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AUTOIONIZATION STATES OF H^- BELOW THE n = 2 LEVEL OF H

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The resonances below the inelastic (n=2) threshold of electron-hydrogen scattering are examined by the projection operator technique of Feshbach. This technique converts the problem to an eigenvalue problem for a projected Hamiltonian in which the autoionization levels of H^- become true bound states. The number of levels of this problem is found to be infinite and cluster at the n=2 level of H. The relative spacings of the levels are identical to the resonances in e-H scattering as derived by Gailitis and Damburg.

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I INTRODUCTION

Recently, O'Malley and Geltman[1] have utilized the projection operator technique of Feshbach[2], as applied to the atomic case by Hahn, O'Malley and Spruch[3], to calculate the compound autoionization states of H^- below the n=2 excitation threshold for e-H scattering. The point of the projection operator, Q, is that it projects out (removes) the ground state of hydrogen from the total wave function, and therefore gives rise only to asymptotically vanishing terms even for a wave function that would otherwise be capable of describing e-H elastic scattering. Thus one can formulate an ordinary eigenvalue problem for the Schrödinger equation with a projected wave function $Q\Psi$:

$$H(Q\Psi) = \mathcal{E}_n (Q\Psi) \tag{1.1}$$

and, following Fano[4], O'Malley and Geltman have shown that at energies E_n close to the eigenvalues $\mathcal{E}_n$ of the above problem,

$$E_n = \mathcal{E}_n + \Delta_n, \tag{1.2}$$

the phase shift associated with the scattering problem, described by Ψ, undergoes an increase of approximately π radians corresponding to resonances in the elastic scattering.

Although an explicit formula for Δ_n was given[1], it involves coupling to the continuum part of Ψ. Thus the O'Malley-Geltman calculations were confined to $\mathcal{E}_n$ below the inelastic (2s) threshold for H^- (e-H scattering) and He (e-He^+ scattering). The neglect of Δ_n would indeed be justifiable as agreement with other scattering calculations[5,6,7] and experiments[8] showed[1]. However, there is a special circumstance in the case of elastic scattering just below the 2s threshold which makes for an infinite number of resonances which cluster on the 2s threshold. This remarkable result was deduced by Gailitis and Damburg[9] on the basis of close-coupling scattering calculations above threshold which were then extrapolated below threshold. The physical basis for this phenomenon derives from the very long range nature of the potential (r^{-2}) which in turn stems from the degeneracy of the 2s and 2p levels of hydrogen (and it is only in this approximation that the infinity of resonances applies). On the other hand the actual calculations of O'Malley and Geltman[1] yielded only two resonances in each channel, which, result although it was in accord with previous predictions of two resonances[6], leaves open the question of whether the higher resonances are present below threshold in the actual spectrum of $Q\Psi$ or whether they appear above the 2s threshold and are only brought below threshold by the uncalculated Δ_n

The formal definition of the projection operator Q as it applies to this problem has been given by Hahn, O'Malley, and Spruch[2]:

$$Q = 1 - P_1 - P_2 + P_1 P_2 \qquad (1.3)$$

$$P_i = |\varphi_0(\underset{\sim}{r_i})\rangle\langle\varphi_0(\underset{\sim}{r_i})| \qquad (1.4)$$

$\varphi_0(\underline{r}_i)$ is the ground state of hydrogen occupied by the i^{th} particle (i = 1,2).

In the next section we shall show that the spectrum of discrete levels of $Q\Psi$ is indeed infinite below threshold, and we shall derive a formula for the relative spacings of $\mathcal{E}_m$ which is identical to that of Gailitis and Damburg[9] for E_m .

II ANALYSIS

We start with a close-coupling wave function for the ^1S state of e-H scattering including 1s-2s-2p states of hydrogen:

$$\Psi = \frac{1}{r_1 r_2}\Big\{\big[\bar{u}(r_1)R_{1s}(r_2) + \bar{v}(r_1)R_{2s}(r_2) + w(r_1)R_{2p}(r_1)\cos\theta_{12}\big] + \big[(1 \rightleftarrows 2)\big]\Big\}, \qquad (2.1)$$

where $R_{n\ell}$ is r times the given radial wave function. A straightforward application of Q on Ψ now yields

$$Q\Psi = \frac{1}{r_1 r_2}\Big\{\big[\bar{v}(r_1)\,R_{2s}(r_2) + w(r_1)\,R_{2p}(r_2)\cos\theta_{12}\big] + \big[(1\rightleftarrows 2)\big]$$

$$- C_v\big[R_{1s}(r_1)\,R_{2s}(r_2) + (1\rightleftarrows 2)\big]\Big\}, \qquad (2.2a)$$

where

$$C_v = \int_0^\infty R_{1s}(r)\,\bar{v}(r)\,dr. \qquad (2.3)$$

Here we note that one can add any amount of R_{2s} to $\bar{u}$ and simultaneously subtract the same amount to R_{1s} from $\bar{v}$ without changing ψ. Thus by selecting this amount as C_v, i.e., by redefining $\bar{u}$ and $\bar{v}$ as given in (2.4):

$$u(r_i) \equiv \bar{u}(r_i) + C_v R_{2s}(r_i) \qquad (2.4a)$$

$$v(r_i) \equiv \bar{v}(r_i) - C_v R_{1s}(r_i), \qquad (2.4b)$$

we find, without having changed Ψ , that

$$Q\Psi = \frac{1}{r_1 r_2}\left\{ v(r_1)\,R_{2s}(r_2) + w(r_1)\,R_{2p}(r_2)\cos\theta_{12} + (1 \rightleftarrows 2)\right\}. \qquad (2.2b)$$

Therefore without any loss of generality we can take (2.2b) as the general form of $Q\Psi$, and we see that it has the desired vanishing asymptotic form below the n=2 threshold:

$$\lim_{r_i \to \infty} Q\Psi = 0. \qquad (2.5)$$

$Q\Psi$ is in fact the close coupling wave function with the 1s term absent. The equations which v and w satisfy may be simply derived from the integro-differential equations for the scattering in the close coupling approximation[10] by dropping all terms depending on u and R_{1s}. At large distances they reduce, for S states, to

$$\left(\frac{d^2}{dr^2} + \mathcal{E}\right) v = \frac{6w}{r^2} \, , \tag{2.6a}$$

$$\left(\frac{d^2}{dr^2} - \frac{2}{r^2} + \mathcal{E}\right) w = \frac{6v}{r^2} \tag{2.6b}$$

These equations may be diagonalized[11] so that two linear combinations of v and w satisfy two uncoupled equations. The one which contains the attractive r^{-2} potential corresponds to

$$F(r) = v(r) + \left(\frac{1-\sqrt{37}}{6}\right) w(r) \, . \tag{2.7}$$

The diagonalized equation is

$$\left(\frac{d^2}{dr^2} + \frac{(\sqrt{37}-1)}{r^2} + \mathcal{E}\right) F(r) = 0 . \tag{2.8}$$

In this equation $\mathcal{E}$ is the energy in rydbergs relative to the 2s threshold. Having gotten the equation in this form, we can appeal to an argument of Landau and Lifshitz[12] to answer affirmatively the question of whether there are an infinite number of bound states of F(r). For they[12] have shown that any problem governed by the potential in (2.8) for large r and well-behaved

for small r has a solution with an infinite number of nodes as $\mathcal{E} \to 0$. Thus for $\mathcal{E}$ negative and small, one can find bound state solutions with any arbitrary number of nodes, i.e., there are an infinite number of bound states with $\mathcal{E} < 0$.

This much was also clear to Damburg and Gailitis[9] as a perusal of their paper shows. The new point thus far has been that the elimination of the 1s state from the close-coupling wave function can be put on a more rigorous basis by a consistent application of the Q operator. Below we shall actually evaluate the eigenvalue spectrum of F.

Letting

$$\epsilon = |\mathcal{E}|, \tag{2.9}$$

one can convince oneself that the solution of (2.8) which vanishes at infinity is

$$F(r) = \sqrt{r}\, H^{(1)}_{i\alpha}(i\epsilon^{1/2} r) \qquad (2.10)$$

where

$$\alpha = \sqrt{(37)^{1/2} - (5/4)} \qquad (2.11)$$

and $H^{(1)}_{i\alpha}$ is the Hankel function

$$H^{(1)}_{\nu}(z) = J_{\nu}(z) + i N_{\nu}(z)$$

J_ν and N_ν are the Bessel and Neumann functions respectively. For large values of r [13]

$$\lim_{r \to \infty} F(r) \propto e^{-\epsilon^{1/2} r}\left(1 - \frac{\alpha^2 + 1/4}{2 r \epsilon^{1/2}} + O\left(\frac{1}{r^2 \epsilon}\right)\right) \qquad (2.12)$$

For values of $r < a$ the equations for F and a second linear combination of v and w, call it $G = v + [(1 + \sqrt{37})/6]w$, will be coupled. They cannot be decoupled by any linear transformation. However, it is certainly possible to define a non-local potential[14] which will describe an uncoupled F(r) down to the origin. This non-local potential can in turn be approximated a local potential $V_e(r)$ at least for values of r slightly below the value of $r = a$ where Eq. (2.6) is valid. Now it can safely be assumed that $V_e(r)$ will continue to decrease (increase in magnitude) until such a point $r = b$ where the centrifugal barrier forces the potential up to infinity. I.e.,

$$|V_e(r)| \geq |V(a)| = \frac{\sqrt{37}-1}{a^2} \quad ; \; b < r < a. \qquad (2.13)$$

Then for any energy satisfying

$$\epsilon \ll \frac{\sqrt{37}-1}{a^2} \quad , \qquad (2.14)$$

the wave function F(r) will be virtually independent of ϵ for $r \leq a$. Let the logarithmic derivative of F(r) at $r = a$, as obtained by integration from the origin in the presence of the actual potential, be defined by

$$t \equiv \frac{1}{F(a)} \cdot \left. \frac{dF(r)}{dr} \right|_{r = a} . \tag{2.15}$$

To repeat, for energies satisfying (2.14), t is virtually independent of ϵ.

This logarithmic derivative must be matched to that of $F(r)$ for $r > a$ in order to obtain the allowed bound states. In this region $F(r)$ is given by (2.10). It is shown below that as long as we only consider energies consistent with (2.14), the small argument expansion of the Hankel function in (2.10) may be used in the vicinity of $r = a$.

To see this we consider the small argument expansion[13]

$$H_\nu^{(1)}(z) = \frac{i}{\sin \nu\pi} \left[e^{-i\nu\pi} \frac{(\frac{1}{2}z)^{\nu}}{\Gamma(1+\nu)} - \frac{(\frac{1}{2}z)^{-\nu}}{\Gamma(1-\nu)} \right] \cdot \left[1 + 0 \left(\frac{|z|^2}{4|\nu+1|} \right) \right] . \tag{2.16}$$

Putting in the imaginary values $\nu = i\alpha$ and $z = i\epsilon^{\frac{1}{2}}r$ yields the explicit expression

$$H_{i\alpha}^{(1)}(i\epsilon^{\frac{1}{2}}r) = \frac{2ie^{\frac{1}{2}\alpha\pi}\sin[\alpha\ln(\frac{1}{2}\epsilon^{\frac{1}{2}}r) - \varphi]}{[\pi\alpha\sinh(\pi\alpha)]^{\frac{1}{2}}}\left[1+O\left(\frac{\epsilon r^2}{4\sqrt{\alpha^2+1}}\right)\right] , \qquad (2.17)$$

where

$$\varphi = \arg[\Gamma(1 + i\alpha)] \quad .$$

It is easily verified that for α given by (2.11) and for $r \approx a$, (2.14) guarantees that

$$\frac{\epsilon r^2}{4\sqrt{\alpha^2+1}} \ll 1 \quad .$$

Therefore, with no further restriction we have, to within a proportionality constant

$$F(r) = \sqrt{r} \sin [\alpha \ln (\tfrac{1}{2} \varepsilon^{\frac{1}{2}} r) - \varphi], \; r \approx a \; , \tag{2.18}$$

and

$$\frac{1}{F(a)} \cdot \frac{dF(r)}{dr} \bigg|_{r=a} = \frac{\alpha}{a} \cot [\alpha \ln (\tfrac{1}{2} e^{\frac{1}{2}} a) - \varphi] + \frac{1}{2a} \; . \tag{2.19}$$

The allowed bound state energies may be found by equating this to t, the value from the interior, and solving for $\varepsilon^{\frac{1}{2}}$ assuming, of course, that t is independent of ε.

$$\varepsilon^{\frac{1}{2}} = \frac{2}{a} \exp \left\{ \frac{1}{\alpha} \left[\cot^{-1}\left(\frac{2ta-1}{2\alpha}\right) + \varphi \pm n\pi \right] \right\} \; , \tag{2.20}$$

where

$$0 \leq \cot^{-1} \chi \leq \pi \quad .$$

Let the energy of the lowest bound state be designated by ϵ_1. If ϵ_1 satisfies (2.14), the successively higher states are given by the recursion relation:

$$\epsilon_{n+1} = e^{-2\pi/\alpha} \epsilon_n \quad , \tag{2.21}$$

as is easily seen from (2.20). Equation (2.21) is identical to the formula for the ratio of resonant energies obtained by Gailitis and Damburg[9]. This relation becomes more accurate with increasing n, because of the decreasing dependence of t on ϵ, and because of the increasing validity of the first order expansion (2.17). We now look at the case n = 1.

O'Malley and Geltman[1] have given for the energy of the lowest lying 's bound state:

$$\epsilon_1 = 0.645 \text{ ev} = 0.0474 \text{ Rydbergs.} \tag{2.22}$$

If this energy is to satisfy (2.14), the matching radius which we choose must satisfy

$$a^2 \ll \frac{\sqrt{37}-1}{\epsilon_1} \approx 107 ,$$

where all lengths are given in Bohr radii. For $a = 5$, (2.14) is satisfied fairly well. However, the extent to which the asymptotic equations are valid at such a small radius is questionable. The potentials coupling in other channels could give 10% effects at $r = 5$ quite easily. But allowing a 10% error in the relation (2.21) for $n = 1$ is not serious, since with ϵ_1 fixed by (2.22) one obtains

$$\epsilon_2 = (0.037 \pm 0.004) \text{ e.v.} \tag{2.23}$$

This result corresponds to a fairly narrowly defined second eigenvalue; namely (relative to the ground state of hydrogen):

$$\mathcal{E}_2 = (10.167 \pm 0.004) \text{ e.v.}$$

Furthermore, since the asymptotic form of the 2s-2p equations, (2.6), contains no exchange terms, Eq. (2.19) must hold for triplet as well as singlet S states (albeit with a different ε_1). For other values of the total angular momentum one has equations similar to (2.6) with altered numerical coefficients of the r^{-2} terms[15]. Only in P and D states will the diagonalization yield a net attractive r^{-2} potential with associated coefficients $\alpha = 1.86$ and 0.75 respectively[16]. With these changes in α, Eq. (2.19) also holds for states of both spins.

In Table I, we summarize the numerical results for the first three resonances for S and P states. The energies are given relative to the ground state of hydrogen (which is appropriate for comparison with resonant energies in the elastic scattering of electrons from hydrogen). The S and P states of both spins are included and the lowest state in each case has been chosen to agree with the calculated results of O'Malley and Geltman[1]. The second states, which in the ^1S case is in accord with the original prediction of two resonances[6,7], then provide a point of comparison with the O'Malley-Geltman result.

It can be seen that our second states particularly in the ^1S case are lower than the corresponding O'Malley-Geltman states. The discrepancy in ϵ_2 is 0.011 e.v. which, by comparison to (2.23) is seen to be a difference of 30%. The qualitative lowering of the levels as we have obtained is almost certainly correct. This is again because of the tremendously long range of the r^{-2} potential. A quantitative estimate of this potential can be obtained by observing when the second term in the asymptotic expansion (2.12) becomes comparable to the first. For any eigenfunction n, we define this value of r by R_n:

$$R_n = \frac{\alpha^2+\frac{1}{4}}{\epsilon_n^{\frac{1}{2}}} \qquad (2.24)$$

In the ^1S case $R_1 \cong 100\ a_0$ where we have explicitly appended the unit of length a_0 (the Bohr radius). Having used a not unusual relative partial wave type variational wave function with up to 25 terms, it is not surprising that O'Malley and Geltman could get an accurate lowest state whose range (25 a_0) is not very much more than an ordinary type bound state wave function. However, the range of the second state (100 a_0) by a conventional variational wave function below the n = 2 threshold at all. There can be little question that the value itself must be too high.

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16. These numbers are given in footnote 16 of T. F. O'Malley, Phys. Rev. 137, A 1668 (1965).

TABLE I

Autoionization levels of H^- (in eV above the ground of hydrogen[a])

State	O'Malley-Geltman[b]	This paper[c]
^1S	9.559	9.559
	10.178	10.1668
	—	10.2016
^3S	10.149	10.149
	10.202	10.2006
	—	10.2036
^1P	10.178	10.178
	10.203	10.2029
	—	10.2037
^3P	9.727	9.727
	10.198	10.1875
	—	10.2032

[a] Our numbers are based upon the rydberg being taken as exactly 13.605 eV.

[b] From reference 1.

[c] This column contains only the first three of the resonances for each state of the infinity of resonances predicted by Eq. (2.19).