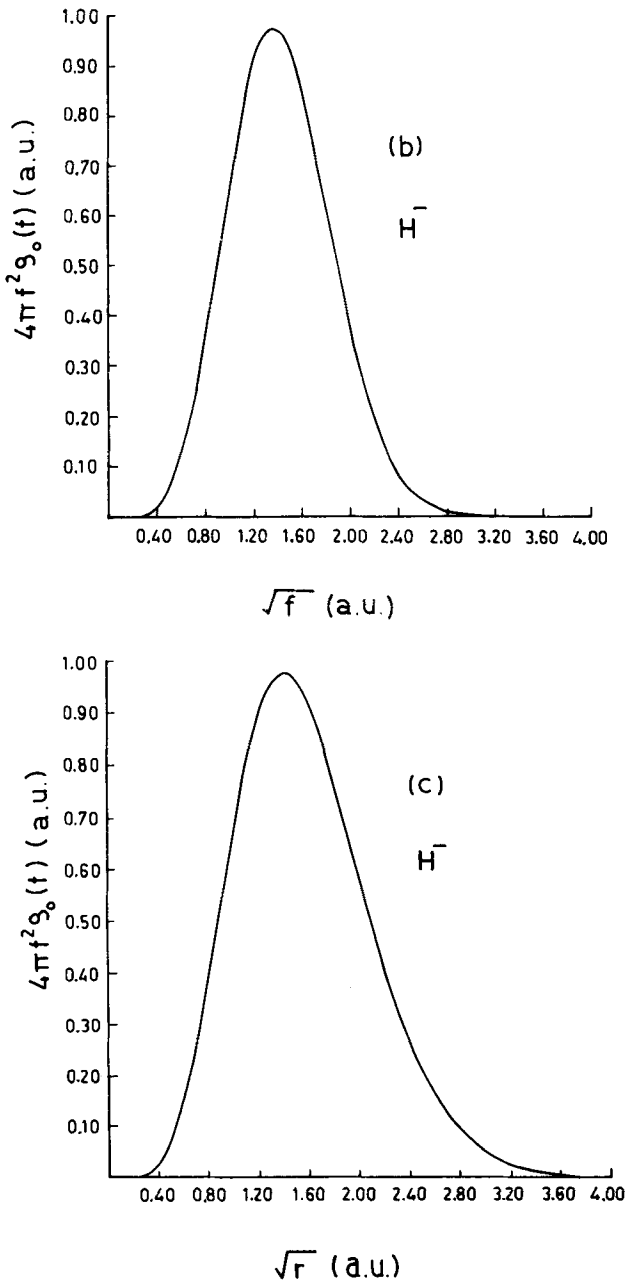
This means that $d^2 f/dr^2$ vanishes when

$$f^4\rho_0^2(f)\frac{d}{dr}\left\{r^2\rho(r)\right\} = r^4\rho^2(r)\frac{d}{df}\left\{f^2\rho_0(f)\right\} \tag{10}$$

Such vanishing need not be at the maxima or minima of the radial density. However, $d^2 f/dr^2 = 0$ at $r = 0$, from (9), since $d/df\{f^2\rho_0(f)\} = 0$ at $r = 0$ and f varies linearly as r for very small r. Figures 1(b) and 2(b) verify these conclusions.
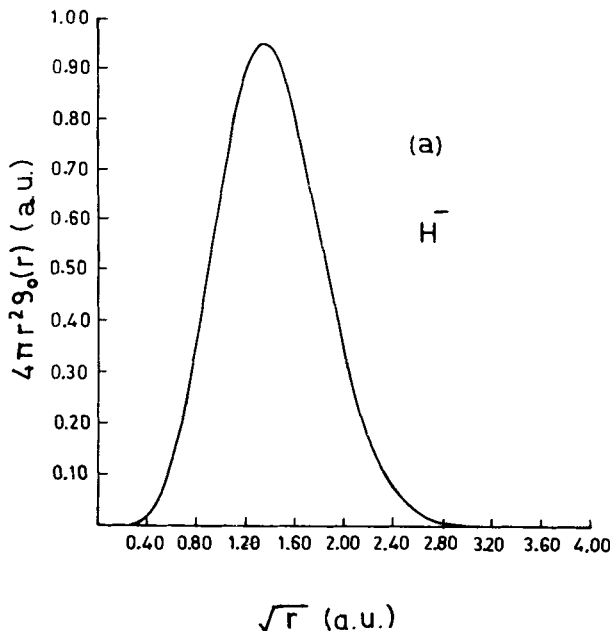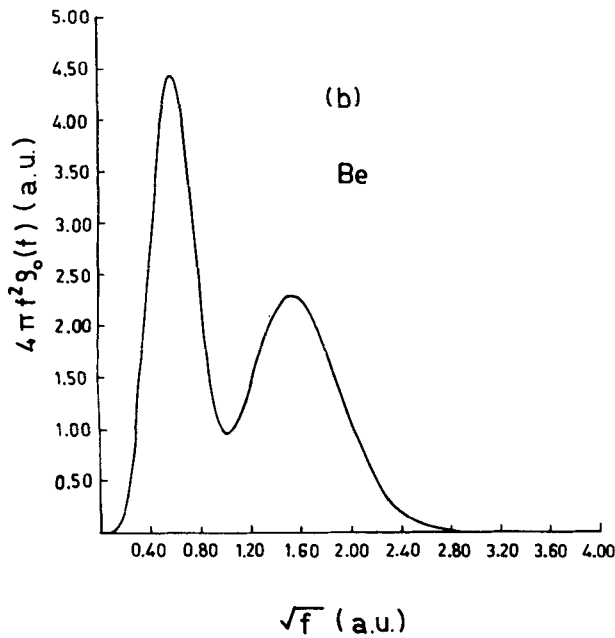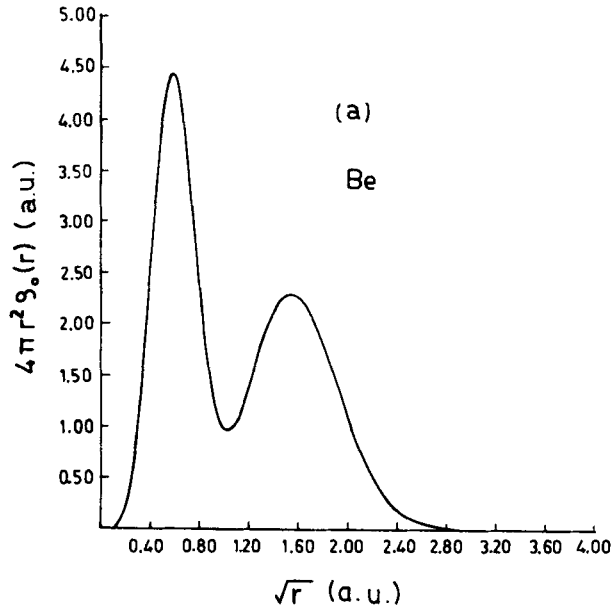
Figure 3. Plot of (a) single-zeta [8] $4\pi r^2 \rho_0(r)$ against $\sqrt{r}$, (b) $4\pi f^2 \rho_0(f)$ against $\sqrt{f}$ and (c) $4\pi f^2 \rho_0(f)$ against $\sqrt{r}$, in a.u., for the Li^+ ion. The plots for the other two-electron systems, H^-, He and Be^{++}, are similar. Plots (a) and (b) are identical but (c) is different. Normalized transformed orbital is employed.

Furthermore, figures 3 and 4 depict $4\pi f^2 \rho_0(f)$ as functions of $r^{1/2}$ and $f^{1/2}$, for Li^+ ion and Be atom. They are also compared with the corresponding single-zeta $4\pi r^2 \rho_0(r)$ plotted against $r^{1/2}$. The plots of $4\pi f^2 \rho_0(f)$ against $f^{1/2}$ and $4\pi r^2 \rho_0(r)$ against $r^{1/2}$ obviously coincide. But those of $4\pi f^2 \rho_0(f)$ against $f^{1/2}$ and $r^{1/2}$ are not identical; the locations of the maxima and minima in the last two plots are slightly

different. Also, the plot against $r^{1/2}$ has a longer tail. This explains why df/dr in (3) goes to ∞ as $r \to \infty$.

In summary, atomic shell structure has been observed in a distance quantity like $f(r)$ whose behaviour is such that $f(r) = 0, \infty$ at $r = 0, \infty$; $df/dr \simeq 1$ at $r = 0$ and goes to ∞ as $r \to \infty$. These conclusions are valid except in the special case of $\rho = \rho_0$ and $f = r$.
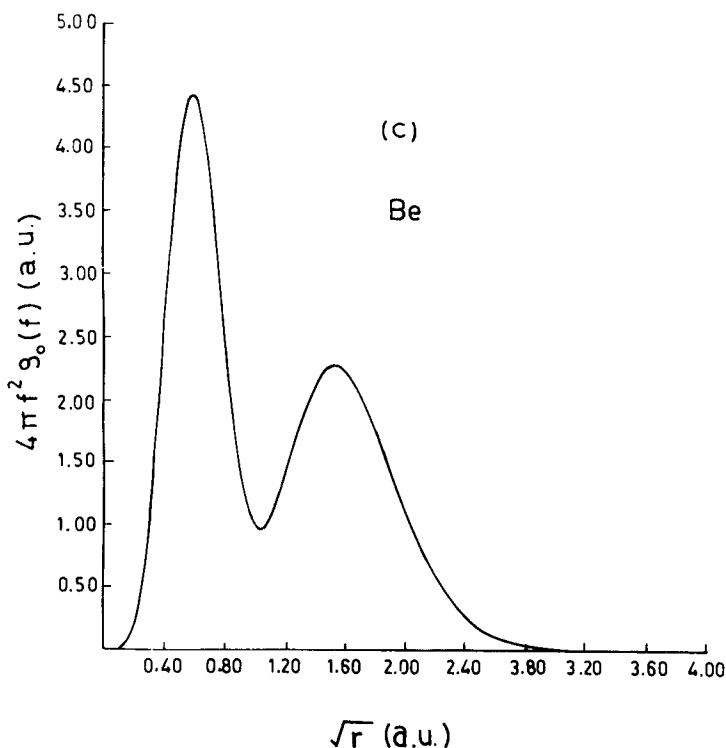
Figure 4. Plot of (a) single-zeta [8] $4\pi r^2 \rho_0(r)$ against $\sqrt{r}$, (b) $4\pi f^2 \rho_0(f)$ against $\sqrt{f}$ and (c) $4\pi f^2 \rho_0(f)$ against $\sqrt{r}$, in a.u., for the Be atom. The plots for the Li atom are similar. Plots (a) and (b) are identical but (c) is different. Orthonormalized transformed orbitals are employed.

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