Autoionization states of Li, Be^+, B^{2+}, and C^{3+}

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The positions and widths of the first few ^2S, $^2P^0$, and ^2D autoionization states of Li, Be^+, B^{2+}, and C^{3+} are calculated. The results are compared with the experimental values where available.

The positions and widths of ^2S, $^2P^0$, and ^2D autoionization states of Li, Be^+, B^{2+}, and C^{3+} below the ^3S threshold of two-electron ions are presented in this paper. The states in Li, Be^+, and B^{2+} have been observed recently by Bruch *et al.*[1] using an ion-beam time-of-flight method; states in Be^+ and B^{2+} have been observed by Rodbro *et al.*[2,3] using fast ion beam excited in single gas collisions. Ziem *et al.*[4] measured the positions of the states of Li by bombarding Li vapor by H^+ and He^+. The optically allowed $^2P^0$ transitions in Li were previously observed in photon absorption in the ground state of Li by Ederer *et al.*[5] Recently ^2S and ^2D transitions of Li have been observed by McIlrath and Lucatorto[6] by first exciting the $1s^22p$ state from $1s^22s$ state by 1-MW dye laser.

The ^2S and $^2P^0$ states in Li have been calculated previously[7] by quasiprojection operator technique. This method was developed by Temkin *et al.*[8] to study the well-known He^- resonance at 19.31 eV. There it was shown that it is possible to construct quasiprojection operators $\hat{P}$ and $\hat{Q}$ for $N+1$ electron systems if the condition of idempotency is relaxed. For $N=2$ the simplest quasiprojection operators are[8]

$$\hat{Q} = 1 - \hat{P}, \tag{1a}$$

$$\hat{P} = \hat{P}_1 + \hat{P}_2 + \hat{P}_3, \tag{1b}$$

where

$$\hat{P}_i = \varphi_0(x^i)\rangle\langle\varphi_0(x^i). \tag{1c}$$

This method has been extended recently[9] to calculate resonances below any discrete target threshold.

$\varphi_0(x^i)$ is the ground state target wave function. x^i indicates the absence of x_i space and spin coordinates from the target wave function. In the present calculation φ_0 is taken to be a closed shell wave function:

$$\varphi_0(\vec{x}_1, \vec{x}_2) = \varphi_0(\vec{r}_1, \vec{r}_2)\chi^0 = (\xi^3/\pi)e^{-\xi(r_1+r_2)}\chi^0(12), \tag{2}$$

where $\xi = Z - \frac{5}{16}$, and Z is the nuclear charge: $\chi^0(12) = (\alpha_1\beta_2 - \alpha_2\beta_1)/\sqrt{2}$.

With this choice of the target wave function, the projection operators are idempotent

$$\hat{P}^2 = \hat{P}, \quad \hat{Q}^2 = \hat{Q}, \tag{3a}$$

so that

$$\hat{P}\hat{Q} = 0. \tag{3b}$$

The eigenvalues ϵ_λ are calculated by the Rayleigh-Ritz variational principle:

$$\delta(\langle\hat{Q}\Phi, H\hat{Q}\Phi\rangle / \langle\hat{Q}\Phi, \hat{Q}\Phi\rangle) = 0. \tag{4}$$

The trial wave function Φ used in this calculation is of the configuration interaction type

$$\Phi = \frac{A}{\sqrt{3}} \sum_i C_i [R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2) R_{n_3 l_3}(r_3) Y(l_1 l_2, l_3; L) + 1 \rightleftharpoons 2]\chi(12;3), \tag{5}$$

where $i = (n_1 l_1, n_2 l_2, n_3 l_3)$ and A is the antisymmetry operator. Y is the angular factor of total angular momentum L, and χ is a spin function

$$\chi(12;3) = [(\alpha_1\beta_2 - \alpha_2\beta_1)/\sqrt{2}]\alpha_3.$$

The trial wave function is symmetric in the first two spatial coordinates indicating that the total wave function is constructed from spin $\vec{0}$ and $\frac{\vec{1}}{2}$

TABLE I. Orbitals used to form various configurations and nonlinear parameter of the lowest Li states.

Orbital	Nonlinear parameters ^2S	$^2P^0$	^2D
$1s$	2.9748	2.9760	2.9841
$2s$	0.6080	0.8405	0.9263
$2s'$	2.3294	2.0292	2.2867
$2p$	1.2068	0.8131	0.7125
$2p'$	3.3250	1.5443	2.3978
$3s$	0.5655	0.8717	1.0577
$3p$	1.0853	0.5644	0.7032
$3d$	1.2670	0.8398	0.7208
$4s$	0.8900	1.3149	1.1446
$4p$	1.2440	0.6414	1.0974
$4d$	1.4912	1.51178	1.6090
$4f$	1.3558	1.7646	
$5s$	2.9774		
$5p$	4.5052		1.1885

to give total spin $\vec{\frac{1}{2}}$. The spin combination of $\vec{1}+\vec{\frac{1}{2}}=\vec{\frac{1}{2}}$ was not considered in constructing the wave function Φ. R_{nl} are the Slater orbitals given by

$$R_{nl}(r) = [(2\alpha_n)^{2n+1}/(2n)!]^{1/2} r^{n-1} e^{-\alpha_n r} . \quad (6)$$

Equation (5) can be written in the symbolic form

$$\Phi = \frac{A}{\sqrt{3}} \sum_i C_i (n_1 l_1 n_2 l_2) n_3 l_3$$

$$= \frac{A}{\sqrt{3}} \sum_i C_i c_i . \quad (7)$$

The orbitals nl used to form the configurations c_i are given in Table I. The configurations c_i used in the wave function for ^2S, $^2P^0$, and ^2D states are given in Table II. The orbitals $5s$ and $5p$ were not used in the wave function Φ for $^2P^0$ states. The orbitals $4f$ and $5s$ were not used in the wave function Φ for ^2D states. The number of terms in the trial wave function ranged up to 35 for ^2S states and 40 for $^2P^0$ and ^2D states. The wave function $\hat{Q}\Phi$ for the autoionization states is obtained by projection with $\hat{Q}$ on Φ.

TABLE II. Configuration used to form the wave function given in Eq. (7).

i	Configurations c_i ^2S	$^2P^0$	^2D
1	$(2s2s)1s$	$(2s2p)1s$	$(2s3d)1s$
2	$(2s1s)3s$	$(2s2p')1s$	$(2s'3d)1s$
3	$(2s3s)1s$	$(2s3p)1s$	$(3s3d)1s$
4	$(2p2p)1s$	$(1s2p)2s$	$(4s3d)1s$
5	$(2p1s)3p$	$(1s2p')2s$	$(1s3d)2s$
6	$(2p3p)1s$	$(1s3p)2s$	$(1s3d)2s'$
7	$(3p3p)1s$	$(3s2p)1s$	$(1s3d)3s$
8	$(3d3d)1s$	$(3s2p')1s$	$(1s3d)4s$
9	$(2p'2p')2s$	$(1s3p)2s'$	$(2p2p)1s$
10	$(2p2s)2p'$	$(2s'2p)1s$	$(2p'2p')1s$
11	$(2p2p')2s$	$(2s'3p)1s$	$(3p3p)1s$
12	$(2s2s')3s$	$(3s3p)1s$	$(4p4p)1s$
13	$(2s'3s)2s$	$(1s2p)3s$	$(2p2p')1s$
14	$(2s'2s')3s$	$(1s2p)2s'$	$(3p2p')1s$
15	$(2p'2p')3s$	$(1s2p')3s$	$(4p2p')1s$
16	$(2s'2s')2s$	$(1s3p)3s$	$(1s2p)2p'$
17	$(1s2s)4s$	$(4s2p)1s$	$(2s4d)1s$
18	$(2s4s)1s$	$(4s3p)1s$	$(2s'4d)1s$
19	$(3s3s)1s$	$(2s4p)1s$	$(3s4d)1s$
20	$(1s2p)4p$	$(1s2s)4p$	$(4s4d)1s$
21	$(2p4p)1s$	$(3s4p)1s$	$(1s4d)2s$
22	$(1s3d)4d$	$(1s3s)4p$	$(1s4d)2s'$
23	$(3d4d)1s$	$(1s2p)4s$	$(1s4d)3s$
24	$(4d4d)1s$	$(1s2p')4s$	$(1s4d)4s$
25	$(4f4f)1s$	$(3d2p)1s$	$(1s3p)2p'$
26	$(1s2s)5s$	$(3d2p')1s$	$(1s4p)2p'$
27	$(2s5s)1s$	$(3d3p)1s$	$(3d3d)1s$
28	$(1s2p)5p$	$(1s2p)3d$	$(4d4d)1s$
29	$(2p5p)1s$	$(1s2p')3d$	$(3d4d)1s$
30	$(1s3s)4s$	$(1s3p)3d$	$(1s4d)3d$
31	$(3s4s)1s$	$(4d2p)1s$	$(2p3p)1s$
32	$(1s3p)4p$	$(4d2p')1s$	$(2p4p)1s$
33	$(3p4p)1s$	$(4d3p)1s$	$(2p5p)1s$
34	$(2p2p')3s$	$(1s2p)4d$	$(3p5p)1s$
35	$(2p3s)2p'$	$(1s2p')4d$	$(4p5p)1s$
36		$(1s3p)4d$	$(1s3p)2p$
37		$(3d4f)1s$	$(1s4p)2p$
38		$(1s4f)3d$	$(1s5p)2p$
39		$(4d4f)4d$	$(1s5p)3p$
40		$(1s4f)4d$	$(1s5p)4p$

Starting from an initial guess of hydrogenic values, the nonlinear parameters associated with the orbitals are varied automatically by the program to obtain the minimum of the desired root of Eq. (4). As an illustration, the optimized nonlinear parameters for the first lowest root of ^2S, $^2P^0$, and ^2D states of Li are given in Table I. The lowest roots ϵ_λ corresponding to ^2S, $^2P^0$, and ^2D states are given in Table III in Rydberg units.

The width of the states is given by the expression:

$$\Gamma = 2k|\langle \hat{P}\psi_c H \hat{Q}\Phi \rangle|^2 . \quad (8)$$

The nonresonant continuum wave functions $\hat{P}\psi_c = \psi_c$ when closed shell target function is used, and it is calculated in the exchange approximation from the ansatz

$$\psi_c = (A/\sqrt{3})\{[u_L(r_1)/r_1] Y_{L0}(\Omega_1)\varphi_0(\vec{r}_2, \vec{r}_3)\chi(23;1)\} , \quad (9)$$

$u_L(r)$ is the scattering function and it is obtained from

$$\int \varphi_0(\vec{r}_2, \vec{r}_3) Y_{L0}(\Omega_1)\chi^*(23;1)(H-E)\psi_c d\Omega_1 d\vec{r}_2 d\vec{r}_3 = 0 , \quad (10)$$

TABLE III. Eigenvalues ϵ_λ (Ry) of Li, Be^+, B^{2+}, and C^{3+}.

System	λ	^2S	$^2P^0$	^2D
Li	1	-10.8090	-10.6214	-10.4596
	2	-10.3877	-10.5072	-10.3251
	3	-10.2945	-10.3636	
Be^+	1	-20.2459	-19.9138	-19.6336
	2	-19.3786	-19.7426	-19.0340
	3	-19.1593	-19.1200	-18.8484
B^{2+}	1	-32.6829	-32.2058	-31.8190
	2	-31.4621	-31.9863	-30.4671
	3	-30.6716	-30.6127	-30.2171
	4	-30.4429	-30.3443	
C^{3+}	1	-48.1209	-47.4970	-47.0046
	2	-46.5480	-47.2315	-44.6307
	3	-44.7249	-44.8103	-44.3105
	4	-44.4779		

TABLE IV. Positions in eV and comparison with the experimental values.

System and state	λ	Position[a]	Width	Other calculations[b]	McIlrath and Lucatorto[c]	Experiment Ziem *et al.*[d]	Experiment Rodbro *et al.*
Li, ^2S	1	56.424	0.0403	56.54	56.31[e]	56.35	
	2	62.156	0.013	62.03	61.992	61.995	
	3	63.425	0.34×10^{-4}	63.23	63.135		
$^2P^0$	1	58.976	0.007[f]	58.96[f]	58.91[g]	58.91	
	2	60.531	0.011	60.60	60.396[g]	60.397	
	3	62.483	0.21×10^{-4}	62.46	62.419[g]	62.425	
^2D	1	61.177	0.005	61.11	61.062	61.065	
	2	63.008	0.75×10^{-3}	62.98	62.899	62.98	
Be^+, ^2S	1	96.129	0.053	96.26			96.0[h]
	2	107.929	0.008	108.13			107.6[h]
	3	110.913	0.008	109.7[i]			112.4[h]
$^2P^0$	1	100.647	0.01	100.42			100.4[h]
	2	102.976	0.017	102.81			102.6[h]
	3	111.447	0.22×10^{-4}				110.9[h]
^2D	1	104.459	0.023	104.51			104.1[h]
	2	112.621	0.002	112.6[j]			112.4[h]
	3	115.143	0.18×10^{-3}	115.8[j]			114.9[h]
B^{2+}, ^2S	1	154.821	0.068	154.95			155.2[k]
	2	171.432	0.009	171.46			170.8[k]
	3	182.187	0.013				
	4	185.299					
$^2P^0$	1	161.312	0.010	160.09			161.7[k]
	2	164.299	0.028	164.05			164.4[k]
	3	182.988	0.51×10^{-4}				
	4	186.639					
^2D	1	166.576	0.027	166.53			167.1[k]
	2	184.970	0.003				
	3	188.371	0.25×10^{-3}				
C^{3+}, ^2S	1	227.103	0.074	227.26			
	2	248.503	0.009	248.40			
	3	273.308	0.027				
	4	276.669					
$^2P^0$	1	235.592	0.013	235.36			
	2	239.204	0.033	238.91			
	3	272.150	0.003				
^2D	1	242.290	0.039	242.15			
	2	274.590	0.002				
	3	278.946	0.75×10^{-6}				

[a] The positions of states of Li are relative to Li ground state at -14.95605 Ry (Ref. 16) and those of Be^+, B^{2+}, and C^{3+} are relative to the ground states of Be^{2+}, B^{3+}, and C^{4+} at -27.31113, -44.06194, and -64.81249 Ry, respectively (Ref. 17). 1 Ry = 13.605826 eV.

[b] Li results of Weiss (quoted in Ref. 6) and other results are from Ref. 12.

[c] McIlrath and Lucartorto, Ref. 6.

[d] Ziem *et al.*, Ref. 4.

[e] Pegg *et al.*, Ref. 11.

[f] Barden *et al.*, Ref. 10, also obtain 58.96 and 0.007 eV for the position and width (see text).

[g] Ederer *et al.*, Ref. 5.

[h] Rodbro *et al.*, Ref. 2.

[i] Bely-Debau *et al.*, Ref. 14.

[j] Bruch, Ref. 15.

[k] Rodbro *et al.*, Ref. 3.

where H is the total Hamiltonian and $E = E_0 + k^2$. E_0 is the ground state energy of the target and k^2 is the energy of the outgoing electron.

Positions and widths of various states are given in Table IV along with the results of other calculations and experiments, where available. The positions are given with respect to the ground state of two-electron target except in the case of Li, where the positions are given with respect to the ground state of Li atom. Some of the results of Li were presented in Ref. 7. The values are slightly different here because the trial wave functions have different sets of configurations compared to the configurations used in Ref. 7. The positions of states in Li have been calculated by Weiss (quoted in Ref. 6). The position and width of $^2P(1)$ state of Li have been calculated by Barden *et al.*[10] They get 58.96 and 0.007 eV for the position and width. The experimental positions obtained by photon absorption[5,6] in $1s^22s$ and $1s^22p$ are given in Table IV except for $^2S(1)$ where the position obtained by Pegg *et al.*[11] is given. The photon absorption experiments should be more accurate than the collision excitation experiments. The agreement between the calculations and these experiments and also of Ziem *et al.*[4] is good.

The positions of the resonances in Be^+, B^{2+}, and C^{3+} are given in Table IV along with the $1/Z$ expansion results of Safronova and Kharitonova.[12] The experimental values of Rodbro *et al.*[2,3] are also given. Again the agreement between the calculations and experiments is good.

The widths of ^2S, $^2P^0$, and ^2D states for the systems studied here are given in Table IV. The widths of the lowest ^2S, $^2P^0$, and ^2D states are found to be much more stable compared to the widths of the higher states as the number of terms is increased or the nonlinear parameters are varied. It is seen that the widths increase as the nuclear charge Z increases. The autoionization rates ($\Gamma/\hbar$) are required in the study of satellite lines[13] in the solar corona; the widths given here should be useful. There is very little information on widths, and it would be desirable to have additional calculations and experimental measurements of the widths of the autoionization states.

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