PHYSICAL REVIEW A, VOLUME 61, 052505

Correlated one-electron and two-electron densities for the ground state of the lithium atom

F. J. Gálvez and E. Buendía
Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain

A. Sarsa
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85827

(Received 3 December 1999; published 10 April 2000)

One- and two-electron densities are calculated for the ground state of the lithium atom starting from a highly accurate Hylleraas-type wave function. An analytical parametrization for those densities is obtained, which allows one to calculate both the form factor and the structure factor. Electronic correlation effects are discussed in terms of these densities and related functions such as the Coulomb hole. The calculation of the densities has been performed by means of the Monte Carlo method.

PACS number(s): 31.25.Eb, 31.15.Ew, 32.10.−f

I. INTRODUCTION

The ground state of the lithium atom has been the focus of extensive computational studies using correlated wave functions. For a compilation of results, see Refs. [1,2], and references therein. All these investigations have been mainly focused on the calculation of accurate values for the nonrelativistic ground-state energy. Other properties such as the one-and two-body densities in position space and the elastic and inelastic scattering factors have also been obtained.

These one-and two-body densities play an important role in the description and understanding of the dynamics of atoms and molecules [3–17]. Electron correlation effects have been studied in terms of the Coulomb hole, i.e., the difference between the correlated and the Hartree-Fock interelectronic densities, and the Hund rules have been interpreted using these densities. Also, the one-body density is the cornerstone of density functional theory. Finally, it is worth mentioning here that the scattering factors have also been analyzed to elucidate the effects of electronic correlations in atomic and molecular systems [18–25].

For an N-electron system, the one-body density is defined as

$$\rho(\vec{r})=\int\frac{|\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)|^2}{\langle\Psi|\Psi\rangle}\sum_i^N\delta(\vec{r}-\vec{r}_i)d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_N \quad (1)$$

and represents the probability density function for the electron-nucleus vector $\vec{r}$. The spherically averaged density is denoted by $\rho(r)$ and the radial charge distribution around the nucleus is given by

$$D(r)=4\pi r^2\rho(r). \quad (2)$$

For the lithium atom, analytic expressions for $D(r)$ have been obtained from both a configuration-interaction (CI) wave function [9] and a Hylleraas-type wave function [11], although in this last case it is necessary to make some restrictions on the basis functions used in the Hylleraas expansion. Accurate values for the electron density at the nucleus, $\rho(0)$, and for the moments $\langle r^n\rangle$ have also been calculated starting from a CI wave function [9] and from explicitly correlated wave functions [12,14].

Two-body properties can be studied in terms of both the interelectronic or intracule, $I(\vec{r}_{12})$, and the center of mass or extracule, $E(\vec{R})$, densities defined as [4]

$$I(\vec{r}_{12})=\int\frac{|\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)|^2}{\langle\Psi|\Psi\rangle}\times\sum_{i<j}^N\delta[\vec{r}_{12}-(\vec{r}_i-\vec{r}_j)]d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_N, \quad (3)$$

$$E(\vec{R})=\int\frac{|\Psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)|^2}{\langle\Psi|\Psi\rangle}\times\sum_{i<j}^N\delta\left(\vec{R}-\frac{\vec{r}_i+\vec{r}_j}{2}\right)d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_N, \quad (4)$$

respectively. These functions are the probability density functions for the relative, $\vec{r}_{12}$, and center of mass, $\vec{R}$, vectors, respectively. Their spherical averages are denoted by $h(r_{12})$ and $d(R)$. The corresponding radial densities are given by

$$P(r_{12})=4\pi r_{12}^2h(r_{12}),$$
$$\Pi(R)=4\pi R^2d(R). \quad (5)$$

In Eqs. (1), (3), and (4) summation over the spin variables is implicit. The numerical difficulties involved in calculating these densities have restricted their calculation with highly accurate wave functions to few-electron atoms. For helium-like systems, very precise wave functions have been obtained by using the variational method. With them benchmark calculations of the interelectronic density have been reported since the work of Coulson and Neilson [3]. For the ground state of the lithium atom information about these densities is much more scarce. Accurate values for some moments of the intracule density $\langle r_{12}^n\rangle$ can be found in [14,15]. A compact analytical formula for the electron-electron radial distribution, obtained from a Hylleraas-type wave function, has been reported [13]. This closed form was obtained by imposing some conditions on the basis set in order to carry out analytically the different integrals involved in the calculation.

This leads to an intracule density that does not reproduce adequately the low-r_{12} region in the atom. For the atoms of the second and third row, the spherically averaged radial electron-pair density $P(r_{12})$ has been obtained within a configuration-interaction scheme [17]. Recently the intracule [16,26] and extracule [27] densities have been calculated starting from explicitly correlated wave functions by means of the Monte Carlo method for atoms from He to Ne.

The elastic scattering (or atomic form) factor $F(\vec{q})$ and the inelastic scattering factor $S(\vec{q})$ in the framework of the first Born approximation can be written in terms of the one- and two-body densities in the form [28]

$$F(\vec{q})=\int \rho(\vec{r})e^{i\vec{q}\cdot\vec{r}}d\vec{r} \tag{6}$$

and

$$S(\vec{q})=\int\int \Gamma(\vec{r}_1,\vec{r}_2)e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}d\vec{r}_1 d\vec{r}_2-|F(\vec{q})|^2+N, \tag{7}$$

respectively. Here, $\Gamma(\vec{r}_1,\vec{r}_2)$ denotes the two-electron density normalized to $N(N-1)$, and $\vec{q}$ is the momentum transfer vector whose magnitude q depends on the wavelength λ of the radiation and the scattering angle 2θ according to $q=(4\pi/\lambda)\sin\theta$. In addition, the spherically averaged elastic and inelastic form factors, $F(q)$ and $S(q)$, may be expressed in terms of $D(r)$ and $P(r_{12})$ as

$$F(q)=\int_0^\infty D(r)j_0(qr)dr \tag{8}$$

and

$$S(q)=2\int_0^\infty P(r_{12})j_0(qr_{12})dr_{12}-|F(q)|^2+N, \tag{9}$$

where $j_0(x)$ is the spherical Bessel function of zero order.

For the lithium atom, correlated values of $F(q)$ and $S(q)$ have been calculated using different variational wave functions [18,20,22,23,25]. The inelastic scattering factor is more sensitive to the effect of electronic correlations than the elastic form factor.

High-quality Hylleraas-type wave functions have been used previously to obtain different properties of the atomic lithium ground state, such as the energy and the expectation values $\langle\Sigma_i\delta(r_i)\rangle$, $\langle\Sigma_{i>j}\delta(r_{ij})\rangle$, $\langle r^n\rangle$, and $\langle r_{12}^n\rangle$, which are related to the single-particle and intracule densities. However, some other quantities, such as the corresponding one- and two-body densities at any point of their interval of definition, or even the inelastic form factor, cannot be directly evaluated. The aim of this work is to calculate spherically averaged one- and two-body densities in position space and both the elastic and inelastic scattering factors for the atomic lithium ground state starting from a very accurate variational Hylleraas-type wave function. The calculations are performed by means of the Monte Carlo method, which allows one to evaluate expectation values of any operator between wave functions of any kind [29]. Therefore no analytical restrictions are imposed on the basis set, its length being limited only by the computational time requirements in the Monte Carlo evaluation of the densities. With the wave function used in this work more than 99.99% of the correlation energy is recovered and the asymptotically correct short and long range behaviors are reproduced. The Monte Carlo single-particle, intracule, and extracule densities are then parametrized by means of simple analytical expressions. This allows one to obtain the elastic and inelastic scattering factors in a simple and closed form. Finally, electron correlation effects on all these quantities will be examined.

The structure of this paper is as follows. In Sec. II we give the wave function we have worked with and some details of the numerical methodology. In Sec. III we present the results obtained in this work. Finally, we give the conclusions in Sec. IV. Unless otherwise indicated, atomic units are used throughout.

II. WAVE FUNCTION AND MONTE CARLO CALCULATIONS

The wave function employed in this work is expanded in terms of Hylleraas-type basis functions

$$\Psi(1,2,3)=\mathcal{A}\sum_{\mu=1}^{M} C_\mu\phi_\mu(\vec{r}_1,\vec{r}_2,\vec{r}_3)\chi_\mu, \tag{10}$$

where $\mathcal{A}$ is the three-electron antisymmetrizer, C_μ are the variationally determined expansion coefficients, and M is the number of basis functions employed. The basis functions $\phi_\mu(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ are of the form

$$\phi_\mu(\vec{r}_1,\vec{r}_2,\vec{r}_3)=e^{-\alpha(r_1+r_2)-\gamma r_3}r_1^{i_\mu}r_2^{j_\mu}r_3^{k_\mu}r_{23}^{l_\mu}r_{31}^{m_\mu}r_{12}^{n_\mu} \tag{11}$$

and χ_μ denotes the possible spin eigenfunctions, which for the doublet states can be one of the two

$$\chi=\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3) \tag{12}$$

or

$$\chi=2\alpha(1)\alpha(2)\beta(3)-\beta(1)\beta(2)\alpha(3). \tag{13}$$

We shall use the parametrization proposed by King and Shoup [30], a 352-term expansion that provides a nonrelativistic ground-state energy of $-7.478\,058$, which is $2\,\mu h$ above the most precise calculation, i.e., a correlation energy of 99.995%. The numerical values of the exponents are $\alpha=2.76$ and $\gamma=0.65$, and the 352 values of the integers $\{i_\mu,j_\mu,k_\mu,l_\mu,m_\mu,n_\mu\}$ which determine the basis set have been taken from [30]. This basis set was chosen by requiring the optimal energy with the fewest possible number of basis functions. More precise expansions have been reported since (see, e.g., [14]) in which the number of basis functions is a factor 5 bigger than in the wave function used in this work, and only one spin basis set is used. The use of such an expansion is prohibitive for our present computational resources. Finally, it is worth mentioning that an advantage of the basis set employed here is that it makes use of the two possible spin eigenfunctions for the ground-state configura-

TABLE I. Monte Carlo (MC) and parametrized (A) values of $\rho(0)$ and $\langle r^n \rangle$ for the ground state of the lithium atom as compared with the corresponding Hartree-Fock (HF) values, and with other correlated values obtained directly from the wave function (HN [30] and Exact [12,14,15]) and from other parametrized single-particle density calculations (KD) [11]. In parentheses we give the statistical error of the MC calculation.

	$\rho(0)$	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$
HF	13.83408	30.21654	5.715475	5.019761	18.63129	94.75963	567.0927
MC		30.3(1)	5.7191(7)	4.9899(6)	18.359(6)	92.63(6)	550.2(6)
HN	13.84150		5.718107	4.989579	18.35514	92.60858	550.2030
Exact	13.84254	30.24097	5.718111	4.989523	18.35462	92.60364	550.0736
A	13.8466	30.2516	5.71855	4.98971	18.3573	92.6229	550.217
KD	13.84170	30.24071	5.718087	4.989765	18.35707	92.62792	550.4163

tion. Therefore the spatial components need to be computed only once and they require no additional computation time.

The one- and two-body densities can be computed with the Monte Carlo method as the expectation values of the different δ operators, such as are shown in Eqs. (1), (3), and (4). We have also calculated the different one- and two-body expectation values $\langle t^n \rangle$, where t stands for r, r_{12}, and R.

The elastic and inelastic form factors may also be calculated by using the Monte Carlo method. This requires evaluation of the expectation value in the variational wave function of the following local operators:

$$f(q;\vec{r}_1,\ldots,\vec{r}_N)=\sum_{k=1}^{N}\frac{\sin(qr_k)}{qr_k},\quad s(q;\vec{r}_1,\ldots,\vec{r}_N)=\sum_{k<l}^{N}\frac{\sin(qr_{kl})}{qr_{kl}}. \tag{14}$$

A major drawback of using these expressions is that, for large q, their highly oscillatory behavior requires very large computing time in order to obtain accurate values for the corresponding form factors. An alternative way to obtain them is to use an analytical expression for both the single-particle and the intracule densities and then to perform their corresponding Fourier transforms. As we shall see below, there is good agreement between the factors calculated in this way and the ones obtained directly.

III. RESULTS

A. Single-particle density

In Table I we present different results for the moments of the single-particle density and for $\rho(0)$. In the first row we show the values obtained within the Hartree-Fock (HF) framework. The results provided by the wave function used in this work are shown in the rows MC and HN. The former indicates the results calculated using the Monte Carlo method while in the latter the integrals are evaluated numerically [30]. In the row labeled as Exact we give the most accurate values for those properties given in the literature [12,14,15]. It can be concluded that the wave function used in this work provides a description of the one-body density of high quality. Also, the MC method provides quite accurate results for these expectation values. In the worst case, $\langle r^{-2} \rangle$, the relative error is 0.2%.

To parametrize the Monte Carlo radial density function $D(r)$ we have used the same analytical form as that obtained by King and Dressel by using a different Hylleraas basis set [11]:

$$D(r)=\sum_{k=1}^{7} e^{-\alpha_k r}\sum_{n=0}^{g_k} a_{k,n}r^n \tag{15}$$

with the restrictions

$$\sum_{k=1}^{7} a_{k,0}=0;\quad \sum_{k=1}^{7}(a_{k,1}-\alpha_k a_{k,0})=0. \tag{16}$$

The numerical values of the parameters α_k and $a_{k,n}$ are given in Table II.

The values of $\rho(0)$ and $\langle r^n \rangle$ calculated with this adjusted density are also shown in Table I (row A), where they are also compared with those obtained from the analytical expression of King and Dressel [11] (row KD). In general the agreement between the parametrized values and the rest is quite good.

B. Intracule density

In Table III we show the values of some radial moments of the intracule density, $\langle r_{12}^n \rangle$, and its value at the coalescence point, $h(0)$. The notation used here for the different rows is the same as in Table I. Again the quality of the results provided by the Monte Carlo method is apparent.

Once we obtained the Monte Carlo interelectronic radial density $P(r_{12})$, we parametrized it by means of the expression

$$P_a(r_{12})=\sum_{k=1}^{3} e^{-\alpha_k r_{12}}\sum_{n=1}^{r_k} b_{k,n}r_{12}^n \tag{17}$$

with the condition $\Sigma_{n=1}^{3} b_{1,n}=0$. This expression was obtained by Dressel and King [13] from a Hylleraas-type wave function in which some restrictions on the powers of r_{ij} were imposed. This leads to a significant loss of precision in the

TABLE II. Coefficients α_k, $a_{k,n}$, $b_{k,n}$, and $c_{k,n}$ for the parametrized single-particle, intracule and extracule densities.

	$\alpha_1=1.30$	$\alpha_2=3.41$	$\alpha_3=5.52$	$\alpha_4=6.82$	$\alpha_5=8.93$	$\alpha_6=11.04$	$\alpha_7=12.34$
$a_{k,0}$	32.61914	−577.6960	1604.013	−4917.567	24949.70	169330.7	−190421.8
$a_{k,1}$	−22.66042	541.4168	378.1069	1037.909	1232.701	−46844.17	−240527.4
$a_{k,2}$	5.101153	−228.4099				−81858.94	−103422.5
$a_{k,3}$	−0.158814						−15470.30
$a_{k,4}$	0.112840						

	$\alpha_1=1.30$	$\alpha_2=3.41$	$\alpha_3=5.52$		$\alpha_1=1.30$	$\alpha_2=3.41$	$\alpha_3=5.52$
$b_{k,1}$	−11998.32	−113864.6	125863.0	$c_{k,1}$	−30559.20	349362.7	−318803.5
$b_{k,2}$	5577.773	253035.4	32281.02	$c_{k,2}$	30577.75	−1074826.	−172065.4
$b_{k,3}$	−1051.250	−196043.1		$c_{k,3}$	−12395.65	2268595.	
$b_{k,4}$	100.5064	133710.7		$c_{k,4}$	2549.599	−2300853.	
$b_{k,5}$	−4.819898	−50206.25		$c_{k,5}$	−262.4857	2174966.	
$b_{k,6}$	0.093133	18353.06		$c_{k,6}$	10.88710	−1207237.	
$b_{k,7}$		−4059.999		$c_{k,7}$		622938.7	
$b_{k,8}$		851.1032		$c_{k,8}$		−179760.2	
$b_{k,9}$		−94.84240		$c_{k,9}$		42657.53	
$b_{k,10}$		8.983948		$c_{k,10}$		−2202.909	

low-r_{12} region. This is not the case for the wave function and for the parametrization of the intracule density obtained here. In Table II we give the numerical values of the parameters $b_{k,n}$ and in Table III (row *A*) we show the values of the intracule density at the origin, $h(0)$, and of the moments $\langle r_{12}^n \rangle$ calculated with the parametrization of this work as compared with the values obtained from the parametrization of Dressel and King [13] (row DK). The great improvement made in the description of the low-r_{12} region is apparent. In addition, these results are in good agreement with those considered exact. An additional test of the quality of the density is given by means of the cusp condition, i.e., the value of the ratio $h'(0)/h(0)$, which should be equal to 1. For our density this ratio is 0.989.

With the adjusted intracule density we have calculated several functions related to it. First, in Fig. 1, we plot the Coulomb hole defined as $\Delta P(r_{12}) = P_c(r_{12}) - P_{\mathrm{HF}}(r_{12})$, where the subscripts *c* and HF mean correlated and Hartree-Fock, respectively. The Coulomb hole takes negative values from the origin up to a given value of r_{12}, then it shows two positive maxima, and, finally, it goes through zero and takes negative values. The first minimum and maximum account for the redistribution of the two electrons in the 1*s* shell while the second maximum and minimum correspond to a pair 1*s*-2*s*. Thus the effect of electronic correlations is to separate the 1*s* pair and to concentrate the relative charge at intermediate interelectronic distances.

We have also calculated the function $h(r_{12}) - h'(r_{12})$,

TABLE III. Monte Carlo (MC) and parametrized *(A)* values for $h(0)$, $\langle r_{12}^n \rangle$, $d(0)$, and $\langle R^n \rangle$ for the ground state of the lithium atom as compared with the corresponding Hartree-Fock (HF) values, and with other correlated values for the intracule density obtained directly from the wave function (HN [30] and Exact [15,14]) and from other parametrized single-particle density calculations (DK) [13]. The value of $d(0)$ in the MC row was obtained by carrying out the integrals numerically. In parentheses we give the statistical error of the MC calculation.

	$h(0)$	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12} \rangle$	$\langle r_{12}^{2} \rangle$	$\langle r_{12}^{3} \rangle$	$\langle r_{12}^{4} \rangle$
HF	0.7842886	5.03229	2.280921	8.689089	37.26414	195.8344	
MC		4.39(1)	2.1998(2)	8.669(1)	36.85(1)	192.2(1)	1156(1)
HN	0.54461		2.198208	8.668507	36.84889	192.10037	1156.022
Exact	0.544329	4.3812	2.1982120	8.6683968	36.847838		
A	0.5461	4.3901	2.1996	8.6693	36.863	192.27	1158.4
DK	0.6354	4.50	2.204	8.680	36.95	192.8	1161

	$d(0)$	$\langle R^{-2} \rangle$	$\langle R^{-1} \rangle$	$\langle R \rangle$	$\langle R^{2} \rangle$	$\langle R^{3} \rangle$	$\langle R^{4} \rangle$
HF	6.274309	20.129172	4.561842	4.344543	9.316035	24.479298	74.19288
MC	6.17243	20.21(3)	4.6013(3)	4.2996(6)	9.145(3)	23.86(1)	71.83(7)
A	6.146	20.223	4.6012	4.300	9.149	23.896	71.662

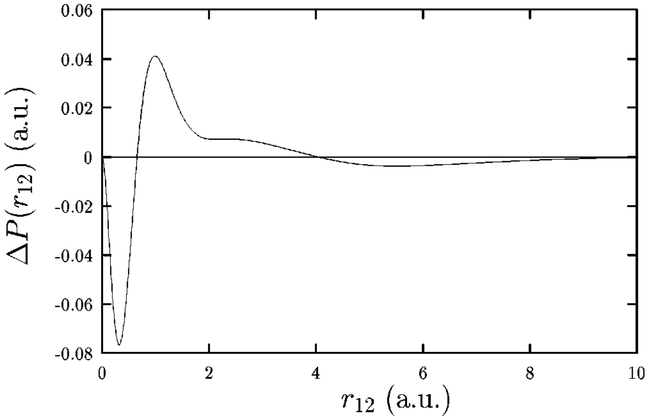

FIG. 1. Coulomb hole $\Delta P(r_{12})$ for the ground state of the lithium atom calculated with the parametrization of Eq. (17).

i.e., the difference between the intracule density and its first derivative. This function is the electron-electron cusp condition spatially extended, similar to the one studied for the single-particle density [31]. This function has been shown to be positive for two-electron systems [32]. With the wave function used in this work we have concluded that this property also holds for the ground state of the lithium atom, as can be seen in Fig. 2, where we compare the correlated function with the Hartree-Fock one. The property $h(r_{12})-h'(r_{12})\geqslant 0$ allowed many inequalities involving $h(0)$ and the radial moments $\langle r_{12}^n\rangle$ to be obtained for two-electron systems [33,34], which now are also available for the lithium atom. The main effect of electronic correlations is to diminish the strength of $h(r_{12})-h'(r_{12})$, which leads to sharper inequalities among $h(0)$ and $\langle r_{12}^n\rangle$ than in the Hartree-Fock framework.

C. Extracule density

The values of the extracule density at the origin, $d(0)$, and of the moments $\langle R^n\rangle$ have been obtained both within the Hartree-Fock framework [35,36] and by using [27] the generalized Jastrow wave functions of Schmidt and Moskowitz [37]. The correlated values of both $d(0)$ and the radial moments of negative order were bigger than the corresponding Hartree-Fock values while the moments of positive order were smaller. A study of the difference function

$$\Delta\Pi(R)=\Pi_c(R)-\Pi_{\rm HF}(R), \tag{18}$$

i.e., the equivalent to the Coulomb hole for this density, showed that this function is positive for small values of R and negative otherwise. That was interpreted by assuming that the electrons seek for a position in which they are on opposite sides of the atom when electronic correlations are considered. This was found to be consistent with the fact that, on average, electronic correlations make the lithium atom smaller and at the same time they reduce the moments of negative order of the interelectronic density. This can be seen by comparing the correlated and the Hartree-Fock values of the moments of both the radial charge distribution and the intracule density.

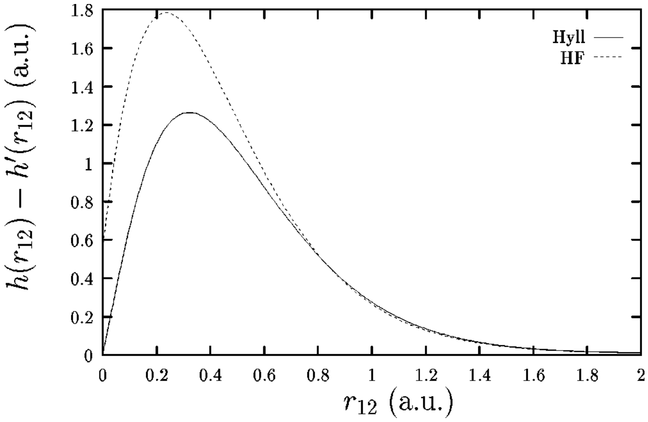

FIG. 2. Cusp condition spatially extended for the intracule density of the ground state of the lithium atom calculated with the parametrization of Eq. (17) as compared with the Hartree-Fock value.

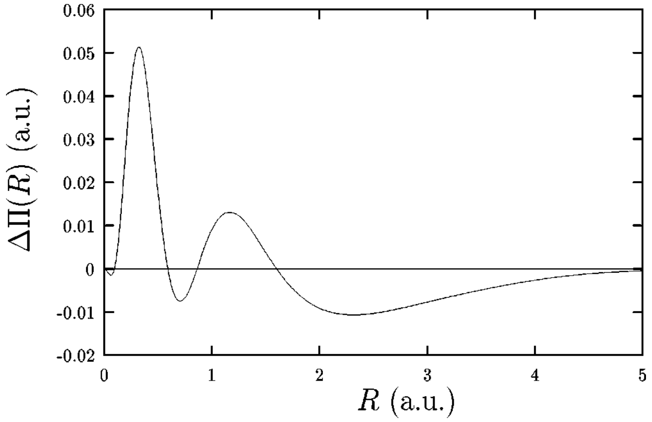

FIG. 3. Difference function $\Delta\Pi(R)$ for the ground state of the lithium atom calculated with the parametrization of Eq. (19).

This picture is confirmed when the more accurate Hylleraas-type wave function is used to calculate the extracule density and its radial moments. In Table III we compare the correlated values of $\langle R^n\rangle$ with the Hartree-Fock values. In Fig. 3 we plot the difference function $\Delta\Pi(R)$. This function presents almost the same behavior here as in [27]. The only difference is that for the Hylleraas wave function the value of $d(0)$, which is the probability of finding two electrons exactly at mirror positions with respect to the nucleus, is 6.172 43, and therefore smaller than the noncorrelated value. Also, there is a tiny region for small R values for which the correlated extracule density is smaller than the Hartree-Fock density (see Fig. 3). This behavior is similar to that found for the helium atom [27]. It is worth mentioning here a recent calculation of $d(0)$ for different atoms and ions using large CI wave functions [38]. In that work it was found that electronic correlations tend to diminish $d(0)$ with respect to the HF value; however, the numerical value reported there is different from the one obtained here.

To parametrize the extracule density we have taken into account that within the Hartree-Fock framework and for the atoms helium to beryllium the relation $d(R)=8h(2R)$ is fulfilled [36]. Although this relation does not necessarily hold in general, it allows one to select a particular form for the extracule density. The quality of this parametrization will be determined in terms of the results that are obtained with it. We have

$$\Pi_a(R)=\sum_{k=1}^{3} e^{-2\alpha_k R}\sum_{n=1}^{r_k} c_{k,n}R^n \tag{19}$$

with the condition $\Sigma_{n=1}^{3} c_{1,n}=0$. The numerical values of the parameters $c_{k,n}$ are given in Table II. The moments $\langle R^n\rangle$ calculated with the Monte Carlo method and those obtained by using the analytical parametrization given by Eq. (19) are reported in Table III, where they are compared with the corresponding Hartree-Fock moments. Both sets of correlated values agree within the statistical error of the MC calculation. Finally, let us mention that the moments $\langle R^n\rangle$ obtained from a generalized Jastrow-type wave function [27] are in good agreement with the values obtained here from the Hylleraas-type wave function.

D. Elastic and inelastic form factors

Both the elastic and the inelastic form factors can be computed directly by means of the MC method by calculating the mean value of the functions of Eq. (14). Due to the oscillating behavior of these functions, this method allows $F(q)$ and $S(q)$ to be obtained with a given precision up to a q_{max}, from where they take less precise values.

Both the elastic and the inelastic form factors can be obtained, once the single-particle and intracule densities are parametrized, by calculating their corresponding Fourier transforms. In this case the expressions for both form factors are

$$\begin{aligned}F_a(q)=&\frac{1}{q}\sum_{k=1}^{7}\sum_{n=1}^{g_k} a_{k,n}(n-1)!\left(\frac{\alpha_k}{q^2+\alpha_k^2}\right)^n\\&\times\sum_{0\leqslant 2j\leqslant n-1}(-1)^j\binom{n}{2j+1}\left(\frac{q}{\alpha_k}\right)^{2j+1}\\&+\frac{1}{q}\sum_{k=1}^{7} a_{k,0}\tan^{-1}\left(\frac{q}{\alpha_k}\right)\end{aligned}\tag{20}$$

and

$$\begin{aligned}S_a(q)=&\frac{2}{q}\sum_{k=1}^{3}\sum_{n=1}^{r_k} b_{k,n}(n-1)!\left(\frac{\alpha_k}{q^2+\alpha_k^2}\right)^n\\&\times\sum_{0\leqslant 2j\leqslant n-1}(-1)^j\binom{n}{2j+1}\left(\frac{q}{\alpha_k}\right)^{2j+1}\\&-|F_a(q)|^2+N.\end{aligned}\tag{21}$$

We have checked that these form factors calculated analytically agree perfectly with the ones obtained by using the MC method directly in that region of q where the MC method provides reliable results within the statistical error employed in this work.

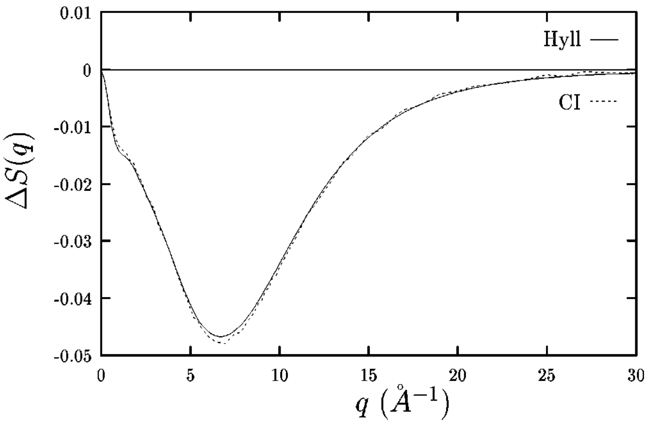

FIG. 4. Comparison between the difference function $\Delta S(q)$ obtained from the parametrized single-particle and intracule densities of this work and from the CI wave function of [23].

The elastic and inelastic form factors obtained from Eqs. (20) and (21) present an excellent agreement with the CI results of Meyer *et al.* [22,23]. In Fig. 4 we plot the difference function $\Delta S(q)=S_c(q)-S_{HF}(q)$ obtained from Eq. (21) as compared with the difference function obtained in [23]. It is apparent that the two curves are practically superimposed. However, the asymptotic behavior of the inelastic form factor is different in the two calculations because, as is known, a wave function such as a CI one that does not satisfy the electron-electron cusp condition can never satisfy the correct asymptotic behavior of the inelastic form factor [19]. The results reported here differ slightly from those of Alexander *et al.* [25] especially at small values of q. As discussed in that paper, this might be due to the fact that the generalized Jastrow wave function employed in that work is insufficiently flexible to describe properly the scattering cross section in that region of q. In fact, in previous work [26] it was found that the wave function used in [25] for the lithium atom provides single-particle and intracule densities that are overestimated for high values of the corresponding variable.

IV. CONCLUSIONS

The single-particle and both the intracule and extracule electron densities have been calculated for the ground state of the lithium atom starting from a highly accurate Hylleraas-type wave function that provides more than 99.99% of the correlation energy. The calculations have been performed by means of the Monte Carlo method. Simple analytical parametrizations have been obtained for those densities. With them the elastic and inelastic form factors have been calculated. The effects of electronic correlation on these quantities and on other functions such as the spatially extended cusp condition have been analyzed.

ACKNOWLEDGMENTS

This work has been partially supported by the Spanish Dirección General de Investigación Científica y Técnica (DGICYT) under Contract No. PB98-1318 and by the Junta de Andalucía. A.S. acknowledges financial support from the Spanish Ministerio de Educación y Cultura.

[1] F. W. King, J. Mol. Struct.: THEOCHEM **400**, 7 (1997).
[2] F. W. King, Adv. At., Mol., Opt. Phys. **40**, 57 (1999).
[3] C. A. Coulson and A. H. Neilson, Proc. Phys. Soc. London **78**, 831 (1961).
[4] A. J. Coleman, Int. J. Quantum Chem. **S1**, 457 (1967).
[5] R. Benesch and V. H. Smith, Jr., Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **26**, 579 (1970).
[6] R. Benesch, J. Phys. B **4**, 1403 (1971).
[7] A. J. Thakkar, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), p. 553.
[8] R. J. Boyd, C. Sarasola, and J. M. Ugalde, J. Phys. B **21**, 2555 (1988).
[9] R. O. Esquivel, A. V. Bunge, and M. A. Nún̄ez, Phys. Rev. A **43**, 3373 (1991).
[10] R. C. McWeeny, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum Press, New York, 1992), p. 47.
[11] F. W. King and P. R. Dressel, J. Chem. Phys. **90**, 6449 (1989).
[12] F. W. King, Phys. Rev. A **40**, 1735 (1989).
[13] P. R. Dressel and F. W. King, J. Chem. Phys. **100**, 7515 (1994).
[14] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **52**, 3711 (1995).
[15] F. W. King, J. Chem. Phys. **102**, 8053 (1995).
[16] J. Cioslowski, B. B. Stefanov, A. Tan, and C. J. Umrigar, J. Chem. Phys. **103**, 6093 (1995), and references therein.
[17] H. Meyer, T. Müller, and A. Schweig, J. Mol. Struct.: THEOCHEM **360**, 55 (1996).
[18] R. Benesch and V. H. Smith, Jr., J. Chem. Phys. **53**, 1466 (1970).
[19] A. J. Thakkar and V. H. Smith, Jr., J. Phys. B **11**, 3803 (1978).
[20] H. Schmider, R. O. Esquivel, R. P. Sagar, and V. H. Smith, Jr., J. Phys. B **26**, 2943 (1993).
[21] J. Wang, R. O. Esquivel, V. H. Smith, Jr., and C. F. Bunge, Phys. Rev. A **51**, 3812 (1995).
[22] H. Meyer, T. Müller, and A. Schweig, Acta Crystallogr., Sect. A: Found. Crystallogr. **51**, 171 (1995).
[23] H. Meyer, T. Müller, and A. Schweig, Chem. Phys. **191**, 213 (1995).
[24] S. A. Alexander, R. L. Coldwell, R. E. Hoffmeyer, and A. J. Thakkar, Int. J. Quantum Chem. **S29**, 627 (1995).
[25] S. A. Alexander, R. L. Coldwell, R. E. Hoffmeyer, and A. J. Thakkar, J. Mol. Struct.: THEOCHEM **388**, 7 (1996).
[26] A. Sarsa, F. J. Gálvez, and E. Buendía, J. Chem. Phys. **109**, 7075 (1998).
[27] F. J. Gálvez, E. Buendía, and A. Sarsa, J. Chem. Phys. **111**, 3319 (1999).
[28] I. Waller and R. D. Hartree, Proc. R. Soc. London, Ser. A **124**, 119 (1929).
[29] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in ab initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[30] F. W. King and V. Shoup, Phys. Rev. A **33**, 2940 (1986).
[31] F. J. Gálvez and I. Porras, Phys. Rev. A **44**, 144 (1991).
[32] J. S. Dehesa, J. C. Angulo, T. Koga, and K. Matsui, Z. Phys. D: At., Mol. Clusters **25**, 9 (1992).
[33] J. S. Dehesa, J. C. Angulo, T. Koga, and K. Matsui, Phys. Rev. A **47**, 5202 (1993).
[34] J. S. Dehesa, J. C. Angulo, T. Koga, and Y. Kasai, Phys. Rev. A **48**, 832 (1993).
[35] T. Koga and H. Matsuyama, J. Phys. B **30**, 5631 (1997).
[36] T. Koga and H. Matsuyama, J. Chem. Phys. **108**, 3424 (1998).
[37] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).
[38] J. M. Mercero, J. E. Fowler, C. Sarasola, and J. M. Ugalde, Phys. Rev. A **59**, 4255 (1999).