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High-lying doubly excited $^1P^o$ states of H^-

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We report a calculation for $^1P^o$ resonance parameters in electron-hydrogen scattering converging on the $N=3$ to 9 hydrogen thresholds. Resonance energy positions and widths are calculated by using a method of complex-coordinate rotation, with quantum numbers K, T, N, and n given to each resonant state. Results are compared with the recent experimental measurements and other theoretical values.

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I. INTRODUCTION

In the present work we report results for the doubly excited $^1P^o$ resonant states in H^- below the $N=9$ hydrogen threshold. The method of complex-coordinate rotation [1] is used in the present investigation. For the intrashell resonance (the two electrons occupy the same shell) and other lower-lying resonances we use Hylleraas-type wave functions to take into account the strong electronic-correlation effects. The present work is an extension of the earlier calculations [2–4]. We investigate the detail convergence behavior such that precise resonance parameters can be established. Our results can be used as standard nonrelativistic values for the lower-lying $^1P^o$ resonances. For the intershell resonances (the two electrons occupy different shells) we report results for $nlml'\,^1P^o$, with $m \ge n$. Products of Slater orbitals are used for wave functions. The use of separable wave functions enables us to have an adequate representation of two electrons where they occupy different configurational spaces. Our results are compared with other calculations and with experimental measurements.

II. WAVE FUNCTIONS AND CALCULATIONS

The wave functions used in this work are of the Hylleraas type for the doubly excited intrashell resonances and lower-lying states,

$$\Phi = \sum_{k,m,n} C_{kmn}\exp[-a(r_1+r_2)]r_{12}^{k} \times[r_1^n r_2^{m+1} Y_{0,0}(1)Y_{1,0}(2) + r_2^n r_1^{m+1} Y_{0,0}(2)Y_{1,0}(1)] , \qquad (1)$$

TABLE I. Convergence behaviors for the $3s3p\,^1P^o(1)$ state in H^-. In the notation of $(KTNn)$, this state is (1133) ($\alpha=0.3$, $\theta=0.35$). The $^1P^o(1)$ state represents the first (lowest) $^1P^o$ resonance below $N=3$ threshold.

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
14	680	−0.125 433 719	0.001 191 42
15	816	−0.125 433 511	0.001 191 42
16	969	−0.125 433 503	0.001 191 47
17	1140	−0.125 433 510	0.001 191 49

where $k+n+m \le \omega$, with ω a positive integer. For $^1P^o$ resonances we use wave functions with up to $\omega=18$, which leads to $M=1330$ terms, where M denotes the total number of terms in the basis functions.

For states in which the two electrons occupy different shells (intershell resonances) and other high-lying states, we use products of Slater orbitals:

$$\Phi = A\sum_{la,lb}\sum_{i,j} C_{a_i,b_j}\eta_{a_i}(r_1)\eta_{b_j}(r_2)Y^{LM}_{la,lb}(1,2)S(\sigma_1,\sigma_2) , \qquad (2)$$

where

$$\eta_{a_i}(r) = r^{na_i}\exp(-\xi_{a_i} r) .$$

In Eq. (2), A is the antisymmetrizing operator, S is a two-particle spin eigenfunction, and the η are individual Slater orbitals. Y is an eigenfunction of the total angular momentum L,

$$Y^{LM}_{la,lb}(1,2) = \sum_{m_{la}}\sum_{m_{lb}} C(la,lb,L;m_{la},m_{lb},M) \times Y_{la,m_{la}}(1)Y_{la,m_{lb}}(2) \qquad (3)$$

with C the Clebsch-Gordan coefficients. For the intershell states, quite extensive basis sets are used for the wave functions. We use a total of 16 s-type, 15 p-type, 14 d-, 13 f-, 10 g-, 9 h-, 8 i-, 5 k-, 3 l-, 2 m-, and 1 n-type orbitals. These orbitals would couple to a total of 987 terms for the $^1P^o$ states.

The Hamiltonians for the H^- system is given by

$$H = -\nabla_1^2 - \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} = T + V , \qquad (4)$$

TABLE II. Convergence behaviors for the $N=3\,^1P^o(2)$ state in H^-. The quantum numbers for this state are (2034) ($\alpha=0.25$, $\theta=0.30$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
16	969	−0.117 143 662	8.918×10^{-6}
17	1140	−0.117 143 640	8.993×10^{-6}
18	1330	−0.117 143 616	8.991×10^{-6}

TABLE III. Doubly excited $^1P^o$ states below the $N=3$ hydrogen threshold. The numbers in brackets in the width column represent the power of 10 by which the preceding number is multiplied.

					Complex rotation[a]		18-state algebraic close coupling[b]		R matrix (15 state)[c]		Adiabatic		Experiment[f]	
State	K	T	N	n	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)[d]	$-E_r$ (Ry)[e]	$-E_r$ (Ry)	Γ (Ry)
$^1P^o(1)$	1	1	3	3	0.125 433 5	2.383[−3]	0.125 43	2.38[−3]	0.125 425	2.51[−3]	0.1253	0.124 42	0.125 20	2.02[−3]
(2)	2	0	3	4	0.117 143 6	1.798[−5]	0.117 14	1.79[−5]	0.117 143	1.8[−5]	0.1168			
(3)	2	0	3	5	0.112 233 4	4.2[−6]	0.112 23	4.36[−6]	0.112 290		0.1121			
(4)	1	1	3	4	0.111 814	1.4[−4]	0.111 80	1.37[−4]	0.111 806	1.33[−4]		0.111 62	0.111 46	1.18[−4]

[a] Present calculation.

[b] Callaway (Ref. [7]).

[c] Pathak, Kingston, and Berrington (Ref. [8]).

[d] Koyama *et al.* (Ref. [9]).

[e] Sadeghpour and Greene (Ref. [10]).

[f] Cohen *et al.* (Ref. [11]).

where r_1 and r_2 are the coordinates of electrons with respect to the nucleus and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. Atomic units are used in this work with energy units in Rydbergs.

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

$$r \rightarrow r\exp(i\theta) \tag{5}$$

and the Hamiltonian can be written as

$$H=T\exp(-2i\theta)+V\exp(-i\theta)\ . \tag{6}$$

Complex eigenvalues are obtained by diagonalizing the transformed Hamiltonian. The resonance parameters are determined by finding stabilized roots with respect to the variation of the nonlinear parameters α, and of the angle θ, with $\theta > \arg(E_{\text{res}})/2$. The complex resonance energy is given by

$$E_{\text{res}}=E_r-i\Gamma/2\ . \tag{7}$$

The theoretical aspects of the complex-rotation method have been discussed in previous publications [1] and will not be repeated here. Instead we only briefly describe the computational procedures. First, we use the stabilization method to obtain optimized wave functions with which complex-coordinate calculations will then 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 [1]. Once the stabilized wave functions for a particular resonance are obtained, a straightforward complex-rotation method is applied, and the so called "rotational paths" are examined. The final resonance parameters, both resonance position and width, are then deduced from the conditions that a discrete complex eigenvalue was stabilized with respect to the nonlinear parameters in the wave functions [Eq. (1)] and with respect to θ. The optimized θ is determined by examining the resonance complex eigenvalue when it exhibits the most stabilized characters. This is usually done by employing smaller basis expansion sets. For example, for the $3s3p$ $^1P^o(1)$ resonance, it is found that when $M=286$ terms ($\omega=10$), the resonance complex eigenvalue would exhibit the most stabilized character, i.e., $\partial|E|/\partial\theta \approx$ minimum at $\alpha=0.3$ and $\theta=0.35$ approximately. Once the optimized value for θ is obtained, we can examine the convergence behaviors for the resonance parameters for different expansion lengths.

For the high-lying $^1P^o$ states, we use separable Slater-type orbital wave functions. The nonlinear parameters in the wave functions are multiplied by a constant scaling parameter α'. The resonance complex eigenvalues are deduced by the stabilization condition with respect to the changes of α' and θ.

III. RESULTS AND DISCUSSIONS

In Table I we show the convergence behaviors for the $3s3p$ $^1P^o(1)$ state. In the notation of quantum numbers ($KTNn$), this state is (1133). In this work we employ

TABLE IV. Convergence behaviors for the $N=4$ $^1P^o(1)$ state in H^-. The quantum numbers for this state are (2144) ($\alpha=0.25$, $\theta=0.30$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
16	969	−0.074 355 892 97	0.001 033 43
17	1140	−0.074 358 836 5	0.001 033 43
18	1330	−0.074 358 904 6	0.001 033 57

TABLE V. Convergence behaviors for the $N=4$ $^1P^o(2)$ state in H^-. The quantum numbers for this state are (3045) ($\alpha=0.20$, $\theta=0.25$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
15	816	−0.068 587 727 6	0.000 018 209 1
16	969	−0.068 588 038 6	0.000 018 182 8
17	1140	−0.068 588 133 7	0.000 018 271 4
18	1330	−0.068 588 052 1	0.000 018 331 8

TABLE VI. Convergence behaviors for the $N=4$ $^1P^o(8)$ state in H$^-$. The quantum numbers for this state are (0144) ($\alpha=0.17$, $\theta=0.20$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
17	1140	−0.062 618 131 4	0.000 102 568
18	1330	−0.062 625 005 1	0.000 101 679
19	1540	−0.062 624 224 0	0.000 107 591

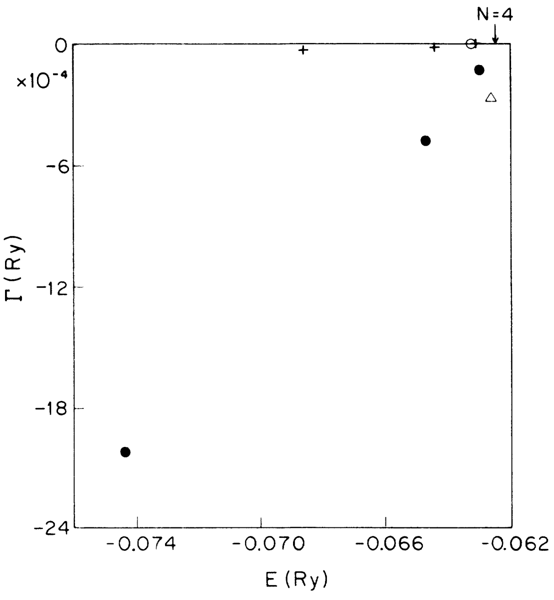

FIG. 1. Resonance complex eigenvalues below the $N=4$ hydrogen threshold: ●, (214*n*) series ($n \geq 4$); △, (014*n*) series ($n \geq 4$); +, (304*n*) series ($n \geq 5$); ○, (104*n*) series ($n \geq 5$).

quantum numbers ($KTNn$) to denote each resonance. The quantum numbers K and T were proposed by Herrick and Sinanoglu [5] and by Lin [6]. Readers are referred to the earlier references for their physical meanings, [2–4]. For the $^1P^o(1)$ resonance [the (1133) state], we fix the nonlinear parameters $\alpha=0.30$ and the optimized θ is found at 0.35 rad approximately. We calculate the complex eigenvalue as a function of ω (and of M). Up to a total of $\omega=17$ ($M=1140$) terms are used for this state. We determine the resonance parameters as $E_r=-0.125\,433\,5\pm1\times10^{-7}$ Ry and $\Gamma/2=0.001\,191\,49\pm1\times10^{-7}$ Ry. Table II shows the convergence behaviors for the $N=3$ $^1P^o(2)$ state [the (2034) state]. The optimized nonlinear parameters are found at $\alpha=0.25$ and $\theta=0.30$ rad. We estimate this state to have parameters of $E_r=-0.117\,143\,6\pm1\times10^{-7}$ Ry and $\Gamma/2=8.99\times10^{-6}\pm1\times10^{-7}$ Ry. The $N=3$ results are summarized in Table III, in which comparisons are made with other calculations and with experimental measurements. It is seen that the present calculations are in excellent agreement with those of the 18-state algebraic close-coupling calculation [7]. The 15-state R-matrix calculation [8] also agrees reasonably well with our results. Table III also shows some adiabatic calculations [9,10]. However, no widths were given in these calculations. Table III also shows a comparison with experimental observations for the (1133) and (1134) states [11]. Adequate agreement is found.

Tables IV–VI show the convergence behaviors for the (2144), (3045), and (0144) states, respectively. We estimate the resonance parameters for the (2144) state as $E_r=-0.074\,358\,9\pm5\times10^{-7}$ Ry, and $\Gamma/2=0.001\,033\,6$ $\pm5\times10^{-7}$ Ry. Similarly the resonance parameters for the (3045) state are determined to be $E_r=-0.068\,588\,1$ $\pm1\times10^{-6}$ Ry and $\Gamma/2=0.000\,018\,3\pm1\times10^{-6}$ Ry. The (0144) state would have resonance parameters of E_r

TABLE VII. Doubly excited $^1P^o$ states below the $N=4$ hydrogen threshold. The numbers is brackets in the width column represent the power of 10 by which the preceding number is multiplied.

		Complex rotation[a]		18-state algebraic close-coupling[b]		15 state R matrix[c]		Adiabatic	
State	$K\ T\ N\ n$	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)[d]	$-E_r$ (Ry)[e]
$^1P^o(1)$	12 1 4 4	0.074 358 9	2.0672[−3]	0.074 33	2.02[−3]	0.074 261	2.49[−3]	0.073 47	0.073 56
(2)	3 0 4 5	0.068 588 1	3.66[−5]			0.068 578	3.60[−5]	0.068 31	
(3)	2 1 4 5	0.064 705	4.88[−4]			0.064 648	4.50[−4]	0.064 22	0.064 16
(4)	3 0 4 6	0.064 397	1.54[−5]			0.064 383	1.60[−5]	0.064 42	
(5)	1 0 4 5	0.063 226	1.19[−5]			0.063 205			
(6)	3 0 4 7	0.063 124	6.3[−6]						
(7)	2 1 4 6	0.062 995	1.294[−4]			0.063 107	9.3[−5]		
(8)	0 1 4 4	0.062 63	2.4[−4]			0.062 703			0.062 88

[a] Present calculation.
[b] Callaway (Ref. [7]).
[c] Pathak, Kingston, and Berrington (Ref. [8]).
[d] Koyama *et al.* (Ref. [9]).
[e] Sadeghpour and Greene (Ref. [10]).

TABLE VIII. Convergence behaviors for the $N=5$ $^1P^o(1)$ state in H^-. The quantum numbers for this state are (3155) ($\alpha=0.20, \theta=0.25$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
15	816	−0.049 027 087 2	0.000 766 233
16	969	−0.049 037 843 6	0.000 767 283
17	1140	−0.049 032 216 6	0.000 772 720
18	1330	−0.049 032 735 3	0.000 766 916

TABLE IX. Convergence behaviors for the $N=5$ $^1P^o(2)$ state in H^-. The quantum numbers for this state are (4056) ($\alpha=0.17, \theta=0.20$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
16	969	−0.045 261 852 5	$2.400\,2\times10^{-5}$
17	1140	−0.045 261 555 5	$2.372\,9\times10^{-5}$
18	1330	−0.045 261 156 0	$2.391\,4\times10^{-5}$

TABLE X. Convergence behaviors for the $N=5$ $^1P^o(3)$ state in H^-. The quantum numbers for this state are (1155) ($\alpha=0.2, \theta=0.25$).

ω	M	E_r (Ry)	$\frac{1}{2}\Gamma$ (Ry)
16	969	−0.043 629 146 0	0.000 506 459
17	1140	−0.043 628 774 9	0.000 506 939
18	1330	−0.043 629 138 7	0.000 506 329

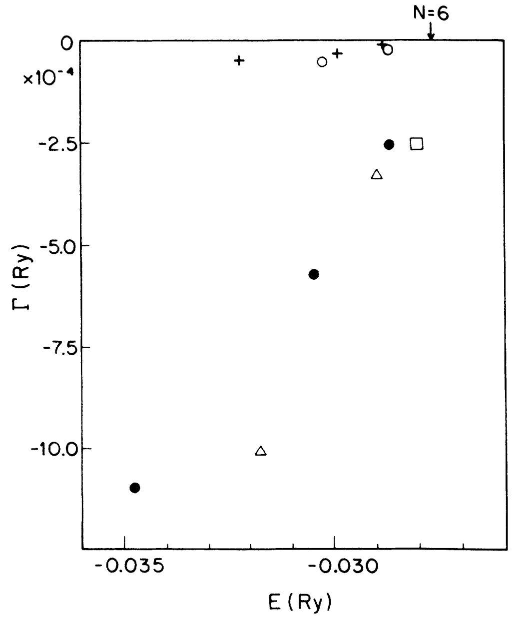

FIG. 3. Resonance complex eigenvalues below the $N=6$ hydrogen threshold: ●, (416n) series ($n\geq6$); △, (216n) series ($n\geq6$); □, (016n) series ($n\geq6$); +, (506n) series ($n\geq7$); ○, (306n) series ($n\geq7$).

$=-0.062\,624\pm1\times10^{-5}$ Ry and $\Gamma/2=0.000\,11\pm1\times10^{-5}$ Ry. We summarize our $N=4$ results in Table VII and in Fig. 1. Also in this table we compare our results with other calculations. It is seen that good agreement is found with the 18-state algebraic close coupling [7] for the (2144) state. As for the 15-state R-matrix cal-

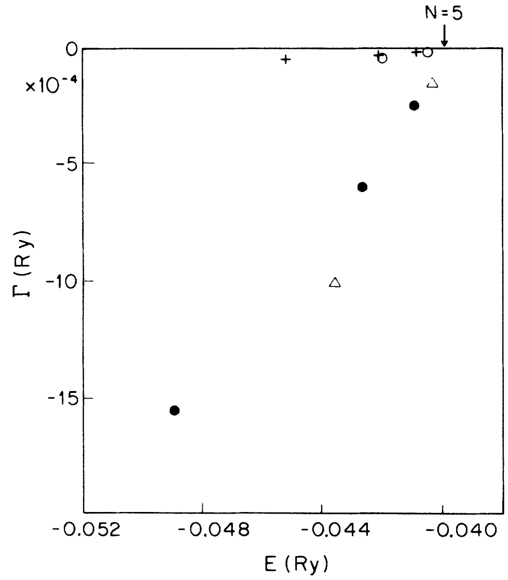

FIG. 2. Resonance complex eigenvalues below the $N=5$ hydrogen threshold: ●, (315n) series ($n\geq5$); △, (115n) series ($n\geq5$); +, (405n) series ($n\geq6$); ○, (205n) series ($n\geq6$).

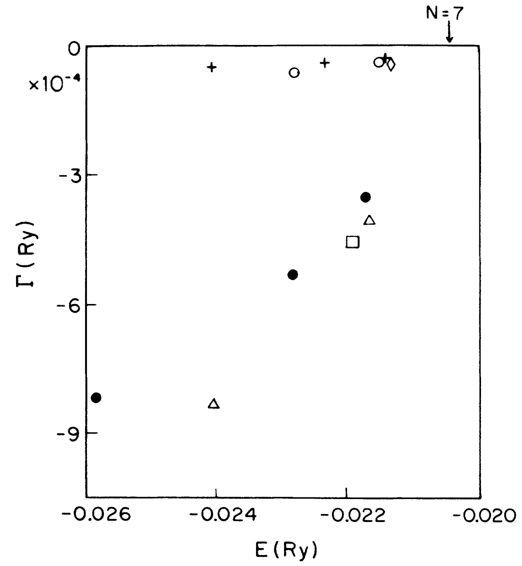

FIG. 4. Resonance complex eigenvalues below the $N=7$ hydrogen threshold: ●, (517n) series ($n\geq7$); △, (317n) series ($n\geq7$); □, (117n) series ($n\geq7$); +, (607n) series ($n\geq8$); ○, (407n) series ($n\geq8$); ◇, (207n) series ($n\geq8$).

TABLE XI. Doubly excited $^1P^o$ states below the $N=5$ hydrogen threshold. The numbers in brackets in the width column represent the power of 10 by which the preceding number is multiplied.

		Complex rotation[a]		Experiment[b]		Adiabatic	
State	$K\ T\ N\ n$	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)[c]	$-E_r$ (Ry)[d]
$^1P^o$(1)	3 1 5 5	0.049 033	1.536[−3]	0.049 036	1.58[−3]	0.049 37	0.049 04
(2)	4 0 5 6	0.045 261	4.86[-5]			0.045 16	
(3)	1 1 5 5	0.043 629	1.012[−3]			0.043 00	
(4)	3 1 5 6	0.042 656	6.0[−4]	0.042 786	1.036[−3]	0.042 69	0.042 60
(5)	4 0 5 7	0.042 140	3.00[−5]			0.042 00	
(6)	2 0 5 6	0.042 063	3.76[−5]			0.041 86	
(7)	3 1 5 7	0.040 939	2.4[−4]	0.041 234	1.05[−3]		0.040 90
(8)	4 0 5 8	0.040 894	1.4[−5]				
(9)	2 0 5 7	0.040 486	1.6[−5]				
(10)	1 1 5 6	0.040 383	1.5[−4]				

[a] Present calculation.
[b] Harris *et al.* (Ref. [12]).
[c] Koyama *et al.* (Ref. [9]).
[d] Sadeghpour and Greene (Ref. [10]).

TABLE XII. Doubly excited $^1P^o$ states below the $N=6$, 7, 8, and 9 hydrogen thresholds. The numbers in brackets in the width column represent the power of 10 by which the preceding number is multiplied.

		Complex rotation		Experiment[a]		Adiabatic	
State	$K\ T\ N\ n$	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)	Γ (Ry)	$-E_r$ (Ry)[b]	$-E_r$ (Ry)[c]
$^1P^o$(1)	4 1 6 6	0.034 727 6	1.1154[−3]	0.034 666	8.53[−4]	0.034 78	0.035 04
(2)	5 0 6 7	0.032 176 7	5.16[−5]			0.032 18	
(3)	2 1 6 6	0.031 746	9.84[−4]			0.031 28	
(4)	4 1 6 7	0.030 41	5.8[−4]	0.030 498	6.03[−4]	0.030 51	0.030 74
(5)	3 0 6 7	0.030 220	5.68[−5]			0.030 09	
(6)	5 0 6 8	0.029 865	3.4[−5]				
(7)	2 1 6 7	0.028 977	3.4[−4]				
(8)	1 0 6 7	0.028 808	1.5[−5]				
(9)	3 0 6 8	0.028 650	2.72[−5]				
(10)	4 1 6 8	0.028 631	2.6[−4]	0.029 188	4.04[−4]		0.029 06
(11)	0 1 6 6	0.027 995	2.6[−4]				
$^1P^o$(1)	5 1 7 7	0.025 838	8.18[−4]	0.025 754	9.11[−4]	0.025 98	0.025 96
(2)	6 0 7 8	0.024 042	8.36[−4]				
(3)	5 1 7 8	0.022 831	5.34[−4]	0.022 578	3.6[−4]	0.023 02	0.023 12
(4)	4 0 7 8	0.022 806	6.24[−5]				
(5)	6 0 7 9	0.022 344	4.66[−5]				
(6)	1 1 7 7	0.021 911	4.58[−4]				
(7)	5 1 7 9	0.021 722	3.56[−4]	0.021 828	1.05[−4]		0.021 76
(8)	3 1 7 8	0.021 640	4.14[−4]				
(9)	4 0 7 9	0.021 481	3.5[−5]				
(10)	6 0 7 10	0.021 463	2.9[−5]				
(11)	2 0 7 8	0.021 376	4.1[−5]				
$^1P^o$(1)	6 1 8 8	0.019 966	6.8[−4]	0.020 034	2.28[−4]		0.020 18
(2)	4 1 8 8	0.018 837	6.9[−4]				
(3)	7 0 8 9	0.018 704	5.2[−5]				
(4)	5 0 8 9	0.017 836	7.0[−5]				
(5)	6 1 8 9	0.017 778	4.76[−4]				
(6)	7 0 8 10	0.017 387	4.80[−5]				
(7)	2 1 8 8	0.017 515	5.18[−4]				
(8)	4 1 8 9	0.016 936	4.15[−4]				
(9)	3 0 8 9	0.016 876	7.2[−5]				0.016 04
$^1P^o$(1)	7 1 9 9	0.015 80	5.4[−4]				
(2)	5 1 9 9	0.015 09	5.1[−4]				

[a] Harris *et al.* (Ref. [12]).
[b] Koyama *et al.* (Ref. [9]).
[c] Sadeghpour and Greene (Ref. [10]).

culation [8], satisfactory agreement also exists, although their width for the (2144) state does differ somewhat with our result.

Tables VIII–X show the convergence behaviors for the (3155), (4056), and (1155) states, respectively. We estimate the (3155) state would have resonance parameters of $E_r=-0.049\,033\pm1\times10^{-5}$ Ry and $\Gamma/2=0.000\,768\pm1\times10^{-5}$ Ry. The (4056) state would lie at $E_r=-0.045\,261\pm1\times10^{-6}$ Ry, with a half-width of $\Gamma/2=2.39\times10^{-5}\pm1\times10^{-6}$ Ry. The (1155) state is determined to be $E_r=-0.043\,629\pm1\times10^{-6}$ Ry and $\Gamma/2=0.000\,506\pm1\times10^{-6}$ Ry. We compare our results with the recent experimental observations [12]. It is seen that the agreement for the (3155) state is very good. Their widths for the (3156) and (3157) states differ from our calculations. It is also noted that their widths for the higher-lying states differ from what might have been expected from a dipole series [13]. We summarize our results for the $N=5$ resonances in Table XI and in Fig. 2. In Table XI, we also show results for some adiabatic calculations using hyperspherical coordinates [9,10]. Our accurate results would provide assessment of merits for these calculations.

In Table XII, we summarize our $^1P^o$ doubly excited states below the $N=6$, 7, 8, and 9 hydrogen thresholds. Our $N=6$ and 7 results are also shown in Figs. 3 and 4, respectively. As compared with the recent experimental observations, it is seen that the resonance positions generally have good agreement. However, differences in widths do exist for some of the high-lying states such as the (4168), (5179), and (6188) states.

In summary, we have carried out an elaborate calculation for doubly excited $^1P^o$ resonance states of H^- below the $N=3$, 4, 5, 6, 7, 8, and 9 hydrogen thresholds. The present accurate results are useful references for other theoretical and experimental works.

ACKNOWLEDGMENT

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