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Wave functions for two- and three-electron atoms and isoelectronic ions

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Abstract. We have developed simple wave functions for two- and three-electron atoms and ions, which have the correct structure when one of the electrons is far away, or when two of the particles are close to each other. These essentially parameter-free wave functions allow us to deduce fairly accurate values for the energies, $\langle r^{2n}\rangle$, for multipolar polarizabilities of two-electron atoms and ions, and for the coefficients of the asymptotic density.

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1 Introduction

Development of simple, analytic wave functions is an important but difficult problem in atomic physics. Generally one uses a basis of convenient, orthonormal state vectors with variational coefficients. The variational approach has achieved a very high level of accuracy in the calculation of He energy levels, and also of Li, in some cases better than 1 part in 10^{15}. The calculations for He were based on the use of logarithmic terms [1–3] in the basis, or doubled basis sets [4]. One also has very accurate values for some excited states [5] and for Li ground state [6]. More recently, it has been emphasized [7–11] that wave functions which incorporate some properties of the exact wave functions provide accurate and useful representations of the energy eigenstates of two-electron systems. These considerations need to be extended to systems with more than two electrons. It may also be mentioned that the general analytical structure of the wave functions is an important guideline in the choice of the basis functions for the variational calculations. A basis chosen with the correct analytic structure of the wave functions has been shown [12] to be very efficient in giving variational energies of a very high level of accuracy.

Here we discuss some useful, local properties of wave functions and develop simple but fairly accurate wave functions for two-electron atoms and ions. We then extend these ideas to develop accurate wave functions for the ground state of three-electron atoms and ions. These wave functions allow us to deduce some important properties of the systems, such as asymptotic densities, expectation values of $\langle r^2\rangle$, multipolar polarizabilities, etc. We will use atomic units unless stated otherwise.

2 Some local properties

Here we briefly discuss some local properties of eigenfunctions of energy. These properties will help us in developing reliable wave functions for the eigenstates.

2.1 Asymptotic wave functions

The Hamiltonian for N-electron atoms and ions is

$$H^{(N)} = \sum_{i=1}^{N} \frac{1}{2}p_i^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i>j}^{N} \frac{1}{r_{ij}}\,, \tag{2.1}$$

where $r_{ij} = \mid \mathbf{r}_i - \mathbf{r}_j \mid$. The energy eigenfunction

$$H^N\,\psi(\mathbf{r}_i) = E\,\psi(\mathbf{r}_i) \tag{2.2}$$

then has the asymptotic behaviour [13,14]

$$\begin{aligned} \psi(\mathbf{r}_i) &\overset{r_1\to\infty}{\longrightarrow} \psi_0^{(N-1)}(\mathbf{r}_2,...,\mathbf{r}_N)\, f_0(\mathbf{r}_1)\,, \qquad (2.3)\\ f_0(\mathbf{r}_1) &= e^{-ar_1}\, r_1^u \left[1 + \frac{(\ell-u)(\ell+u+1)}{2ar_1} + \ldots\right] \\ &\quad \times Y_\ell^m(\theta_1,\phi_1)\,, \\ a &= [\,2(E_0^{(N-1)} - E)\,]^{1/2}\,, \\ u &= \frac{Q_{N-1}}{a} - 1\,, \end{aligned}$$

where $\psi_0^{(N-1)}(\mathbf{r}_2,...,\mathbf{r}_N)$ is the ground-state wave function of the $(N-1)$-electron system with energy $E_0^{(N-1)}$, Q_{N-1} is the charge seen by the electron 1 when it is far away, and ℓ is the angular-momentum quantum number of electron 1 when it is far away. It is important to note that the asymptotic behaviour depends only on the separation energy $E_0^{(N-1)} - E$ of the last electron and the charge Q_{N-1} of the core seen by this electron when it is far away.

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2.2 Wave functions for $r_1 \to 0$

When electron 1 is close to the nucleus, the Schroedinger equation can be written in the form

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right)\psi^{(N)} = O\,(1)\,, \tag{2.4}$$

where the terms on the right-hand-side are finite order terms for $r_1 \to 0$. Keeping other variables fixed, we expand $\psi^{(N)}$ in terms of spherical harmonics,

$$\psi^{(N)} = \sum_{\ell,m} G_{\ell m}(r_1) Y_\ell^m(\theta_1, \phi_1) \tag{2.5}$$

and project out the ℓ, m state to get

$$\frac{\mathrm{d}^2}{\mathrm{d}r_1^2}\left[\,r_1 G_{\ell m}(r_1)\,\right] - \frac{\ell(\ell+1)}{r_1} G_{\ell m}(r_1) + 2Z\, G_{\ell m}(r_1) \longrightarrow O\,(r_1^{\ell+1}) \text{ for } r_1 \to 0. \tag{2.6}$$

Substituting

$$G_{\ell m}(r_1) = r_1^\ell\,(\,a_0 + a_1 r_1 + ...) \tag{2.7}$$

into equation (2.6), one obtains

$$a_1 = -\frac{Z}{\ell+1}\,a_0. \tag{2.8}$$

One usually applies this condition to the dominant s-wave terms for which

$$a_1(\ell = 0) = -Z a_0(\ell = 0)\,. \tag{2.9}$$

2.3 Wave function for $r_{12} \to 0$

When electrons 1 and 2 are close to each other, we go to the centre-of-mass frame of electrons 1 and 2 whose reduced mass is 1/2, so that

$$\left(-\nabla_{12}^2 + \frac{1}{r_{12}}\right)\psi^{(N)} = O(1)\,. \tag{2.10}$$

We again expand in terms of spherical harmonics,

$$\psi^{(N)} = \sum_{\ell,m} G_{\ell m}(r_{12})\, Y_\ell^m(\theta_{12}, \phi_{12}) \tag{2.11}$$

and project out the ℓ, m state to get

$$\frac{\mathrm{d}^2}{\mathrm{d}r_{12}^2}\left[\,r_{12} G_{\ell m}(r_{12})\,\right] - \frac{\ell(\ell+1)}{r_{12}} G_{\ell m}(r_{12}) - G_{\ell m}(r_{12}) \longrightarrow O\,(r_{12}^{\ell+1}) \text{ for } r_{12} \to 0. \tag{2.12}$$

Substituting

$$G_{\ell m}(r_{12}) = r_{12}^\ell\,(\,b_0 + b_1 r_{12} + ...) \tag{2.13}$$

into equation (2.12) one obtains

$$b_1 = \frac{1}{2(\ell+1)} b_0\,. \tag{2.14}$$

When the two electrons are in the singlet state they are in relative ℓ even states and when they are in the triplet state, they are in relative ℓ odd states. Therefore the leading contribution for $r_{12} \to 0$ is from the $\ell = 0$ term for the singlet states, and from the $\ell = 1$ term for the triplet states, so that one has for $r_{12} \to 0$,

$$\begin{aligned}\psi^{(N)} &\longrightarrow b_0\left(1 + \frac{1}{2} r_{12}\right) \quad \text{for singlet} \\ &\longrightarrow b_0\, r_{12}\left(1 + \frac{1}{4} r_{12}\right) \quad \text{for triplet}\,.\end{aligned} \tag{2.15}$$

These are described as cusp conditions.

3 Two-electron wave functions

For a two-electron atom or ion with nuclear charge Z, the Schroedinger equation is

$$\begin{aligned}&H\,\psi = E\,\psi\,,\\ &H = \frac{1}{2}(\,p_1^2 + p_2^2\,) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}\,.\end{aligned} \tag{3.1}$$

We develop model wave functions for different states which incorporate the local properties we have discussed.

3.1 Ground-state wave function

We propose a wave function of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = A\,[\,e^{-Zr_1}\,e^{-ar_2}\,g(r_2) + e^{-Zr_2}\,e^{-ar_1}\,g(r_1)\,]\,f(r_{12})\,, \tag{3.2}$$

where A is the normalization constant. We take

$$a = [\,2(-Z^2/2 - E)\,]^{1/2}\,, \tag{3.3}$$

with E being the total energy of the system, to ensure the correct asymptotic, exponential behaviour in equation (2.3). The energy E is determined iteratively by calculating the average value of H,

$$E\ =\ \frac{\langle\psi\mid H\mid\psi\rangle}{\langle\psi\mid\psi\rangle}\,. \tag{3.4}$$

The factor $g(r_i)$ is introduced to incorporate the required threshold behaviour in equation (2.9) and in the intermediate $-r$ region. It may be noted that for He and positive ions Li$^+$, etc., the exponent a is large, and the power u of r_1 in equation (2.3) is small and may be left out. For H$^-$, a is quite small and u is -1. Therefore we consider different $g(r_i)$ for the two cases.

3.2 Behaviour for $r_i \to 0$

For He and the positive ions, we take

$$g(r_i) \;=\; 1 \,+\, c\,e^{-Z' r_i}, \quad Z' = Z - 5/16. \tag{3.5}$$

The choice of Z' in the exponent ensures that when the electron is outside the remaining core, which in the variational description implies $r_i > 1/Z'$, the function

$$\begin{aligned}\tilde{g}(r_i) &= e^{-a r_i} g(r_i) \\ &= e^{-a r_i}\left(1 + c e^{-Z' r_i}\right)\end{aligned} \tag{3.6}$$

is dominated by the leading asymptotic exponential term $e^{-a r_i}$. The constant c is determined by the coalescence condition in equation (2.9) which implies

$$\frac{(1+c)a + cZ'}{1+c} \;=\; Z\,, \tag{3.7}$$

or

$$c = \frac{(Z-a)}{Z' + a - Z}\,. \tag{3.8}$$

For the negative ion H^-, we take

$$g(r_i) \;=\; (1 - e^{-b r_i})/r_i\,, \tag{3.9}$$

which has the required asymptotic power r_i^{-1} in equation (2.3). For ensuring the correct behaviour in equation (2.9) for $r_i \to 0$, we require

$$e^{-a r_i}(1 - e^{-b r_i})/r_i \to b(1 - Z r_i) \quad \text{for} \quad r_i \to 0\,, \tag{3.10}$$

which leads to the relation

$$b \;=\; 2\,(Z - a)\,, \quad Z = 1\,. \tag{3.11}$$

This determines $g(r_i)$ in equation (3.9) for negative ions.

3.3 Behaviour for $r_{12} \to 0$

It has been found [15] that

$$f(r_{12}) = 1 - \frac{1}{1+2\lambda} e^{-\lambda r_{12}} \tag{3.12}$$

provides a good description of the correlation between the two electrons. It incorporates the cusp condition in equation (2.15):

$$f(r_{12}) = \frac{2\lambda}{1+2\lambda}\left(1 + \frac{1}{2} r_{12}\right) \quad \text{for} \quad r_{12} \to 0. \tag{3.13}$$

Furthermore, the parameter λ was estimated [15] from a perturbative approach to be well represented by

$$\lambda = \frac{5Z}{12} - \frac{1}{3}\,. \tag{3.14}$$

3.4 Results for the ground state

We now have the wave function in equation (3.2) for the ground state. The function $g(r_i)$ is given in equation (3.5) for He and positive ions, with the parameter c given in equation (3.8), and in equation (3.9) for H^- with the parameter b determined by equation (3.11), and the correlation function $f(r_{12})$ is given by equation (3.12) along with λ as quoted in equation (3.14). The parameter a which depends on E, and the energy E taken to be the average energy,

$$E\langle\psi \mid \psi\rangle = \langle\psi \mid -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \mid \psi\rangle\,, \tag{3.15}$$

are determined iteratively. There are no free parameters in the wave functions.

The wave function in equation (3.2) for He and positive ions with $g(r_i)$ given in equation (3.5) is of the form

$$\psi = \sum A_i\, e^{(-u_i r_1 - v_i r_2 - w_i r_{12})}\,, \tag{3.16}$$

so that

$$\begin{aligned}\langle\psi \mid \psi\rangle &= \sum_{i,j} A_i A_j \\ &\times \int \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2\, e^{[-(u_i+u_j) r_1 - (v_i+v_j) r_2 - (w_i+w_j) r_{12}]}\,.\end{aligned} \tag{3.17}$$

The expectation value of H is given by

$$\begin{aligned}\langle\psi \mid H \mid \psi\rangle &= \sum_{i,j} A_i A_j \\ &\times \int \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2\, e^{[-(u_i+u_j) r_1 - (v_i+v_j) r_2 - (w_i+w_j) r_{12}]} \\ &\times \left[-u_i^2 - w_i^2 + \frac{2(u_i - Z)}{r_1} + \frac{(2w_i + 1)}{r_{12}} \right. \\ &\left. - u_i w_i \frac{(r_1^2 - r_2^2 + r_{12}^2)}{r_1 r_{12}}\right]\,.\end{aligned} \tag{3.18}$$

These expressions involve integrals of the type

$$\begin{aligned}&I_{n_1,n_2,n_3}(u,v,w) = \\ &\int \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2\, r_1^{n_1}\, r_2^{n_2}\, r_3^{n_3}\, e^{(-u r_1 - v r_2 - w r_3)} = \\ &(-\mathrm{d}/\mathrm{d}u)^{n_1+1}(-\mathrm{d}/\mathrm{d}v)^{n_2+1}(-\mathrm{d}/\mathrm{d}w)^{n_3+1} \\ &\times \frac{16\pi^2}{(u+v)(v+w)(w+u)}\,.\end{aligned} \tag{3.19}$$

This allows us to obtain the energies in a closed analytic form. The energy expressions for the negative ion H^- wave function in equation (3.2) with $g(r_i)$ given in equation (3.9) are reduced to a similar form by using the identity

$$\frac{e^{-ar} - e^{-br}}{r} = \int_a^b e^{-ar}\,\mathrm{d}a\,. \tag{3.20}$$

Table 1. Parameter c, normalization constant A for the wave function in equation (3.2), $-E^{\rm tot}$, ratio $-2T/V$ of expectation values of twice the kinetic energy and potential energy, expectation values of r^2, r^4 for the ground state of two-electron atoms and ions, and the essentially exact variational energies from reference [16].

	c	A	$-E^{\rm tot}$	$-E^{\rm tot}$(exact)	$-2T/V$	$\langle r^2\rangle$	$\langle r^4\rangle$
H^-	-	0.1992	0.52533	0.52775	1.011	25.33	1846
He	0.6376	0.8489	2.90175	2.90372	0.992	2.388	7.912
Li^+	0.3148	3.1383	7.27677	7.27991	0.992	0.889	1.028
Be^{2+}	0.2092	8.590	13.6517	13.65557	0.992	0.462	0.273
B^{3+}	0.1567	17.43	22.0266	22.03097	0.994	0.283	0.102
C^{4+}	0.1253	30.85	32.4015	32.40625	0.994	0.191	0.0460
N^{5+}	0.1043	49.81	44.7764	44.78146	0.996	0.137	0.0238
O^{6+}	0.0891	75.27	59.1514	59.15660	0.996	0.104	0.0135
F^{7+}	0.0782	108.2	75.5264	75.53171	0.996	8.10×10^{-2}	8.24×10^{-3}
Ne^{8+}	0.0695	149.5	93.9013	93.90681	0.996	6.50×10^{-2}	5.50×10^{-3}

The energies are again available in a closed analytic form.

The wave functions also allow us to calculate the expectation values $\langle r^2\rangle$, $\langle r^4\rangle$, etc. The expectation value $\langle r^2\rangle$ is related to the diamagnetic susceptibility χ,

$$\chi = -\frac{1}{6}\langle r^2\rangle \,. \tag{3.21}$$

The results are given in Table 1. They are in fairly good agreement with the results of elaborate calculations. For example, with our zero-parameter wave function, we get $E = -2.90175, -7.2768, -13.6517$ for the total energies of He, Li^+, Be^{2+}, which may be compared with the essentially exact values of -2.90372, -7.2799, -13.6556, respectively, obtained from variational calculations [16]. For H^-, we get $E = -0.5253$ from the parameter-free wave function, to be compared with the value of -0.5276 from the variational calculations [16]. The expectation values for $\langle r^n\rangle$ are also quite good. Our values of $\langle r^2\rangle$ for He and Li^+ are 2.39 and 0.889, and the value of $\langle r^4\rangle$ for He is 7.91, to be compared with the corresponding values of 2.39, 0.892, and 7.93, respectively from the accurate variational wave functions [16]. Since our wave functions incorporate the correct asymptotic behaviour, the results for higher values of n are particularly reliable. Apart from the accuracy of the predicted energies, one can judge the quality of the model wave function in terms of the virial theorem. For the exact wave functions the virial theorem requires that the ratio $-2\langle T\rangle/\langle V\rangle$ should be 1. As can be observed from the results in Table 1, our values for this ratio are quite close to 1.

3.5 Wave functions for excited states

We can also write simple, useful expressions for lowest energy wave functions with $L = 1, 2, ...$ incorporating the threshold and cusp conditions in equations (2.9, 2.14), and the asymptotic behaviour. The suggested wave functions are

$$\begin{aligned}\psi(\mathbf{r}_1,\mathbf{r}_2) = A\,[\,&e^{-Zr_1}\, e^{-ar_2}\, r_2^{\ell}\, P_\ell(\cos\theta_2)\\ &\pm e^{-Zr_2}\, e^{-ar_1}\, r_1^{\ell}\, P_\ell(\cos\theta_1)\,]\, f_\pm(r_{12})\,,\end{aligned} \tag{3.22}$$

Table 2. Variational values of parameter λ, normalization constant A, energies predicted, and experimental energies for some excited states of He and Li^+.

	state	λ	A	$-E^{\rm tot}$	$-E^{\rm expt}$
He	$2\,^1P$	0.80	0.1130	2.12336	2.12390
	$2\,^3P$	0.90	0.1197	2.13042	2.13324
	$3\,^1D$	0.50	2.855×10^{-3}	2.05560	2.05566
	$3\,^3D$	0.40	2.895×10^{-3}	2.05562	2.05568
Li^+	$2\,^1P$	1.35	1.1669	4.9922	4.9935
	$2\,^3P$	1.50	1.2444	5.0220	5.0279

where the + is for singlet states and − is for triplet states. For the correlation functions we take

$$\begin{aligned} f_+(r_{12}) &= 1 - \frac{1}{1+2\lambda_+} e^{-\lambda_+ r_{12}} \quad \text{singlet states}\,,\\ f_-(r_{12}) &= 1 - \frac{1}{1+4\lambda_-} e^{-\lambda_- r_{12}} \quad \text{triplet states}\,, \end{aligned} \tag{3.23}$$

which satisfy equation (2.14) for $\ell = 0, 1$ respectively, for $r_{12} \to 0$. The constant a in equation (3.22) is determined from the asymptotic condition in equation (2.3),

$$a = [\,2(-Z^2/2 - E)\,]^{1/2}\,, \tag{3.24}$$

where E is determined iteratively to give

$$E = \frac{\langle \psi \mid H \mid \psi\rangle}{\langle \psi \mid \psi\rangle}\,, \tag{3.25}$$

with the Hamiltonian in equation (3.1). The remaining parameter $\lambda_\pm$ are determined variationally. These 1-parameter results are given in Table 2, and are in good agreement with the experimental values of the energies. For example, our predicted values for the energy of the singlet $2\,^1P$ state of He is -2.1234 which is to be compared with the experimental value of -2.1239.

Table 3. Values of D_1, D_2 for the perturbed wave function in equation (3.30) and the calculated values of the polarizabilities α_ℓ and hyperpolarizabilities B for H^-, He, Li^+, Be^{++} along with the results from other calculations.

	H^-	He	Li^+	Be^{++}
$D_1(\ell=1)$	2.128	0.3302	0.1972	0.1411
$D_2(\ell=1)$	0.37	0.979	0.407	0.220
$D_1(\ell=2)$	1.419	0.2287	0.1346	0.0957
$D_2(\ell=2)$	-0.03	0.544	0.239	0.138
$D_1(\ell=3)$	1.064	0.1750	0.1022	0.0724
$D_2(\ell=3)$	-0.07	0.336	0.165	0.0970
α_1	220	1.370	0.191	0.0517
α_1 (other)	$(211\text{-}215)_a$	$(1.383)_b$	$(0.192)_c$	$(0.051)_d$
α_2	1.08×10^4	2.407	0.109	0.0146
α_2 (other)	–	$(2.443)_b$	$(0.111)_d$	$(0.0149)_d$
α_3	1.38×10^6	10.60	0.154	0.0104
$-B$	7.54×10^5	7.75	0.114	7.52×10^{-3}
$-B$ (other)	–	$(7.333)_e$	$(0.121)_e$	$(8.39 \times 10^{-3})_e$

a: Reference [19], *b*: reference [17], *c*: reference [18], *d*: reference [8], *e*: reference [20].

3.6 Multipolar polarizabilities and hyperpolarizabilities

Our wave functions can also be used to calculate multipolar polarizabilities and hyperpolarizabilities. In the presence of a perturbative multipolar potential, the perturbation to the wave function, $\delta\psi_\ell$, satisfies the inhomogeneous equation

$$(H - E)\,\delta\psi_\ell = [\,r_1^\ell\,P_\ell(\cos\theta_1) + r_2^\ell\,P_\ell(\cos\theta_2)\,]\,\psi\,, \tag{3.26}$$

where H is the unperturbed Hamiltonian given in equation (3.1), and ψ is the unperturbed wave function given in equation (3.2). The multipolar polarizability α_ℓ is given by

$$\alpha_\ell = 2\,\langle\psi\mid[\,r_1^\ell\,P_\ell(\cos\theta_1) + r_2^\ell\,P_\ell(\cos\theta_2)\,]\mid\delta\psi_\ell\rangle. \tag{3.27}$$

For obtaining a good representation for $\delta\psi_\ell$, we observe that equation (3.26) implies the asymptotic behaviour,

$$\delta\psi_\ell \overset{r_1\to\infty}{\longrightarrow} D_1\,r_1^{\ell+1-\ell_0}\,P_\ell(\cos\theta_1)\,A\,e^{-ar_1-Zr_2}, \tag{3.28}$$

$$D_1 = \frac{1}{a(\ell+2-\ell_0-Q_1/a)}\,,\quad Q_1 = Z-1\,, \tag{3.29}$$

where A is the normalization constant of the unperturbed wave function in equation (3.2), and ℓ_0 is equal to 0 for He and positive ions, and is equal to 1 for H^-. We therefore take

$$\delta\psi_\ell = [\,(D_1 r_1 + D_2)\,r_1^{\ell-\ell_0} P_\ell(\cos\theta_1)\,A\,e^{-ar_1-Zr_2} \\ +(D_1 r_2 + D_2)\,r_2^{\ell-\ell_0}\,P_\ell(\cos\theta_2)\,A\,e^{-ar_2-Zr_1}]\,f(r_{12})\,, \tag{3.30}$$

with $f(r_{12})$ being the correlation function given in equation (3.12). The constant D_2 is determined by requiring that this function satisfies the equation

$$\langle\delta\psi_\ell\mid(H - E)\mid\delta\psi_\ell\rangle = \\ \langle\delta\psi_\ell\mid[\,r_1^\ell\,P_\ell(\cos\theta_1) + r_2^\ell\,P_\ell(\cos\theta_2)\,]\mid\psi\rangle \tag{3.31}$$

obtained by taking the scalar product of the relation in equation (3.26) with $\delta\psi_\ell$. The values of the parameter D_1, D_2, and the values of the polarizabilities are given in Table 3. The polarizabilities are generally in good agreement with the results of other calculations [8,17,18]. Since the polarizabilities of H^- are very sensitive to the input separation energy of the last electron, we have taken the experimental value of 0.0276 as the input separation energy for H^-. For this input energy the normalisation constant A is 0.2125 and the predicted value of the dipolar polarizability of H^- is 220 which may be compared with the value of 211-215 from earlier calculations [19].

The wave functions $\delta\psi_\ell$ in equation (3.30) can be used for calculating hyperpolarizability B defined as

$$B = -2T_{121} - 4T_{112}\,, \tag{3.32}$$

where

$$T_{121} = \langle\delta\psi_1\mid[\,r_1^2\,P_2(\cos\theta_1) + r_2^2\,P_2(\cos\theta_2)\,]\mid\delta\psi_1\rangle \tag{3.33}$$

$$T_{112} = \langle\delta\psi_1\mid[\,r_1\,P_1(\cos\theta_1) + r_2\,P_1(\cos\theta_2)\,]\mid\delta\psi_2\rangle\,. \tag{3.34}$$

The predicted values of B are given in Table 3. The value of 7.696 for He is close to the value of 7.327 from other calculations [20]. Since our wave functions have the correct asymptotic behaviour, we expect that our predicted values are quite reliable.

4 Three-electron wave functions

The general approach based on the local properties of energy eigenfunctions can be extended to develop wave functions of atoms and ions with three electrons.

We consider a wave function

$$\psi(1,2,3) = G\,[\,\phi(1,2)\eta(3) \\ +\phi(2,3)\eta(1) + \phi(3,1)\eta(2)\,]\,F(1,2,3)\,. \tag{4.1}$$

Here, $\phi(i,j)$ are the two-electron wave functions we developed earlier (correlation part is in F),

$$\phi(i,j)=\sum_{k=1}^{2} c_k[\,e^{-Zr_i}e^{-a_k r_j}+e^{-Zr_j}e^{-a_k r_i}\,] \\ \times[\,\alpha(i)\beta(j)\;-\;\beta(i)\alpha(j)\,]/2^{1/2}\,, \tag{4.2}$$

where

$$a_1\;=\;[2(-Z^2/2-E_2)]^{1/2}\,, \tag{4.3}$$

E_2 being the ground-state energy of the two-electron ion,

$$c_1\;=\;1\,, \tag{4.4}$$

$$a_2=a_1+Z',\quad Z'=Z-5/16\,, \tag{4.5}$$

$$c_2=\frac{(Z-a_1)}{Z'+a_1-Z}\,, \tag{4.6}$$

as required by the threshold behaviour in equation (3.8), and α and β are the spin-up and spin-down state vectors of the electrons. The function η is taken to be

$$\eta(i)=r_i^2\left(r_i+\frac{d}{u-2}\right)^{u-2}e^{-ar_i}\alpha(i)\,. \tag{4.7}$$

Imposing the asymptotic behaviour in equation (2.3), we get

$$\begin{aligned} a&=[\,2(E_2-E)\,]^{1/2}\,,\\ u&=\frac{Z-2}{a}-1\,,\\ d&=-\frac{u(u+1)}{2a}\,. \end{aligned} \tag{4.8}$$

Finally, the correlation function F is taken to be

$$\begin{aligned} F(1,2,3)&=f(1,2)\,f(2,3)\,f(3,1)\,,\\ f(i,j)&=1-\frac{1}{1+2\lambda}e^{-\lambda r_{ij}}\,,\\ \lambda&=\frac{5Z}{12}-\frac{1}{3}\,, \end{aligned} \tag{4.9}$$

where $f(i,j)$ is the two-electron correlation function in equation (3.12) with λ given in equation (3.14). It must be emphasized that there are no free parameters in the wave function, but the wave function satisfies the correct exchange properties, the correct asymptotic properties for $r_i\to\infty$ and the correct threshold properties for $r_i\to 0$ or $r_{ij}\to 0$.

It is straightforward to calculate the expectation value of the energy

$$E\;=\;\frac{\langle\psi\mid T+V\mid\psi\rangle}{\langle\psi\mid\psi\rangle}\,. \tag{4.10}$$

Table 4. Input values of $-E_2, a_i, c_i$ of two-electron wave functions in equation (4.2), input values of the ionisation energy which is nearly equal to the output values of the ionisation energy, normalization constant G, average value of r^2, and the coefficient Nc_0^2 of the asymptotic radial density in equation (4.12), for Li, Be$^+$, B^{++}, along with the accurate variational values $-E_{\rm var}^{\rm tot}$ from a: reference [6], b: reference [21].

	Li	Be$^+$	B^{++}
$-E_2$	7.277	13.652	22.0273
a_1	2.357	3.3622	4.3652
a_2	4.619	6.3123	8.0056
c_1	1	1	1
c_2	0.3974	0.2758	0.2112
$E_{\rm in}^{\rm ion}(eV)$	5.3912	18.21	37.93
$E_{\rm out}^{\rm ion}(eV)$	5.334	18.16	37.86
$-E_{\rm out}^{\rm tot}$	7.4732	14.320	23.4193
$-E_{\rm var}^{\rm tot}$	$(7.47806)_a$	$(14.3247)_b$	$(23.4245)_b$
G	0.4303	3.828	17.86
$\langle r^2\rangle$	17.35	6.45	3.32
Nc_0^2	0.660	8.04	42.0

The evaluation of the kinetic energy is simplified by using the identity [9]

$$\int(\phi\,f)\,\nabla^2\,(\phi\,f){\rm d}\tau=\int[f^2\,\phi\,\nabla^2\,\phi-\phi^2\,(\nabla f)\cdot(\nabla f)]\,{\rm d}\tau \tag{4.11}$$

which follows from simplifying the left-hand side and integrating by parts.

The integrations are carried out numerically. The calculated values of the parameters and the predicted values of the energy for Li, Be$^+$, B^{++} are given in Table 4. The energies are generally in good agreement with the accurate variational calculations [6,21]. For Li, the predicted values are -7.473 ± 0.0015 a.u. for the total energy, 5.33 ± 0.04 eV for the ionisation energy with the uncertainties being due to estimates of errors in numerical integrations, and the corresponding variational values [6] are -7.4781 a.u. and 5.39 eV, respectively. The predictions for Be$^+$ and B^{++} are of similar quality. Other quantities of importance are the normalization constant G, and the coefficient Nc_0^2 of the asymptotic radial density

$$\rho_r(r)\overset{r\to\infty}{\longrightarrow}\;Nc_0^2\,r^{2(u+1)}\,e^{-2ar}\,. \tag{4.12}$$

We have also given the calculated values of $\langle r^2\rangle$ which are related to the diamagnetic susceptibility χ as in equation (3.21). Our value of 17.4 for $\langle r^2\rangle$ of Li is fairly close to the corresponding value of 18.355 from the accurate variational wave functions [6]. Since our wave functions have the correct asymptotic behaviour, we expect the predicted values of the coefficient Nc_0^2 of the asymptotic radial density, and of $\langle r^2\rangle$ to be fairly reliable.

5 Conclusions

Wave functions of the atoms and ions have simple structures when one of the electrons is far away, or when it is close to the nucleus, or when two electrons are close to each other. These properties provide important guidelines in the construction of simple, analytic wave functions of atoms and ions. We have constructed relatively simple wave functions satisfying these properties for two-electron atoms and ions. These wave functions without any free parameters give fairly accurate values for the energies and for the average values $\langle r^{2n} \rangle$. We have also presented a simple method based on asymptotic behaviour of perturbed wave functions, for obtaining accurate values for the multipolar polarizabilities and hyperpolarizabilities. The two-electron wave functions are then used to construct three-electron wave functions, incorporating the asymptotic and threshold conditions. These three-electron wave functions provide fairly accurate values for the energies, the average values $\langle r^{2n} \rangle$, and for the coefficients of asymptotic densities. The simplicity of the wave functions and the accuracy of their predictions demonstrate the importance of the asymptotic and threshold behaviours in the development of the wave functions.

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