Variational Calculation of the Scattering of Electrons of Nearly Zero Energy by Hydrogen Atoms*

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The cross section for the scattering of electrons by hydrogen atoms at zero energy has been calculated by using a variational principle of the Hulthén-Kohn type. For singlet scattering we have used a three-parameter trial function which reduces to an H⁻ wave function at small electron separations and which has the correct asymptotic form. To calculate triplet scattering we use an antisymmetrized version of the same trial function. The effective range for singlet scattering is determined from the scattering length already calculated and the known value of the electron attachment energy for H⁻. For triplet scattering we use an energy-dependent trial function to determine the effective range. Using the calculated values of the above parameters, we find the cross section as a function of energy for the range 0–0.02 volt.

1. INTRODUCTION

THE problem of the scattering of electrons by hydrogen atoms has a certain intrinsic interest because of the high hydrogen concentration in stellar atmospheres. Just as important is the fact that this problem serves as a sort of model for the general problem of the scattering of electrons by atomic systems. Any approximation methods one devises for the more difficult problems of the scattering by heavier atoms can be tried out with hydrogen, and the results can be compared either with experimental data or with more accurate calculations that can be made for this three-body system.

Some experiments have been done on the elastic scattering of electrons by atomic hydrogen,[1,2] and numerous calculations have also been tried.[3] Unhappily, the experiments do not go down to energies below 1.5 electron volts, and none of the calculations attempted has been specifically designed to take advantage of the known properties of the proton plus two-electron system where the total energy of the system is approximately equal to the binding energy of the hydrogen atom.

The difficulty in dealing with the low-energy scattering of electrons by hydrogen atoms is that none of the interactions can be considered small; thus, no perturbation procedure is possible. In addition, it is difficult to take into account the polarization of the hydrogen atom by the incoming electron. The central idea of this paper is to take advantage of the fact that

we know something about the polarization of the atom by the incoming electron, namely, that a negative hydrogen ion exists with an attachment energy of $\frac{3}{4}$ of an electron volt. This experimental fact has two consequences. The first is that this bound state so close to zero energy will dominate the zero-energy scattering cross section. The second conclusion is that the wave function of H⁻ should be a good description of the system of two electrons plus a proton when all three particles are close together. Such a wave function should be particularly useful in a variational principle.

In Sec. 2 we discuss the problem we are going to solve and the variational principle we shall use. In Sec. 3 we shall give the results for singlet and triplet scattering at zero energy using two different trial functions. In Sec. 4 we discuss the way in which the known results of the singlet and triplet scattering lengths and the attachment energy of H⁻ enable us to extend our results to higher energies. In the final section we compare our work with the previous literature.

2. VARIATIONAL PRINCIPLE

In order to solve the problem of the scattering of electrons by hydrogen atoms, we must solve the differential equation,

$$L\Psi(\mathbf{r}_1,\mathbf{r}_2)=0, \qquad (1)$$

subject to the boundary condition that as $\mathbf{r}_1$ or $\mathbf{r}_2$ goes to infinity, the solution should consist of an incident plane wave in one particle times a bound state function of the other, plus an outgoing spherical wave in the coordinates of one of the electrons times a bound state wave function in the coordinates of the other. The operator L is

$$L=\nabla_1^2+\nabla_2^2+2\left(\frac{k^2}{2}-\frac{1}{2}+\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{r_{12}}\right), \qquad (2)$$

where we have set $\hbar=m=e=1$. In this system of units, the unit of length is the Bohr radius and the unit of energy is twice the ionization energy of hydrogen. The quantity k^2 is the kinetic energy of the incident electron; $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons, and $\mathbf{r}_{12}$

¹ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 12.
² Bederson, Hammer and Malamud (to be published).
³ H. S. W. Massey and B. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951); W. P. Allis and P. M. Morse, Phys. Rev. **44**, 269 (1933); J. McDougall, Proc. Roy. Soc. (London) **A136**, 549 (1932); S. Chandrasekhar and F. H. Breen, Astrophys. J. **103**, 41 (1946). T. Kato, Progr. Theoret. Phys. Japan **6**, 394 (1951); S. S. Huang, Phys. Rev. **76**, 477 (1950).

is equal to $r_1 - r_2$. The mass of the proton is taken to be infinite.

Since we shall be interested in the scattering at zero energy, we need concern ourselves only with the s phase shift. However, the potential in (1) is not spherically symmetric hence there is some difficulty about introducing a phase shift. The method for doing this has been discussed by Kohn[4] and we shall repeat the relevant portions of his paper as applied to the problem at hand.

The asymptotic form of the wave function can be written as

$$\Psi^\mu = \sum_i N_i P_i \phi_i \left(\alpha_i{}^\mu \frac{e^{-ik_i r_i}}{r_i} - \beta_i{}^\mu \frac{e^{ik_i r_i}}{r_i} \right). \quad (3)$$

In (3), where P_i represents the normalized angular wave function of relative motion, N_i is a normalization constant so chosen that $|\alpha_i{}^\mu|^2$ represents the probability flux of the incoming electron, and ϕ_i is a bound state hydrogenic wave function. The superscript μ represents a possible mode of collision. In our case, there are two possible modes of collision, one in which electron 1 is incident, and the other in which electron 2 is incident.

In the particular problem we are considering, namely, the scattering of electrons by hydrogen atoms near zero energy, the index i runs over 1 and 2. Only the zero angular momentum wave function need be considered. The coefficients $\alpha_1{}^2$ and $\alpha_2{}^1$ are equal to zero; the coefficient $\beta_1{}^1$ is connected with the amplitude for direct scattering and $\beta_2{}^1$ is connected with the amplitude for exchange scattering. The S matrix is defined as the matrix connecting $\alpha_i{}^\mu$ and $\beta_i{}^\mu$, as follows:

$$\beta_i{}^\mu = \sum_j S_{ij} \alpha_j{}^{(\mu)}. \quad (4)$$

In the representation we have used, the S matrix is not diagonal. From the symmetry of our problem, we know that $S_{11} = S_{22}$ and that $S_{12} = S_{21}$. In order to diagonalize S, we must transform it with the matrix

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}. \quad (5)$$

This means that the basis for the diagonal representation of S is

$$\frac{1}{\sqrt{2}} \begin{pmatrix} \Psi^{(1)} + \Psi^{(2)} \\ \Psi^{(1)} - \Psi^{(2)} \end{pmatrix}. \quad (6)$$

These are the same linear combinations which are required to satisfy the Pauli principle. We now introduce the proper phases as the diagonal elements of S, such that

$$S_{11}' = e^{2i\delta_1}, \quad S_{22}' = e^{2i\delta_2}. \quad (7)$$

These considerations are relevant to our problem in the following way: in order to introduce phases for the scattering problem, two s phases are required, one representing the phase shift for singlet scattering, and the other for triplet scattering. The former is characterized by a symmetric wave function in coordinate space, the latter by an antisymmetric one.

The variational principle used here is one that has previously been derived by Kohn[4] or can be derived by a simple generalization of the method used by Kato.[3] It states that if we define

$$X \equiv k \cot\delta = k \cot\delta^t - \int \Psi^t L \Psi^t d\tau_1 d\tau_2, \quad (8)$$

where δ^t is the trial phase shift, then X is stationary with respect to the variations of trial functions Ψ^t subject to the condition that their asymptotic form is

$$\Psi^t \underset{r_1 \to \infty}{\longrightarrow} \frac{1}{(8\pi)^{\frac{1}{2}}} \frac{1}{r_1} [\cos k r_1 + k \cot\delta^t \sin k r_1] \phi_0(r_2), \quad (9)$$

$\phi_0(r)$ being the ground state wave function for hydrogen. Its asymptotic form, where r_2 goes to infinity, is

$$\Psi^t \underset{r_2 \to \infty}{\longrightarrow} \pm \frac{1}{(8\pi)^{\frac{1}{2}}} \frac{1}{r_2} [\cos k r_2 + k \cot\delta^t \sin k r_2] \phi_0(r_1); \quad (10)$$

the plus or minus sign obtains, depending on whether we are considering singlet or triplet scattering. There are two separate stationary expressions of the form of Eq. (8) which have to be separately calculated with symmetric and antisymmetric trial functions, respectively.

3. RESULTS FOR ZERO-ENERGY SCATTERING

As we have explained in the introduction, the trial function used in the stationary expression (8) for singlet scattering should reduce to an H^- wave function when the electrons are close to one another, and to the correct asymptotic form (9) and (10) when they are separated. We first concentrated on zero-energy singlet scattering and used a wave function of the form

$$\Psi^t = A(e^{-\alpha r_1} e^{-\beta r_2})$$

$$+ \frac{1}{(8\pi)^{\frac{1}{2}}} \left[B(1 - e^{-\gamma r_2}) + \frac{(1 - e^{\gamma r_2})^2}{r_2} \right] \frac{1}{\pi^{\frac{1}{2}}} e^{-r_1}$$

$$\pm \frac{1}{(8\pi)^{\frac{1}{2}}} \left[B(1 - e^{-\gamma r_1}) + \frac{(1 - e^{-\gamma r_1})^2}{r_1} \right] \frac{1}{\pi^{\frac{1}{2}}} e^{-r_2}. \quad (11)$$

The α and β that we chose are the best ones for H^- and have been determined by Chandrasekhar[5] to be $\alpha = 1.03925$ and $\beta = 0.28309$. It probably would have been better to have left the α and β as free parameters, but this would have made the calculation very cumbersome. By taking the limit of (9) as $k \to 0$, we can see

[4] W. Kohn, Phys. Rev. **74**, 1763 (1948).

[5] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

TABLE I. Results for singlet and triplet scattering.

	X_0	γ	A	B
Singlet	−0.1226	0.12	0.0414	−0.1282
Triplet	−0.4251	0.46	0.00557	−0.4256

that B represents $\lim_{k\to 0}(k\cot\delta^t)$. A, B, and γ were the parameters which were varied. The actual procedure we used was to substitute (11) into (8), and then to carry out the integrations. When this was done, $k\cot\delta$ was expressed as a function of A, B, and γ. We then eliminated A and B by the relations

$$\partial(k\cot\delta)/\partial A = 0 = \partial X_0/\partial A,$$
$$\partial(k\cot\delta)/\partial B = 0 = \partial X_0/\partial B, \tag{12}$$

where X_0 is the stationary value of $\lim_{k\to 0}(k\cot\delta)$. Having eliminated two of the parameters algebraically we plotted X_0 as a function of γ and determined the stationary point from the plot. The numerical calculations are quite involved and were carried out with the aid of Burroughs E-101 computer.

For triplet scattering we have no guide, as we do in the singlet case, as to what would be an intelligent choice of trial function, but since we do not expect that the triplet scattering will contribute much, we have merely taken the antisymmetric combination of the same one-electron wave functions that has been used in (11). The results of the calculation are summarized in Table I.

Our next attempt was to improve the singlet cross section calculation by taking a more complicated H⁻ wave function, one that depends explicitly on r_{12}. Our trial function to be used in the stationary expression (8) is

$$\Psi^t = A(1+cr_{12})[e^{-\alpha r_1}e^{-\beta r_2}+e^{-\beta r_1}e^{-\alpha r_2}]$$
$$+\frac{1}{(8\pi)^{\frac{1}{2}}}\left[B(1-e^{-\gamma r_2})+\frac{(1-e^{-\gamma r_2})^2}{r_2}\right]\frac{1}{\pi^{\frac{1}{2}}}e^{-r_1}$$
$$+\frac{1}{(8\pi)^{\frac{1}{2}}}\left[B(1-e^{-\gamma r_1})+\frac{(1-e^{-\gamma r_1})^2}{r_1}\right]\frac{1}{\pi^{\frac{1}{2}}}e^{-r_2}. \tag{13}$$

$$c=0.31214, \quad \alpha=1.07478, \quad \beta=0.47758.$$

The results obtained for singlet scattering by using this trial function are summarized in Table II.

We did not attempt to complicate the calculation for triplet scattering since we have no reason to believe that the more complicated trial function would improve

TABLE II. Results obtained for singlet scattering by using r_{12}-dependent trial functions.

	X_0	γ	A	B
Singlet	−0.1291	0.07	0.0308	−0.1472

the results. Besides, the triplet cross section seemed to be quite small at zero energy.

The limit as $k\to 0$ of $k\cot\delta$ equals $-1/a$, where a is the scattering length. The singlet and triplet cross sections in terms of the scattering lengths are

$$Q_s=4\pi a_s{}^2, \quad Q_t=4\pi a_t{}^2. \tag{14}$$

The total cross section is given by

$$Q=\tfrac{1}{4}Q_s+\tfrac{3}{4}Q_t. \tag{15}$$

The results for the total cross section are given in Table III.

Thus it is seen that the triplet cross section contributes only about 20% of the total at zero energy, and that the inclusion of an explicit r_{12} dependence in singlet trial function lowers of the cross section by about 10%.

4. RESULTS NEAR ZERO ENERGY

By a slight generalization of the argument used in potential scattering,[6] it is easy to show that in the three-body problem which we are considering, the

TABLE III. Total cross sections at zero energy.

	$\tfrac{1}{4}Q_s$	$\tfrac{3}{4}Q_t$	Q
Using trial function Eq. (11)	$66.54\,\pi a_0{}^2$	$16.61\,\pi a_0{}^2$	$83.15\,\pi a_0{}^2$
Using trial function Eq. (13)	$60.00\,\pi a_0{}^2$	$16.61\,\pi a_0{}^2$	$76.61\,\pi a_0{}^2$

effective range formula holds for each of the phase shifts,

$$k\cot\delta_{t,s}=-\frac{1}{a_{t,s}}+\tfrac{1}{2}r_{0t,0s}k^2,$$

$$r_{0t,0s}=\left\{\begin{matrix}\text{triplet}\\\text{singlet}\end{matrix}\right\}\text{effective range.} \tag{16}$$

Again, by arguments similar to those used in the one-body problem, it is possible to show that in the event that a negative ion exists, there is a relation between the attachment energy, the scattering length and the effective range given by

$$\epsilon=(1/a)+\tfrac{1}{2}r_0\epsilon^2, \quad \epsilon=\text{attachment energy.} \tag{17}$$

Having now calculated the scattering length, we could calculate the effective range if we knew the attachment energy for H⁻. The best value is one which Hylleraas and Midtdal[7] have found, as corrected by Branscomb,[8] to give 0.756 electron volts. In our units this is $\epsilon=0.236$. Substituting this and the previously calculated value of a_s into (17), we find the values for r_{0s} as given in Table IV.

[6] J. Blatt and V. W. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952), pp. 57 ff.
[7] E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).
[8] L. Branscomb (private communication).

TABLE IV. Singlet effective ranges.

	Trial function Eq. (11)	Trial function Eq. (13)
r_{0s}	$4.04a_0$	$3.85a_0$

Since the only bound state of H^- is a singlet state, we have no similar argument which would enable us to determine the triplet scattering length. What we have done in this paper is to use an energy-dependent trail function of the form

$$\Psi = A\left[e^{-\alpha r_1}e^{-\beta r_2} + e^{-\beta r_1}e^{-\gamma r_2}\right]$$

$$+\frac{1}{(8\pi)^{\frac{1}{2}}}\frac{1}{r_1}[\cos kr_1(1-e^{-\gamma r_1})^2$$

$$+k\cot\delta^t\sin kr_1(1-e^{-\gamma r_1})]\frac{1}{\pi^{\frac{1}{2}}}e^{-r_2}$$

$$+\frac{1}{(8\pi)^{\frac{1}{2}}}\frac{1}{r_2}[\cos kr_2(1-e^{-\gamma r_2})^2$$

$$+k\cot\delta^t\sin kr_2(1-e^{-\gamma r_2})]\frac{1}{\pi^{\frac{1}{2}}}e^{-r_1}. \quad (18)$$

We then expand the result in powers of k^2, and obtain

$$X = k\cot\delta = f(A,B,\gamma) + g(A,B,\gamma)k^2. \quad (19)$$

From (16), we note that

$$\partial X/\partial k^2 = +\tfrac{1}{2}r_0. \quad (20)$$

If we now take the derivative of (19) with respect to k^2 and take the limit as k^2 approaches zero, we have

$$\left(\frac{\partial X}{\partial k^2}\right)_0 = \left(\frac{\partial f}{\partial A}\right)_0\left(\frac{\partial A}{\partial k^2}\right)_0 + \left(\frac{\partial f}{\partial B}\right)_0\left(\frac{\partial B}{\partial k^2}\right)_0$$

$$+\left(\frac{\partial f}{\partial \gamma}\right)_0\left(\frac{\partial \gamma}{\partial k^2}\right)_0 + g(A,B,\gamma)_0, \quad (21)$$

where the subscript 0 indicates that the value of the functions is to be taken when $k^2=0$. But the extremal nature of X_0 means that we have evaluated it at the points where

$$(\partial f/\partial A)_0 = (\partial f/\partial B)_0 = (\partial f/\partial \gamma)_0 = 0. \quad (22)$$

Comparing (20), (21), and (22), we see that

$$(\partial X/\partial k^2)_0 = g(A,B,\gamma)_0 = \tfrac{1}{2}r_0. \quad (23)$$

Thus, using an energy-dependent trial function we

TABLE V. Singlet and triplet effective ranges.

	Singlet	Triplet
r_0	3.11	0.808
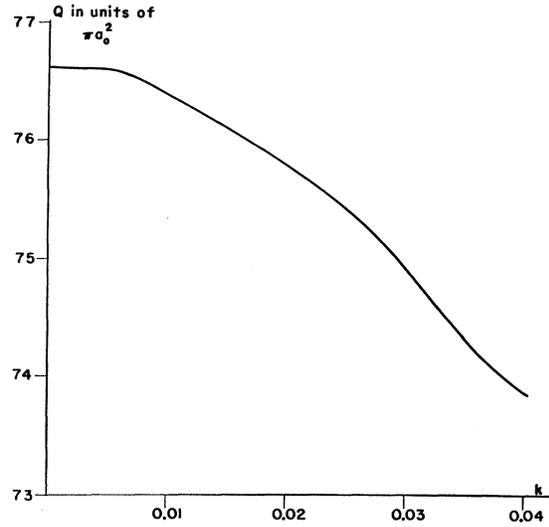
FIG. 1. Total cross section vs wave number.

obtain the results for r_0 as given in Table V. We see that this gives a value of the effective range in the case of singlet scattering which is about 30% smaller than the more accurate calculation using the known attachment energy. It is to be expected that the latter method of calculating the effective range is not quite as accurate since the trial function we use becomes worse as we proceed away from zero energy. As we have said before, since the triplet scattering is relatively unimportant, we feel that the error incurred is
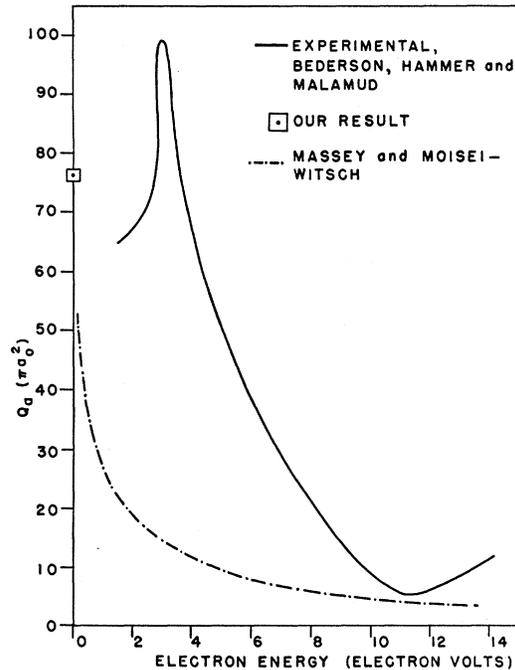
FIG. 2. Comparison of calculated and experimental results for the scattering of electrons by hydrogen atoms.

small. We have used the value of $r_{0s}=3.85$ and $r_{0t}=0.808$. The results are plotted in Fig. 1.

We have plotted the results only up to $k=0.04$, since we feel that the validity of the effective-range formula can be guaranteed only in regions where $k^2 \ll 1/r_0^2$.

5. COMPARISON WITH OTHER RESULTS AND CONCLUSIONS

There are no experimental results for the scattering of electrons by hydrogen atoms in the vicinity of zero energy; Bederson, Hammer, and Malamud[2] have obtained a cross section of 65π at 1.5 electron volts. The relationship of their results to ours is shown in Fig. 2.

Of the calculations that have been made, the one by Massey and Moiseiwitsch[3] is closest to the one reported here. However, the authors do not emphasize the scattering at zero energy, nor do they report any results in the neighborhood of zero energy. It is difficult to estimate how to extrapolate their results. However, the values of $k \cot\delta$ calculated by them fall on a straight line both for the singlet and for the triplet case. If one extends this straight line to zero energy, one obtains a value of 64.6π, in contrast to our value of 76.6π. The higher value that we have obtained seems more in accord with the experimental results.

One other observation should be made. The results of McDougall,[3] Chandrasekhar and Breen[3] and Kato[3] for the scattering of an electron by the Hartree field of the hydrogen atom give a value of the zero-energy cross section of about 350π, which has always seemed too large. Since these authors do not include an exchange interaction in the Hartree-Fock sense, it is reasonable to suppose that their calculation is an approximation to the singlet cross section. This means that their value must be weighted with the statistical weight of $\frac{1}{4}$. The triplet cross section, as we have seen, is very small at zero energy and therefore the value obtained by considering the scattering by the Hartree field at the atom seems surprisingly good.

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Nuclear Level Densities*

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By using the statistical methods originally due to Bethe, the predictions for the densities of nuclear energy levels at excitation energies around 8 Mev are examined for two different versions of the shell model. A crude method is used to take into account the effects of shell structure. The assumed form of the theoretical expression for the density of nuclear energy levels is employed to analyze the data from slow-neutron resonance experiments and from fast (n,γ) cross sections. In contrast to earlier results, for the necessary potential radius, it is found that either the static diffuse potential with a radius of $\sim 1.2 \times 10^{-13} \times A^{\frac{1}{3}}$ cm, or the diffuse velocity-dependent potential based on the Johnson-Teller model with a radius of $\sim 1.4 \times 10^{-13} \times A^{\frac{1}{3}}$ cm, leads to fair agreement with the above experiments. In each case the values of the thickness of the surface layer on the nuclear potential and the magnitude of the spin-orbit coupling are taken to be those previously found to give close agreement with the experimental shell-model level sequences.

The level-density expressions used here lead to an energy dependence which is in even stronger disagreement with those derived from various excitation function and inelastic scattering experiments than the empirical formula of Blatt and Weisskopf. It is argued that this anomaly may cast more light on the use of the statistical theory of nuclear reactions than on the validity of the expression for nuclear level densities.

I. INTRODUCTION

IGO and Wegner,[1] and others,[2] have pointed out that there exists an anomaly in the various measurements of nuclear level densities: different nuclear-reaction experiments give evidence about the energy dependence and the dependence on mass number A which seems contradictory. However, the statistical theory of nuclear reactions[3] is employed to analyze these experiments so that it is far from certain which of the many assumptions involved is breaking down. Besides the steadily increasing evidence for "direct interactions"[2,4] or noncompound-nucleus processes,

[1] G. Igo and H. E. Wegner, Phys. Rev. 100, 1309 (1955).

[2] See, e.g., Brookhaven Conference on the Statistical Aspects of the Nucleus, January, 1955, BNL-331 (C-21) (unpublished).

[3] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952).

[4] Austen, Butler, and McManus, Phys. Rev. 92, 350 (1953); R. M. Eisberg and G. Igo, Phys. Rev. 93, 1039 (1954); R. M. Eisberg, Phys. Rev. 94, 739 (1954).