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Doubly excited shape resonances in H^-

Y. K. Ho*
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

A. K. Bhatia
Laboratory for Astronomy and Solar Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

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The method of complex-coordinate rotation is used to investigate doubly excited shape resonances in H^-. We calculate resonance parameters for the ${}^1P^o$ shape resonance lying above the $n=2$ hydrogen threshold using Hylleraas-type wave functions. Comparisons are made with experimental measurements and with other theoretical calculations. In addition, we also report a calculation for ${}^3P^o$ and ${}^1D^e$ shape resonances lying above the $n=3$ hydrogen threshold.

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I. INTRODUCTION

A shape resonance in e^--H scattering is the result of the incoming electron being trapped by a potential well formed by the attractive static and polarization potentials between the incoming electron and the excited hydrogen atoms, and a repulsive angular-momentum barrier. Such a potential well may be able to support both Feshbach-type resonances and shape resonances lying above the excitation thresholds of hydrogen atoms. One ${}^1P^o$ shape resonance lying above the $n=2$ threshold has been observed in experiments. The shape resonance has been studied by the New Mexico team [1–3] in photodetachment experiments and in $1S$-$2S$ and $1S$-$2P$ excitation experiments by McGowan, Williams, and Curley [4] and by Williams [5,6]. On the theoretical side several methods have been applied to study the ${}^1P^o$ shape resonance. These methods include different variants of close-coupling approximations [7–9]: pseudostate close coupling combined with a multichannel J-matrix technique [10]; an 18-state (pseudo- and real atomic state) algebraic variational close-coupling calculation [11]; and an R-matrix calculation [12]. Other methods to investigate this shape resonance include the group-theoretical approach [13,14], hyperspherical-coordinate studies [15], and the complex-coordinate rotation method in which products of orthogonal Laguerre functions were used [16]. In comparing the results for Ref. [11] and Ref. [16], it is found that while the energies obtained by using the algebraic close-coupling calculation and that of the complex rotation calculation agree reasonably well, the difference for their widths is quite substantial. It seems an independent calculation for this state is worthwhile. In the present work, the method of complex-coordinate rotation [17] is used to investigate the ${}^1P^o$ shape resonance lying above the $n=2$ hydrogen threshold. Hylleraas-type wave functions are used to take into account the strong electronic correlation effects. In Sec. II we present our wave functions and calculations. Results are shown in Sec. III. In addition to the $n=2\ {}^1P^o$ shape resonance we have also investigated ${}^3P^o$ and ${}^1D^e$ shape resonances lying above the $n=3$ hydrogen threshold. Results are also shown in Sec. III.

II. WAVE FUNCTIONS AND CALCULATIONS

For ${}^{1,3}P^o$ wave functions we use Hylleraas type [18]

$$\Psi=\sum_{k,m,n} C_{kmn}\exp[-\alpha(r_1+r_2)]r_{12}^n[r_1^k r_2^{m+1}Y_{00}(1)Y_{10}(2)\pm r_2^k r_1^{m+1}Y_{10}(1)Y_{00}(2)] \tag{1}$$

with $k+m+n\le\omega$, a positive integer, or zero, and Y is the usual spherical harmonics.

In Eq. (1), r_1 and r_2 denote the coordinates for electrons 1 and 2, respectively, and r_{12} represents the coordinates between the two electrons.

For ${}^1D^e$ wave functions, we also use Hylleraas type [19]

$$\Psi=(f+\tilde{f})[-\mathcal{D}_2^{0+}(\theta,\phi,\psi)+\sqrt{3}\cos(\theta_{12})\mathcal{D}_2^{2+}(\theta,\phi,\psi)]+(f-\tilde{f})\sqrt{3}\sin(\theta_{12})\mathcal{D}_2^{2-}(\theta,\phi,\psi)$$
$$+(g+\tilde{g})[-\cos(\theta_{12})\mathcal{D}_2^{0+}(\theta,\phi,\psi)+\sqrt{3}\mathcal{D}_2^{2+}(\theta,\phi,\psi)]\ , \tag{2}$$

where $\mathcal{D}$ are the rotational harmonics, depending on the symmetric Euler angles θ,ϕ,ψ [20]. The trial radial functions f and g are of the Hylleraas form and are given by

$$f(r_1,r_2,r_{12})=e^{-\alpha r_1-\beta r_2}r_2^2\sum_{k,m,n\ge 0}^{N/2}C_{kmn}^{(1)}r_1^k r_2^m r_{12}^n\ , \tag{3a}$$

and

$$g(r_1,r_2,r_{12})=e^{-\alpha r_1-\beta r_2}r_1 r_2\sum_{k,m,n\ge 0}^{N/2}C_{kmn}^{(2)}r_1^k r_2^m r_{12}^n\ . \tag{3b}$$

It is implied that

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TABLE I. Convergence behavior for the $n=2\,{}^1P^o$ shape resonance in H^- ($\alpha=\beta=0.50$ and $\theta=0.7$).

ω	N	E_r (Ry)	$\frac{\Gamma}{2}$ (Ry)
15	816	−0.248 693	0.000 734
16	969	−0.248 690	0.000 715
17	1140	−0.248 704	0.000 702
18	1330	−0.248 719	0.000 688

$$\tilde{f}(r_1,r_2,r_{12})=f(r_2,r_1,r_{12}) \tag{4a}$$

and

$$\tilde{g}(r_1,r_2,r_{12})=g(r_2,r_1,r_{12}) \;, \tag{4b}$$

with $k+m+n\leq\omega$, where k,m,n are positive integers or zero.

The Hamiltonian for the electron-hydrogen system is given by

$$H=-2\nabla_1^2-2\nabla_2^2-2/r_1-2/r_2+2/r_{12}=T+V \;. \tag{5}$$

Atomic units are used in the present calculation, with the energy units in rydbergs (Ry).

In the complex-coordinate rotation method, the radial coordinates are rotated through an angle θ:

$$r\rightarrow r\exp(i\theta) \;, \tag{6}$$

and the Hamiltonian can be written as

$$H=T\exp(-2i\theta)+V\exp(-i\theta) \;. \tag{7}$$

The eigenvalues are calculated by diagonalizing the expression

$$E=\langle\Phi H\Phi\rangle/\langle\Phi\Phi\rangle \;, \tag{8}$$

wherein the wave function is real. Since the rotated Hamiltonian is complex, complex eigenvalues are obtained. The resonance parameters are determined by finding a root which is stable with respect to the variation of the nonlinear parameters α,β, and the angle θ, provided it is greater than $\arg(E_{\rm res})/2$. The complex resonance energy is given by

$$E_{\rm res}=E_r-i\Gamma/2 \;. \tag{9}$$

The theoretical aspects of the complex-coordinate rotation method [17] have been discussed in previous publications. For the computational procedures we first use the stabilization method to obtain optimized wave functions with which complex-coordinate calculations will be carried out. The use of the stabilization method as a first step for the method of complex-coordinate rotation has been demonstrated in a review [17]. Once the stabilized wave functions for a particular resonance are obtained, a straightforward complex-coordinate rotation method is applied, and the so-called "rotational paths" are examined after the complex transformation $r\rightarrow r\exp(i\theta)$ is made. We determine the optimized θ by examining the resonance complex eigenvalue when it exhibits the most stabilized characters. This is usually done by employing smaller basis expansion sets. Once the optimized value for θ is obtained, we can examine the convergence behaviors for the resonance parameters for different expansion lengths.

TABLE II. Comparison of theoretical calculations for the $n=2\,{}^1P^o$ shape resonance.

Method	E_r (Ry)	$\frac{\Gamma}{2}$ (Ry)	Author
Complex-coordinate, Hylleraas functions	$-0.248\,72\pm5\times10^{-5}$	$0.000\,69\pm5\times10^{-5}$	Present calculation
18-state close coupling	−0.248 79	0.000 735	Callaway [11]
Complex-coordinate orthogonal Laguerre functions	−0.248 70	0.000 52	Wendoloski and Reinhardt [16]
R matrix	−0.248 656	0.001 16	Pathak, Kingston, and Berrington [12]
3-state close coupling plus correlation	−0.248 675	0.000 555	Macek and Burke [8]

TABLE III. The ${}^1P^o$ shape resonance of H^- measured above the $n=2$ level of 10.198 92 eV. The reduced rydberg for hydrogen atoms is used for energy conversion (1 Ry = 13.598 56 eV).

E_r (eV)	Γ (eV)	Method	Author
		Theory	
0.0177	0.0141	Complex-coordinate, orthogonal Laguerre functions	Wendoloski and Reinhardt [16]
0.0165	0.0200	18-state close coupling	Callaway [11]
0.0183	0.0315	R matrix	Pathak, Kingston, and Berrington [12]
0.0174	0.0188	Complex-coordinate, Hylleraas functions	Present calculation
		Experiment	
0.018 ±0.002	0.022 ±0.003	Excitation cross sections (2P)	Williams [6]
0.016 ±0.002	0.021 ±0.003	Excitation cross sections (2S)	Williams [6]

III. RESULTS AND DISCUSSIONS

We use Hylleraas-type wave functions to calculate the $n=2\,{}^1P^o$ shape resonance. Using $N=969$ terms ($\omega=16$) the optimized θ at which the complex eigenvalue is found to be stable is at $\theta=0.7$. It is noted that such an optimized θ for a shape resonance is larger than those for Feshbach resonances (see Ref. [18], for example). Apparently, the use of the larger value of θ enables the cut in the complex energy plane to be rotated farther away from the shape resonance. Table I shows the convergence behavior when different expansion lengths are used. We deduce the resonance parameters as $E_r=(-0.248\,72\pm5\times10^{-5})$ Ry, and $\Gamma/2=(0.000\,69\pm5\times10^{-5})$ Ry. It should be mentioned that our calculation is not a bound calculation. The estimated errors are deduced from the stabilization characters of the complex eigenvalues. In Table II we compare our results with other theoretical calculations. It is seen that our parameters compare quite well with those of the 18-state algebraic close-coupling calculation [11]. Other earlier calculations for the ${}^1P^o$ shape resonance can be found in a review by Risley [21]. In comparing with various theoretical calculations, we should point out that the results shown in Table II are obtained basically using two different approaches. The first, like the complex-coordinate rotation, as employed in the present calculation and that in Ref. [16], calculates the resonance pole in the complex energy plane directly. The second, like the 18-state close coupling or the R-matrix approach, calculates the S matrix on the real energy axis near the resonance pole and fits the eigenphase sums to a resonance formula to obtain the resonance position and width. For a shape resonance occurring near and above a threshold, the nonresonance background changes rapidly. In the fitting procedure to extract the resonance parameters some assumptions of unknown validity have to be made about such a rapidly changing background.

Table III shows a comparison of our results with those obtained in the electron-impact excitation experiments [6]. Parameters obtained in both 2S and 2P excitation cross sections are shown here. It is seen that our results lie within the experimental errors. In the comparison with experiment, a proper perspective should be made here. The excitation cross sections are measured at real energies and the results were fitted to a model to yield the resonance positions and widths. An ideal theoretical procedure is to calculate cross sections and the results should

TABLE IV. Energy separation Δ between the ${}^1P^o$ shape and Feshbach resonances (see text for detailed discussion). The width is for the shape resonance.

Quantity	Photodetachment experiment [2]	Present calculation
Δ (eV)	0.046±0.0006	0.0460±0.0007
Γ (eV)	0.0222±0.0006	0.0188±0.0014

TABLE V. Convergence behavior for the ${}^3P^o$ shape resonance lying above the H ($n=3$) threshold ($\alpha=\beta=0.33$ and $\theta=0.6$).

ω	N	E_r (Ry)	$\frac{\Gamma}{2}$ (Ry)
15	816	−0.109 432	0.000 851
16	969	−0.109 460	0.000 844
17	1140	−0.109 475	0.000 839
18	1330	−0.109 484	0.000 843
19	1540	−0.109 490	0.000 851

TABLE VI. Comparison of the $^3P^o$ shape resonance above the H ($n=3$) threshold (threshold energy $=-0.111\,11$ Ry).

Quantity	Complex coordinate	28-state close coupling (Callaway [25])	R matrix (Pathak, Kingston, and Berrington [12])
E_r (Ry)	$-0.109\,49$ $\pm 5\times10^{-5}$	-0.1092	-0.1106
$\frac{\Gamma}{2}$ (Ry)	8.5×10^{-4} $\pm 5\times10^{-5}$	8.45×10^{-4}	6.0×10^{-6}

then be folded with the experimental beam width to compare with experiment. Since we have not done so, the comparison shown in Table II has an unknown error due to such difficulty.

Next we compare our results with those obtained in the photodetachment experiment. Special care must be taken for such a comparison. The experimental energy scale was calibrated such that the peak of their narrow $^1P^o$ Feshbach resonance below the $n=2$ hydrogen threshold was adjusted to that calculated in Ref. [10]. However, because more accurate theoretical calculations for the $^1P^o$ Feshbach resonance have appeared in the literature since then, it is better in a consistent manner to compare the energy separation between the Feshbach and shape resonances. Table IV shows the comparison. In the table Δ is defined as $\Delta=E(\text{shape})-E(\text{Feshbach})$, and the theoretical value of $E(\text{Feshbach})=-0.252\,099\,2$ Ry is taken from a recent complex-coordinate calculation [22]. To convert into eV, the reduced rydberg for hydrogen atoms 1 Ry $=13.598\,420$ eV is used (see Ref. [23]). It is seen that the theoretical energy separation of 0.0460 ± 0.0007 eV is in excellent agreement with the experimental value of 0.046 ± 0.0006 eV. The widths for the $^1P^o$ shape resonance, however, do show some differences even if both estimated errors are taken into consideration. Again, the comparison shown in Table III has an unknown error due to the theoretical difficulty, as was discussed in the last paragraph.

A $^3P^o$ shape resonance lying above the $n=2$ threshold was recently reported by Cortes *et al.* [24]. These authors used a stabilization method to estimate the resonance energy but no width was reported. We have investigated the existence of such a shape resonance, but have been unable to obtain a stabilized complex eigenvalue (both in E_r and Γ) lying above the $n=2$ threshold. This may be due to the narrowness of its width. The two electrons of this state would occupy different configurational spaces, and the width for such a state usually is quite narrow. More works are needed before the existence of the $^3P^o$ resonance lying above the hydrogen $n=2$ threshold can be established.

In addition to the $n=2$ $^1P^o$ shape resonance, we have also examined shape resonances lying above the $n=3$ hydrogen threshold. Hylleraas-type wave functions are used to calculate $^3P^o$ and $^1D^e$ resonances. We have identified stabilized complex eigenvalues for these states lying above the $n=3$ hydrogen threshold. Table V shows the convergence behaviors for the $^3P^o$ state. We deduce the resonance parameters as $E_r=(-0.109\,49\pm5\times10^{-5})$ Ry, and $\Gamma/2=(8.5\times10^{-4}\pm5\times10^{-5})$ Ry. A comparison with those of R-matrix calculations [12] is shown in Table VI. It is seen that our width differs significantly with that in Ref. [12]. Our results are in good agreement with a recent 28-state algebraic close-coupling calculation [25].

Table VII shows the convergence behaviors for the $^1D^e$ resonance when different expansion lengths are used. We deduce the resonance parameters as $E_r=(-0.102\,50\pm5\times10^{-5})$ Ry and $\Gamma/2=(0.005\,77\pm5\times10^{-5})$ Ry. This

TABLE VII. Convergence behaviors for the $^1D^e$ shape resonance above the $n=3$ hydrogen threshold ($\alpha=\beta=0.33$).

ω	N	E_r (Ry)	$\frac{\Gamma}{2}$ (Ry)
		$\theta=0.5$	
15	888	$-0.102\,507$	0.005 761
16	1050	$-0.102\,484$	0.005 767
17	1230	$-0.102\,488$	0.005 759
18	1430	$-0.102\,502$	0.005 758
		$\theta=0.6$	
15	888	$-0.102\,563$	0.005 573
16	1050	$-0.102\,477$	0.005 762
17	1230	$-0.102\,479$	0.005 800
18	1430	$-0.102\,498$	0.005 770

TABLE VIII. Doubly excited states with $K=0$ and $T=0$ (see Ref. [26]) associated with the H ($n=3$) threshold (threshold energy $=-0.111\,11$ Ry).

State	K	T	E_r (Ry)	$\frac{\Gamma}{2}$ (Ry)	Resonance
$^1S^e$	0	0	$-0.112\,277$	8.2×10^{-5}	Feshbach [27]
$^3P^o$	0	0	$-0.109\,49$ $\pm5\times10^{-5}$	8.5×10^{-4} $\pm5\times10^{-5}$	Shape
$^1D^e$	0	0	$-0.102\,50$ $\pm5\times10^{-5}$	5.77×10^{-3} $\pm5\times10^{-5}$	Shape

$^1D^e$ state and the $^3P^o$ state are believed to be members of a rotor series with quantum numbers $K=0$ and $T=0$ (see Table VIII). The lowest member of such a rotor series, the $^1S^e$ state, was, however, found to lie below the threshold and became a Feshbach resonance [27]. Callaway [25] has also found a $^1D^e$ shape resonance lying about the $n=3$ threshold. In a 28-state algebraic close-coupling calculation, he obtained resonance energy $E_r=-0.1025$ Ry, which is identical to ours, but with a smaller half-width of $\Gamma/2=0.002\,115$ Ry.

In summary, we have carried out a complex-coordinate calculation for shape resonances in H^- using Hylleraas-type wave functions. Our $^1P^o$ shape resonance lying about the $n=2$ threshold is found to be in good agreement with an 18-state close-coupling calculation and with electron-impact excitation experiments. We have also reported a calculation for $^1D^e$ and $^3P^o$ shape resonances lying above the $n=3$ hydrogen threshold. Our results are useful references for future theoretical and experimental works.

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*Present address: Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei, Taiwan, Republic of China.

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