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Simplified variational method for P-wave electron-hydrogen scattering

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The simplified Kohn-Feshbach variational method is used to study the phase shifts for the P-wave electron-hydrogen system. Unlike earlier calculations where the curve fitting is used to calculate the width and the shift for a resonance state, we obtained these quantities by direct integration. This permits us to study the variation of $\Gamma(E)$ and $\Delta(E)$ in the resonance region and a well-defined resonance energy position can be found. In the elastic region we obtained two resonances each for triplet and singlet states. These resonance positions compare favorably with previous accurate calculations.

I. INTRODUCTION

The study of electron-hydrogen low-energy scattering has been of special interest in the past because it is one of the simplest three-body problems for which a comparison between theoretical and experimental results can be made. Among many theoretical methods proposed to solve such a problem, the variational approach has received much attention. The variational method developed by Kohn[1] has been used to compute accurate S- and P-wave phase shifts[2,3] for electron-hydrogen elastic scattering. However, these calculations encountered some difficulties, for example, the occurrence of spurious singularities in the computation. Although Schwartz[2] has shown that these singularities can be controlled and that accurate results can still be obtained, the presence of this feature is basically undesirable. It is also very difficult to use Kohn's method to obtain convergent results in the closed-channel resonance region. To account for these difficulties, other variational procedures have been developed, for example, by Harris[4] and by Nesbet.[5] More recently a variational method based on the Feshbach formulation[6] was proposed.[7,8] In its application it was found that the difficulties encountered in Kohn's method did not appear. Furthermore, the quasiminimum nature of the Kohn-Feshbach method, i.e., the calculated phase shift gives a lower bound to the true phase shift, is suggested by Hahn[7] and numerically investigated by Truhlar and Smith[8] and Chung and Chen.[7] However, in the variational method the evaluation of continuum-continuum matrix elements can become very difficult for higher partial waves. In the earlier paper,[9] we have shown that these difficult integrals can be completely avoided without compromising in the accuracy of the results, thus further reducing the computational effort of the Kohn-Feshbach method. Some preliminary results have been presented. In this work we extend the application of this method to the calculation of widths and shifts for closed-channel resonances.

II. FESHBACH EQUATIONS AND CLOSED-CHANNEL RESONANCES

In the Feshbach formalism, the Schrödinger equation becomes

$$(PHP-E)P\Psi=-PHQ\Psi\ , \qquad (1)$$

$$(QHQ-E)Q\Psi=-QHP\Psi\ , \qquad (2)$$

where P and Q are the open-channel and closed-channel projection operators, respectively. The variation functional constructed from these equations is

$$[J_P]=J_{Pt}-\langle P\Psi|PHP-E|P\Psi\rangle-\langle P\Psi|PHQ|Q\Psi\rangle$$
$$-\langle Q\Psi|QHP|P\Psi\rangle\ , \qquad (3)$$

$$[J_Q]=\langle Q\Psi|QHQ-E|Q\Psi\rangle+\langle Q\Psi|QHP|P\Psi\rangle$$
$$+\langle P\Psi|PHQ|Q\Psi\rangle\ , \qquad (4)$$

where J_{Pt} is an appropriate term of the variational principle.[10] For elastic scattering it takes the form $\frac{1}{2}k\tan\theta$, where k represents the linear momentum and θ is the phase shift. These functionals are obtained by introducing trial functions for $P\Psi$ and $Q\Psi$ with sets of linear parameters. A set of equations is obtained by optimizing the functionals. Some of these equations involve continuum-continuum integrals which are most difficult to evaluate. The essence of the simplified variational method is that these integrals can be avoided without affecting the accuracy of the result. This procedure is discussed in Ref. 9.

Feshbach has shown that the closed-channel resonances are associated with the occurrence of the eigenvalues of the QHQ operator. Therefore, to treat the resonance which corresponds to a particular ϵ_n, we define a new set of projection operators

$$Q'=|\phi_n\rangle\langle\phi_n|\ , \qquad (5)$$

$$P' = 1 - Q' \ , \tag{6}$$

where ϕ_n is the eigenfunction of QHQ. Using this pair of projection operators the Schrödinger equation leads to

$$(E - \epsilon_n)Q'\Psi = Q'HP'\Psi \tag{7}$$

and

$$(E - P'HP')P'\Psi = P'HQ'\Psi \ . \tag{8}$$

This pair of equations can be solved to give[11]

$$Q'\Psi = \Lambda_n \phi_n \ , \tag{9}$$

where

$$\Lambda_n = \langle \phi_n | H | P'\Psi \rangle / (E - \epsilon_n) \ , \tag{10}$$

and

$$P'\Psi = \Psi_E^+ + \Lambda_n \frac{1}{E - P'HP'} P'H\phi_n \ . \tag{11}$$

Here Ψ_E^+ is the solution of $(E - P'H'P')P'\Psi_E^+ = 0$. Substituting Eq. (11) into Eq. (10), we get

$$\Lambda_n = \langle \phi_n | H | \Psi_E^+ \rangle / (E - \epsilon_n - \Delta_n + \tfrac{1}{2} i \Gamma_n) \ , \tag{12}$$

where

$$\Gamma_n = 2\pi |\langle \phi_n | H | \Psi_E^+ \rangle|^2 \ , \tag{13}$$

and

$$\Delta_n = \mathrm{P} \int \frac{|\langle \phi_n | H | \Psi_\epsilon^+ \rangle|^2}{E - \epsilon} d\epsilon \ . \tag{14}$$

The total wave function can now be written as

$$\Psi = \Psi_E^+ + \Lambda_n \frac{1}{E - P'HP'} P'H\phi_n + \Lambda_n \phi_n \ . \tag{15}$$

The appearance of the complex form in the last equation is superficial since Eq. (15) can immediately be reduced to

$$\Psi = e^{-i\beta} \left[\cos\beta \Psi_E^+ + \sin\beta \left(\mathrm{P} \int \Psi_\epsilon^+ \frac{\langle \Psi_\epsilon^+ | H | \phi_n \rangle}{(E - \epsilon)} d\epsilon + \phi_n \right) \times (\pi \langle \Psi_E^+ | H | \phi_n \rangle)^{-1} \right] \ , \tag{16}$$

where

$$\tan\beta = \frac{\frac{1}{2}\Gamma_n}{(E - \epsilon_n - \Delta_n)} \ . \tag{17}$$

Excluding the trivial phase factor, expression (16) is identical to that derived by Fano.[12] As can be found in the literature,[13] the width Γ_n of a resonance state is usually determined by making a nonlinear least-squares fit with[13]

$$\delta = a + bE + \tan^{-1}[\tfrac{1}{2}\Gamma_n / (E_{\mathrm{res}} - E)] \ , \tag{18}$$

where δ is the total phase shift, and a and b are the parameters to be determined from the curve-fitting process. However, Eq. (13) suggests that Γ_n can be calculated by direct integration if Ψ_E^+ can be calculated explicitly. In Eq. (18) Γ_n has been assumed to be a constant with respect to the energy, whereas it is actually energy dependent as clearly indicated in the Feshbach formalism. Thus, the investigation of the variation of $\Gamma_n(E)$ in the resonance region becomes a point of interest.

To compute Ψ_E^+ we note that the last term on the right-hand side of Eq. (15) is simply the nth eigenfunction of QHQ. The second term arises from the interaction of ϕ_n with the continuum as well as all the other ϕ_j's where $j \neq n$. This term is orthogonal to ϕ_n. Therefore, if we can remove the ϕ_n component from the trial function for $Q\Psi$, the solution thus obtained will neither contain ϕ_n nor its interaction term. To see this we write

$$(P'HP' - E)P'\Psi_E^+ = [(P + Q - Q')H(P + Q - Q') - E] \times (P + Q - Q')\Psi_E^+ = 0 \ . \tag{19}$$

This can be separated into

$$(PHP - E)P\Psi_E^+ = -PH(Q - Q')\Psi_E^+ \ , \tag{20a}$$

$$[(Q-Q')H(Q-Q') - E](Q - Q')\Psi_E^+ = -(Q - Q')HP\Psi_E^+ \ . \tag{20b}$$

Since the structure of Eqs. (20a) and (20b) are the same as Eqs. (1) and (2), a pair of functionals similar to those of Eqs. (3) and (4) can be constructed without much effort. Solution of these functionals by variational method gives Ψ_E^+, which can be used to compute $\Gamma_n(E)$ using Eq. (13). The shift then follows from algebraic computation. We know that

$$|\Lambda_n|^2 = |\langle \phi_n | \Psi \rangle|^2 = \frac{\Gamma_n / 2\pi}{(E - \epsilon_n - \Delta_n)^2 + \frac{1}{4}\Gamma_n^2} \ . \tag{21}$$

Since Γ_n and $|\langle \phi_n | \Psi \rangle|^2$ can be explicitly calculated, the shift Δ_n in the resonance position can be computed from Eq. (21) by simple algebra. A more precise resonance position can thus be obtained from

$$E_{\mathrm{res}} = \epsilon_n + \Delta_n(E_{\mathrm{res}}) \ . \tag{22}$$

$\Delta_n(E)$ is usually a slowly varying and monotonic function in the resonance region and therefore, E_{res} can easily be obtained by a graphic method. This will be shown and discussed in Sec. III along with other results. This method permits one to locate the resonance position without actually looking into the resonance phase shifts.

III. RESULTS AND DISCUSSION

The trial wave function used for the open-channel segment in the present work is given by

$$P\Psi = e^{-r_1}\Phi(r_2) | 01JM \rangle \pm 1 \longrightarrow 2 \ , \tag{23a}$$

where $J=1$, $M=0$, and

$$\Phi(r)=\sum_{j=1}^{N} d_j r^j e^{-tr}+(1-e^{-tr})^2 j_1(kr) - \tan\theta\,(1-e^{-tr})^3 n_1(kr)\ , \tag{23b}$$

where θ is the phase shift and j_1 and n_1 are the regular and irregular spherical Bessel functions, respectively; t is a nonlinear parameter which only affects the speed of convergence and not the converged result. For the closed-channel trial wave function we assume[7]

$$Q\Psi=Q\sum_{l=0}^{L}\sum_{i,j} C_{ijl}(r_1^i r_2^j\, e^{-(\beta r_1+\alpha r_2)} \times |l\,l+1\,JM\rangle \pm 1 \leftrightarrow 2)\ , \tag{24a}$$

where

$$Q=1-|\Psi_{100}(r_1)\rangle\langle\Psi_{100}(r_1)|-|\Psi_{100}(r_2)\rangle\langle\Psi_{100}(r_2)|\ ; \tag{24b}$$

Ψ_{100} is the ground-state wave function of the hydrogen atom. The nonlinear parameters α and β have to be determined by optimizing the variation functional.

The most accurate results for electron-hydrogen elastic P-wave phase shifts are obtained by Armstead who has used 56- to 84-term Hylleraas-type wave functions and Kohn's variational method. In the earlier paper, we have shown that the triplet phase shifts given by a simple separable trial function such as the one in Eqs. (23) and (24) agree excellently with Armstead's result. In the singlet case, our phase shift differs from his result mainly in the third or fourth decimal place. This indicates that the correlation effect is slightly more important in the singlet state as compared with that in the triplet state. However, a comparison with the results of Seiler[13] *et al.* who used the variational method proposed by Harris and Nesbet and $1s$-$2s$-$2p$-type trial wave function shows that the improvement of our result is generally over 90%. Our result is also better as compared with that of Gailitis.[14] The result for the singlet phase shifts and the comparison is given in Table I and Fig. 1. From Table I it is clear that two resonances are observed in spite of the fact that both are quite narrow. Armstead's calculation failed to obtain convergence in this energy region.

To determine the resonance positions for both triplet and singlet states we used the method described in Sec. II. We solved the eigenvalue problem variationally for QHQ to obtain ϕ_n and ϵ_n. Next, the ϕ_n component was removed from the total trial wave function to obtain Ψ_E^+. $\Gamma(E)$ was then explicitly calculated from Eq. (13) followed by the computation of $\Delta(E)$. Finally, to find E_{res} from Eq. (22) we defined $y=E$ and $y=\epsilon_n+\Delta(E)$ and

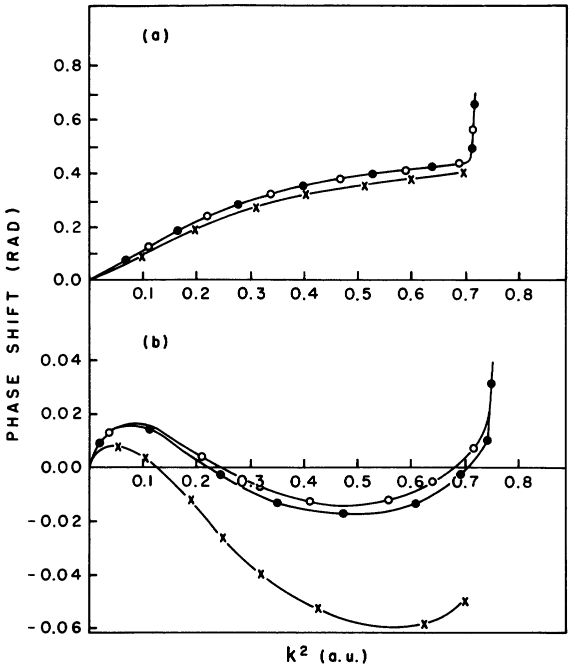

FIG. 1. (a) Triplet P-wave and (b) singlet P-wave phase shifts for electron-hydrogen elastic scattering. (*x*), $1s$-$2s$-$2p$ close-coupling calculations, open circles (○), Armstead's work, and closed circles (●), present work.

TABLE I. Singlet P-wave phase shifts (in radians) for electron-hydrogen scattering. The number in the parentheses indicates the uncertainty in the last figure quoted.

k^2 (a.u.)	Armstead[a]	SOC[b]	Gailitis[c]	Present work
0.01	0.006	0.004	0.0046	0.005 782
0.04	0.0146		0.0142	0.014 45
0.09	0.0163	0.004		0.015 50
0.16	0.0096		0.0079	0.008 46
0.25	−0.0014	−0.028	−0.0037	−0.002 87
0.36	−0.010			−0.013 029
0.49	−0.014	−0.059	−0.0178	−0.017 225
0.64	−0.005	−0.058	−0.0104	−0.009 544
0.70				−0.000 78
0.712	0.006			−0.001 882
0.715	0.0073			0.002 616
0.720	0.009		0.0017	0.003 924
0.7396	0.019			0.010 573
0.748 04				0.040(1)
0.748 05				1.084
0.748 06				2.9799(5)
0.748 09				3.0607(3)
0.749 96				6.168 18
0.749 97				6.170 68

[a] Reference 3.
[b] Reference 13.
[c] Reference 14.

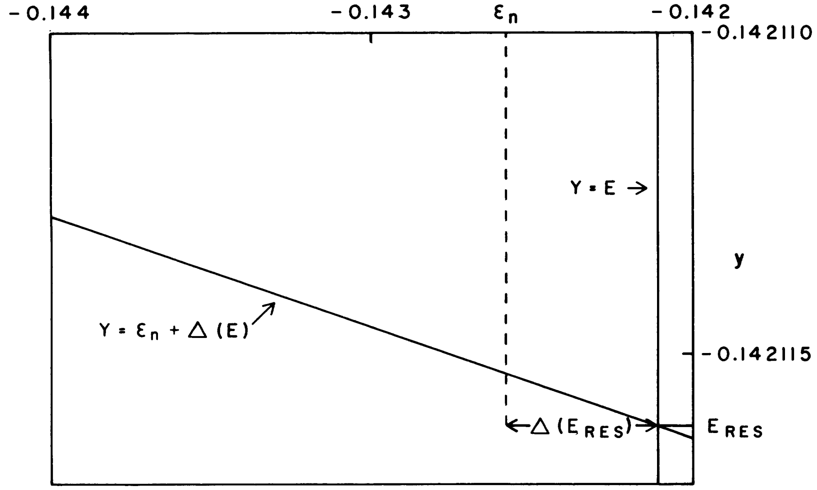

FIG. 2. Determination of the resonance position and the shift for the ^3P(1) resonance (in a.u.).

looked for the intersection of these two lines. We found this method considerably simpler as compared to the one commonly used[13] especially for relatively broad resonances. This graphic method is shown in Fig. 2. It should be noted here that Dirks and Hahn[15] also used a graphic method to search for positron-hydrogen scattering resonance, but their procedure is considerably different than the one we have used here.

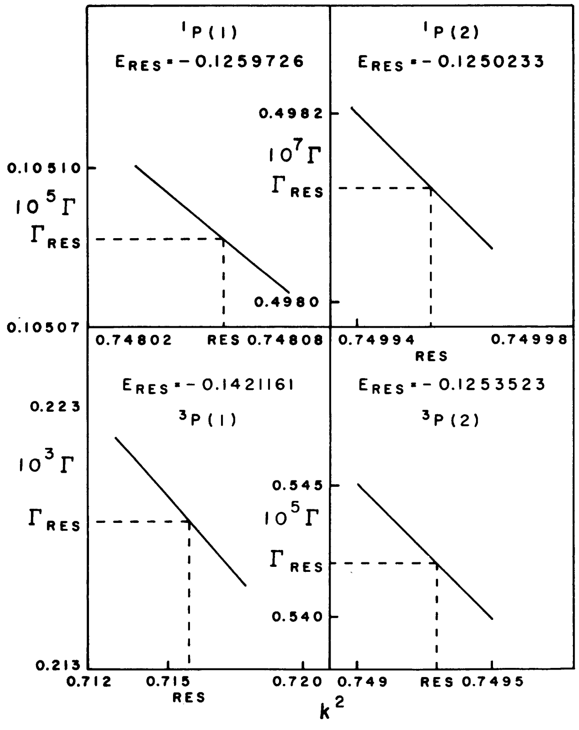

FIG. 3. Energy dependence of the widths of ^1P and ^3P resonances for elastic e-H scattering (in a.u.).

Once E_{res} is determined, $\Gamma(E_{\text{res}})$ can also be determined. This is shown in Fig. 3. The results are summarized in Table II. In these calculations a 57- or 62-parameter $Q\Psi$ is used. If more parameters are used, ϵ_n can be lowered further. For example, for ^1P resonances we obtain -0.125 998 and -0.125 029 a.u. using 76 parameters. Among the earlier works available[16,17] the best ϵ_n for the lowest ^3P state is obtained by Bhatia and Temkin[16] using a 56-parameter correlation function. It is lower than our result by 1.4×10^{-5} a.u. On the other hand, the result of Bhatia *et al.*,[17] who included correlations explicitly, is considerably higher than our result. Reference 16 quotes only the result for the lowest ^3P resonance.

The resonance states for the P-wave electron-hydrogen scattering have been studied by several authors in the past. Burke and Schey[18] have made a $1s$-$2s$-$2p$ close-coupling calculation. This is further improved by introducing correlation terms in the wave function.[19] Burke *et al.* also made a pseudostate computation for this system.[20] More recently, Seiler *et al.*[13] have studied the resonances using the variational method. The results are presented in Table III. Because of the conversion factor the quoted results of Refs. 13, 18, and

TABLE II. Resonance energies and width (in a.u.) for P-wave electron-hydrogen scattering. The superscript indicates the power of 10 with which each number should be multiplied.

		ϵ_n	Width	Shift	E_{res}
^1P	1	−0.125 975 8	0.1051^{-5}	0.316^{-5}	−0.125 972 6
	2	−0.125 023 4	0.4981^{-7}	0.72^{-7}	−0.125 023 3
^3P	1	−0.142 583 5	0.2187^{-3}	0.4674^{-3}	−0.142 116 1
	2	−0.125 361 7	0.5401^{-5}	0.94^{-5}	−0.125 352 3

TABLE III. Resonance energies and width (in eV) for electron-hydrogen scattering. For Refs. 13, 18, and 20 the conversion factor is changed from 13.605 35 to 13.597 47 eV. See Refs. 18 and 21.

	References	${}^1P(1)$	${}^1P(2)$	${}^3P(1)$	${}^3P(2)$	
$E_{\rm res}$	Present work	10.1717	10.1975	9.7326	10.1885	
	13	10.179	10.198	9.762	10.196	Algebraic 1*s*-2*s*-2*p* close-coupling calculation
	18	10.173	···	9.762	···	1*s*-2*s*-2*p* close-coupling approximation [a]
	18	10.171	···	9.734	···	1*s*-2*s*-2*p* +correlation [a]
	20	···	···	9.753	···	1*s*-2*s*-2*p* +pseudostates
	16	···	···	9.733	···	Hylleraas wave function + polarized orbital
	22	···	···	9.71 ± 0.03	···	Experimental
		10.18 ± 0.03	···	9.76 ± 0.03	···	Experimental [b]
Γ	Present work	2.86×10^{-5}	1.355×10^{-6}	5.948×10^{-3}	1.469×10^{-4}	
	13	2.42×10^{-5}	2.06×10^{-7}	7.98×10^{-3}	4.28×10^{-5}	
	18	2.26×10^{-5}	···	7.97×10^{-3}	···	
	18	4.50×10^{-5}	···	5.94×10^{-3}	···	
	20	···	···	5.71×10^{-3}	···	
	16	···	···	6.30×10^{-3}	···	
	22	···	···	>0.009	···	

[a] These results are actually quoted in Ref. 18(b).

[b] J. R. Risley, A. K. Edwards, and R. Geballe, Phys. Rev. A 9, 1115 (1974). A most complete compilation of experimental and theoretical results for electron-hydrogen scattering resonances is included in this reference.

20 have been changed. Neglecting the relativistic effect we use 13.59747 eV as the ionization energy of the hydrogen.[21] For the lowest ${}^3P$ state, our result agrees excellently with the correlation wave-function calculation and the agreement with experiment is slightly improved. In Ref. 16, the width is also obtained by integrating Eq. (13) in which Ψ_E^+ is replaced by the result of a polarized-orbital approximation. They obtained 9.733 eV for the resonance position in close agreement with this work and Ref. 19, but their resonance width is slightly larger. It appears that the width ob-

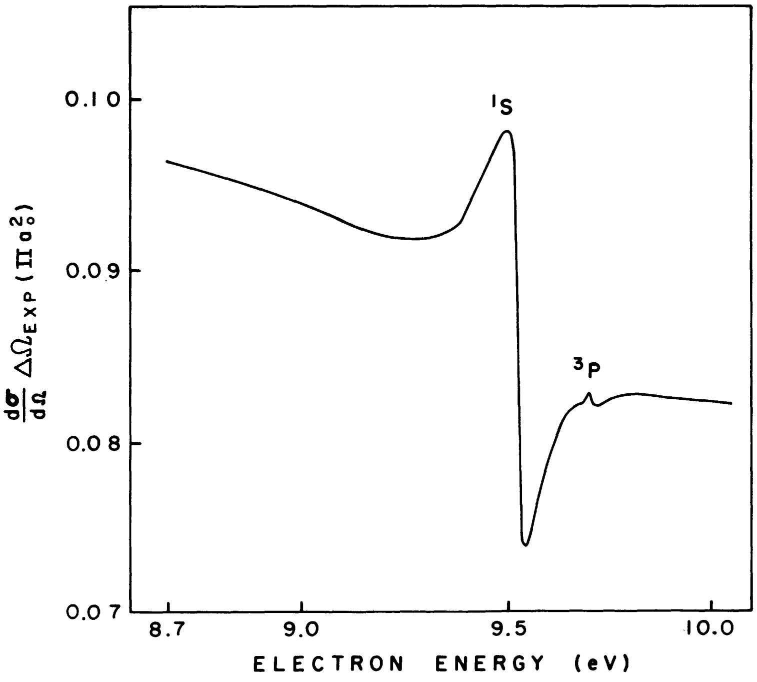

FIG. 4. *S*- and *P*-wave contribution to the total calculated cross section in the closed-channel resonance region viewed from $\theta = 90°$, $\Delta\theta = 90°$, and $\Delta\Phi = 15°$.

tained in the experiment is somewhat larger than the more accurate computations.

The lowest ^1P resonance position calculated in this work agrees closely with the correlation calculation of Burke and Taylor[19] but the width lies between that of Ref. 19 and Seiler *et al.* (see Table III). The second resonances of the triplet and singlet states was studied by Seiler *et al.*[13] Their result is somewhat different from ours. For these cases, the resonance positions and widths computed in the present work can be considered more reliable. This is because more radial correlation is included in the $Q\Psi$ of Eq. (24a) than the $2s$ and $2p$ target states used in the wave function of Ref. 13. These resonances are not reported in the numerically integrated close-coupling calculations, perhaps because they are too narrow to be easily determined.

It is perhaps worthwhile to mention that the shift $\Delta(E)$ is very sensitive to the trial function used for $Q\Psi$. For example, if we use a less flexible trial function for $Q\Psi$ so that ϵ_n is somewhat higher, we obtain a slightly larger $\Delta(E)$. This feature is also seen in some of the earlier work.[23] Figure 4 shows the S- and P-wave contributions to the total scattering cross section.

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