

Saddle-point complex-rotation method for the $(1s\ 2s\ 2s)^2S$ resonance in He^- , Li I, Be II, and B III

Brian F. Davis

Department of Chemical and Physical Sciences, University of North Carolina at Wilmington, Wilmington, North Carolina 28403-3297

Kwong T. Chung

Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

(Received 14 November 1983)

The saddle-point complex-rotation method is tested for a three-electron system by calculating the $(1s\ 2s\ 2s)^2S$ resonance in He^- , Li I, Be II, and B III. The energy position and width obtained for this resonance are well converged for a wide range of rotation angles and nonlinear parameters for all atomic systems considered. To obtain higher accuracy, the relativistic and mass polarization corrections are also calculated. The results are compared with those of the most accurate theoretical calculations and experiments. For Be II, the agreement between the theoretical widths is very poor. Experimental data are needed to confirm the correct theoretical value.

I. INTRODUCTION

Recently, a saddle-point complex-rotation method for calculating the position and width of a closed-channel resonance was proposed.¹ This method combines two different techniques for dealing with atomic resonances. The saddle-point technique^{2,3} yields the essential part of the closed-channel component of a resonant wave function. If the open-channel component is combined with this closed-channel component, then the small "shift" from the saddle-point energy to the resonance position and the width could be obtained. However, the inclusion of this nonsquare-integrable component could present computational difficulties. On the other hand, the complex-rotation method^{4,5} is capable of generating the resonance position and width with only the use of square-integrable basis functions. In Ref. 1 it was shown that this saddle-point complex-rotation method yields accurate results for two-electron resonances in helium. The complex eigenvalue was found to be very stable with respect to the rotation angle and the nonlinear parameter of the scattered electron in the open-channel component. Indeed, the good convergence of the complex eigenvalue is the merit of this present method, and it is probably due to the preoptimization of the closed-channel basis functions by the saddle-point technique.

In this paper we continue to investigate the saddle-point complex-rotation method by applying it to a three-electron system, the $(1s\ 2s\ 2s)^2S$ resonance in He^- , Li I, Be II, and B III. We chose this resonance because experimental results for the width of He^- are available for comparison, and also because this resonance has been the proving ground for many other theoretical methods. We calculate it for Li I, Be II, and B III in order to observe the isoelectronic trends and to stimulate further experimental interest in measuring the width of this resonance for these systems.

II. RESULTS

The nonrelativistic Hamiltonian for the three-electron system in atomic units (a.u.) is given by

$$H_0 = \sum_{i=1}^3 \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{\substack{i,j=1 \\ i < j}}^3 \frac{1}{r_{ij}}, \quad (1)$$

where Z is the nuclear charge and r_{ij} is the interelectron distance. The rotated Hamiltonian is obtained by scaling each radical coordinate by $e^{i\theta}$, i.e., r_j becomes $r_j e^{i\theta}$ where θ is the angle of rotation. If we refer to the N -electron radial coordinates collectively as R_N and the corresponding angular variables as Ω_N , then the form of our rotated trial wave function becomes

$$\psi = \sum_j C_j \phi_j(R_3 e^{i\theta}, \Omega_3) + A \sum_k D_k \psi_g(R_2 e^{i\theta}, \Omega_2) U_k(\vec{r}), \quad (2)$$

where the C_j and D_k are linear variation parameters and A is an antisymmetrization operator. In the first term, which represents the closed-channel component, the ϕ_j are optimized, antisymmetrized configuration-interaction basis functions with the "proper" $1s$ vacancy built in. For Li I, Be II, and B III, the basis functions in the closed-channel components result from previous saddle-point calculations for the $(1s\ 2s\ 2s)^2S$ states.⁶ For He^- they are determined in this investigation. To obtain a converged result for these closed-channel components, up to 14 partial waves and 97 linear parameters have been used (see Ref. 6). In the second term, which represents the open-channel component, ψ_g is the $(1s\ 1s)^1S$ two-electron target state. The $U_k(\vec{r})$, which form a one-dimensional complete set for representing the scattered s -wave electron, are given by

TABLE I. Energy of the eight-term, three-partial-wave ($1s1s$) 1S target state and comparison with Pekeris's value (in a.u.).

System	E_g^{NR} (This work)	E_g^{NR} Pekeris (Ref. 8)	E_g^{rel}
He	-2.900 869	-2.903 724	-2.903 800
Li II	-7.276 970	-7.279 913	-7.280 484
Be III	-13.651 410	-13.655 566	-13.657 643
B IV	-22.027 384	-22.030 972	-22.036 504

$$U_k(\vec{r}) = r^k e^{-\gamma r}, \quad (3)$$

where γ is a nonlinear variation parameter.

With this ψ , the width and shift are calculated by the standard variation method

$$\delta \frac{\langle \psi | H_0(\theta) | \psi \rangle}{\langle \psi | \psi \rangle} = 0. \quad (4)$$

In the above expression the unconjugated $e^{i\theta}$ is used in the complex conjugated wave function. For a more detailed description of the above procedure, the interested reader is referred to Ref. 1.

An accurate target-state wave function ψ_g should be used in the wave function given by Eq. (2) when carrying out the complex-rotation computation. Although the two-electron ($1s1s$) 2S wave function can easily be calculated to high precision, this wave function would need a large number of terms to account for the correlation effect.⁷ This, in turn, would make the three-electron complex-rotation calculation prohibitively time consuming. On the other hand, a very crude target-state wave function might lead to inaccuracy. To compromise, we chose to use a three-partial-wave, eight-term function to represent the target states. Compared with the nonrelativistic results of Pekeris,⁸ the energy of these wave functions are higher by 0.0029–0.0041 a.u. The energies for the eight-term target states and their comparison to Ref. 8 are given in Table I.

For an accurate determination of the total energy for the three-electron resonances we also calculated the contribution from relativistic and mass polarization effects. These are obtained by evaluating the expectation values of the following operators⁹ with the saddle-point wave functions

$$H_1 = -\frac{1}{8}\alpha^2 \sum_{i=1}^3 p_i^4 \quad (5)$$

(mass correction),

$$H_2 = \frac{\pi}{2}\alpha^2 \sum_{i=1}^3 Z\delta(\vec{r}_i) \quad (6)$$

(Darwin term),

$$H_3 = -\pi\alpha^2 \sum_{\substack{i,j=1 \\ i < j}}^3 \left(1 + \frac{8}{3}\vec{s}_i \cdot \vec{s}_j\right)\delta(\vec{r}_{ij}) \quad (7)$$

(Fermi contact term),

$$H_4 = -\frac{1}{2}\alpha^2 \sum_{\substack{i,j=1 \\ i < j}}^3 \frac{1}{r_{ij}} \left[\vec{p}_i \cdot \vec{p}_j + \frac{\vec{r}_{ij} \cdot (\vec{r}_{ij} \cdot \vec{p}_i) \vec{p}_j}{r_{ij}^2} \right] \quad (8)$$

(retardation),

$$H_5 = \frac{1}{M} \sum_{\substack{i,j=1 \\ i < j}}^3 \vec{p}_i \cdot \vec{p}_j \quad (9)$$

(mass polarization).

In these equations, α is the fine-structure constant, Z is the nuclear charge, and M is the nuclear mass approximated by

$$M = \{[Z(1.008 142) + N(1.008 982)]1836\} / 1.008 142. \quad (10)$$

For the atomic systems of interest, He⁻, Li I, Be II, and B III, the number of neutrons N are 2, 4, 5, and 6, respectively.

In Table II we present the results obtained with the saddle-point wave functions for the different ions. In this table E_{sp} is the saddle-point energy, L is the number of angular partial waves used in the expansion of the saddle-point wave function, N is the total number of terms used, and q is the optimized parameter in the $1s$ vacancy orbital,

$$\phi_{1s} = Ce^{-qr}, \quad (11)$$

where C is a normalization constant. It is interesting to note that $q \approx Z - \frac{1}{2}$, indicating that the $1s$ vacancy is approximately half shielded from the nucleus by the $1s$ electron. $\langle H_1 + H_2 \rangle$, $\langle H_3 \rangle$, $\langle H_4 \rangle$, and $\langle H_5 \rangle$ are the results of the first-order perturbation theory for the operators given in Eqs. (5)–(9), respectively. We note that the relativistic and mass polarization corrections vary smoothly as a function of nuclear charge.

In the complex-rotation computation, the inclusion of 15 terms in the open-channel component [i.e., k runs from

TABLE II. Relativistic correction, mass polarization, shift, and width of the ($1s2s2s$) 2S resonances (in a.u., for notation see text).

	E_{sp}	L	N	q	$\langle H_1 + H_2 \rangle$ (10^{-3})	$\langle H_3 \rangle$ (10^{-5})	$\langle H_4 \rangle$ (10^{-6})	$\langle H_5 \rangle$ (10^{-6})	Δ (10^{-4})	E	Γ (10^{-3})
He ⁻	-2.191 617 7	10	67	1.45	-0.1133	0.04	0.01	1.193	-0.287	-2.191 758	0.4250
Li I	-5.405 219 0	10	79	2.48	-0.6266	0.47	0.4	0.673	0.071	-5.405 833	1.3541
Be II	-10.122 718 2	14	97	3.48	-2.1114	1.67	1.4	-0.342	0.620	-10.124 750	1.9475
B III	-16.341 007 8	10	85	4.48	-5.3733	4.16	4.1	-2.278	1.230	-16.346 215	2.2855

TABLE III. Convergence of the resonant energy E_r and width Γ of $\text{Li I } (1s2s2s)^2S$ as a function of rotation angle θ (in radians) and nonlinear parameter γ using the saddle-point complex-rotation method; here, x is given in the body of the table. For energy $E_r = (-5.4052119 + 10^{-7}x)$ a.u. and for width $\Gamma = (0.0013541 + 10^{-7}x)$ a.u.

		θ					
γ		0.2	0.3	0.4	0.5	0.6	0.7
E_r	1.50	26	0	0	-1	-1	-3
	1.875	16	0	0	0	-1	-1
	2.25	20	0	0	0	0	2
	2.265	15	0	0	0	-1	-6
	3.00	-37	-2	0	0	2	15
Γ	1.50	-8	-1	0	-1	-1	2
	1.875	30	1	0	0	0	0
	2.25	19	1	0	0	0	-1
	2.625	-44	-2	0	0	2	9
	3.00	-4	-2	0	-1	-4	3

0 to 14 in Eq. (2)] yields a converged complex energy, $E_r - i\Gamma/2$. This convergence for the resonant energy E_r and width Γ is shown in Table III for the case of Li. This table demonstrates that the complex eigenvalue is very stable over a wide range of rotation angles θ and nonlinear parameters γ . If the nonlinear parameter γ is scaled to the other charges Z from Li I by the prescription

$$\gamma' = \frac{Z}{3}\gamma, \quad (12)$$

then similar convergences are obtained for He^- , Be II, and B III.

The final results for the 2S resonances are also given in Table II. The shift from the saddle-point energy to the resonance position is defined by

$$\Delta \equiv E_r - E_{\text{sp}}. \quad (13)$$

The total energy E in this table is defined by

$$E = E_{\text{sp}} + \Delta + \langle H_1 + H_2 + H_3 + H_4 + H_5 \rangle. \quad (14)$$

We note that the shift changes steadily as a function of nuclear charge, from -0.78 meV for He^- to $+1.67$ meV for B III. The shift is smallest for the neutral lithium atom, i.e., $+0.19$ meV. The width also increases smoothly as a function of nuclear charge.

It is worthwhile to point out that the shift depends sensitively on the accuracy of the closed-channel wave function used in the computation. The small shifts shown in this table seem to justify the inner-shell vacancy picture which is the foundation of the saddle-point technique.

III. COMPARISON WITH THEORY AND EXPERIMENT

A comparison of our results with other calculations and experiments is given in Table IV. The resonance position in this work is quoted in electron volts above the two-electron relativistic ground-state energy given in Table I. The conversion from atomic units to electron volts is accomplished with the infinite-mass rydberg, -13.605826

eV, which is appropriate when comparing with scattering data.¹⁰

For He^- all the theoretical calculations¹¹⁻¹⁵ for the 2S resonance position seem to be in good agreement. In many references, the resonance position is given in terms of the energy above the ground state of the helium atom. But the actual value used for this energy is not quoted in these references. This makes a precise comparison between the theoretical results difficult. A few of the earlier results quoted in Table IV have been adjusted using the reference energy of Table I. Our He^- energy lies on the lower end of the theoretical results. It gives slightly better agreement with the experiments.¹⁶⁻²⁰ The width of this work agrees closely with that of Ehrhardt *et al.*¹⁷

For Li I no experimental results for the width are available, and to our knowledge only Bhatia and Temkin²¹ and Bhatia²² have published theoretical values. They obtained widths of 0.0423 and 0.0403 eV, respectively. Our result, 0.0369 eV, agrees better with the more recent value of Bhatia.²² The experimental results for the energy of Rassi *et al.*²³ and Rødbro *et al.*²⁴ are slightly higher than those of Pegg *et al.*²⁵ and Ziem *et al.*²⁶ Our calculated result is in better agreement with that of Refs. 23 and 24.

For Be II there is a very large range of calculated widths,²⁷⁻²⁹ from 0.02 to 0.09 eV. Unfortunately no experimental result for the width of this system is available to resolve this large discrepancy.

Kelly,²⁷ Nicholaides *et al.*,²⁹ and Bhatia²² calculated the width with the golden-rule formula. This is accomplished by calculating a matrix element between the closed-channel and open-channel components. Kelly²⁷ and Nicholaides *et al.*²⁹ used a multiconfiguration Hartree-Fock function for the closed channel, and a Hartree-Fock function for the open channel. Bhatia²² used a configuration interaction function derived from the quasiprojection operator technique for the closed-channel component, and he combined a scattering function computed from the static-exchange approximation with his closed-shell target state for the open channel. Kelly's²⁷ result, 0.093 eV, is to be compared with the 0.083-eV result

TABLE IV. Comparison of energy and width of the $(1s2s2s)^2S$ resonance for He^- , Li I , Be II , and B III .

		Energy (eV)	Width (meV)	Ref. no.	Author; method	
He^-	Theory	19.376 ^a	11.56		This work	
		19.403 ^a	12.13	11	Junker and Huang; complex rotation	
		19.4	13.9	12	Temkin <i>et al.</i> ; quasiprojection operator	
		19.402 ^a	11.72	11	Junker; complex rotation	
		19.38	11.5	13	Ormonde and Golden; close coupling	
		19.4	15	14	Sinfailam and Nesbet; variational	
		19.398	12	15	Bain <i>et al.</i> complex rotation	
		19.365	11.0	30	Hummer and Norcross; close coupling	
		Expt.	19.3	17.5±2.5	16	Andrick and Ehrhardt; transmission
			19.3		17	Ehrhardt <i>et al.</i> ; transmission
	19.30±0.01		8±2	18	Golden and Zecca; transmission	
		19.367±0.009	9±1	19	Cvejanovic <i>et al.</i> ; transmission	
		19.35±0.02	13	20	Golden <i>et al.</i> ; transmission	
Li I	Theory	51.012 ^a	36.85		This work	
		51.000 ^a	42.3	21	Bhatia and Temkin; quasiprojection operator	
		51.049 ^a	40.3	22	Bhatia; quasiprojection operator	
		51.15			A. W. Weiss (quoted in Ref. 22)	
	Expt.	51.04			Junker (quoted in Ref. 25)	
		50.92±0.03		25	Pegg <i>et al.</i> ; projectile-electron spectroscopy	
		50.92±0.01		26	Ziem <i>et al.</i> ; projectile-electron spectroscopy	
		51.004±0.015		23	Rassi <i>et al.</i> ; projectile-electron spectroscopy	
	50.97±0.05		24	Rødbro <i>et al.</i> ; beam-gas spectroscopy		
Be II	Theory	96.136 ^a	53.00		This work	
		96.185 ^a	53	22	Bhatia	
		96.737 ^a	92.93	27	Kelly; Multiconfiguration Hartree-Fock (MCHF)	
		97.94	20.5	28	Palmquist <i>et al.</i> ; Greens function	
		96.230 ^a	83;23	29	Nicolaides <i>et al.</i> ; MCHF	
	Expt.	96.10±0.1		24	Rødbro <i>et al.</i> ; beam-gas spectroscopy	
	B III	Theory	154.842 ^a	62.19		This work
154.972 ^a			68	22	Bhatia; quasiprojection operator	
154.95				22	Weiss (quoted in Ref. 22)	
Expt.		154.94±0.1		24	Rødbro <i>et al.</i> ; beam-gas spectroscopy	

^aThese theoretical results are quoted relative to the relativistic ground-state energy of Table I.

of Nicolaides *et al.*,²⁹ where both calculations employed the same closed-channel wave function. These results do not agree with the present result of 0.053 eV. When Nicolaides *et al.*²⁹ included more correlation in their closed-channel wave function, their calculated width dropped to 0.023 eV which also does not agree with the present work.

Palmquist *et al.*²⁸ used a Green function approach with Siegert boundary conditions to calculate the resonance parameters via a complex energy. Their calculated width, 0.021 eV, agrees with the 0.023-eV result of Nicolaides *et al.*²⁹ and disagrees with our result. Their calculated energy, 97.94 eV, is very high as compared to experiment and other theory. This is probably due to a lack of completeness in their "Slater-type orbital plus one Siegert orbital"

basis, which does not adequately account for the electron correlation.

Bhatia's calculated width, 0.053 eV, is in excellent agreement with the present work. This is interesting. The two calculations are similar in that the basis sets used to expand the closed-channel component of the wave function are more complete as compared to the other calculations. It appears that accounting for the electron correlation is essential for a well converged result for the width of this 2S resonance.

Nicolaides *et al.*²⁹ also calculated the shift Δ , which results from the interaction of the closed-channel component of the resonant wave function with the open-channel component through the Hamiltonian. Their result, -0.0015 a.u., is more than 20 times larger than our

result of $+0.000064$ a.u. This shows clearly that the closed-channel component of this work is far more accurate than that of Ref. 29.

For B III, fewer theoretical and experimental results exist for comparison. The calculated results of Bhatia,²² Weiss (see Ref. 22), and this work all lie within the experimental uncertainty quoted by the only experimental result of Rødbro *et al.*²⁴ Our result lies at the low end of the quoted uncertainty while the other calculations are closer to the line center. Our lower result is, for the most part, due to the inclusion of the relativistic effects which are absent in Ref. 22. Finally, our calculated width, 62 meV, is in reasonable agreement with Bhatia's result of 68 meV for this system.

IV. SUMMARY

In this work the saddle-point complex-rotation method is used to perform detailed calculations for the $(1s2s2s)^2S$ resonance in He⁻, Li I, Be II, and B III. This method utilizes saddle-point configuration-interaction basis functions which include the proper vacancy orbitals for the closed-channel component of the resonant wave function. A

complex rotation is then carried out after including the open-channel component in order to obtain the width and the small shift from the saddle-point energy to the resonance position. We found that the resulting complex eigenvalue is very stable over a wide range of rotation angles and nonlinear parameters in the open-channel component.

To obtain higher accuracy, the relativistic and mass polarization corrections for each atomic system are also considered. These results are then compared with the most accurate theoretical calculations and experiments. For He⁻, Li I, and B III the theoretical calculations and experiments are in satisfactory agreement. However, for Be II agreement between the theoretical widths is very poor. It would be very interesting to have this width measurement carried out so that the correct theoretical result could be verified.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation Grant No. PHY-82-06490.

-
- ¹K. T. Chung and B. F. Davis, *Phys. Rev. A* **26**, 3278 (1982).
²K. T. Chung, *Phys. Rev. A* **20**, 1743 (1979).
³K. T. Chung and B. F. Davis, *Phys. Rev. A* **22**, 835 (1980).
⁴E. Balslev and J. M. Combes, *Commun. Math. Phys.* **22**, 280 (1971).
⁵B. F. Davis and K. T. Chung, *Int. J. Quantum Chem.* **14**, No. 4 (1978).
⁶B. F. Davis and K. T. Chung, *J. Phys. B* **15**, 3113 (1982); K. T. Chung and R. Bruch, *Phys. Rev. A* **28**, 1418 (1983); K. T. Chung, *ibid.* **25**, 1596 (1982).
⁷B. F. Davis and K. T. Chung, *Phys. Rev. A* **25**, 1328 (1982).
⁸C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).
⁹H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), p. 181.
¹⁰A. K. Bhatia and A. Temkin, *Phys. Rev. A* **11**, 2018 (1975).
¹¹B. R. Junker and C. L. Huang, *Phys. Rev. A* **18**, 313 (1978); B. R. Junker, *ibid.* **18**, 2437 (1978).
¹²A. Temkin, A. K. Bhatia, and J. N. Bardsley, *Phys. Rev. A* **5**, 1663 (1972).
¹³S. Ormonde and D. E. Golden, *Phys. Rev. Lett.* **31**, 1161 (1973).
¹⁴A. L. Sinfailam and R. K. Nesbet, *Phys. Rev. A* **6**, 2118 (1972).
¹⁵R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukumar, *J. Phys. B* **7**, 2189 (1974).
¹⁶D. Andrick and H. Ehrhardt, *Z. Phys.* **192**, 99 (1966).
¹⁷H. Ehrhardt, L. Lauhans, and F. Linder, *Z. Phys.* **214**, 179 (1968).
¹⁸D. E. Golden and A. Zecca, *Phys. Rev. A* **1**, 241 (1970); D. E. Golden and A. Zecca, *Rev. Sci. Instrum.* **42**, 210 (1971).
¹⁹S. Cvejanovic, J. Comer, and F. H. Reed, *J. Phys. B* **7**, 468 (1974).
²⁰D. E. Golden, F. D. Schowengerdt, and J. Macek, *J. Phys. B* **7**, 478 (1974).
²¹A. K. Bhatia and A. Temkin, *Phys. Rev. A* **13**, 2322 (1976).
²²A. K. Bhatia, *Phys. Rev. A* **18**, 2523 (1978).
²³D. Rassi, V. Pejcev, and K. J. Ross, *J. Phys. B* **10**, 3535 (1977).
²⁴M. Rødbro, R. Bruch, and P. Bisgaard, *J. Phys. B* **12**, 2413 (1979).
²⁵D. J. Pegg *et al.*, *Phys. Rev. A* **12**, 1330 (1975).
²⁶P. Ziem, R. Bruch, and N. Stolterfoht, *J. Phys. B* **8**, L480 (1975).
²⁷H. P. Kelly, *Phys. Rev. A* **9**, 1582 (1974).
²⁸M. Palmquist, P. L. Altick, J. Richter, P. Winkler, and R. Yaris, *Phys. Rev. A* **23**, 1795 (1981).
²⁹C. A. Nicolaides, Y. Komninos, and D. R. Beck, *Phys. Rev. A* **27**, 3044 (1983).
³⁰D. G. Hummer and D. W. Norcross, *Bull. Am. Phys. Soc.* **24**, 1183 (1979).