Low Energy Electron-Hydrogen Scattering

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The effective range theory is developed for electron-hydrogen scattering. The scattering length $a_s$ and the effective range $r_{0s}$ of the singlet state are determined by making use of the accurate solution of the H$^-$ ion state, as

$$a_s = 7.03, \quad r_{0s} = 3.37 \text{ (in atomic unit)}.$$

The scattering length $a_t$ and the effective range $r_{0t}$ of the triplet state are calculated from the zero energy solution by a variation-perturbation method. The results are $a_t = 2.34, r_{0t} = 1.29$.

§ 1. Introduction

The scattering of an electron by a hydrogen atom is the simplest and the most fundamental problem among electron-atom scatterings. Apart from the direct application of the result to the exploration of the physical condition of celestial bodies, to the researches of discharge phenomena and so on, it has an important theoretical significance as a test of various approximations used in the calculations in more complicated collision problems pertaining to a complex atom.

The method of calculation for the problem of electron-hydrogen scattering at low energies has been improved by many authors. The Born and distorted wave approximation in a central field of a hydrogen atom gave a rather poor result, for one finds the same cross-section for both the singlet and the triplet states, and also the zero phase-shift for the zero energy limit. The solution of the Hartree-Fock type equation including the exchange effect was obtained accurately by a numerical method.

Subsequent calculations taking the polarization into account showed that the Hartree-Fock approximation gives a fairly good result, especially for the triplet state, but a more refined calculation is needed for the singlet state.

A powerful method for treating a low energy scattering, so-called the effective range theory, was put forward by Schwinger and Bethe for the nucleon-nucleon scattering, according to which the scattering process is described completely by two quantities—the scattering length $a$ and the effective range $r_0$. These quantities are calculated from the wave-function of the state for the zero energy of the incident particle, or by the function of the bound state if the system has a stable bound state with small binding energy such as the deuteron-state for two nucleons. In the case of electron-hydrogen scattering, there also exists a H$^-$ state with a very small affinity, and its state function is calculated quite accurately by the variational method due to Hylleraas. We shall
find $a_s$, $r_{0s}$ for the singlet state using this function $\psi_0$ (actually using Hart-Herzberg function) of the ion state. The values of $a_s$, $r_{0s}$ obtained are estimated to be very accurate, because the binding energy (affinity) of $H^-$ is very small (~0.028) compared with the kinetic energy of the electron inside the Bohr radius, and also because of the reliability of the $H^-$-function.

For the triplet state, no such handy function exists, so that we have to construct the wave function of the zero energy state to find $a_s$, $r_{0s}$. This function is calculated together with that for the singlet state by a variation-perturbation method which is, in a sense, a mixed use of both the variational method for Hartree-Fock and the second Born approximation, and provides improvements on them.

§2 recapitulates the results of calculations hitherto obtained, from the standpoint of the effective range theory, and gives the values of $a_s$, $r_{0s}$ determined from the function of the negative ion state. In §3 the variation-perturbation method is described to find $a$ and $r$ from the solution of the zero energy state. §4 contains the summary and the conclusion.

§2. Effective range theory

The Schrödinger equation for the system of a hydrogen atom and an electron is, in atomic units,

$$\left\{ \frac{d}{dr} + \frac{1}{r} + \frac{1}{r^2} - \frac{1}{r_{0s}} + E \right\} \psi(r_1, r_2) = 0. \tag{1}$$

The atomic electron in a hydrogen atom in the ground state is described by a function $\phi(r)$ which satisfies

$$\left\{ \frac{d}{dr} + \frac{1}{r} \right\} \phi(r) = 0, \tag{2}$$

$$\int \phi(r)^2 dr = 1,$$

so that

$$\phi(r) = e^{-r/\sqrt{\pi}}.$$

We shall normalize the function $\psi(r_1, r_2)$ as

$$\psi(r_1, r_2) \rightarrow \phi(r_2) \frac{\sin(kr_2 + \delta_\pm)}{r_2 \sin \delta_\pm} \quad \text{for} \quad r_2 \rightarrow \infty,$$

$$\rightarrow \pm \phi(r_2) \frac{\sin(kr_1 + \delta_\pm)}{r_1 \sin \delta_\pm} \quad \text{for} \quad r_1 \rightarrow \infty, \tag{3}$$

where $\pm$ correspond to the singlet and the triplet states respectively. The total cross-section is given by

$$\sigma = \frac{1}{4} \sigma_\uparrow + \frac{3}{4} \sigma_\downarrow, \quad \sigma_\pm = \frac{4\pi}{k^2(1 + \cot^2 \delta_\pm)}. \tag{4}$$
To express this cross-section in terms of the quantities arising in the effective range theory, the following function, which is equal to the asymptotic form of $\psi(r_1, r_2)$, is introduced:

$$u(r_1, r_2) = \phi(r_1) \frac{\sin(kr_1 + \theta_1)}{r_2 \sin \theta_2} \pm \phi(r_2) \frac{\sin(kr_2 + \theta_2)}{r_1 \sin \theta_1}.$$  

(5)

Then, following the procedure taken by Bethe in his paper, it is found that

$$k_a \cot \theta_a - k_b \cot \theta_b = \frac{(k_a^2 - k_b^2)}{8\pi} \int_0^\infty (u_\alpha u_\beta - \psi_\alpha \psi_\beta) d r_1 d r_2$$

$$\pm \frac{1}{2\pi} G(k_a, \theta_a) \{F(k_b, \theta_b) - 2\pi \phi(0)\}$$

$$\mp \frac{1}{2\pi} G(k_b, \theta_b) \{F(k_a, \theta_a) - 2\pi \phi(0)\},$$  

(6)

where the extra terms

$$F(k, \theta) = \frac{\sin(kr + \theta)}{r^2 \sin \theta} dr$$

$$G(k, \theta) = \frac{\sin(kr + \theta)}{r \sin \theta} dr$$

arise from the exchange.

Putting $k_0 = 0$, and expanding according to the powers of $k_a^2 = k_b^2$,

$$k \cot \theta = - \frac{1}{a} + \frac{r_0}{2} k^2 + O(k^4)$$  

(7)

is obtained, where $a$ is the scattering length determined from the asymptotic form of zero-energy state $\psi_0(r_1, r_2)$:

$$u_\alpha(r_1, r_2) = \phi(r_1) (1 - r_2/a) \pm \phi(r_2) (1 - r_1/a),$$  

(8)

and $r_0$ is the effective range given by

$$r_0 = \frac{1}{4\pi} \int_0^\infty (u_\alpha^2 - \psi_\alpha^2) d r_1 d r_2 \mp 8 (1 - 2/a)^2.$$  

(9)

The cross-section is expressed as

$$\sigma = \frac{4\pi a^2}{1 + a (a - r_0) k^2 + (a r_0 / 2) k^4}.$$  

(10)

For the singlet state, the cross-section can also be expressed by using the function of the negative ion state $\psi_\alpha(r_1, r_2)$. For that, (6) is extended to the negative energy state by putting $k_0 = -i \gamma$, $\cot \theta_0 = -i$. The result is

$$k \cot \theta = - \gamma + \frac{\rho}{2} (\gamma^2 + k^2) + O((\gamma^2 + k^2)^2),$$  

(11)

where

$$\rho = \frac{1}{\gamma} - \frac{1}{4\pi} \int_0^\infty \psi_\alpha^2 d r_1 d r_2,$$  

(12)
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\[ \psi_{\frac{1}{2}}(r_1, r_2) \rightarrow u_{\frac{1}{2}}(r_1, r_2) = \phi(r_1) \exp(-\gamma r_2) + \phi(r_2) \exp(-\gamma r_1), \quad (13) \]

and the cross-section is given by

\[ \sigma_+ = \frac{4\pi}{(r^2 + k^2)[1 - \gamma \rho + \rho^2 (r^2 + k^2) / 4]} . \quad (14) \]

If \( \rho = r_0 \) ("shape-independent" assumption) is assumed, the following relation holds:

\[ \gamma = \frac{1}{a_s} + \frac{r_{0s} \gamma^2}{2} . \quad (15) \]

The numerical values of \( a, r_0 \) estimated from the existing data of calculations by various authors will be tabulated below.

A) Massey-Moiseiwitsch. They included the exchange and performed two kinds of variational calculations, the one neglecting, and the other including the polarization. The data for \( k = 0 \) being not given, \( a \) and \( r_0 \) are estimated from those of \( k = 0.1, 0.2, \) and 0.3.

B) Borowitz-Greenberg. They used 3-parameter trial functions for the zero energy state. The asterisk indicates the values deduced from (15) for \( a_s \) obtained by the variational method and \( \gamma = 0.236 \) estimated by Branscomb, and \( \dagger \) those calculated from energy dependent approximate functions.

C) Seaton. He tried various methods in solving the zero energy state. The values, polarization neglected, are deduced from the accurate numerical integration including the exchange, and, polarization included, from the 3-parameter trial function.

D) We solved the zero energy equation by a method described in the next section. \( r_0 \) is calculated by (9).

E) We also calculated \( \rho \) by (12), using the 20-parameter function of Hart-Herzberg,\(^5\) which is normalized according to (13) with \( \gamma = 0.236, \) and

\[ \rho = 3.37 \leq r_0 \]

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\( a_s \) and \( r_{0s} \) polarization neglected
\( a_s \) and \( r_{0s} \) polarization included
\( r_{0s} \) first approximation
\( r_{0s} \) second approximation
is found. This value of \( \rho \) may be fairly accurate, in view of the reliability of the \( H^- \) function. Then (15) gives

\[
a_e = 7.03.
\]

We shall mention the applicability of the effective range theory to the electron-hydrogen scattering. To ensure the validity of the approximation assumed here, the contribution from the third term of (7) (or (11)) must be estimated. However, we feel that this approximation seems to be valid when the incident energy (and also the binding energy) of the electron is smaller than the kinetic energy of the electron inside the Bohr radius. If this is the case, the result: \( a_e = 7.03 \) will be very accurate, with an error possibly within a few percents.

§ 3. Variation-perturbation method

As has been remarked in the introduction, our problem of three bodies with two electrons and an infinitely heavy nucleus is the simplest of the many-body problems in quantum mechanics. But we have not on hand even a full knowledge of the analytical property of the state function at the singularities. The most effective approach practicable at the present stage would be the variational method. Indeed, for the \( H^- \) ion, very accurate calculations\(^5\) have been performed with a large number of parameters. On the other hand, in the scattering problem, only three parameters have been employed,\(^3\) among which only one is responsible for the polarization. It would be worth while to look into the effect of polarization in a more systematic way.

The second Born approximation is certainly one of the powerful methods to see the general tendency of this effect.\(^6\) However, for the low energy electron, this is not a convenient method to give a good approximation. Here an attempt is given to solve the problem by a mixed use of the Born approximation and the variational method, which is also equivalent to finding \( F_n \) approximately, when the exact solution is expressed in a form\(^7\)

\[
\psi(r_1, r_2) = \left( \sum_n + \int \right) \{ \phi_n(r_2) F_n(r_1) \pm \phi_n(r_1) F_n(r_2) \}.
\]

The general idea has already been put forward in a paper\(^8\) by one of the authors (T. O.). Here the procedure is described briefly, with a special attention to the degree of approximation.

Now the problem is to solve the equation

\[
H \psi_k(r_1, r_2) = E_k \psi_k(r_1, r_2),
\]

\[
E_k = -\frac{1}{2} + \frac{k^2}{2}, \quad H = -\frac{A_1}{2} - \frac{A_2}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}},
\]

where \( \psi_k \) is normalized as \( \langle \psi_k, \psi_k \rangle = \delta(k - k') \), the inner product \( \langle \varphi, \psi \rangle \) being defined as \( \int \int \varphi(r_1, r_2) \psi(r_1, r_2) \, dr_1 \, dr_2 \). Let an approximate solution in the Hartree-Fock approximation be
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\[ \psi_{00}(r_1, r_2) = \phi_0(r_1) f(r_2) \pm \phi_0(r_2) f(r_1), \quad \phi_0(r) = e^{-r}/\sqrt{\pi}, \]  

where \( f(r) \) is taken, with two adjustable parameters \( a \) and \( b \), as

\[ f(r) = (1/r) \left\{ (1-e^{-r}) (1+be^{-r}) -r^a \right\}. \]

Let the other approximate functions to constitute a complete system corresponding to excited states of the hydrogen atom \( \phi_n \) be

\[ \psi_{n,k} = \frac{1}{2\pi} \left\{ \phi_n(r_1) \frac{\sin kr_2}{r_2} \pm \phi_n(r_2) \frac{\sin kr_1}{r_1} \right\}, \]

(19)
to which the ion state \( \psi_g \) will also be included. Then we find

\[ \psi_{0,0} = \psi_{0,0} - \sum_{n=0}^{\infty} \left( \frac{\psi_{n,k}(H+\frac{1}{2})}{E_{n,k} - E_{0,0}} \right) \psi_{n,k} dk \]

\[ + \frac{2}{r^2} (\varphi_g, (H+1/2) \psi_{0,0}) \varphi_g + O(\delta \psi_{0,0}, \delta \psi_{t,k}), \]

(20)

where \( E_{0,0} = -1/2, E_{n,k} = k^2/2 - 1/2(n+1)^2 \). The order of the errors is estimated as follows. Let the error of \( \psi_{n,k} \) be \( \delta \psi_{n,k} \sim J \), which cannot be very small for the low energy collision, and \( \delta \psi_g \) is expected to be less than \( J \). \( \varphi_{0,0} \), with two adjustable parameters, may have smaller error \( \epsilon \) compared with \( J \). Thus, taking

\[ \mathcal{F}_{0,0} = \psi_{0,0} + O(\epsilon \cdot J) \]

(21)
as the trial function to be put into the variational expression, the scattering length \( a \) is then calculated from

\[ -1/a = -1/a_1 + (1/4\pi) (\varphi_g, (H-E_{0,0}) \varphi_g) + O(\delta \varphi_2 \cdot \delta \varphi_3) \]

(22)

where \( a_1 \) is the scattering length determined by the asymptotic behavior of the trial function \( \varphi_1 \). The approximate value of \( a \) is determined by taking \( \varphi_1 = \varphi_2 = \varphi_{0,0} \) (first approx.), \( \varphi_1 = \mathcal{F}_{0,0}, \varphi_2 = \varphi_{0,0} \) (second approx.), \( \varphi_1 = \varphi_2 = \mathcal{F}_{0,0} \) (third approx.), for which \( 1/a \) will contain the errors \( \epsilon^2, \epsilon^2 J, \epsilon^2 J \) respectively. (In the Born approximation the unperturbed functions are used for both \( \varphi_1 \) and \( \varphi_2 \).) The second approximation in the Table is calculated retaining only \( n=0 \) (ground state) and 1 (2s of hydrogen atom) in the summation. The parameters in (18) are determined by the Hulthen variational method as \( a_1 = 9.02, b_2 = -0.396, a_1 = 2.350, b_1 = 0.312 \).

\section*{§4. Summary}

a) Singlet state. The effective range theory is developed for e—H scattering. According to the theory, the effective range has been calculated by making use of the H—ion wave function, which was obtained by Hart and Herzberg very accurately, by the variational method. The effective range is found to be \( r_0 = 3.37 \). Using the binding
energy (affinity) of $H^-$ 0.0278 which was obtained by Midtdal and Hylleraas with the variational method, the scattering length is found to be $a_s=7.03$. The values of $a_s$, $r_0$ obtained are estimated to be very accurate, the errors will be of the order of a few percents, because of the reliability of the $H^-$-function and also because the binding energy (affinity) of $H^-$ is very small ($\sim 0.028$) compared with the kinetic energy ($\sim 1$) of the electron inside the Bohr radius (namely, the validity of the effective range theory in the very low energy region). It is to be noted that this agrees well with Seaton's value $a_s=7.01$, (which has an error of within 10% according to the author's estimate). On the other hand, the value $a_s=7.88$ determined from the zero energy function cannot be much relied upon, since the effect from higher excited states may not be negligible.

b) Triplet state. In this state, the effect of polarization is automatically taken into account to some extent by the anti-symmetrization of the state function, so that the first approximation $a_t=2.350$, $r_0=1.29$ may not be a bad value. The accurate value of $a_t$ in this approximation, according to Seaton, is 2.347. By including the $2s$ state only as the excited state, $a_t=2.346$ is obtained, whereas Seaton obtained $a_t=2.33$ in his calculation including the polarization.

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