Projection-Operator Approximation for Autoionization States in the Inelastic Scattering Region

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(Received 8 June 1972)

A projection-operator technique is used to investigate the resonance states of two-electron systems in the inelastic scattering energy region. Computations are carried out for the P autoionization states for He and the H^- ion in the $n = 2$ to $n = 3$ energy region. The results are compared with previous calculations and experiments. For the ^1P resonance of He, very good agreement is obtained as compared with the accurate measurement of Madden and Codling.

INTRODUCTION

The study of the autoionization state of atomic systems has generated vast interest in the past.[1] In the last decade great advances have been made both experimentally and theoretically. For example, the success of the close-coupling calculation[2] predicted the existence of closed-channel resonances. The projection-operator formalism of Feshbach[3] also puts these resonance phenomena of a firm theoretical ground. Most investigation so far are limited to the elastic scattering energy region where the projection-operator technique has demonstrated its effectiveness repeatedly.[4-6] In the inelastic scattering region, theoretical investigations are few and only very limited successes[7-9] have been reported, and to my knowledge no projection-operator techniques were applied. Experimentally, accurate measurements have been made in this region, for example, for electron-atom collision.[10] For helium, perhaps the most accurate measurements for resonance states is the spectroscopy experiment by Madden and Codling.[11] For ^1P states in the $n = 2$ to $n = 3$ energy region, they observe at least six resonances. No theoretical investigations have been made to interpret their result quantitatively.

In the present work, we will use the projection-operator approximation to investigate the P resonance states in the $n = 2$ to $n = 3$ energy region for the H^- and He systems. For ^1P resonance states of helium, dipole transition matrix elements will be calculated to compare with the experimental observation.

PROJECT-OPERATOR FORMALISM

In the Feshbach formalism, the Schrödinger equation becomes[3]

$$\left(PHP + PHQ \frac{1}{E - QHO} QHP - E\right) P\Psi = 0 , \tag{1}$$

where P and Q are the open- and closed-channel projection operators, respectively. A spectral decomposition can be made for the optical potential. Using ϕ_n, the eigenfunction of QHQ, we have

$$\left(PHP + \sum_n \frac{PH\phi_n\rangle\langle\phi_n HP}{E - \epsilon_n} - E\right) P\Psi = 0 . \tag{2}$$

It is clear from Eq. (2) that the closed-channel resonance arises when the energy E approaches one of the eigenvalues of QHQ.

In the neighborhood of an isolated resonance, one can study the solution of the Schrödinger equation as follows: We define a pair of new projection operators[12]

$$Q' = |\phi_n\rangle\langle\phi_n| , \tag{3a}$$

$$P' = 1 - Q' . \tag{3b}$$

In this case,

$$(E - \epsilon_n) Q'\Psi = Q' HP'\Psi , \tag{4}$$

i.e.,

$$Q'\Psi = \Lambda_n \phi_n , \tag{5}$$

where

$$\Lambda_n = \langle \phi_n| H| P'\Psi\rangle/(E - \epsilon_n) . \tag{5a}$$

Equation (1) becomes

$$(E - P'HP') P'\Psi = \Lambda_n P'H\phi_n . \tag{6}$$

Therefore

$$P'\Psi = \psi_0^{(+)} + \Lambda_n \frac{1}{E - P'HP'} P'H\phi_n , \tag{7}$$

where $\psi_0^{(+)}$ is the solution to the homogeneous equation. Inserting Eq. (7) into Eq. (5a), we obtain

$$\Lambda_n = \frac{\langle \phi_n| H| \psi_0^{(+)}\rangle}{E - \epsilon_n + \langle \phi_n| HP'[1/(E - P'HP')]P'H| \phi_n\rangle} . \tag{8}$$

The total wave function is now given by

$$\Psi = \psi_0^{(+)} + \Lambda_n \frac{1}{E - P'HP'} P'H\phi_n + \Lambda_n \phi_n . \tag{9}$$

The first term on the right-hand side represents the background continuum. The second term comes from the coupling of ϕ_n to the continuum. To investigate the dipole radiation to the ground state, we need to compute the dipole matrix element $|\langle \Psi | \vec{r} | \psi_{gr} \rangle|^2$, where ψ_{gr} is the ground-state wave function. In the present work, we shall neglect the contribution from the background continuum. Furthermore, we neglect the coupling term on the assumption that it is relatively small in the part of coordinate space where ψ_{gr} is large. The "oscillator-strength density" becomes

$$f_{n0} = 2m(E_n - E_{gr})|\Lambda_n|^2 |\langle \phi_n | \vec{r} | \psi_{gr} \rangle|^2 . \tag{10}$$

From Eq. (8) we have

$$|\Lambda_n|^2 = \frac{\Gamma_n/2\pi}{(E - \epsilon_n - \Delta_n)^2 + (\Gamma_n/2)^2} , \tag{11}$$

where Δ_n is the shift of the resonance position from ϵ_n and Γ_n is the width of the resonance state. It is apparent that $|\Lambda_n|^2$ is only significant within a small energy region for small Γ_n. To compare with the line intensity we integrate over the neighborhood of a resonance. Assuming Δ_n and Γ_n are essentially constant over a very small energy range,

$$\int_{\Delta E} |\Lambda_n|^2 dE \simeq \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{1}{x^2 + 1} dx = 1 . \tag{12}$$

Hence

$$F_{n0} = \int f_{n0} dE \simeq 2m(E_n - E_{gr})|\langle \phi_n | \vec{r} | \psi_{gr} \rangle|^2/\hbar^2 . \tag{13}$$

Although Eq. (11) seems to suggest a Lorentz distribution of line intensity, this is due only to the approximation we have made. The interference with the continuum can change the structure of line intensity considerably.[13]

TRIAL FUNCTION

Since ϕ_n decays exponentially at large distances the most effective trial function for two-electron atomic system is probably the Hyllerass-type wave function. They include the correlation of the two electrons explicitly. These have been used in computing ϵ_n's by Bhatia et al.[5] However, for resonances in the inelastic scattering energy region, the two electrons are further apart; the inclusion of r_{12} coordinate in the wave function becomes less important. Other types of trial functions usually used are the Slater orbitals,[5] hydrogenic functions, and Sturium functions.[6] Each method has some advantages as well as disadvantages. Recently, a more flexible configuration-interaction trial function was adopted to calculate the resonances in the elastic scattering region; excellent results were reported.[14] Following this choice, we assume

$$\phi_n = \sum_{k,m} \sum_l C_{kml} (r_1^k r_2^m e^{-(zr_1/3 + \beta r_2)})$$

$$\times |JMl\, l+1\rangle \pm 1 \mp 2)$$

$$+ \sum_{k,m} \sum_{l=0}^{1} C_{kml} (r_1^k r_2^m e^{-(zr_1/3 + \beta r_2)})$$

$$\times |JMl+1\, l\rangle \pm 1 \mp 2) , \tag{14}$$

where z is the nuclear charge and the second summation ensures that the $3p - ns$- and $3d - np$-type wave functions are properly included. In the present calculation $J = 1$, $M = 0$ is taken. To use a simpler notation, Eq. (14) can be written

$$\phi_n = \sum_{k,m,l} C_{kml} \zeta_l (k, m, \tfrac{1}{3}z, \beta) . \tag{15}$$

In the $n = 2$ to $n = 3$ energy region, $1s$, $2s$, $2p$ all belong to the open channel. Therefore,

$$Q = [1 - P_{1s}(1) - P_{2s}(1) - P_{2p}(1)]$$

$$\times [1 - P_{1s}(2) - P_{2s}(2) - P_{2p}(2)] . \tag{16}$$

The P_{nl}'s are defined as

$$P_{nl}(1) = \sum_{m=-l}^{l} |\psi_{nlm}(\vec{r}_1)\rangle \langle \psi_{nlm}(\vec{r}_1)| \tag{17}$$

and ψ_{nlm} is the hydrogenlike wave function. To operate these projection operators on our trial function, we notice that

$$[p_{1s}(1) + P_{1s}(2)] \zeta_l(k, m, \alpha, \beta)$$

$$= \delta_{l0} \left(\frac{\zeta_l(k, 0, \alpha, 1)(m+2)!}{(\beta+1)^{m+3}} \right.$$

$$\left. + \frac{\zeta_l(0, m, 1, \beta)(k+2)!}{(\alpha+1)^{k+3}} \right) , \tag{18}$$

where δ_{l0} is the Kronecker δ. Similar results can be obtained for P_{2s} and P_{2p}. The Hamiltonian of our system is

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - (z/r_1) - (z/r_2) + (1/r_{12}) . \tag{19}$$

Utilizing Eq. (18), the computation for the integral $\langle Q\Psi | H - E | Q\Psi \rangle$ can be greatly simplified.

RESULT AND DISCUSSION

For the lowest ^1P resonance of helium, the optimized value for β is close to $\tfrac{1}{3}z$. To avoid the secular equation becoming too singular, the second summation in Eq. (14) is neglected. With a three partial wave and 18 parameter wave function, we obtain -0.3331 a.u. for the energy eigenvalue for this state. If 35 parameters are included, ϵ_n become -0.33554 a.u. The lowest result -0.33583 a.u. is obtained by using a four partial wave and 76 parameter trial function. The experiment of Madden and Codling gives -0.33294 (± 0.00150) a.u. for the position of maximum line intensity. This

TABLE I. ^1P autoionization states of helium in the $n=2$ to $n=3$ energy region (in a.u.). N is the number of linear parameters, β is the value of the nonlinear parameter, and L is the number of partial waves used. $(-M)$ indicates $(0.1)^M$.

Level sequence	N	β	L	ϵ_n	$N_{sp}/N_{pd}/N_{df}$	$|\langle\phi_n|z_1+z_2|\psi_{gr}\rangle|^2$	Series	E_{max} (expt)[a]
1	76	0.71	4	−0.335 827	0.506/0.482/0.012	3.31(−4)	(+)	−0.332 94 (150)
2	75	0.39	3	−0.286 020	0.761/0.232/0.007	5.44(−7)	A	
3	75	0.48	3	−0.282 839	0.436/0.363/0.201	5.04(−5)	B	
4	75	0.36	3	−0.271 126	0.410/0.548/0.042	1.71(−4)	(+)	−0.269 80 (46)
5	75	0.36	3	−0.267 505	0.227/0.589/0.175	2.97(−7)	C	
6	75	0.26	3	−0.257 441	0.733/0.255/0.012	4.42(−7)	A	
7	75	0.26	3	−0.251 206	0.570/0.224/0.206	2.30(−6)	B	
8	75	0.24	3	−0.250 481	0.221/0.644/0.135	9.03(−5)	(+)	−0.249 86 (46)
9	75	0.22	3	−0.248 004	0.250/0.573/0.177	2.50(−8)	C	
10	75	0.22	3	−0.244 912	0.148/0.349/0.503	1.21(−8)	D	
11	80	0.22	3	−0.244 371	0.701/0.281/0.016	3.78(−7)	A	
12	80	0.20	3	−0.240 497	0.251/0.668/0.081	4.53(−5)	(+)	−0.240 24 (46)
13	80	0.20	3	−0.240 215	0.541/0.204/0.249	1.62(−6)	B	
14	80	0.18	3	−0.239 123	0.250/0.568/0.182	1.23(−7)	C	
15	80	0.18	3	−0.237 648	0.151/0.345/0.504	5.45(−8)	D	
16	80	0.15	3	−0.236 924	0.629/0.358/0.013	2.76(−10)	A	
17	80	0.14	3	−0.234 350	0.164/0.785/0.051	1.77(−5)	(+)	−0.234 93 (46)

[a]Madden and Codling, see Ref. 11. The number in the parentheses gives the standard deviation in the last few digits quoted.

discrepancy is due to two factors: First, the shift Δ_n is not computed in the present calculation; second, the resonance position differs from the maximum-intensity position, i.e., $E_{res}=E_{max}-\Gamma_n/q_n$. For this state Γ_n is relatively large and q_n is positive[13] hence, E_{res} is considerably lower than the experimental value E_{max}. In this connection, it is interesting to note that in Ref. 13 the estimated value for Γ/q is 0.0016 a.u. for this state. The only other theoretical calculation is carried out by Taylor and Burke[8] using $1s$-$2s$-$2p$ plus 20 correlation functions. Their result gives 0.0075 a.u. for the width and −0.334 a.u. for the energy of this state. Since no closed-channel states were included in their computation, the agreement between the two computations should be considered

satisfactory.

For higher resonances, the second summation in Eq. (14) is included. In these calculations, we used up to 75 or 80 parameters in the trial function. Considerably more autoionization states are obtained as compared with the lines observed in the experiment. Theoretically speaking, there might be five possible resonance series in this energy region. This arises from the linear combination of $3s$-np, $3p$-ns, $3p$-nd, $3d$-np, $3d$-nf basis. The observed series should correspond to the most prominent series. To demonstrate this point, we need first to classify the energy states into various series. We then compute the dipole matrix element $|\langle\phi_n|z_1+z_2|\psi_{gr}\rangle|^2$ for each series, and finally compare the observed energy positions with our

TABLE II. ^3P Autoionization states of helium in the $n=2$ to $n=3$ energy region (in a.u.) for notation see Table I.

Level sequence	β	N	$|\langle\phi_n|z_1+z_2|\psi_{3S}\rangle|^2$	ϵ_n	$N_{sp}/N_{pd}/N_{df}$	Series
1	0.75	76	9.04(−2)	−0.351 790	0.821/0.178/0.001	(+)
2	0.69	76	8.72(−3)	−0.310 951	0.180/0.750/0.069	A
3	0.38	75	1.85(−2)	−0.280 094	0.770/0.216/0.005	(+)
4	0.38	75	1.00(−2)	−0.278 847	0.422/0.541/0.037	B
5	0.34	75	1.48(−3)	−0.260 328	0.205/0.652/0.143	A
6	0.32	75	2.65(−3)	−0.258 022	0.451/0.248/0.301	C
7	0.28	80	8.64(−3)	−0.255 412	0.757/0.234/0.008	(+)
8	0.28	80	4.35(−3)	−0.253 502	0.375/0.564/0.061	B
9	0.24	75	1.10(−4)	−0.245 305	0.193/0.400/0.407	D
10	0.25	80	9.77(−4)	−0.244 932	0.250/0.582/0.167	A
11	0.22	80	9.37(−4)	−0.243 748	0.340/0.239/0.417	C
12	0.205	80	4.81(−3)	−0.243 294	0.765/0.225/0.010	(+)
13	0.205	80	2.26(−3)	−0.242 118	0.328/0.0591/0.080	B

TABLE III. P autoionization state of H⁻ in the $n=2$ to $n=3$ energy region (in a.u.). For notation see Table I.

	Level sequence	β	N	ϵ_n	L	E_{res} (Burke et al.)[a]	E_{res} (expt.)[b]
	1	0.30	76	$-0.062\,468$	4	-0.0621	-0.0622 ± 0.0007
^1P	2	0.13	75	$-0.058\,583$	3		
	3	0.06	75	$-0.056\,109$	3		
	4	0.07	75	$-0.055\,832$	3		
	1	0.31	76	$-0.068\,292$	4	-0.0677	-0.0667 ± 0.0007
^3P	2	0.11	75	$-0.057\,483$	3	$-0.057\,23$	
	3	0.09	75	$-0.056\,332$	3		
	4	0.06	75	$-0.055\,876$	3		

[a]See Ref. 7.   [b]See Ref. 10.

calculation.

To help us identify each series of resonances, we compute the contribution from each partial wave to the normalization. We impose the condition

$$\langle \phi_n \mid \phi_n \rangle = N_{sp+pd} + N_{pd+dp} + N_{df} + \cdots = 1 \qquad (20)$$

and compare the ratio of $N_{sp+ps} : N_{pd+dp} : N_{df}$. The results are given in Table I.

In this table, we list 17 ^1P resonances in the $n=2$ to $n=3$ energy region. For convenience of discussion we classify the five series as (+), A, B, C, D series. The ground-state wave function ψ_{gr} is a 65 parameter configuration-interaction wave function; it gives -2.9028 a.u. for the energy of the ground state. We compare the five resonance states whose level positions lie very close to the observation lines; these belong to the (+) series. The dipole matrix elements for these series are considerably larger than those of the unobserved states. The only exception is the lowest B series, which has not been reported in the experiment. This may be understandable since the transition from the two lowest states in the (+) series are much more intense and the width of these two states are relatively large. In general, the agreement between the result in Table I and those of experiment must be considered as very good.

For the ^3P resonances of helium, no detailed experimental observations have been reported. In Table II, we list 13 resonance states. Since transition to the ground state is forbidden, we compute the dipole matrix element to the $2\,^3S$ state which has an extremely long lifetime. The wave function

we used for this state is similar to that of the ground state; it gives -2.175214 a.u. for the energy of the $2\,^3S$ state. This is to be compared with the most accurate value of -2.175229 a.u. by Pekeris[15] and by Chung and Hurst.[16] The lowest resonance calculated by Taylor and Burke[8] gives -0.350 a.u. for resonance energy. The result here for the same state gives -0.35179 a.u. The dipole matrix element in Table II seems to suggest that the transition line here will be more intense than those observed in the ^1P case. The transition wavelength should be between 230 to 250 Å. Since $2\,^3S$ has a long lifetime, it would be of interest to see this experiment being carried out.

I have also computed the P autoionization states of H⁻ in the $n=2$ to $n=3$ energy region. The results are given in Table III. For the lowest ^1P resonance we obtain -0.0625 a.u. for the energy of this state; this is to be computed with the experimental result -0.0622 ± 0.0007 a.u. of Mc-Gowan et al.[10] Burke, Ormonde, and Whitaker[7] use a six-state close-coupling calculation and obtain -0.0621 a.u. No higher members of resonances are reported in their work. For the lowest ^3P resonance, we obtain -0.0683 a.u. for the energy as compared with -0.0677 a.u. by Burke et al.[7] The experimental results give -0.0667 ± 0.0007 a.u. In our calculation β values range from 0.31 to 0.06. Four autoionization states are obtained for triplets as well as singlets. As we decrease β, more autoionization states appear. These states, however, are extremely close to the threshold; no effort has been made to calculate them.

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Minimum-Variance Method for Potential Scattering

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(Received 26 May 1972)

In variational solutions of differential or integral equations the variance integral and variance sum provide measures of the inadequacy of the trial function. For certain potential-scattering problems the variance integral can be used to derive rigorous upper and lower bounds to the phase shift. In more general scattering problems, the study of the variance sum or integral gives a check on the convergence of the standard variational calculations, and an alternative criterion for choosing the best trial function. Results are shown for an attractive exponential potential.

I. INTRODUCTION

The standard variational principles[1] for scattering are the extensions of the Rayleigh-Ritz principle by Hulthén,[2] Kohn,[3] and Rubinow.[4] Similar methods have been suggested more recently by Harris and Michels.[5] These methods share several unsatisfactory features.

(a) Convergence of the results can be misleading. As the number of variational parameters is increased, the results obtained by the standard techniques may converge rapidly to a common value, but there is no guarantee that this is the correct value. It is easy to construct an example of a calculation where convergence to the wrong value is achieved. For example, in studying e-H collisions at an energy of 0.005 a.u. (0.14 eV), we obtained the results shown in Table I. For each of the three standard techniques, the phase shift is given for trial functions with three, six, and 12 parameters. In each case the convergence is fast, and the three answers for the 12-term function agree to eight significant figures. However, the correct value for the phase shift, as given by Schwartz, is 2.551, in contrast to the value of 2.396 obtained by each of these methods. The explanation for this discrepancy is that the trial wave functions were constrained so that no matter how many adjustable parameters were introduced, one of the two indistinguishable electrons was always in the $1s$ hydrogenic state. Thus the result should converge to the one-state-exchange approximation value, as indeed it does.

In performing this calculation we deliberately restricted the trial wave functions so that they do not span the whole function space. In more serious calculations, of course, one tries to ensure that the trial functions span the whole space as best one can. However, the standard techniques are unable to indicate whether this desired spanning of the function space actually has been achieved. Hopefully, the variational theorem ensures that we have chosen the best possible wave function within the space spanned by the trial function, but the variational theorem assuredly does not tell us how important the rest of the function space may be.

(b) The standard methods do not give upper and lower bounds on the phase shift. This difficulty clearly is related to difficulty (a); the problem of obtaining rigorous bounds will be discussed in Sec. III.

(c) The wave functions obtained by these methods may be relatively poor for other purposes, such as photoionization studies, even though they give good phase shifts.

(d) The application of the standard theories to systems with many electrons and several open

TABLE I. Phase shifts of e-H scattering at $k = 0.1$ a.u.

No. of parameters	Hulthén	Kohn	Rubinow
3	2.365 97	2.355 72	2.341 94
6	2.395 64	2.395 66	2.395 64
9	2.395 789	2.395 788	2.395 792
12	2.395 818 2	2.395 818 2	2.395 818 2