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Resonances in Multichannel Scattering*

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The formalism of Feshbach as used by O'Malley and Geltman for finding resonances in elastic electron-hydrogen scattering is extended to more than one channel. A result of Feshbach's is rederived. It is found that resonances occur in all open channels at the same energy and with the same width. Infinities of "resonances" are found below the higher N levels in electron-hydrogen scattering, and recurrence relations determining the relative positions of the higher resonances are found.

I. INTRODUCTION

IN recent years, resonances in elastic scattering have received much attention in the field of electron scattering by atoms. This began with the theoretical discovery by Burke and Shey[1] of an elastic scattering resonance in the scattering of electrons by atomic hydrogen in its ground state. This was quickly followed by other calculations[2] confirming the first resonance and finding others. In all these methods the resonances were obtained by solving a complicated set of equations for the phase shift as a function of energy. Since the resonances are all very narrow, very many energy points were necessary, and there is no guarantee with this method that resonances have not been missed.

More recently, O'Malley and Geltman[3] have used a formalism of Feshbach[4] in which the definition of a resonance is made more precise. But more to the point, the approximate calculation of the position of the resonance is reduced to finding the lowest eigenvalues of some Hamiltonian. O'Malley and Geltman used the method to reproduce the approximate positions of the elastic resonances in electron-hydrogen scattering. In this paper we extend the idea to multichannel scattering so that resonances in excitation processes are described. An interesting result of Feshbach's is derived but given slightly different emphasis; that is, if a resonance occurs in any one state amplitude (for instance for the elastic scattering), it will also occur in *all* the other states (the excitation amplitudes will also be resonant) at the same energy and with the same width.

The formal derivation is presented in the next section. Unlike O'Malley and Geltman who used a standing-wave formalism to obtain expressions for the tangent of the phase shift (K matrix), an outgoing wave formalism is used here so that the connection with the cross sections can be made more directly. In Sec. III an application is made to resonances in electron-hydrogen scattering just below each of the higher thresholds. There is a single infinite sequence of resonances below the $n=2$ threshold for total angular momentum equal to zero. It is also found that there is the same kind of sequence below the $n=3$ level, but that below the $n=4$ and higher levels there are multiple sequences.

II. FORMAL DERIVATION

The starting point of our discussion is, of course, the Schrödinger equation

$$(E-H)\psi^{(+)}=0 \tag{1}$$

with the boundary conditions

$$\lim_{r_0\to\infty}\psi^{(+)}(0,1\cdots)\to\sum_{n=0}^{N}\left(e^{i\mathbf{k}_0\cdot\mathbf{r}_0}\delta_{n0}+f_{n0}(\hat{r}_0,\hat{k}_0)\frac{e^{ik_nr_0}}{r_0}\right)\times\phi_n(1\cdots z)\,, \tag{2}$$

where the ϕ_n are the bound-state wave functions of the target and the $f_{n0}(\hat{r}_0,\hat{k}_0)$ are the amplitudes for the transition from the initial state, 0, to the state n. k_n is the momentum available to the outgoing particle when the target is left in the nth state. We have assumed that only the $(N+1)$ lowest states may be excited. The next step is the definition of a projection operator P and its complement $Q=1-P$, such that P projects out of $\psi^{(+)}$ all of the open-channel components of $\psi^{(+)}$. The construction of this projection operator has been discussed in many places,[4] and we shall not dwell upon it here. The wave function for the open-channel part of ψ is then $P\psi$. It satisfies the Schrödinger equation

$$[EP-P\mathcal{H}P]P\psi^{(+)}=0\,, \tag{3}$$

where

$$\mathcal{H}=H+HQ\frac{1}{E+i\eta-QHQ}QH\,. \tag{4}$$

The infinitesimal $i\eta$ has been inserted to make the outgoing-wave boundary condition more explicit.

The operator $Q[E+i\eta-QHQ]^{-1}$ may be represented by

$$\frac{Q}{E+i\eta-QHQ}=\sum_\nu\frac{u_\nu(01\cdots z)u_\nu^*(0'1'\cdots z')}{E_\nu+i\eta-\epsilon_\nu}\,, \tag{5}$$

where the u_ν are the complete (in the space of Q) normalized set of eigenfunctions of QHQ and ϵ_ν are their

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[1] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 149 (1962).

[2] See K. Smith, National Bureau of Standards Report (1965) for a comprehensive review.

[3] T. F. O'Malley and S. Geltman, Phys. Rev. **137**, A1344 (1965).

[4] H. Feshbach, Ann. Phys. (N. Y.) **19**, 287 (1962).

eigenvalues. One might expect the spectrum of the ϵ_ν to start at W_{N+1}, the energy of the lowest state of the target which cannot be excited, and go up since Q forbids the target from lying below W_{N+1}. However, the system of target plus projectile may form one or more "bound" states with the Hamiltonian QHQ. These states will cause resonances. For the sake of clarity let us suppose only one such state exists and call it u_0,

$$\mathcal{H}=\left[H+\sum_{\nu\neq 0}\frac{Hu_\nu u_\nu{}^*H}{E-\epsilon_\nu+i\eta}\right]+\frac{Hu_0u_0{}^*H}{E-\epsilon_0+i\eta}. \tag{6}$$

We denote the term in the bracket by $\hat{H}$. Then suppose the solution to

$$[EP-P\hat{H}P]P\hat{\psi}_{k_0}{}^{(+)}=0 \tag{7}$$

is known. Then the solution to Eq. (3) can be written

$$P\psi^{(+)}=P\hat{\psi}^{(+)}+\hat{G}^{(+)}Hu_0>\frac{1}{E-\epsilon_0+i\eta}\langle u_0HP\psi^{(+)}\rangle, \tag{8}$$

where $\hat{G}^{(+)}$ is the outgoing wave Green's function,

$$[EP-P\hat{H}P]\hat{G}^{(+)}=P. \tag{9}$$

The last term in Eq. (8) is a separable potential so that the solution of Eq. (8) is immediately

$$P\psi^{(+)}=P\hat{\psi}^{(+)}+\hat{G}^{(+)}Hu_0> \frac{1}{E-\epsilon_0-\langle u_0H\hat{G}^{(+)}Hu_0\rangle+i\eta}\langle u_0HP\hat{\psi}^{(+)}\rangle. \tag{10}$$

The amplitude for scattering is then obtained from the asymptotic form of $\hat{G}$.[5]

$$f_{n0}(\hat{k}_n,\hat{k}_0)=\hat{f}_{n0}(\hat{k}_n,\hat{k}_0)-\frac{1}{4\pi}\frac{\langle\hat{\psi}_{k_n}{}^{(-)}PHu_0\rangle\langle u_0HP\hat{\psi}_{k_0}{}^{(+)}\rangle}{E-\epsilon_0-\langle u_0H\hat{G}^{(+)}Hu_0\rangle+i\eta}, \tag{11}$$

where $P\hat{\psi}_{k_n}{}^{(-)}$ is the time-reversed wave function with incoming-wave boundary conditions and where f_{n0} is the amplitude obtained from $\hat{\psi}^{(+)}$. The differential cross section is then

$$\frac{d\sigma_{n0}}{d\Omega}=\frac{k_n}{k_0}\left|\hat{f}(\hat{k}_n,\hat{k}_0)-\frac{1}{4\pi}\frac{\langle\hat{\psi}_{k_n}{}^{(-)}PHu_0\rangle\langle u_0HP\hat{\psi}_{k_0}{}^{(+)}\rangle}{E-\epsilon_0-\langle u_0H\hat{G}^{(+)}Hu_0\rangle+i\eta}\right|^2. \tag{12}$$

If $\hat{f}_{n0}$, $\langle\hat{\psi}_{k_n}{}^{(-)}PHu_0\rangle\langle u_0HP\hat{\psi}_{k_0}{}^{(+)}\rangle$ and $\langle u_0H\hat{G}^{(+)}Hu_0\rangle$ are all slowly varying functions of energy in the vicinity of $E\simeq\epsilon_0$ (there is no reason for rapid variation of these quantities), then the second term in (12) makes the cross section vary rapidly. Equation (12) may be simplified as

$$\frac{d\sigma_{n0}}{d\Omega}=\frac{k_n}{k_0}\left\{\hat{f}_{n0}(\hat{k}_n,\hat{k}_0)+\frac{1}{(E-\epsilon_0-\Delta)^2+\Gamma^2/4}\times[|A_{n0}|^2-2\,\mathrm{Re}\hat{f}_{n0}{}^*A_{n0}(E-\epsilon_0-\Delta-i\Gamma/2)]\right\}, \tag{13}$$

where

$$\langle u_0H\hat{G}^{(+)}Hu_0\rangle=\Delta-i\Gamma/2, \tag{14}$$

$$\langle\hat{\psi}_{k_n}{}^{(-)}PHu_0\rangle\langle u_0HP\hat{\psi}_{k_0}{}^{(+)}\rangle=A_{n0}. \tag{15}$$

This is a typical Breit-Wigner shape. Note that the resonant energy is not the eigenvalue ϵ_0 but is slightly shifted by Δ. However, Δ is independent of n so that all amplitudes are resonant at the *same energy*. Their widths Γ are also identical.

It might be thought that the limitation in Eq. (6) in which only one eigenstate of QHQ was separated off would limit the application to S states. Otherwise, u_0 would be $(2L+1)$-fold degenerate and it would seem that $(2L+1)$ terms must be included in the last term of Eq. (6). These states will differ only by their magnetic quantum number and since $P\psi^{(+)}$ is an eigenfunction of L_z (along the direction of incident momentum), only one of the $(2L+1)u_0$ will couple to $P\psi^+$ and the above analysis applies.

If more than one state of QHQ must be included, then the step leading from (8) to (10) must be generalized slightly and the resonance structure becomes more complex.

We note that if u_0 is an $L=0$ eigenstate, only $L=0$ components of $\hat{\psi}^{(+)}$ will couple and the resonance will occur in the S wave part of σ_{n0}. Similar remarks apply for higher values of L.

The elastic resonances recently observed[6] in the scattering from various atoms occur just below excitation thresholds and are very probably those described here. It would be of interest to look at the inelastic cross sections at the same energies to confirm the appearance of the resonances in other channels.

III. EXAMPLE OF ELECTRON-HYDROGEN SCATTERING

O'Malley and Geltman have used the one-state standing wave analog of the preceding section to calculate ϵ_0 for the problem of electron-hydrogen scattering. They obtain an eigenvalue for the singlet S channel at 9.559 eV above the ground state of H which is 0.645 eV below the $n=2$ threshold. Burke and Schey's[1] $1s$-$2s$-$2p$ close coupling approximation yields 9.61 eV for the position of the resonance. This last number is an approximation to $\epsilon_0+\Delta$, indicating that Δ is of the order of 0.05 eV. Temkin and Walker[7] used the formalism of O'Malley and Geltman to show that there is an infinite sequence

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[5] M. Gell-Mann and M. L. Goldberger, Phys. Rev. **131**, 679 (1963).

[6] C. E. Kuyatt, J. Arol Simpson, and S. R. Mielczarek, Phys. Rev. **138**, A385 (1965).

[7] A. Tempkin and J. F. Walker, Phys. Rev. **140**, A1520 (1965).

of eigenvalues of QHQ below the $n=2$ threshold, and that for the higher ones the ratio of successive ones is

$$\lim_{j\to\infty} \epsilon_{j+1}/\epsilon_j = e^{-2\pi/\alpha'}, \quad \alpha' = (\surd 37 - 5/4)^{1/2}. \qquad (16)$$

These results were obtained previously by a different method by Gailitis and Damburg.[8] Whether any one of these eigenvalues corresponds to a true resonance is still a moot point. The energy shift of the jth resonance,

$$\Delta_j = \mathrm{Re}\langle u_j H \hat{G}^{(+)} H u_j \rangle, \qquad (17)$$

may shift the position of the resonance above the $n=2$ threshold, in which case it is no longer a resonance. We shall see below that the fact that there are an infinite number of eigenvalues ϵ_j below the $n=2$ threshold is a direct result of the degeneracy of the $2s$ and $2p$ levels. These are, of course, not exactly degenerate but are split by the Lamb shift so the infinity of levels is cut off.

We shall illustrate the multichannel aspect of this formalism by looking for resonances in electron-hydrogen scattering below the $n=N$ thresholds ($N=3, 4\cdots$). This requires that one find the eigenvalues of QHQ where Q projects out the $n<N$ components of ψ. We shall not attempt the lengthy problem of finding the lowest eigenvalue, but we merely show that there are an infinity of such eigenvalues similar to the infinity below the $n=2$ level and we obtain the result analogous to Eq. (16). We use the Rayleigh-Ritz principle to obtain the eigenvalues

$$\epsilon = \frac{\langle \psi QHQ\psi \rangle}{\langle \psi Q\psi \rangle} = \frac{\langle \psi_Q H \psi_Q \rangle}{\langle \psi_Q \psi_Q \rangle}. \qquad (18)$$

Here ψ is any trial function and ψ_Q is a trial function orthogonal to P. We take the form for singlet or triplet

$$\psi_Q = (1 \pm X_{12}) \sum_n \phi_n(\mathbf{r}_1) F_n(\mathbf{r}_2), \qquad (19)$$

where X_{12} is the coordinate exchange operator, ϕ_n are hydrogenic states, and F_n are undetermined functions. The sum runs over all states above the $n=N$ level, but we need only the $n=N$ level here. The calculation is much easier when the expansion is made an angular momentum eigenfunction. Thus Eq. (19) becomes

$$\psi_Q{}^{L,M} = (1 \pm X_{12}) \sum_{\substack{l_1 m_1 \\ l_2 m_2}} \phi_{N l_1 m_1}(\mathbf{r}_i) \frac{1}{r_2} u_{l_2}(r_2) Y_{l_2 m_2}(\hat{r}_2) \times \langle l_1 m_1 l_2 m_2 | L M l_1 l_2 \rangle, \qquad (20)$$

where the last factor is the usual vector-coupling coefficient and u_l is now only a radial function. Variation of Eq. (18) with respect to the functions u_l yields the close-coupling equations[9] which at large distances become[10]

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \epsilon\right) u_l = \frac{2}{r^2} \sum_{l'} A_{ll'} u_{l'}, \qquad (21)$$

where ϵ is the energy below the $N=3$ resonance. Here $A_{ll'}$ is a real symmetric matrix given by

$$A_{l_2 l_2'} = \left(\int_0^\infty dr\, r^3 R_{N l_2} R_{N l_2'}\right) \sum_{l_1 l_1' m_1 m_1' m_2 m_2'} \langle L M l_2 l_1 | l_2 m_2 l_1 m' \rangle \times \langle l_2 m_2 l_1 m_1 | \hat{r}_1 \cdot \hat{r}_2 | l_2' m_2' l_1' m_1' \rangle \times \langle l_2' m_2' l_1' m_1' | L M l_2' l_1' \rangle. \qquad (22)$$

We further simplify by looking at S-wave resonances, $L=M=0$. In that case the only nonvanishing elements are

$$A_{l,l+1} = A_{l+1,l} = \tfrac{3}{2} N (l+1) \left[\frac{N^2 - (l+1)^2}{4(l+1)^2 - 1}\right]^{1/2}. \qquad (23)$$

Equation (21) can be uncoupled by diagonalizing the matrix

$$B_{ll'} = l(l+1)\delta_{ll'} + 2A_{ll'}. \qquad (24)$$

The resultant equations are

$$\left[\frac{d^2}{dr^2} - \frac{b_j}{r^2} - \epsilon\right] v_j = 0, \quad j = 1\cdots N \qquad (25)$$

where the b_j are the eigenvalues of the matrix B. Positive b_j represent repulsive potentials which cannot result in positive ϵ and so are of no interest here. A variation of Sturm's theorem[11] can be used to show that there is at least one negative eigenvalue and that for $N>3$ there is more than one negative eigenvalue. We first note that the eigenvalues b_j are all real and distinct (otherwise one of the off-diagonal elements would vanish). Sturm's theorem applied here can be stated as follows: Let D_q, $q=0,1,\cdots,N$, be the determinant of the qth minor of B with $D_0=1$. Then the number of sign changes in the sequence $D_0 D_1 \cdots D_N$ with zeros discarded is the number of negative eigenvalues of B. The recurrence relation

$$D_{q+1} = D_q q(q+1) - 9N^2 q^2 \left(\frac{N^2 - q^2}{4q^2 - 1}\right) D_{q-1},$$
$$D_{-1} = 0,$$

greatly aids in computing the D_q. The first few are given by

$$\begin{aligned} D_0 &= 1, \\ D_1 &= 0, \\ D_2 &= -3N^2(N^2-1), \\ D_3 &= -18N^2(N^2-1), \\ D_4 &= 27N^2(N^2-1)[(9/35)N^2(N^2-9)-8]. \end{aligned} \qquad (26)$$

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[8] M. Gailitis and R. Damburg, Proc. Phys. Soc. (London) **82**, 192 (1963).

[9] K. Omidvar, Phys. Rev. **133**, A970 (1964).

[10] Rydberg units are used here.

[11] L. E. Dickson, *New First Course in the Theory of Equations* (John Wiley & Sons, Inc., New York, 1939), p. 83.

TABLE I. Eigenvalues b for the first few states.

N	b	α
2	-5.08	2.20
3	-16.20	3.99
4	-33.32	5.75
	-5.34	2.26
5	-56.45	7.50
	-20.67	4.52
6	-85.57	9.24
	-42.02	6.46
	-1.63	1.17

Thus for $N=2$ there is one sign change, the one negative eigenvalue. For $N=3$ there is still only one negative eigenvalue. However, for $N=4$ there are two sign changes and so two distinct negative eigenvalues. For higher N, Eq. (26) shows that there are still at least two negative eigenvalues. The remaining analysis is identical to that given in Refs. 6 and 7 for the resonances below the $n=2$ levels Briefly, it utilizes the result of Landau and Lifshitz[12] that an equation which behaves like Eq. (25) with negative $b<\frac{1}{4}$ at large distances has an infinite number of bound states. For the very highly excited bound states, the bulk of the wave function lies in the region where this asymptotic form (25) applies, and its solution can be used to get the dependence of the eigenvalue on the quantum number. The result is

$$\lim_{s\to\infty}\frac{\epsilon_{s+1}{}^{(j)}(N)}{\epsilon_s{}^{(j)}(N)}=e^{2\pi/\alpha_j(N)},\quad \alpha_j(N)=[|b_j(N)|-\tfrac{1}{4}]^{1/2}. \tag{27}$$

Thus, when there is more than one negative eigenvalue of B there will be more than one sequence of infinite eigenvalues of QHQ below the Nth threshold. In Table I we show all the negative eigenvalues and their corresponding values of α_j for the first few N.

Again we should point out that whether these constitute true resonances is in doubt. The value of the lowest eigenvalue of QHQ can be determined by a calculation analogous to that of O'Malley and Geltman with a Q chosen to project out the levels below N, or by a close coupling calculation which includes the levels up to and including N.

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I am indebted to Dr. R. von Holdt for an illuminating discussion of Sturm's theorem and for obtaining the eigenvalues quoted above.

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[12] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958), p. 118 ff.

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Resonant Electron Capture in Small-Angle Collisions of Ar^+ on Ar and Ne^+ on Ne†

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Measurements of the electron capture probability P_0 have been made for single collisions of Ar^+ ions with neutral Ar atoms and Ne^+ ions with neutral Ne atoms, the latter measurements being an extension of work previously reported by this laboratory. The incident ions ranged in energy from 200 eV to 4 keV, the scattered particles being detected at angles ranging from 0.75° to 15° in the laboratory coordinates. A charge analysis of the scattered particles has yielded values of P_0 as a function of the incident ion energy T and scattering angle θ; in both cases P_0 is found to oscillate rapidly as a function of θ, with some dependence upon T also. The periodicity of P_0 as a function of T and θ is consistent with a description of the collision wherein the electronic state of the ion-atom system changes adiabatically and is a superposition of symmetric and antisymmetric energy eigenstates of the diatomic molecular ion. The data are discussed in terms of this description, yielding empirical values of an integral I, defined as the energy difference ΔE between these two eigenstates, integrated over the collision path of relative motion. For the range of collisions studied, I varied from about 6 to 26 eV-Å in the case of Ar^+ on Ar, and from about 5 to 25 eV-Å in the case of Ne^+ on Ne. An approximate functional dependence of ΔE upon internuclear separation R is also obtained, although there is some evidence that ΔE may also depend upon the relative collision speed v in the case of the Ar^+-on-Ar collisions. It is proposed that the ΔE measured for the gentler collisions which produce no excitation of either atomic system is the energy difference between the Π_g and Π_u states of the quasimolecule.

1. INTRODUCTION

THE measurements presented in this paper are a continuation of work previously performed in this laboratory and reported upon in a paper,[1] hereinafter called I. The present measurements of Ne^+ on Ne are an extension of that earlier work to lower incident ion energy T and smaller scattering angle θ. A brief preliminary report of the Ar^+ on Ar measurements presented here was given in another paper.[2]

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[1] P. R. Jones, P. Costigan, and G. Van Dyk, Phys. Rev. **129**, 211 (1963).

[2] P. R. Jones, G. Van Dyk, and N. Eddy, in *Proceedings of The Third International Conference on the Physics of Electronic and Atomic Collisions*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 862.