Vol 17 No 11, November 2008
1674-1056/2008/17(11)/4175-05

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Wavefunction and energy of the $1s^2 2snl$ configuration in a beryllium atom*

Huang Shi-Zhong(黄时中)†, Ma Kun(马 堃), Yu Jia-Ming(于加明), and Liu Fen(刘 芬)

College of Physics and Electrical Information, Anhui Normal University, Wuhu 241000, *China*

(Received 16 April 2008; revised manuscript received 2 June 2008)

A new set of trial functions for $1s^2 2snl$ configurations in a beryllium atom is suggested. A Mathematica program based on the variational method is developed to calculate the wavefunctions and energies of $1s^2 2sns$ ($n = 3 - 6$) configurations in a beryllium atom. Non-relativistic energy, polarization correction and relativistic correction which include mass correction, one- and two-body Darwin corrections, spin-spin contact interaction and orbit-orbit interaction, are calculated respectively. The results are in good agreement with experimental data.

Keywords: beryllium atom, wavefunction, energy
PACC: 3130J, 0420F, 3120T

1. Introduction

Much work[1−9] has been done to investigate the energy structures in excited states of a beryllium-like atom, a complex four-electron atomic system. In 1993 and 1994, the energies and fine structures of $1s^2 2snl$ (nl = 2p, 3s, 3p, 3d) excited states in a beryllium atom were calculated with a full-core plus correlation method by Zhu and Chung,[1,2] and in 1994 and 1999, systematic multiconfiguration Hartree–Fock results for the $2s^2\ {}^1S_0 \rightarrow 2s2p^3P_1$ intercombination line of C III in the Breit–Pauli approximation, and Breit–Pauli results for energy levels, lifetimes, and some transition data for all levels of $2s^2$, 2s2p, $2p^2$, 2s3s, 2s3p and 2s3d configurations of the Be-like spectrum were reported , separately, by Fischer,[3] and Tachiev and Fisher.[4] In 2000, the energy levels and oscillator strengths for transitions between the levels of the $1s^2 2s^2$, $1s^2 2s2p$ and $1s^2 2p^2$ states of a Be-like atom were calculated with the configuration interaction method by Kingston and Hibbert.[5] In 2004 and 2005, the Rayleigh–Ritz variational calculation with a multiconfiguration-interaction wavefunction was used to obtain the energies of excited state $1s^2 2s2p^3P$ in a beryllium-like O^{4+} and $1s^2 2s^2$, $1s^2 2p^2$ configurations of the Be-like C III by Han and Zhang,[6] and Han and Lu.[7] The same method was utilized to obtain the relativistic energies and fine structures of the high-lying core-excited states ${}^5P(n)(n = 1 - 7)$ and ${}^5S^o(m)(m = 1 - 5)$ for a Be-like boron and carbon by Gou and Wang[8] in 2004. And the low-lying state $1s^2 2p^2 {}^3P$ for beryllium isoelectronic sequence ($Z = 4 - 10$) was investigated by Gu *et al*[9] in 2006.

In all the work above, the calculated energies are in good agreement with experimental data. The wavefunction, however, is another story, and almost no correct wavefunction has been reported explicitly. For a many-electron atomic system, it is desirable to construct wavefunctions such that they are simple in calculation and can present energies comparable with the experimental data. Recently, such new wavefunctions have been constructed for the $1sns$ ($n = 2 - 5$) configurations of a helium atom,[10] where the key point is to substitute modified hydrogen-like radial wavefunctions for Slater-type radial wavefunction, and the former is constructed by adding variational parameters each to corresponding terms of the general Laguerre polynomial in a hydrogen-like radial wavefunction. The advantage is that the new wavefunction contains only a few parameters but can present reasonable calculated energies. In this paper, we extend this method to a four-electron atomic system. A new set of trial functions for $1s^2 2sns$ configurations in a beryllium atom is suggested, and based on those functions and variational method, a Mathematica program is developed to calculate the energies of $1s^2 2sns$ ($n = 3 - 6$) configurations in a beryllium atom. Both

*Project supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China (Grant No 2005LXAH06) and the Research Foundation of Education Bureau of Anhui Province, China (Grant Nos KJ2008A145 and 2002HBL05).

†E-mail: huangsz@mail.ahnu.edu.cn

non-relativistic energies and polarization correction and relativistic corrections which include mass correction, one- and two-body Darwin corrections, spin–spin contact interaction and orbit–orbit interaction, are taken into consideration. The calculated results are compared with the experimental data.

2. Theory

2.1. Wavefunction and non-relativistic energy

The non-relativistic Hamiltonian of beryllium atom is (in atomic unit)

$$H_{\rm NR} = \sum_{i=1}^{4}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i=1}^{4}\sum_{j>i}\frac{1}{r_{ij}}, \qquad (1)$$

where Z is the nuclear charge. According to the Rayleigh–Ritz variational method, the non-relativistic energy of many-electron atoms can be expressed as

$$E_{NR} = {\rm Min}\frac{\langle {\rm LSM_L M_S}|\, H_{\rm NR}\, |{\rm LSM_L M_S}\rangle}{\langle {\rm LSM_L M_S}\mid {\rm LSM_L M_S}\rangle}, \qquad (2)$$

where $|{\rm LSM_L M_S}\rangle$ denotes the Racah wavefunction of many-electron atoms, which is usually expressed as a linear combination of Slater wavefunctions.[11] For the $1s^2 2sns$ configuration in a beryllium atom, the related Racah wavefunctions are

$$\left|{}^3S,0,1\right\rangle = \frac{1}{\sqrt{4!}}\|\psi_{1s0^+}(\boldsymbol{x}_1)\psi_{1s0^-}(\boldsymbol{x}_2)\psi_{2s0^+} \times(\boldsymbol{x}_3)\psi_{ns0^+}(\boldsymbol{x}_4)\|, \qquad (3a)$$

and

$$\left|{}^1S,0,0\right\rangle = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{4!}}\left\|\psi_{1s0^+}(\boldsymbol{x}_1)\psi_{1s0^-}(\boldsymbol{x}_2)\psi_{2s0^+} \times(\boldsymbol{x}_3)\psi_{ns0^-}(\boldsymbol{x}_4)\right\| - \frac{1}{\sqrt{2}}\frac{1}{\sqrt{4!}}\left\|\psi_{1s0^+} \times(\boldsymbol{x}_1)\psi_{1s0^-}(\boldsymbol{x}_2)\psi_{2s0^-}(\boldsymbol{x}_3)\psi_{ns0^+}(\boldsymbol{x}_4)\right\|, \qquad (3b)$$

where $\|\ldots\|$ represents a 4×4 determinant, with $\psi_{1s0^+}(\boldsymbol{x}_1)\psi_{2s0^-}(\boldsymbol{x}_2)\psi_{2s0^+}(\boldsymbol{x}_3)\psi_{ns0^+}(\boldsymbol{x}_4)$ being a diagonal term, and $\psi_{n_j l_j m_{l_j} m_{s_j}}(\boldsymbol{x}_i)$ is the single-electron wavefunction in the form of a product of single-electron radial, angular and spin wavefunctions

$$\psi_{n_j l_j m_{l_j} m_{s_j}}(\boldsymbol{x}_i) = R_{n_j l_j}(r_i)\, Y_{l_j m_{l_j}}(\theta_i\phi_i)\, \chi_{m_{s_j}}(\sigma_i). \qquad (4)$$

Substituting Eq.(3) into Eq.(2), and carrying out the angular integrations and spin summations by virtue of irreducible tensor theory, it is found that the non-relativistic energies of $1s^2 2sns$ configurations in a beryllium atom can be expressed as the following summations of radial integrations:

$$E_{\rm NR}({}^3S) = {\rm Min}\Big[2I(1{\rm s}) + I(2{\rm s}) + I(3{\rm s}) + F^{(0)}(1{\rm s},1{\rm s}) + 2F^{(0)}(1{\rm s},2{\rm s}) - G^{(0)}(1{\rm s},2{\rm s}) + 2F^{(0)}(1{\rm s},ns) - G^{(0)}(1{\rm s},ns) + F^{(0)}(2{\rm s},ns) - G^{(0)}(2{\rm s},ns)\Big], \qquad (5a)$$

and

$$E_{\rm NR}({}^1S) = {\rm Min}\Big[2I(1{\rm s}) + I(2{\rm s}) + I(3{\rm s}) + F^{(0)}(1{\rm s},1{\rm s}) + 2F^{(0)}(1{\rm s},2{\rm s}) - G^{(0)}(1{\rm s},2{\rm s}) + 2F^{(0)}(1{\rm s},ns) - G^{(0)}(1{\rm s},ns) + F^{(0)}(2{\rm s},ns) + G^{(0)}(2{\rm s},ns)\Big], \qquad (5b)$$

where

$$I(nl) = \frac{1}{2}\int_0^\infty rR_{nl}(r)\left[-\frac{{\rm d}^2}{{\rm d}r^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r}\right] rR_{nl}(r){\rm d}r, \qquad (6a)$$

$$F^{(k)}(n_i l_i, n_j l_j) = \int_0^\infty {\rm d}r_1 R^2_{n_i l_i}(r_1) r_1^2 \times \left[\int_0^{r_1}\frac{r_2^k}{r_1^{k+1}} R^2_{n_j l_j}(r_2) r_2^2 {\rm d}r_2 + \int_{r_1}^\infty \frac{r_1^k}{r_2^{k+1}} R^2_{n_j l_j}(r_2) r_2^2 {\rm d}r_2\right], \qquad (6b)$$

and

$$G^{(k)}(n_i l_i, n_j l_j) = \int_0^\infty {\rm d}r_1 R_{n_i l_i}(r_1) R_{n_j l_j}(r_1) r_1^2 \times \left[\int_0^{r_1}\frac{r_2^k}{r_1^{k+1}} R_{n_i l_i}(r_2) R_{n_j l_j}(r_2) r_2^2 {\rm d}r_2 + \int_{r_1}^\infty \frac{r_1^k}{r_2^{k+1}} R_{n_i l_i}(r_2) R_{n_j l_j}(r_2) r_2^2 {\rm d}r_2\right]. \qquad (6c)$$

The accuracy of the calculated non-relativistic energy of $1s^2 2snl$ configurations in a beryllium atom depends on the accuracy of the radial wavefunctions $R_{nl}(r)$. In this paper, a new set of trial radial functions for $1s^2 2snl$ configurations in a beryllium atom are suggested as

$$R_{1s}(r) = 2\sqrt{a^3}e^{-ar}, \tag{7}$$

and

$$\begin{aligned} & R_{nl}(r) \\ = & N_{nl} \exp\left(-\frac{b_n r}{n}\right) \sum_{\nu=0}^{n-1} \\ & \times \frac{n! C_\nu}{\nu!(n-\nu-1)!(\nu+1)!} \left(-\frac{2b_n r}{n}\right)^\nu, \ (n \geq 2), \end{aligned} \tag{8}$$

where a and b_n are the effective screen parameters for 1s and nl ($n \geq 2$) electrons respectively, $C_\nu (\nu = 0, 1, \ldots n-2)$ are variational parameters (C_{n-1} is set as unity), N_{nl} is the normalization coefficient and satisfies

$$\int_0^\infty R_{nl}^2(r) r^2 \mathrm{d}r = 1. \tag{9}$$

The key point of constructing the new radial functions is to add variational parameters (C_ν) each to their corresponding term of the general Laguerre polynomial in a hydrogen-like radial function for the open-shell electrons.

According to Eqs.(5)–(8), a Mathematica program based on the Rayleigh–Ritz variational method is developed to calculate the effective screen parameters a and b_n, the variational parameters $C_\nu (\nu = 0, 1, \ldots, n-2)$, and the non-relativistic energies of $1s^2 2snl$ ($n = 3-6$) configurations in a beryllium atom. The calculated results are listed in Table 1.

Table 1. Parameters and non-relativistic energies of $1s^2 2snl$ configurations in a beryllium atom [Unit: $2 * 13.605804\,\mathrm{eV}$].

n		a	b_2	b_n	$C_0/(2s)$	$C_0/(nl)$	$C_1/(nl)$	$C_2/(nl)$	$C_3/(nl)$	$C_4/(nl)$	E_{NR}
3	^3S	3.68725	2.47698	1.57467	0.949021	0.785794	0.90269				–14.4424
	^1S	3.68739	2.49784	0.725419	0.963100	0.658192	0.942642				–14.3776
4	^3S	3.68727	2.44310	1.33442	0.962402	0.767106	0.890264	0.976413			–14.3695
	^1S	3.68741	2.46083	0.706638	0.969682	0.643216	0.925823	0.995382			–14.3485
5	^3S	3.68727	2.43438	1.203740	0.968707	0.769518	0.892465	0.975666	1.00517		-14.3456
	^1S	3.68737	2.44670	0.700833	0.972789	0.634487	0.920272	0.998610	1.01210		–14.3364
6	^3S	3.68727	2.43151	1.11914	0.972017	0.777387	0.899334	0.981178	1.01491	1.01700	–14.3349
	^1S	3.68734	2.43996	0.699193	0.974502	0.628974	0.919203	1.00438	1.02444	1.01820	–14.3302

2.2. Polarization correction

It is well known that the radial functions are related to the potentials of the electrons. In the non-relativistic Hamiltonian of Eq.(1), only Coulomb potentials are considered, this is a good approach to inner-shell electrons, for the open-shell electrons, however, the dipole potential originating from polarization is important, which has been widely recognized in the theory of the weakest bound electron potential model.[12,13] For the $1s^2 2snl$ configurations of a beryllium atom, the dipole potential of the open-shell nl electron can be expressed as

$$\Delta V_P = -\frac{k(k+1)}{2r^2}, \tag{10}$$

where k is an adjustable parameter. The polarization correction to the non-relativistic energy is

$$\begin{aligned} E_P &= \langle \gamma L S M_L M_S | \, \Delta V_P \, | \gamma L S M_L M_S \rangle \\ &= -\frac{k(k+1)}{2} \int_0^\infty R_{nl}^2(r) \mathrm{d}r. \end{aligned} \tag{11}$$

By applying the variational method to the total energy $E_{NR} + E_P$, it is found that the parameter k can be approximately expressed as

$$k = \begin{cases} (n-4)/2 & (\text{for } ^3S \text{ States}) \\ (n-1)/2 & (\text{for } ^1S \text{ States}) \end{cases} \tag{12}$$

The calculated results of the polarization correction are listed in Table 2.

Table 2. Polarization corrections of $1s^2 2snl$ configurations in a beryllium atom (Unit: $2 * 13.605804\,\mathrm{eV}$).

n		3	4	5	6
E_P	^3S	0.0147165	0.0000000	–0.0055293	–0.0075606
	^1S	–0.0221793	–0.0169238	–0.0139229	–0.0119425

2.3. Relativistic correction

The relativistic correction Hamiltonian of beryllium atom is

$$H_{\rm RS} = H_{\rm MC} + H_{\rm D1} + H_{\rm D2} + H_{\rm SSC} + H_{\rm OO}, \quad (13)$$

where $H_{\rm MC}$ is the mass correction, $H_{\rm D1}$ the one-body Darwin correction, $H_{\rm D2}$ the two-body Darwin correction, $H_{\rm SSC}$ the spin-spin contact interaction, and $H_{\rm OO}$ the orbit-orbit interaction that vanishes for $1s^2 2sns$ configurations of a beryllium atom. In a tensor expression, their concrete forms are[11]

$$H_{\rm MC} = -\frac{\alpha^2}{8}\sum_i \nabla_i^4, \quad (14a)$$

$$H_{\rm D1} = \frac{\alpha^2 Z}{8}\sum_i \frac{\delta(r_i)}{r_i^2}, \quad (14b)$$

$$H_{\rm D2} = -\frac{\alpha^2}{4}\sum_{j>i}\frac{\delta(r_i - r_j)}{r_i^2}\sum_k (2k+1) \times \left[C_i^k \cdot C_j^k\right], \quad (14c)$$

and

$$H_{\rm SSC} = -\frac{2\alpha^2}{3}\sum_i\sum_{j>i}\frac{\delta(r_i - r_j)}{r_i^2}\boldsymbol{s}_i \cdot \boldsymbol{s}_j \times \sum_k (2k+1)\left[C_i^k \cdot C_j^k\right]. \quad (14d)$$

The relativistic correction to the non-relativistic energy can be expressed as

$$\Delta E_{\rm RS}(\gamma{\rm LS}) = \Delta E_{\rm MC} + \Delta E_{\rm D1} + \Delta E_{\rm D2} + \Delta E_{\rm SSC}, \quad (15)$$

where

$$\Delta E_{\rm MC} = \langle \gamma {\rm LSM_L M_S} | H_{\rm MC} | \gamma {\rm LSM_L M_S} \rangle, \quad (16a)$$

$$\Delta E_{\rm D1} = \langle \gamma {\rm LSM_L M_S} | H_{\rm D1} | \gamma {\rm LSM_L M_S} \rangle, \quad (16b)$$

$$\Delta E_{\rm D2} = \langle \gamma {\rm LSM_L M_S} | H_{\rm D2} | \gamma {\rm LSM_L M_S} \rangle, \quad (16c)$$

and

$$\Delta E_{\rm SSC} = \langle \gamma {\rm LSM_L M_S} | H_{\rm SSC} | \gamma {\rm LSM_L M_S} \rangle. \quad (16d)$$

Carrying out the angular integrations and spin summations by utilizing the irreducible tensor theory,[14] it is found that for $1s^2 2sns$ configurations of a beryllium atom we have

$$\Delta E_{\rm MC}(^3S) = \Delta E_{\rm MC}(^1S) = -\frac{1}{8}\alpha^2 \sum_{i=1}^4 \left\langle \nabla_i^2 R_{n_i l_i}(r) \,\middle|\, \nabla_i^2 R_{n_i l_i}(r) \right\rangle, \quad (17a)$$

$$\Delta E_{\rm D1}(^3S) = \Delta E_{\rm D1}(^1S) = \frac{Z\alpha^2}{8}\sum_{i=1}^4 \delta(l_i, 0)\, R^2_{n_i l_i}(0), \quad (17b)$$

$$\Delta E_{\rm SSC}(^3S) = -2\Delta E_{\rm D2}(^3S) = \frac{1}{2}\alpha^2 \left[F(1s,1s) + F(1s,2s) + F(1s,ns)\right], \quad (17c)$$

and

$$\Delta E_{\rm SSC}(^1S) = -2\Delta E_{\rm D2}(^1S) = \frac{1}{2}\alpha^2 \left[F(1s,1s) + F(1s,2s) + F(1s,ns) + 2F(2s,ns)\right] \quad (17d)$$

where

$$\nabla_i^2 \equiv \frac{{\rm d}^2}{{\rm d}r^2} + \frac{2}{r}\frac{\rm d}{{\rm d}r} - \frac{l_i(l_i+1)}{r^2}, \quad (18a)$$

and the radial integration $F(n_1 l_1, n_2 l_2)$ is defined as

$$F(n_1 l_1, n_2 l_2) = \iint R^2_{n_1 l_1}(r_1) R^2_{n_2 l_2}(r_2) \times \delta(r_1 - r_2) r_2^2 {\rm d}r_1 {\rm d}r_2. \quad (18b)$$

By using the new radial functions presented in Eqs.(7) and (8) and the values of a, b_n and C_ν listed in Table 1, the relativistic corrections can be calculated straightforwardly, the results are listed in Table 3. The calculated results of non-relativistic energy, polarization correction, relativistic correction, total energy and experimental date[15] are listed in Table 4.

Table 3. Relativistic corrections of $1s^2 2sns$ configurations in a beryllium atom [Unit: $2 * 13.605804\,\mathrm{eV}$].

n		$M_c(\alpha^2)$	$D_1(\alpha^2)$	$D_2(\alpha^2)$	SSC(α^2)	OO(α^2)	E_R
3	^3S	–234.803	204.125	–6.58952	13.1790	0	–0.00128342
	^1S	–234.886	204.174	–6.58634	13.1727	0	–0.00128543
4	^3S	–234.557	203.947	–6.57753	13.1551	0	–0.00128043
	^1S	–234.696	204.059	–6.58293	13.1659	0	–0.00128162
5	^3S	–234.512	203.928	–6.57742	13.1548	0	–0.00127906
	^1S	–234.617	204.012	–6.58202	13.1640	0	–0.00127989
6	^3S	–234.503	203.931	–6.57842	13.1568	0	–0.00127840
	^1S	–234.576	203.990	–6.58176	13.1635	0	–0.00127896

Table 4. Energies of $1s^2 2sns$ configurations in a beryllium atom [Unit: $2 * 13.605804\,\mathrm{eV}$].

n		E_{NR}	E_P	E_R	E	NIST[15]	Dif.
3	^3S	–14.4424	0.0147165	–0.00128342	–14.4290	–14.4311	0.0021
	^1S	–14.3776	–0.0221793	–0.00128543	–14.4010	–14.4192	0.0182
4	^3S	–14.3695	0.0000000	–0.00128043	–14.3708	–14.3745	0.0037
	^1S	–14.3485	–0.0169238	–0.00128162	–14.3667	–14.3711	0.0044
5	^3S	–14.3456	–0.0055293	-0.00127906	–14.3524	–14.3539	0.0015
	^1S	–14.3364	–0.0139229	–0.00127989	–14.3516	–14.3525	0.0009
6	^3S	–14.3349	–0.0075606	–0.00127840	–14.3438	–14.3441	0.0003
	^1S	–14.3302	–0.0119425	–0.00127896	–14.3434	–14.3434	0.0000

3. Discussion and conclusion

From Table 4, we can see that the calculated results are in good agreement with experimental date, since the differences are less than 0.005 a.u. except that of $1s^2 2s3s\,^1S$ state (0.0182 a.u.), where in which case the wavefunction might be more distorted. It implies that the new trial wavefunctions suggested in this paper, in most cases, approach the actual atomic wavefunctions.

It is noticeable, however, that only the cases where all the open-shell electrons are s electrons are considered in the present work. Whether or not the suggested trial wavefunctions are suitable for p, d, f ..., electrons deserves to be further investigated.

In conclusion, a new set of trial functions of $1s^2 2sns$ configurations in a beryllium atom is suggested. A Mathematica program based on the variational method is developed to calculate the energies of $1s^2 2sns (n = 3 - 6)$ configurations in a beryllium atom. Non-relativistic energies, polarization correction and relativistic corrections are calculated. The results are in good agreement with experimental data.

References

[1] Chung K T and Zhu X W 1993 *Phys. Rev.* A **48** 1944
[2] Chung K T and Zhu X W 1994 *Phys. Rev.* A **50** 3818
[3] Fischer C F 1994 *Phys. Scr.* **49** 323
[4] Tachiev G and Fischer C F 1999 *J. Phys.* B: *At. Mol. Opt. Phys.* **32** 5805
[5] Kingston A E and Hibbert A 2000 *J. Phys.* B: *At. Mol. Opt. Phys.* **33** 693
[6] Han L H and Zhang R 2004 *J. At. Mol. Phys.* **21** 441 (in Chinese)
[7] Han L H and Lu P F 2005 *J. At. Mol. Phys.* **22** 606 (in Chinese)
[8] Gou B C and Wang F 2004 *Phys. Rev.* A **69** 042513
[9] Gu J, Zhang M, Chen J and Gou B C 2006 *J. At. Mol. Phys.* **23** 606 (in Chinese)
[10] Huang S Z, Ma K, Wu C Y and Ni X B 2008 *Acta Phys. Sin.* (in Chinese)
[11] Huang S Z 2005 *Theory of Atomic Structure* (Hefei: China USTC Press) (in Chinese)
[12] Zheng N W, Ma D X, Yang R Y, Zhou T, Wang T and Han S 2000 *J. Chem. Phys.* **113** 1681
[13] Zheng N W, Zhou T, Wang T, Ma D X, Yang R Y and Lin X 2001 *Chin. J. Chem. Phys.* **14** 292 (in Chinese)
[14] Ma K, Huang S Z, Ni X B, Wu C Y and Hu J 2008 *J. At. Mol. Phys.* (to be published, No.20060031)
[15] *NIST Atomic Spectra Database. Energy Levels Data* [DB]. National Institute of Standards and Technology.2001.09.09 http://physics.nist.gov/cgi-bin/AtData/display.ksh