Energies, fine structures and transition wavelengths of the core-excited states in Be$^+$ ions

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Abstract   The fine structures of doubly excited resonances of lithium-like beryllium are calculated using the saddle-point and saddle-point complex-rotation methods. A restricted variational method is used to obtain a more accurate value for the nonrelativistic energy. Relativistic and mass polarization corrections to the resonance energy are included. Transition wavelengths are also calculated and compared with other theories and experimental results.

Keywords: fine structures, resonance, transition wavelengths, Be$^+$ ions.

The calculation of energies and spectra of doubly and triply excited resonances is very challenging because of strong electron correlation effects and an infinite number of open channels associated with these resonances, which means that more accurate theoretical calculation results are required. The high resolution Auger spectra of lithiumlike doubly and triply excited states were reported by Rødbro et al. in 1979[1]. Three years later, these resonances were calculated using the saddle-point variation method[2]. Afterwards, Piangos and Nicolaides[3] calculated the radiative lifetimes of triply excited states of the Li isoelectronic sequence, using the state-specific theory method. In 1995, Kiernan[4] and Azuma[5] et al. reported the observations of many higher-lying $^2P^0$ resonances of hollow lithium using different experimental techniques. In the studies of Chung and Gou[6~8], the saddle-point complexrotation method was used to calculate the energy and width of some triply excited resonances. Diehl et al.[9] and Cubaynes et al.[10] made high-precision measurements for the energies and widths of triply excited states $^2P^0$, ^2S, and ^2P. The Hartree-Fock configuration interaction (HF-CI), multi-configuration Dirac-Fock (MCDF), and R-matrix methods were used to identify these resonances, respectively. We[11] have also calculated the energies and fine structures of these resonances.

In Ref. [2], the number of linear parameters was limited to about 100, the energy was calculated with a more limited closed-channel wave function and the shift from its interaction with continua was not included. The widths, relativistic corrections, and fine structures were not considered in Ref. [2] either. With the improvement of computing resources we can now perform much more elaborate calculations to improve the accuracy.

1 Theoretical method

The LS[2] coupling scheme is used in the present work. The nonrelativistic Hamiltonian is given

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in atomic units.

$$\hat{H}_0 = \sum_{i=1}^{3}\left[-\frac{1}{2}\nabla_i^2 - \frac{4}{r_i}\right] + \sum_{\substack{i,j=1 \\ i<j}}^{3}\frac{1}{r_{ij}}. \tag{1}$$

In general, the saddle-point wave function of a core excited three-electron system[12] can be written as

$$\Psi_b(1,2,3) = A\sum C_{mnk}^{l_1,l_2,L_{12},l_3}\cdot[1-P_{1s}(r_1)]\cdot[1-P_{1s}(r_2)]\cdot[1-P_{1s}(r_3)]$$
$$\cdot\,\phi_{mnk}(r_1,r_2,r_3)\cdot Y_{l_1,l_2,L_{12},l_3}^{LM}(r_1,r_2,r_3)\cdot X(1,2,3), \tag{2}$$

where A is the antisymmetrization operator, $Y_{l_1,l_2,L_{12},l_3}^{LM}(r_1,r_2,r_3)$ the angular part, $X(1,2,3)$ the spin part, and $\phi_{mnk}(r_1,r_2,r_3)$ is the radial part. The radial basis functions are slater orbitals:

$$\phi_{mnk}(r_1,r_2,r_3) = r_1^m r_2^n r_3^k\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_3). \tag{3}$$

In Eq. (2) the projection operator is given by

$$P_{1s}(r_i) = \mid\phi_0(r_i)><\phi_0(r_i)\mid, \tag{4}$$

where the vacancy orbital is

$$\phi_0(r) = \left(\frac{q^3}{\pi}\right)^{1/2}\exp(-qr). \tag{5}$$

Using the saddle-point variational method, of which q is a parameter determined in the energy maximization processes, the linear parameters C and the nonlinear parameters α_i, β_i, γ_i in Eqs. (2) and (3) are determined in the energy optimization processes, we obtain the basic wave function $\Psi_b(1,2,3)$ and the corresponding saddle-point energy E_b.

To further improve the calculation of energy, we expand the total wave function into

$$\Psi_b'(1,2,3) = D_0\Psi_b(1,2,3) + \Psi_e(1,2,3), \tag{6}$$

where $\Psi_e(1,2,3)$, as a function to saturate the functional space, takes the same form as $\Psi_b(1,2,3)$, with each of nonlinear parameters in the basis function of $\Psi_e(1,2,3)$ being optimized in the restricted variational calculation.

The total energy is further improved by including the mass polarization effect and relativistic corrections. The explicit expressions of these perturbation operators are given in Ref. [13] (including corrections to the kinetic energy $\hat{H}_{KE}$, the Darwin term $\hat{H}_{DT}$, the electron-electron contact term $\hat{H}_{EECT}$, the orbit-orbit interaction $\hat{H}_{OO}$, and mass polarization effect $\hat{H}_{MP}$).

$$E_{REL} = \langle\Psi_b\mid\hat{H}_{KE} + \hat{H}_{DT} + \hat{H}_{EECT} + \hat{H}_{OO} + \hat{H}_{MP}\mid\Psi_b\rangle, \tag{7}$$

$$E_{total} = E_b + E_{RV} + E_{REL} + E_s, \tag{8}$$

where E_{RV} is the sum of the contribution from each of the Ψ'_e s.

The complex energy obtained from $\Psi(1,2,3)$, $E-i\Gamma/2$ gives the position and the width of the resonance. The difference, $E_s = E - E_b$, represents the shift from the saddle-point energy to the resonance energy[14].

The fine structure perturbation operators are given by

$$\hat{H}_{FS} = \hat{H}_{SO} + \hat{H}_{SS} + \hat{H}_{SOO}, \tag{9}$$

where the spin-orbit $\hat{H}_{SO}$, spin-other-orbit $\hat{H}_{SOO}$, and spin-spin $\hat{H}_{SS}$ are given in Reference [13].

The wave function for calculating the fine-structure splitting[13] in the LSJ representation is

$$\Psi_{LSJJ_z} = \sum_{MS_z} \langle LSMS_z \mid JJ_z \rangle \Psi_b(1,2,3). \tag{10}$$

The fine-structure correction to the center-of-gravity energy can be calculated by the first-order perturbation theory,

$$(\Delta E_{FS})_J = \langle \Psi_{LSJJ_z} \mid \hat{H}_{FS} \mid \Psi_{LSJJ_z} \rangle, \tag{11}$$

with

$$E_{CG} = \frac{\sum_J (2J+1)E_J}{\sum_J (2J+1)}, \tag{12}$$

where E_{CG} is the energy for the total angular momentum J state.

The fine-structure splitting is given by

$$v_{J \to J-1} = [(\Delta E_{FS})_J - (\Delta E_{FS})_{J-1}]/hc. \tag{13}$$

The transition wavelengths are calculated by

$$\lambda_{ki} = \frac{hc}{E_k - E_i} = \frac{1}{2R\Delta E_{ki}}, \tag{14}$$

where R is the Rydberg constant.

2   Result and discussion

The thirteen core-excited Be$^+$ systems studied in the present work are the lowest $^4P^0$, the lowest four $^2S^e$, five $^2P^0$, and three $^2D^e$ resonances. The wave functions are much larger than those in Ref. [2], and more angular-spin components are included. As a consequence, the improvement of E_b (the saddle-point energy) over that of Ref. [2] ranges from -0.002 to -0.005 a.u. These energies are further improved by the restricted variation method with E_{RV}, and the total improvement E_{RV} ranges from -0.0000187 to -0.0000996 a.u.

The saddle-point energy is calculated from the closed channel part of the wave function. It differs from the resonance position by a shift (E_s), which comes from the interaction of the closed- and open-channel wave functions. These shift energies range from -0.0000478 to 0.0005698 a.u. The total nonrelativistic term energy is obtained by adding E_{RV}, the shift E_s, and the energy upper bound E_b.

In addition to the shifts E_s and E_{RV}, the energy of these resonances is further corrected by the mass polarization and relativistic perturbations. The relativistic perturbation operators considered in this work are: the correction to the kinetic energy (P^4), the Darwin term, the electron-electron contact term and the orbit-orbit interaction. The mass polarization perturbation operator is accurate to all orders, the relativistic corrections are calculated using the first-order perturbation theory. To make a comparison with the experiment[1], the relativistic energies of these resonances are given in Fig. 1, which shows that the energies predicted in this work agree quite well with the experimental results.
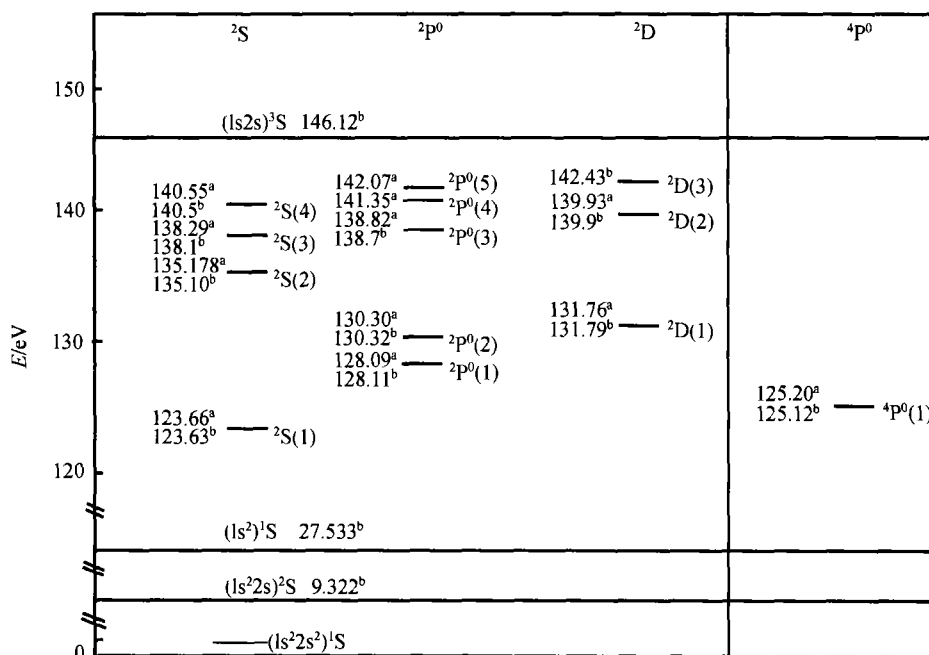

Fig. 1   Energy level diagram for autoionising core-excited states Be$^+$ with configuration 1s2lnl'. (a) This work; (b) Ref. [1].

The energies in Fig. 1 are the center-of-gravity energies. Taking into account the effects of the spin-orbit, spin-other-orbit, and spin-spin interactions, we obtained the energies of the fine-structure resolved J levels. The shift values of the various J levels from the center-of-gravity energy is given in Table 1.

Furthermore we calculated the radiative wavelengths from these resonances. The results are shown in Fig. 2. Our results are in reasonable agreement with those of Ref. [3]. These results of core-excited states for lithium-like beryllium system can be a very useful reference for future experiments.
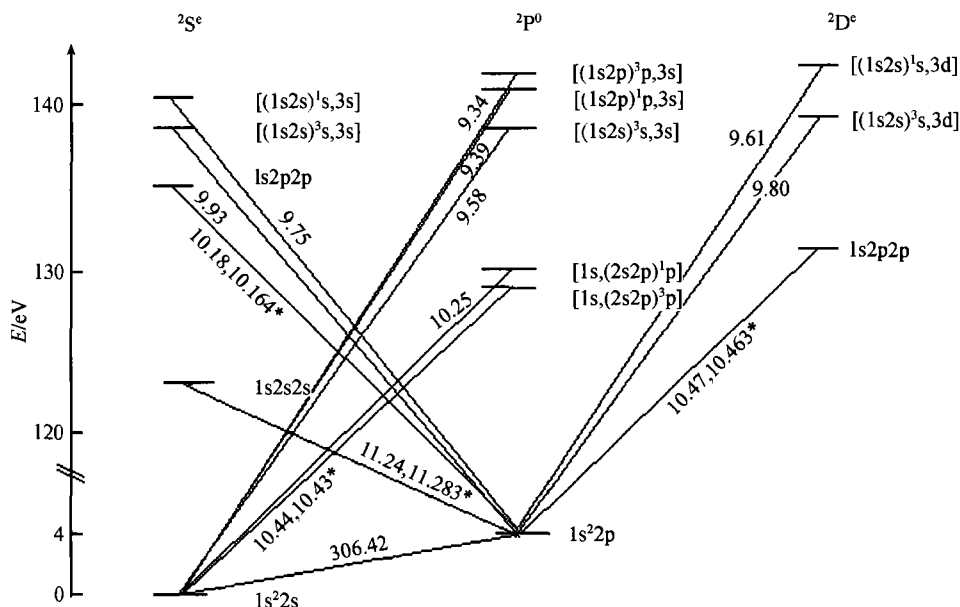
Fig. 2   Transition wavelengths(nm) associated with doubly core-excited states in Be^+ ions. * Reference [3].

Table 1   Fine-structure correction to the center-of-gravity energy (E_{CG}) and splitting ($v_{J\to J-1}$)

^2L	E_{CG}/a.u.	ΔE_J $J = L - 1/2$	ΔE_J/a.u. $J = L + 1/2$	ΔE_J $J = L + 3/2$	$v_{3/2-1/2}$ /cm^{-1}	$v_{5/2-3/2}$ /cm^{-1}
$[1s,(2s2p)^3p]^2P^0$	-9.962354	-0.0000394	0.0000197		13.0	
$[1s,(2s2p)^1p]^2P^0$	-9.881158	0.0000195	-0.0000097		-6.4	
$[(1s2s)^3s,3p]^2P^0$	-9.568031	0.0000160	-0.0000080		-5.3	
$[(1s2s)^1s,3p]^2P^0$	-9.474980	0.0000049	-0.0000025		-1.6	
$[(1s2p)^3p,3s]^2P^0$	-9.448378	-0.0000275	0.0000138		9.1	
$(1s2p2p)^2D$	-9.827540	0.0000605	-0.0000403			-22.1
$[(1s2s)^3s,3d]^2D$	-9.527338	0.0000040	-0.0000027			-1.5
$[(1s2s)^1s,3d]^2D$	-9.435846	-0.0000158	0.0000105			5.8
$(1s2s2p)^4P^0$	-10.068618	0.0000029	-0.0000251	0.0000158	-6.12	9.0

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