

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.

I. INTRODUCTION

RECENTLY, O'Malley and Geltman¹ 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 using 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 $Q\Psi$:

$$QH(Q\Psi) = \mathcal{E}_n(Q\Psi), \quad (1.1)$$

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,

$$E_n = \mathcal{E}_n + \Delta_n, \quad (1.2)$$

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 calculations⁵⁻⁷ and experiments⁸ showed.¹ However,

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¹ T. F. O'Malley and S. Geltman, *Phys. Rev.* **137**, A1344 (1965).

² H. Feshbach, *Ann. Phys. (N.Y.)* **5**, 537 (1958); **19**, 287 (1962).

³ Y. Hahn, T. F. O'Malley, and L. Spruch, *Phys. Rev.* **128**, 932 (1962).

⁴ U. Fano, *Phys. Rev.* **124**, 1866 (1961).

⁵ K. Smith, R. McEachran, and P. Fraser, *Phys. Rev.* **125**, 553 (1962). P. G. Burke and H. M. Schey, *ibid.* **126**, 149 (1962). P. G. Burke, D. D. McVicar, and K. Smith, *Phys. Rev. Letters* **11**, 559 (1963); *Proc. Phys. Soc. (London)* **84**, 749 (1964).

⁶ A. Temkin and R. Pohle, *Phys. Rev. Letters* **10**, 22, 268 (E)

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 (a similar clustering occurs below the threshold of all excited states of hydrogen). This remarkable result was deduced by Gailitis and Damburg⁹ 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 Geltman¹ yielded only two eigenvalues 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 eigenvalues are present below threshold in the actual spectrum of QHQ or whether the infinity of resonances are brought below threshold only by the uncalculated Δ_n .

The formal definition of the projection operator Q as it applies to this problem has been given by Hahn,

(1963). A. Temkin, National Aeronautics and Space Administration Technical Report No. NASA TN D-1720, 1963 (unpublished). In the erratum of the first paper, p. 268 (E), as well as TN D-1720 E. Holgøien, *Proc. Phys. Soc. (London)* **71**, 357 (1958) was erroneously credited with having found a second autoionization level of H^- . After the appearance of the letter, Holgøien (private communication) did find a second $1S$ autoionization level of H^- at 10.17 eV.

⁷ A. Temkin, *Proceedings of the III International Conference on the Physics of Electronic Collisions*, edited by M. R. C. McDowell (John Wiley & Sons, Inc., New York, 1964), p. 107.

⁸ S. M. Silverman and E. N. Lassette, Ohio State University Research Foundation Report No. 9, RF Project 464, Columbus, Ohio; *J. Chem. Phys.* **40**, 1265 (1964). R. P. Madden and K. Codling, *Phys. Rev. Letters* **10**, 516 (1963). J. A. Simpson, S. R. Mielczarek, and J. Cooper, *J. Opt. Soc. Am.* **54**, 269 (1964). C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, *Phys. Rev.* **138**, A385 (1965). G. J. Schulz, *Phys. Rev. Letters* **13**, 583 (1964).

⁹ M. Gailitis and R. Damburg, *Proc. Phys. Soc. (London)* **82**, 192 (1963). See, for example, also A. I. Baz', *Zh. Eksperim. i Teor. Fiz.* **36**, 1762 (1959) [English transl.: *Soviet Phys.—JETP* **36**, 1256 (1959)].

O'Malley, and Spruch²:

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

$$P_i = |\varphi_0(\mathbf{r}_i)\rangle\langle\varphi_0(\mathbf{r}_i)|. \quad (1.4)$$

$\varphi_0(\mathbf{r}_i)$ 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 QHQ is indeed infinite below threshold, and we shall derive a formula for the relative spacings of \mathcal{E}_n which is identical to that of Gailitis and Damburg⁹ for E_n .

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:

$$\Psi = (1/r_1 r_2) \{ [u(r_1)R_{1s}(r_2) + v(r_1)R_{2s}(r_2) + w(r_1)R_{2p}(r_1)\cos\theta_{12}] + [(1 \rightleftharpoons 2)] \}, \quad (2.1)$$

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

$$Q\Psi = (1/r_1 r_2) \{ [v(r_1)R_{2s}(r_2) + w(r_1)R_{2p}(r_2)\cos\theta_{12}] + [(1 \rightleftharpoons 2)] - C_v [R_{1s}(r_1)R_{2s}(r_2) + (1 \rightleftharpoons 2)] \}, \quad (2.2)$$

where

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

The last term (in square brackets) in Eq. (2.2) is seen to be a short-range (exponentially damped) term. It can therefore only contribute short-range terms to the coupled integro-differential equations that one would derive from $Q\Psi$ and therefore does not destroy the necessary property

$$\lim_{r_1 \rightarrow \infty} Q\Psi = 0. \quad (2.4)$$

Furthermore, it will not alter the long-range form of the coupled equations that would be obtained from a form of (2.2) with the last term absent. In other words the long-range form of the equations for v and w are the same as those in the $1s$ - $2s$ - $2p$ close-coupling approximation¹⁰ when all terms depending on u and R_{1s} are

¹⁰ I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. **53**, 654 (1957). The close coupling equations are given in a very explicit form by K. Omidvar, Phys. Rev. **133**, A970 (1964).

It was originally thought that the last term in Eq. (2.2) could be omitted from the entire equations; however, this depends on there being enough freedom in the equations for a solution to exist such that v is orthogonal to R_{1s} . This being a bound-state problem, however, it cannot be taken for granted that such freedom in v exists. We are indebted to P. G. Burke for conversations on this point. He has found it necessary to modify the short-range part of the $2s$ - $2p$ close-coupling equations in a manner which is presumably equivalent to incorporating the last term of Eq. (2.2).

The suggestion that the resonant energies of the scattering problem would correspond to the discrete spectrum of the closed-channel part of the close-coupling equations was first made by H. S. W. Massey [cf. footnote 23a of P. G. Burke and H. M. Schey, Ref. 5]. Thus the argument which we present here can be

dropped. For S states they are

$$(d^2/dr^2 + \mathcal{E})v = 6w/r^2, \quad (2.5)$$

$$(d^2/dr^2 - 2/r^2 + \mathcal{E})w = 6v/r^2. \quad (2.6)$$

These equations may be diagonalized¹¹ so that two linear combinations of v and w satisfy two uncoupled equations with an attractive and repulsive r^{-2} potential respectively. The one which contains the attractive r^{-2} potential corresponds to

$$F(r) = v(r) + \frac{1}{6} [1 - (37)^{1/2}] w(r). \quad (2.7)$$

The diagonalized equation is

$$(d^2/dr^2 + [(37)^{1/2} - 1]/r^2 + \mathcal{E})F(r) = 0. \quad (2.8)$$

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 Lifshitz¹² to answer affirmatively the question of whether there are an infinite number of bound states of $F(r)$. For they¹² 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 $\mathcal{E} \rightarrow 0$. 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 Gailitis⁹ 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

$$\epsilon = |\mathcal{E}|, \quad (2.9)$$

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

$$F(r) = r^{1/2} H_{i\alpha}^{(1)}(i\epsilon^{1/2}r), \quad (2.10)$$

where

$$\alpha = [(37)^{1/2} - (5/4)]^{1/2} \quad (2.11)$$

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

$$H_{\nu}^{(1)}(z) = J_{\nu}(z) + iN_{\nu}(z);$$

J_{ν} and N_{ν} are the Bessel and Neumann functions respectively. For large values of r

$$\lim_{r \rightarrow \infty} F(r) \propto e^{-\epsilon^{1/2}r} \left[1 - \frac{\alpha^2 + \frac{1}{4}}{2r\epsilon^{1/2}} + O\left(\frac{1}{r^2\epsilon}\right) \right]. \quad (2.12)$$

considered a justification of Massey's suggestion on the basis of the Q -operator formalism.

¹¹ M. J. Seaton, Proc. Phys. Soc. (London) **77**, 174 (1961).

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

¹³ W. Magnus and F. Oberhettinger, *Formulas and Theorems for the Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 16.

For values of $r < a$ the equations for F and a second linear combination of v and w , call it

$$G = v + \frac{1}{6}[1 + (37)^{1/2}]w,$$

will be coupled. They cannot be decoupled by any linear transformation. However, it is certainly possible to define a nonlocal potential¹⁴ which will describe an uncoupled $F(r)$ down to the origin. This nonlocal potential can in turn be approximated by 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. Therefore,

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

Then for any energy satisfying

$$\epsilon \ll [(37)^{1/2} - 1]/a^2, \quad (2.14)$$

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

$$t \equiv [1/F(a)]dF(r)/dr|_{r=a}. \quad (2.15)$$

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 expansion¹³

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

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

$$H_{i\alpha}^{(1)}(i\epsilon^{1/2}r) = \frac{2ie^{3\alpha\pi} \sin[\alpha \ln(\frac{1}{2}\epsilon^{1/2}r) - \varphi]}{[\pi\alpha \sinh(\pi\alpha)]^{1/2}} \times \left[1 + O\left(\frac{\epsilon r^2}{4(\alpha^2+1)^{1/2}}\right) \right], \quad (2.17)$$

where

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

¹⁴ M. Mittleman, Ann. Phys. (N. Y.) 14, 94 (1961).

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

$$[\epsilon r^2/4(\alpha^2+1)^{1/2}] \ll 1.$$

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

$$F(r) = r^{1/2} \sin[\alpha \ln(\frac{1}{2}\epsilon^{1/2}r) - \varphi], \quad r \approx a, \quad (2.18)$$

and

$$\frac{1}{F(a)} \frac{dF(r)}{dr} \Big|_{r=a} = \frac{\alpha}{a} \cot[\alpha \ln(\frac{1}{2}\epsilon^{1/2}a) - \varphi] + \frac{1}{2a}. \quad (2.19)$$

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

$$\epsilon^{1/2} = \frac{2}{a} \exp\{\alpha^{-1}[\cot^{-1}((2ta-1)/2\alpha) + \varphi \pm n\pi]\}, \quad (2.20)$$

where

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

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:

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

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 Geltman¹ have given for the energy of the lowest lying ¹S bound state:

$$\epsilon_1 = 0.645 \text{ eV} = 0.0474 \text{ Ry}. \quad (2.22)$$

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

$$a^2 \ll [(37)^{1/2} - 1]/\epsilon_1 \approx 107,$$

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

$$\epsilon_2 = (0.037 \pm 0.004) \text{ eV}. \quad (2.23)$$

[It should be understood that the error estimate of 10% in the accuracy of Eq. (2.21) between ϵ_1 and ϵ_2 is a subjective estimate which could conceivably err on the small side. We believe, however, that it is quite a liberal

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

$$\epsilon_2 = (10.167 \pm 0.004) \text{ eV.}$$

Furthermore, since the asymptotic form of the $2s\text{-}2p$ 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 are 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 eV 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

¹⁵ The Gaillitis-Damburg spacing formula, Ref. 9, was derived originally for the 1S state. P. G. Burke and K. Smith, p. 89 of the conference proceedings quoted in Ref. 7, were the first to extend it to P states.

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 Ref. 1.

^c This column contains only the first three of the eigenvalues for each state of the infinity of eigenvalues predicted by Eq. (2.21). The actual number of levels is finite and cuts off when the energy separation of the autoionization states becomes comparable to the Lamb-shift splitting of the $n=2$ level of H . (See, for example, Ref. 9.)

the first. For any eigenfunction n , we define this value of r by R_n :

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

In the 1S case $R_1 \cong 25 a_0$ and $R_2 \cong 100 a_0$, 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 parameters, 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 ($100 a_0$) is so large that it is surprising indeed that it could be obtained by a conventional variational wave function below the $n=2$ threshold at all.

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