

ON THE THEORY OF ELECTRON CAPTURE
IN He + H⁺ COLLISIONS

By

LOH-YI CHANG

Bachelor of Science

National Taiwan University

Taiwan, China

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Thesis Approved:

H. G. Armstrong

Thesis Adviser

E. E. Kolthoff

J. C. Todd

W. J. Lewis

R. B. Deal

J. H. Buzze

Dean of the Graduate School

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CHAPTER I

GENERAL THEORY

1. INTRODUCTION

The differential scattering of ions by atoms or molecules in the energy range of keV has been studied in a number of cases.¹⁻⁶ The scattered particles have been analyzed at "moderately large" angles of deflection (around 5°). It has been observed that the plot of differential cross sections for various processes, such as, electron capture, electron strippings, etc., exhibits, in many cases, pronounced resonances. Recently many theoretical accounts for these phenomena have been given with some success by means of classical and semi-classical methods, as well as by some modified Born's methods.⁷⁻¹⁵ A unique method has been developed more recently by B. Roth¹⁶ for the $H + H^+$ electron capture process. Essentially this is a perturbation method with more emphasis placed on the nuclei. As the Coulomb wave function for the collision becomes modified by the presence of the electron, the electron configurations of the initial state and the capture state are coupled together strongly over the region where the interatomic interaction is great. While there are still some discrepancies between the observed electron capture probability, P_0 , vs collision energy curve, nevertheless, the theory almost pin-points the observed resonance peaks and anti-peaks.

In the present paper Dr. B. Roth's theory has been extended formally for many-electron atoms. A symmetric formulation is given to allow coupling among more than two electronic configurations, for it is speculated that such a thing might happen on various occasions. In Chapter II the problem of the $\text{He} + \text{H}^+ \rightarrow \text{He}^+ + \text{H}$ electron capture process has been studied in detail. Calculations of resonance peaks and anti-peaks were compared with great success, with the experimental data of Ziemba, et al.³ Some qualitative discussions on the general shape (mainly the damping) of P_0 vs energy curve have also been ventured. In Appendix A the interatomic interaction terms, using hydrogenic wave functions, have also been evaluated, and calculations in connection with the He and H atoms have been made.

2. THE HAMILTONIAN OPERATOR

Consider two atoms of nuclear masses M_1 and M_2 and atomic numbers Z_1 and Z_2 . the Hamiltonian operator for such a system in atomic units is,

$$\begin{aligned} \mathcal{H} = & \frac{1}{2M_1} \Delta_{R_1} + \frac{1}{2M_2} \Delta_{R_2} + \frac{Z_1 Z_2}{|\vec{R}_1 - \vec{R}_2|} + \frac{1}{2} \sum_{i=1}^n \Delta_i - \sum_{i=1}^n \frac{Z_1}{|\vec{R}_1 - \vec{r}_i|} \\ & + \frac{Z_2}{|\vec{R}_2 - \vec{r}_i|} + \sum_{ij}' \frac{1}{r_{ij}}, \quad \sum_{ij}' \equiv \sum_i \sum_j \quad i \neq j \end{aligned} \quad (1)$$

where \vec{R}_1 , \vec{R}_2 , \vec{r}_j and r_{ij} are respectively as follows:

\vec{R}_1 : The position vector of nucleus 1

\vec{R}_2 : The position vector of nucleus 2

\vec{r}_j : The position vector of the j^{th} electron

r_{ij} : The distance between the i^{th} electron and the j^{th} electron

n : The number of electrons of the system

At large interatomic distances where the two atoms may be realized as two non-interacting systems, assume that nucleus 1 and n_1 electrons form a stable atomic system (atom 1) and nucleus 2 and n_2 electrons form another system (atom 2). Furthermore, if there is no ionization, one may subdivide \mathcal{H} into the following groups:

$$\mathcal{H} = H + h_1 + h_2 + V_1$$

where

$$\begin{aligned} H &= H(\vec{R}_1, \vec{R}_2) = \frac{1}{2M_1} \Delta_1 + \frac{1}{2M_2} \Delta_2 - \frac{Z_1 Z_2}{|\vec{R}_1 - \vec{R}_2|} \\ h_1 &= h_1(\vec{R}_1, \vec{r}_i^{(1)}) = \frac{1}{2} \sum_{i=1}^{n_1} \Delta_i + \sum_{i=1}^{n_1} \frac{Z_1}{r_i} - \sum_{ij=1}^{n_1} \frac{1}{r_{ij}} \\ h_2 &= h_2(\vec{R}_2, \vec{\zeta}_k^{(2)}) = \frac{1}{2} \sum_{k=1}^{n_2} \Delta_k + \sum_{k=1}^{n_2} \frac{Z_2}{\zeta_k} - \sum_{ij=1}^{n_2} \frac{1}{r_{ij}} \\ V &= V(\vec{R}_1, \vec{R}_2, \vec{r}_i^{(1)}, \vec{\zeta}_k^{(2)}) = - \sum_{i=1}^{n_1} \frac{Z_1}{r_i} - \sum_{i=1}^{n_1} \sum_{k=1}^{n_2} \frac{1}{r_{ik}} \end{aligned} \quad (2)$$

$\Sigma^{(1)}$ represents the summation over the electrons of atom 1, and $\Sigma^{(2)}$ represents the summation over the electrons of atom 2. $\vec{r}_i^{(1)}$, and $\vec{\zeta}_k^{(2)}$ are the position vectors of the i^{th} and the k^{th} electrons of atom 1 and atom 2 as measured from their corresponding nuclei.

It has to be noticed that there are only $n_1 + n_2 + 2$ particles in the two-atom system. Consequently, there are only $n_1 + n_2 + 2$ independent position vectors. In the subsequent discussion, however, the following vectors will all be used:

$$\vec{r}_1, \vec{r}_2, \vec{\zeta}_k, \vec{r}_i^{(1)}, \vec{\zeta}_k^{(2)}, \vec{r}_i^{(2)}, \vec{\zeta}_k^{(1)}, \vec{R}_1, \vec{R}_2, \vec{R}_1', \vec{R}_2', \vec{r}_{ij}, \vec{R}, \vec{R}'$$

where

$$(M_1 + n_1) \vec{R}'_1 = M_1 \vec{R}_1 + \sum_{i=1}^{n_1} (1) \vec{r}_i \quad (1)$$

$$(M_2 + n_2) \vec{R}'_2 = M_2 \vec{R}_2 + \sum_{k=1}^{n_2} (2) \vec{r}'_k$$

$$\vec{R} = \vec{R}'_1 - \vec{R}'_2$$

$$\vec{R}' = \vec{R}'_1 - \vec{R}'_2$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j = \vec{R} - \vec{\zeta}_k - \vec{r}_i = \vec{R} - \vec{\zeta}_i + \vec{r}_k$$

$$\vec{r}'_i = \vec{R}'_1 - \vec{r}_i$$

$$\vec{\zeta}_k = \vec{R}'_2 - \vec{r}'_k$$

Among the four separate operators only h_1 and h_2 can be expressed in terms of mutually independent coordinates, namely $\vec{R}'_1, \vec{r}_i^{(1)}$ and $\vec{R}'_2, \vec{\zeta}_k^{(2)}$. Consequently, if φ_1 and φ_2 are some eigenfunctions of h_1 and h_2 respectively, then it follows that $\varphi_1 \varphi_2$ is also an eigenfunction of the operator $h_1 + h_2$. However, since H is a function of R_1 and R_2 , the eigenfunction of the operator \hat{H} cannot generally be expressed as the product of the eigenfunctions of h_1, h_2 and H .

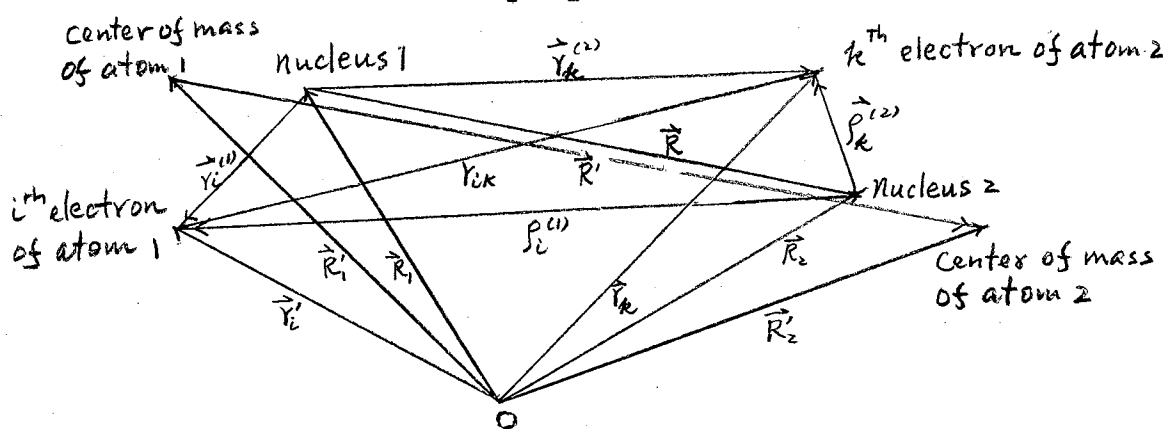


Figure 1. The Coordinate System

3. SOLUTION TO THE SCHRÖDINGER EQUATION

If E is the total energy of the two-atom system, then the corresponding Schrödinger equation is

$$\psi = E\psi \quad (4)$$

or,

$$(H = h_1 + h_2 - E)\psi = -V\psi \quad (4a)$$

In case of atomic collision one seeks for the solutions to the above equation with the following asymptotic form:

$$\psi = I + S, \quad |\vec{R}_1 - \vec{R}_2| \rightarrow \infty \quad (5)$$

where I stands for the incoming wave

and S stands for the scattered wave.

Since V vanishes at large interatomic distances, one therefore obtains the following equations for I and S ,

$$\begin{aligned} (H + h_1 + h_2)_\infty I &= EI \\ (H + h_1 + h_2)_\infty S &= E'S \end{aligned} \quad R \rightarrow \infty \quad (6)$$

In other words, both I and S , solutions to equation (6), must be some linear combinations of ϕ_∞ , where ϕ_∞ is an eigenfunction of the operator

$$(H + h_1 + h_2)_\infty \equiv (H + h_1 + h_2), \quad R \rightarrow \infty$$

To solve the equation (5) for the collision problem, one may first expand ψ in terms of the eigenfunctions of $(H + h_1 + h_2)$, and then solve equation (4a) treating V as some perturbation. The solution so obtained will then be regrouped into I and S for large interatomic distances. Consequently, there are two key considerations in the above-mentioned approach to the atomic collision problem: (1) to find a

suitable set of approximate eigenfunctions $\{\bar{\phi}_\alpha\}$ of $(H + h_1 + h_2)_\infty$, (2) to solve (4a) using the chosen set as the basis for expansion of ψ .

4. THE BORN APPROXIMATION^{17,18}

Usually there is no closed-form expression for $\bar{\phi}$, where $\bar{\phi}$ is an eigenfunction of $(H + h_1 + h_2)$, except in the limiting case when R tends to infinity. If at large interatomic distances atom 1 and atom 2 are in some definite states, for example a and b , then one may write the following equation for the eigenfunction of $(H + h_1 + h_2)_\infty$ where $\varphi_a^{(1)}(\vec{r}_i^{(1)})$ and $\varphi_b^{(2)}(\vec{r}_k^{(2)})$ are the corresponding atomic wave functions.

$$\bar{\phi}_\infty = F_\infty(\vec{R}') \varphi_a^{(1)}(\vec{r}_i^{(1)}) \varphi_b^{(2)}(\vec{r}_k^{(2)}) \quad (7)$$

where

$$H_\infty F_\infty(\vec{R}') = \epsilon_{ab} F_\infty(\vec{R}') \quad (7a)$$

$$h_{1\infty} \varphi_a^{(1)}(\vec{r}_i^{(1)}) = \epsilon_a^{(1)} \varphi_a^{(1)}(\vec{r}_i^{(1)}) \quad (7b)$$

$$h_{2\infty} \varphi_b^{(2)}(\vec{r}_k^{(2)}) = \epsilon_b^{(2)} \varphi_b^{(2)}(\vec{r}_k^{(2)}) \quad (7c)$$

$$E = \epsilon_{ab} + \epsilon_a^{(1)} + \epsilon_b^{(2)}$$

and where

$$H_\infty = H \quad R \rightarrow \infty$$

$$h_{1\infty} = h_1 \quad R \rightarrow \infty$$

$$h_{2\infty} = h_2 \quad R \rightarrow \infty$$

Furthermore, the asymptotic condition on F requires that in the center of mass system,

$$F(\vec{R}') = e^{i\vec{K}_\infty \vec{R}'} = e^{iK_\infty Z'} \quad (8a)$$

for an incoming plane wave, and

$$F(\vec{R}) = \frac{e^{iK_{ab} R'}}{R'} f_{ab}(\theta) \quad (8b)$$

for the scattered wave, and

$$K_{ab}^2/2\mu = E - (\epsilon_a^{(1)} + \epsilon_b^{(2)}) \quad (8c)$$

where the subscript "oo" indicates that both atoms were in the ground states for the incoming wave.

As a first approximation one may take

$$\{\Phi_{ab} \equiv F_{\infty}(\vec{R}') \varphi_a^{(1)}(\vec{r}_i^{(1)}) \varphi_b^{(2)}(\vec{r}_i^{(2)})\}$$

as a complete set of eigenfunctions of $(H + h_1 + h_2)$.

Now, one may expand ψ as follows:

$$\psi \equiv \sum_{ab} \Phi_{ab} = \sum_{ab} F_{ab}(\vec{R}') \varphi_a^{(1)}(\vec{r}_i^{(1)}) \varphi_b^{(2)}(\vec{r}_i^{(2)}) \quad (9a)$$

$$= (e^{iK_{oo}Z'} + \frac{e^{iKabR'}}{R'} f_{oo}(\theta)) \varphi_o^{(1)}(\vec{r}_i^{(1)}) \varphi_o^{(2)}(\vec{r}_i^{(2)}) \quad (9b)$$

$$+ \sum_{\substack{ab \\ a+b \neq 0}} \frac{e^{iKabR'}}{R'} f_{ab}(\theta) \varphi_a^{(1)}(\vec{r}_i^{(1)}) \varphi_b^{(2)}(\vec{r}_i^{(2)}) \quad (9b)$$

By substituting the above-expansion for ψ into equation (4a) and solving for the F_{ab} 's, treating V as a perturbation term, one has the following set of simultaneous equations:

$$HF_{ab} = \sum_{ab} \langle a'b' | v | \psi \rangle \quad (10)$$

where

$$\langle a'b' | v | \psi \rangle = \int \varphi_{a'}^{(1)}(\vec{r}_i^{(1)}) \varphi_{b'}^{(2)}(\vec{r}_i^{(2)}) V \psi_{\pi_i^{(1)} \pi_k^{(2)}} d\tau_i^{(1)} d\tau_k^{(2)} \quad (10a)$$

By taking

$$\psi = e^{iK_{oo}Z'} \varphi_o^{(1)}(\vec{r}_i^{(1)}) \varphi_o^{(2)}(\vec{r}_i^{(2)}) \quad (11)$$

equation (10) becomes reduced to the normal form of Born approximation. Therefore, the validity of Born approximation rests heavily on the completeness and the orthonormality of the chosen set of expansion $\{\Phi_{\infty}\}$. However, although it is quite obvious that the set is complete, its orthonormality is not always beyond question.

5. THE ORTHONORMALITY OF Φ_{ab} 's

In order that any set of eigenfunctions of $(H + h_1 + h_2)$ be orthonormal in the space of all the electronic as well as the nuclear coordinates, the following condition must be satisfied:

$$(\alpha|\alpha') \equiv \int \Phi_{\alpha'}^* \Phi_{\alpha} \prod_i \pi_i^{(1)} d\tau_i^{(1)} \prod_k \pi_k^{(2)} d\tau_k^{(2)} d\vec{R}_1 d\vec{R}_2 = \delta_{\alpha\alpha'} \quad (12)$$

It is clear that in the region where $|\vec{R}_1 - \vec{R}_2|$ is small, the orthonormality of the set of section 3 is very doubtful. This explains the failure of Born approximation in treating some atomic collision processes. Unless some approximate forms are to be used for the Φ 's, integral (12) cannot be evaluated analytically. Fortunately, such analytical evaluations are not always necessary to establish the criterion. To further clarify this point, let us consider the following examples:

$$a. \quad H_{(1)} + H_{(2)}^+ \rightarrow H_{(1)}^+ + H_{(2)} \quad (\text{ground state})$$

Referring to their electronic states before the impact, designate H as atom 1 and H^+ as atom 2. Let $W(\vec{r})$ be the ground state wave function for the hydrogen atom,

$$F_{\infty} W(\vec{r}) = \Phi_{\alpha}, \quad F_{\infty} W(\vec{r}') = \Phi_{\alpha'}$$

Concerning the energy of the two-atom system, Φ_{α} and $\Phi_{\alpha'}$ are degenerate electronic configurations. On the other hand, they do form

definite states at large interatomic distances. The non-vanishing contribution to integral (12) comes, therefore, from the region where the two nuclei are close together, as can be seen in the following integral:

$$\langle \alpha | \alpha' \rangle = \int \phi_{\alpha}^* \phi_{\alpha'} d\mathbf{r} = e^{-R} \left[\frac{1}{3} R^2 + R + 1 \right]$$

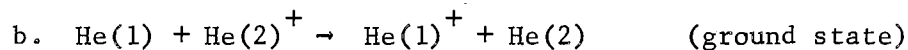
It has been noticed that the following two linear combinations of electronic configurations (LCAO, linear combination of atomic orbitals) form a much better orthonormal set for the ϕ 's.¹⁶

$$F_{\infty}^{\pm}(\vec{R}') (W(\vec{r}) \pm W(\vec{r}')) = \phi^{\pm}$$

The success of the above LCAO's in treating the hydrogen-proton collision problem can be accounted for in the following manner. Firstly, the orthonormality of the two LCAO's is secured by the fact that the two electronic configurations $W(\vec{r})$ and $W(\vec{r}')$ are orthonormal states for large interatomic distances.

$$\int (W(\vec{r}) + W(\vec{r}')) (W(\vec{r}) - W(\vec{r}')) d\vec{r} = 0, \quad R \gg 1$$

Secondly, for small r 's the two LCAO's coincide with the singlet and the triplet Heitler-London wave functions for H_2^+ .¹⁹

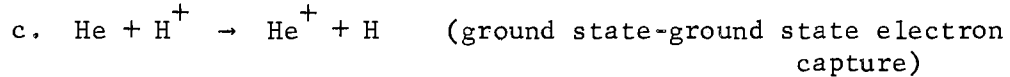


Let $U(\vec{r}_1, \vec{r}_2)$ and $V(\vec{r}_3)$ be the spatial wave function for He and He^+ respectively, and $S(123) = \frac{1}{2} (\alpha_1\beta_2 - \alpha_2\beta_1)\alpha_3$ be the corresponding spin eigenfunction. The following six electronic configurations for the two-atom system are energy degenerate configurations. They form definite electron capture and electron exchange states for large values of R .

$$(0\ 0) = U(\vec{r}_1, \vec{r}_2) V(\vec{r}_3) S(1\ 2\ 3)$$

$$\begin{aligned}
(1\ 0) &= U(\vec{r}_2 \vec{r}_3) V(\vec{\zeta}_1) S(2\ 3\ 1) \\
(2\ 0) &= U(\vec{r}_3 \vec{r}_1) V(\vec{\zeta}_2) S(3\ 1\ 2) \\
(0\ 1) &= U(\vec{\zeta}_1 \vec{\zeta}_2) V(\vec{r}_3) S(1\ 2\ 3) \\
(1\ 1) &= U(\vec{\zeta}_2 \vec{\zeta}_3) V(\vec{r}_1) S(2\ 3\ 1) \\
(2\ 1) &= U(\vec{\zeta}_3 \vec{\zeta}_1) V(\vec{r}_2) S(3\ 2\ 1)
\end{aligned}$$

Different methods have been used to couple the above six configurations in order to form an orthonormal set. However, drastic approximations must be used at various stages of calculation and the results are not as good as in the hydrogen-proton case.²⁰



The energy levels before and after the electron capture, unlike the above cases, are not equal. According to strict Born approximation, the electron capture probability is extremely small. However, experimental results indicate differently. The following three configurations are almost degenerate ones:

$$\begin{aligned}
(0\ 0) &= U_{\text{He}}(\vec{r}_1 \vec{r}_2) S(1\ 2) \\
(0\ 1) &= U_{\text{He}^+}(\vec{r}_2) W(\vec{\zeta}_1) S(1\ 2) \\
(1\ 1) &= U_{\text{He}^+}(\vec{r}_1) W(\vec{\zeta}_2) S(1\ 2)
\end{aligned}$$

where

$$S(1\ 2) = \frac{1}{2} (\alpha_1 \beta_2 - \alpha_2 \beta_1)$$

and where

U_{He} : Ground state atomic wave function of He

U_{He^+} : Ground state atomic wave function of He⁺

$$E = E_{00} - E_{11} = E_{00} - E_{01} = 24.595^{\text{ev}} - 13.595^{\text{ev}} = 11^{\text{ev}}$$

It can be shown by direct integration that the transition probability between the two $\text{He}^+ + \text{H}$ configurations (01) and (11) is very large and highly oscillatory in the region of small values of R . Therefore, they should be almost be considered as one configuration.

$$\frac{1}{N} [(01) + (11)] = \frac{1}{N} (U_{\text{He}} + (\vec{r}_2) W(\vec{c}_1) + U_{\text{He}} + (\vec{r}_1) W(\vec{c}_2)) S \quad (12)$$

The other combination

$$\frac{1}{N} [(01) - (11)] = \frac{1}{N} (U_{\text{He}} + (\vec{r}_2) W(\vec{c}_1) - U_{\text{He}} + (\vec{r}_1) W(\vec{c}_2)) S' \quad (12)$$

$$S' (12) = \frac{1}{2} (\alpha_1 \beta_2 + \alpha_2 \beta_1)$$

is ruled out, since

$$\langle S(12) | S' (12) \rangle = 0$$

The normalization constant N can be evaluated in the following manner.

For large collision parameters the interatomic distance is always large so that

$$\int [(01) + (11)]^* [(01) + (11)] d\vec{r}_1 d\vec{r}_2 = 2$$

$$N = 1/(2)^{\frac{1}{2}}$$

On the other hand, for small collision parameters the interatomic distance could be very small in time. Consequently, because of the high transition probability between the two $\text{He}^+ + \text{H}$ configurations

$$\int [(01) + (11)]^* [(01) + (11)] dr_1 dr_2 \approx 4$$

$$N = \frac{1}{2}$$

In general, N should have a value between $\frac{1}{2}$ and $(\frac{1}{2})^{\frac{1}{2}}$.

If there exists a group of electronic configurations of the two-atom system, which form definite states for large values of R with close laying energy levels, then some LCAO's among these configurations must be chosen such that their orthonormality be secured for all values

of R . To solve the collision problem, a set of $\bar{\phi}$'s based on this LCAO's will give better results than those of Born approximation.

CHAPTER II

He + H⁺ → He⁺ + H COLLISION

1. THE WAVE EQUATION

The Hamiltonian for the system in the center of mass coordinate system of the two atoms is

$$\mathcal{H} = \frac{1}{2\mu} \Delta_R + \frac{1}{2} \Delta_1 + \frac{1}{2} \Delta_2 - \frac{2}{R} + \frac{2}{r_1} + \frac{2}{r_2} + \frac{1}{\zeta_1} + \frac{1}{\zeta_2} + \frac{1}{r_{12}} \quad (13)$$

where

$$\mu = M_{\text{He}} M_{\text{H}} / (M_{\text{He}} + M_{\text{H}})$$

The following form for ψ , the solution to the wave equation corresponding to \mathcal{H} , can be used for the electron capture process if one neglects the center of mass correction,

$$\psi = F_o(\vec{R}) \varphi_o + F_e(\vec{R}) \varphi_c \quad (14)$$

where (Cf. Sec. 4, c, Chapter I).

$$\varphi_o = (00) = U_{\text{He}}(\vec{r}_1, \vec{r}_2)$$

$$\varphi_c = \frac{1}{N} ((01) + (11)) = \frac{1}{N} [U_{\text{He}} + (\vec{r}_2) W(\vec{\zeta}_1) + U_{\text{He}} + (\vec{r}_1) W(\vec{\zeta}_2)]$$

The spin eigenfunction is omitted, for it is unchanged throughout the entire collision process.

Corresponding to the electronic configurations (00), (01), and (11), may be subdivided as follows (Cf. Sec. 1, Chapter I):

$$(00): \mathcal{H} = H + h_{\text{He}} + V(00)$$

$$(01): \mathcal{H} = H + h_{(01)\text{He}^+} + h_{(01)\text{H}} + V_{(10)}$$

$$(11): \mathcal{H} = H + h_{(11)\text{He}^+} + h_{(11)\text{H}} + V_{(11)} \quad (15)$$

where

$$H = \frac{1}{2\mu} \Delta_R - \frac{2}{R}$$

$$h_{\text{He}} = \frac{1}{2} (\Delta_1 + \Delta_2) + \frac{2}{r_1}$$

$$h_{(01)\text{He}^+} = \frac{1}{2} \Delta_1 + \frac{2}{r_1}$$

$$h_{(11)\text{He}^+} = \frac{1}{2} \Delta_2 + \frac{2}{r_2}$$

$$h_{(01)\text{H}} = \frac{1}{2} \Delta_2 + \frac{1}{\zeta_2}$$

$$h_{(11)\text{H}} = \frac{1}{2} \Delta_1 + \frac{1}{\zeta_1}$$

and where

$$V_{(00)} = \frac{1}{\zeta_1} + \frac{1}{\zeta_2}$$

$$V_{(01)} = \frac{2}{r_2} + \frac{1}{\zeta_1} - \frac{1}{r_{12}}$$

$$V_{(11)} = \frac{2}{r_1} + \frac{1}{\zeta_2} - \frac{1}{r_{12}}$$

Therefore, in place of equation (10) one has,

$$H_o F_o = V(0/0)F_o + V(0/C)F_c$$

$$H_c F_c = V(C/0)F_o + V(C/C)F_c \quad (16)$$

where

$$H_o = H + K_o^2/2\mu$$

$$H_c = H + K_c^2/2\mu$$

According to equation (8c)

$$K_o^2/2\mu - K_c^2/2\mu = E_{\text{He}^+} - E_{\text{H}^+}$$

where E_{He^+} and E_{H^+} are the ionization energies of the He and H atoms.

Further

$$V(010) = \int (00) v_{(00)}(00) dt_1 dt_2$$

$$V(01c) = V(c10)$$

$$= \frac{1}{N} \left\{ \int (01) v_{(10)}(00) dt_1 dt_2 + \int (11) v_{(11)}(00) dt_1 dt_2 \right\}$$

$$= \frac{2}{N} \int (01) v_{(10)}(00) dt_1 dt_2$$

$$= \frac{2}{N} \int (11) v_{(11)}(00) dt_1 dt_2$$

$$V(c1c) = \frac{1}{N} \left\{ \int (01) v_{(10)}(01) dt_1 dt_2 + \int (11) v_{(11)}(01) dt_1 dt_2 \right.$$

$$\left. + \int (01) v_{(10)}(11) dt_1 dt_2 + \int (11) v_{(11)}(01) dt_1 dt_2 \right\}$$

$$= \frac{2}{N} \left\{ \int (11) v_{(11)}(11) dt_1 dt_2 + \int (01) v_{(10)}(11) dt_1 dt_2 \right\}$$

2. THE CASE OF STRONG COUPLING

A more simplified version of equation (16) may be obtained by imposing upon it the following assumptions:

I. $V(0/0) = (C/C)$

II. $K_o = K_c$

The justification of these assumptions will be discussed later. Equation (16) now becomes

$$H_o F_o = V(0/0) F_o + V(C/0) F_c$$

$$H_o F_c = V(C/0) F_o + V(0/0) F_c \quad (17)$$

According to equation (9) the asymptotic conditions of F_o and F_c require for large values of R that

$$\begin{aligned}
F_o &\sim e^{iKoZ} + \frac{e^{iKoR}}{R} f_o(\theta) \\
F_c &\sim \frac{e^{iKoR}}{R} f_c(\theta)
\end{aligned} \tag{18}$$

By adding and subtracting the coupled equations (17), one arrives at the following de-coupled forms:

$$H_o(F_o \pm F_c) = [V(O/O) \pm V(C/O)] (F_o \pm F_c) \tag{19}$$

One assumes for solutions to the above equations that

$$\begin{aligned}
F_o + F_c &= \frac{1}{2} (I + SC^+(R)) \\
F_o - F_c &= \frac{1}{2} (I + SC^-(R))
\end{aligned} \tag{20}$$

where I is essentially the Coulomb solution to the operator H_o for incident wave and S is that for scattered wave, i.e.,

$$I \sim e^{iKoZ}$$

$$S \sim (e^{iKR}/R) \times f(\theta)$$

It is evident that this solution is compatible with the asymptotic condition (18). $C^\pm(R)$ are functions of R and approach to constants (complex in general) as S approaches to its asymptotic form. For collision energies in the kev range, the difference between S and its asymptotic expression becomes vanishingly small when the values of R go beyond the Bohr radius of the atom. Therefore, it is reasonable to assume that the C(R)'s are slow varying functions such that their second and higher order derivatives are negligible. On substituting equation (20) into equation (19),

$$H_o(I + SC^\pm(R)) = (V(O/O) \pm V(C/O))(I + SC^\pm(R))$$

since

$$H_o I = H_o S = 0$$

and

$$\Delta S C^{\pm}(R) = C^{\pm}(R) \Delta S + S \Delta C^{\pm}(R) + (\nabla S)(\nabla C^{\pm}(R))$$

Therefore, equation (20a) becomes

$$\left(\frac{1}{2\mu}\right) (S \Delta C^{\pm}(R) + (\nabla S)(\nabla C^{\pm}(R))) = (V(0/0) \pm V(C/0))(I + S C^{\pm}(R)) \quad (20b)$$

If one neglects terms of order K^{-1} and retains only terms containing $C(R)$ and $dC(R)/dR$'s in equation (20b), then one obtains the following differential equation for the C 's.

$$dC^{\pm}(R)/dR = 1/2ik(V(0/0) \pm V(C/0))(C^{\pm}(R) = 2I/S) \quad (21)$$

Since I is a much faster oscillating function than the C 's, the $2S/I$ term contributes negligibly when equation (21) is integrated, then

$$\begin{aligned} dC^{\pm}(R)/dR &= 1/2ik(V(0/0) \pm V(C/0))C^{\pm}(R) \\ C^{\pm}(R) &= e^{-(i/2k)(\varphi_0(R) \pm \zeta_c(R))} \end{aligned} \quad (22)$$

where

$$\begin{aligned} \varphi_0(R) &= \int_0^R V(0/0) dR \\ \varphi_c(R) &= \int_0^R V(C/0) dR \end{aligned} \quad (23)$$

Now one is ready to evaluate the electron capture probability P_0 . According to equations (14), (18) and (22), P_0 is given as

$$P_0 = \frac{1F_c^2}{1F_0^2 + 1F_c^2}$$

Since by our assumption (Cf. equation (14))

$$1F_0^2 + 1F_c^2 = 1f(\theta)1^2$$

Therefore,

$$\begin{aligned} P_0 &= \sin^2 \varphi_c / 2k \\ \varphi_c &= \varphi_c(00) \end{aligned} \quad (24)$$

The energies corresponding to the maxima and minima of P_0 are given by solving the equation

$$\varphi_c / 2k = \frac{1}{2} n\pi, \quad n = 1, 2, 3, \dots \quad (25)$$

with odd n 's corresponding to maxima and even n 's to minima. A useful relation between k , which is the center of mass system of He and H in atomic units, and the collision energy E , which is in the laboratory system in kev's, can be derived as follows:²¹

$$E^{\text{kev}} / 27.210^{-3} = E^{\text{amu}}$$

$$k = \frac{K_{\text{cm}}}{\mu} = \frac{K_{\text{H}}(\text{CM})^*}{M_{\text{H}}}$$

$$K_{\text{H}} = (\text{CM}) = M V (\text{CM})$$

$$V_{\text{H}} = \frac{4}{5} V_{\text{lab}}^*, \quad V_{\text{lab}} = \frac{2M_{\text{H}} E_{\text{lab}}}{M_{\text{H}}}$$

Therefore

$$k^{\text{amu}}_{\text{c.m.}} = 0.16 (E^{\text{kev}}_{\text{lab}})^{\frac{1}{2}}$$

Table 1 and Figure 2 give a comparison of the calculations based upon equation (25) and the experimental results of Ziemba, et al.³

The ground state He wave function obtained by Hylleraas, employing the variation method, is used to evaluate the interaction terms of equation (23). One must bear in mind that the justification of the variation method rests solely on the ground state ionization energy. However, on account of the ionization energy of an atom, the behavior of the "tail" part of the atomic wave function is not very critical. Therefore, the meaningfulness of the Hylleraas wave function in the evaluation of the interaction term is at times debatable. This contributes to some discrepancies in Table 1.

TABLE I

COMPARISON OF CALCULATED K WITH MEASURED K*

n	N=2			N = (2) ^{1/2}			N = 1.6			
	K(calc)	Δk^{**}	$\frac{\Delta k}{k(\text{exp})}$	k(calc)	Δk^{**}	$\frac{\Delta k}{k(\text{exp})}$	kk(calc)	Δk^{**}	$\frac{\Delta k}{k(\text{exp})}$	k(exp)
1(Max)	1.044	+0.088	+ 0.7%	1.480	+0.444	+43%	1.293	+0.257	+25%	1.036
2(min)	0.516	-0.059	-10.2%	0.738	+0.163	+28%	0.640	+0.075	+13%	0.575
3(Max)	0.347	-0.077	-18%	0.498	+0.074	+17%	0.431	+0.007	+1.6%	0.424
4(min)	0.258	-0.062	-19%	0.369	+0.049	+15%	0.320	0.000	0.00%	0.320
5(Max)	0.208	-0.058	-22%	0.286	+0.040	+15%	0.259	-0.007	-2.6%	0.266
6(min)	0.172	-0.049	-22%	0.246	+0.025	+11%	0.213	-0.008	-3.6%	0.221
7(Max)	0.149	-0.046	-24%	0.212	+0.017	+ 8.7%	0.185	-0.010	-5.1%	0.195

* The evaluation of integral (23) is given in Appendix A which includes electron-electron interaction. It is interesting to know that the electron-electron interaction is about 16% of the total interaction.

** $\Delta k = k(\text{calc}) - k(\text{exp})$

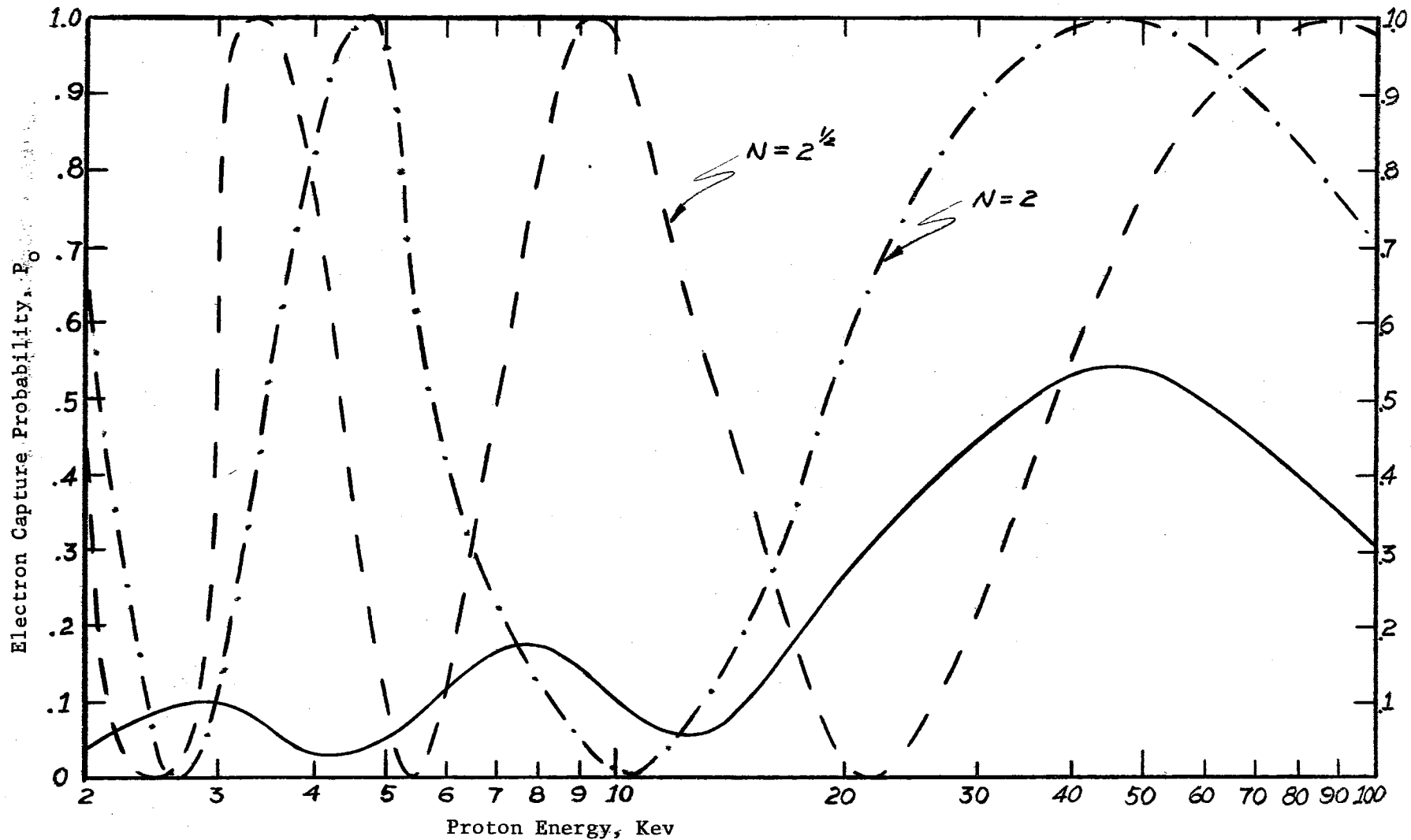


Figure 2. The $\text{He} + \text{H}^+ \longrightarrow \text{He}^+ + \text{H}$ Electron Capture Probability, P_0 , vs. Incident Energy, E_{lab} , in kev

The experimental curve drawn by Ziemba et al., is reproduced here as full line.
 The dashed lines are based on Table I and Equation (24).

Nevertheless, it is quite clear that the $N = 2$ set gives a better account of the experimental data of high collision energy, and the $N = (2)^{\frac{1}{2}}$ set gives a better account of the experimental data of low collision energy. (This is in agreement with the argument of Sec. 4, c, Chapter I.) In general, N will mainly depend upon how close the two nuclei get (the impact parameter), and consequently, N will depend upon the collision energy or K_0 . (For reasons mentioned in the last paragraph, no attempt has been made to establish a functional relation to N on K_0 based upon the Hylleraas wave function of He atom.)

For the best over-all fit with experimental data, N should have a value of around 1.6. Interestingly, if one neglects the electron-electron interaction $V(C/O)$, N would have to be approximately 1.35, which is under the theoretical lower bound of N , $(2)^{\frac{1}{2}} = 1.41$ to get the best fit.

3. THE DIFFERENCE BETWEEN $V(O/O)$ and $V(C/C)$

If one drops assumption I of the last section, equation (17) becomes

$$H_0 \begin{pmatrix} F_0 \\ F_c \end{pmatrix} = (V(ij)) \begin{pmatrix} F_0 \\ F_c \end{pmatrix} \quad (26)$$

where

$$(V(ij)) = \begin{pmatrix} V(O/O) & V(C/O) \\ V(C/O) & V(C/C) \end{pmatrix}$$

It can be shown that this coupled equation also gives exact resonance between the electronic configurations φ_0 and φ_c .

If (a_{ij}) is a diagonalizing matrix of $(V(I/J))$, equation (25) can be decoupled so that

$$\begin{aligned}
 a_{11} H_o F_o + a_{12} H_o F_c &= \frac{1}{2ik} W^+(R) G^+(R) \\
 a_{21} H_o F_o + a_{22} H_o F_c &= \frac{1}{2ik} W^-(R) G^-(R)
 \end{aligned} \tag{27}$$

where

$$\begin{aligned}
 G^+(R) &= a_{11} F_o + a_{12} F_c \\
 G^-(R) &= a_{21} F_o + a_{22} F_c
 \end{aligned}$$

and W^\pm are such that

$$\begin{vmatrix}
 V(O/O) - W & V(C/O) \\
 V(C/O) & V(C/C) - W
 \end{vmatrix} = 0$$

Therefore,

$$W^\pm(R) = \frac{1}{2} \{V(O/O) + V(C/C) \pm \sqrt{[V(O/O) - V(C/O)]^2 + 4V^2(C/O)}\}$$

In general the a_{ij} 's are functions of R . Since, for collision energy in the kev range, the F 's approach their asymptotic expression very rapidly, it is again reasonable to assume that the a_{ij} 's are slow varying functions. Therefore equation (27) can be written approximately as follows:

$$H_o G^\pm(R) = \frac{W^\pm}{2ik} G^\pm(R) \tag{28}$$

Here again one assumes for solutions to the above equations that

$$G^\pm = \frac{1}{2} (I + SC^\pm(R)) \tag{29}$$

and imposes upon the C 's the same asymptotic conditions. One obtains, consequently, the differential equations for the C 's.

$$\frac{d}{dR} C^\pm(R) = \frac{1}{2ik} W^\pm(R) C^\pm(R) \tag{30}$$

or

$$C^\pm(R) = e^{-\frac{i}{2k} \varphi^\pm(R)}$$

$$\varphi^{\pm}(R) = \int_0^R W^{\pm}(R') dR'$$

To evaluate the electron capture probability, let

$$(a_{ij}) = (a_{ij})^{-1}$$

i.e.,

$$F_o = \alpha_{11}G^+ + \alpha_{21}G^-$$

$$F_c = \alpha_{21}G^+ + \alpha_{22}G^- \quad (31)$$

Therefore,

$$(\alpha_{ij}) \begin{pmatrix} W^+ & 0 \\ 0 & W^- \end{pmatrix} = (V(ij))$$

One set of α 's is given by

$$\alpha_{11}/\alpha_{12} = V(C/O)/(W^+ - V(C/O)) = (W^+ - V(C/C))/V(C/O)$$

$$\alpha_{22}/\alpha_{21} = (W^- - V(O/O))/V(C/O) = V(C/O)/(W^- - V(C/C))$$

For large values of R, $V(O/O) - V(C/C)$ vanishes more rapidly than $V(C/O)$. Therefore, in the limiting case

$$F_o = G^+ + G^-$$

$$F_c = G^+ - G^- \quad (32)$$

Consequently,

$$P_o = \sin^2 \varphi' / 2k \quad (33)$$

where

$$\varphi' = \int_0^{\infty} \sqrt{[V(O/O) - V(C/C)]^2 - 4V^2(C/O)} dR .$$

Therefore, the removal of assumption I of the last section will not change the resonance pattern of P_o curve. Furthermore, judging from the comparison of Table 1, the value of φ' ought to be very close to

that of φ , i.e., $V(0/0) \approx V(C/C)$. This semi-empirical consideration justifies our assumption I.

4. THE CENTER OF MASS CORRECTION

Different authors have shown that the expansion of ψ in equation (14) is not an exact solution to the operator even in the asymptotic region where the interaction terms vanish.^{11,14,16} For improved approximations, correction terms, known as the center of mass correction, have to be introduced. For the present problem one may use the method due to Roth.¹⁶ In place of $F_o(R)$ and $F_c(R)$ one should write $F_o(R')$ and $F_c(R'')$. R' is approximately the distance from the proton H^+ to the center of mass of He atom and R'' is approximately the distance between the center of mass of H to that of He^+ . For small angle scattering (θ_{lab} around 5° , for example) the following relations hold approximately true. (Cf. equation (3), Chapter I)

$$\vec{kR} \rightarrow \vec{kR} - k(\vec{r}_1 + \vec{r}_2) \hat{R} \quad \text{For configuration (00)}$$

$$KR' = KR - k(\vec{r}_1 + \vec{r}_2) \hat{R}$$

$$\vec{kR}'' = \vec{kR} - k(\vec{r}_1 - \vec{r}_2) \hat{R}$$

For configuration (01)

$$KR'' = KR - k(\vec{r}_1 - \vec{r}_2) \hat{R}$$

$$\vec{kR}'' = \vec{kR} - k(\vec{r}_2 - \vec{r}_1) \hat{R}$$

For configuration (11)

$$KR'' = KR - k(\vec{r}_2 - \vec{r}_1) \hat{R}$$

Since the C 's are slow varying functions, one may write for the center of mass correction functions F_o and F_c as follows:

$$F_o(R') = F_o(R) e^{-ik(\vec{r}_1 + \vec{r}_2) \hat{R}} \quad \text{For configuration (00)}$$

$$F_o(R'') = F_o(R) e^{ik(\vec{r}_1 - \vec{r}_2) \hat{R}} \quad \text{For configuration (01)}$$

$$F_c(R'') = F_c(R)e^{-ik(\vec{r}_2 - \vec{\zeta}_1) \cdot \hat{R}} \quad \text{For configuration (11)}$$

Therefore, equation (14) becomes

$$\psi = F_o(R')(00) + F_c(R) \left[(10)e^{iK(\vec{r}_1 - \vec{\zeta}_2) \cdot \hat{R}} + (11)e^{iK(\vec{r}_2 + \vec{\zeta}_1) \cdot \hat{R}} \right]$$

and equation (19) becomes

$$\begin{aligned} H_o F_o &= V(0/0)F_o(R) + [V_R(C/0) + iV_I(C/0)]F_c(R) \\ H_c F_c &= [V_R(C/0) - iV_I(C/0)]F_o(R) + [V_R(C/C) + iV_I(C/C)]F_c(R) \end{aligned} \quad (34)$$

where

$$\begin{aligned} V_R(C/0) &= \frac{1}{N} \left\{ \int (01)V_{10}(00) \cos k(\vec{r}_2 + \vec{\zeta}_2) \cdot \hat{R} dt_1 dt_2 \right. \\ &\quad \left. + \int (11)V_{11}(00) \cos k(\vec{r}_1 + \vec{\zeta}_1) \cdot \hat{R} dt_1 dt_2 \right\} \\ &= \frac{2}{N} \int (01)V_{10}(00) \cos k(\vec{r}_2 + \vec{\zeta}_2) \cdot \hat{R} dt_1 dt_2 \\ V_I(C/0) &= \frac{2}{N} \int (01)V_{10}(00) \sin k(\vec{r}_2 + \vec{\zeta}_2) \cdot \hat{R} dt_1 dt_2 \\ V_R(C/C) &= \frac{2}{N} \left\{ \int (01)V_{10}(10) dt_1 dt_2 \right. \\ &\quad \left. + \int (01)V_{10}(11) \cos k(\vec{r}_1 + \vec{\zeta}_1 - \vec{r}_2 - \vec{\zeta}_2) \cdot \hat{R} dt_1 dt_2 \right\} \\ V_I(C/C) &= \frac{2}{N} \int (01)V_{10}(11) \sin k(\vec{r}_1 + \vec{\zeta}_1 - \vec{r}_2 - \vec{\zeta}_2) \cdot \hat{R} dt_1 dt_2 \end{aligned}$$

In view of the remarks of the last section, assume once again that, unlike the cases in sections 2 and 3, equation (34) can only be decoupled partially by adding and subtracting the coupled equations

$$\begin{aligned} H_o(F_o + F_c) &= (V(0/0) + V_R(C/0))(F_o + F_c) \\ &\quad - iV_I(C/0)(F_o - F_c) + iV_I(C/C)F_c \end{aligned} \quad (35)$$

$$\begin{aligned} H_o(F_o - F_c) &= (V(0/0) - V_R(C/0))(F_o - F_c) \\ &\quad + iV_I(C/0)(F_o + F_c) - iV_I(C/C)F_c \end{aligned}$$

If one assumes for solutions to the above equations of the coupled form those given by equation (20), the equation for the C's becomes

$$\frac{dC^+}{dR} = \frac{1}{2ik} \{ [V(0/0) + V_R(C/0)]C^+ - iV_I(C/0)C^- + iV_I(C/C)(C^+ - C^-) \} \quad (36)$$

$$\frac{dC^-}{dR} = \frac{1}{2ik} \{ [V(0/0) - V_R(C/0)]C^- + iV_I(C/0)C^+ - iV_I(C/C)(C^+ - C^-) \}$$

Unless all the imaginary parts of the interaction term vanish, the above equations do not lead to sinusoidal solutions for the C's of the form

$$e^{i\varphi/k}$$

φ : real-valued function

Rather, the real-valued function should be replaced by a complex function ϕ .

$$\phi = z^\pm + ig^\pm \quad (37)$$

where both z^\pm and g^\pm are real-valued functions.

Equation (24) becomes,

$$\begin{aligned} P_0 &= (e^{iz^+ - g^+} - e^{iz^- - g^-})(e^{iz^+ - g^-} - e^{-iz^- - g^-})/4 \\ &= \frac{1}{2} (e^{-2g^+} + e^{-2g^-} - e^{-(g^+ + g^-)} \cos(z^+ - z^-)) \end{aligned} \quad (38)$$

According to equation (24) the P_0 vs collision energy curve will oscillate between 1 and 0. On the other hand, one would expect some damping of this curve due to the real-valued exponential factors. Furthermore, the center of mass correction damping should be approximately symmetrical about the line $P_0 = \frac{1}{2}$. P_0 vs collision energy curves in the $H + H^+$ and $He + He^+$, etc., cases where similar nuclei are involved, all show damping of this kind. In case of $He + H^+$ collision a different kind of damping on the P_0 vs collision energy curve has been observed. Experimental results of Ziemba et al.,³ indicated a strong asymmetric damping of P_0 curve near the low energy and (about 1 kev) where only the

peaks of P_o are strongly damped. A qualitative discussion on the origin of this asymmetric damping will be given in the next section.

5. PARTIAL COUPLING

If one assumes only ground state transitions, then

$$E_{\text{He}^+} - E_{\text{H}^+} = 11^{\text{ev}} = 0.41^{\text{amu}}$$

Now let

$$K_c - \Delta K = K_o$$

Then the law of conservation of energy requires that

$$\frac{1}{2\mu} K_o^2 - \frac{1}{2\mu} (K_o - \Delta K)^2 = .41$$

or

$$\Delta K = 0.41/k$$

for ΔK is a small quantity and ΔK^2 is negligible.

For collision energies in the kev range, K_c is of the order of 1,000 and ΔK is of the order of 1. However, from a pure wave-mechanistic point of view, the smallness of ΔK does not give a complete justification of assumption II as given in Section 1 of this chapter. If one assumes monochromatic waves for both F_o and F_c , the coupled solution of the form given by equation (20) is not compatible with the asymptotic conditions of F_o and F_c , since they will be completely decoupled due to their different wave numbers.

Although there is no exact theory about the collision diameter for atomic collision, it is reasonable to assume that the strong coupling between atomic states φ_o and φ_c occurs only within a small region, with a diameter of the order of one Bohr radius (= 1 in amu) around the

nucleus.²² It is interesting to note that in the case of He + H⁺ collision, F₀ (the initial wave) and F_c (the captured wave) differ only by a few wave lengths within the sphere of one Bohr radius for collision energies of kev range. In this region both F₀ and F_c must be described as wave packets with band widths governed by the uncertainty principle

$$\Delta k \Delta R = 1$$

where Δk is approximately the band width of the wave packets and ΔR can be interpreted as the collision diameter for the electron capture process.

Unless $\Delta K = 0$, coupling between F₀ and F_c can only be achieved partially through the overlapping of the two wave packets. Since the wave number difference ΔK is inversely proportional to k and in turn inversely proportional to the collision energy, the overlapping between F₀ and F_c will increase as the collision energy increases. This explains, at least qualitatively, the asymmetric damping of the P₀ vs. collision energy plot in the He + H⁺ case. For relatively low collision energy, the overlapping between P₀ and P_c is very small, and the scattered wave is essentially in the initial state ϕ_0 . As the collision energy increases, the overlapping becomes greater. Therefore, the peaks of P₀ will then rise.

6. CONCLUSION

The close agreement in Table 1 between the observed P₀ peaks and anti-peaks and the theoretical values reflects the validity of the theory developed in Chapter I and the simplifying assumptions made in the last few sections. It is interesting to know that in the experiments of Ziemba et al.,³ P₀ was determined by measuring the fraction of

neutral scattered hydrogen atoms, without regard to states of excitations of both H and He^+ . The seemingly over-simplified assumption, namely, that all the atomic states are ground states, leads, however, to surprisingly good results. This can be explained by considering the orthogonality of the excited states. According to the argument and remarks in the last section, the ground state wave function ψ_0 and any excited state wave function ψ_n will have nuclear wave functions F_0 and F_n with almost identical wave numbers. This fact enables them to be coupled together very strongly for small interatomic distances. Therefore, for small interatomic distances these states will be coupled together to form an almost single state rather than two or more orthogonal states. As the interatomic distances grow larger, the coupling between them will become weaker and eventually vanish at infinity. However, meanwhile the interatomic interactions will also diminish and become negligible. One has to bear in mind, though, that the above remarks hold true only, as indicated in the last section, in the case of relatively large collision energies (in the kev range).

One should also know that the theory so far developed applies equally well when more than two atomic states are involved. In this case the matrix equation (26) should be properly extended to rank n , where n is the number of states involved. In general, numerical evaluations will be needed to solve the appropriate equations.

To account for the exact shape of the P_0 vs collision energy curve, both the effect of center of mass correction as well as partial coupling have to be considered. Equation (36) has to be solved for ζ^\pm and g^\pm in order to find the center of mass corrected P_0 expression (equation (38)).

Furthermore, this P_0 has to be further modified by the effect of partial coupling.

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APPENDIX A. THE EVALUATION OF INTERACTION TERMS

1. THE ELECTRON-NUCLEUS INTERACTION

If one substitutes into integral (10a) an appropriate expansion of ψ , for example equation (11) for the Born approximation, integral (10a) will be reduced to a more manageable form, one which contains some linear combination of the following general terms:

$$V(a'b'/ab) = V_o(a'b'/ab) + U(a'b'/ab)$$

$$V_o(a'b'/ab) = \int \varphi_{a'}^{(1)*}(\vec{r}_i^{(1)}) \varphi_{b'}^{(2)*}(\vec{\zeta}_k^{(2)}) V_o \varphi_a^{(1)}(\vec{r}_i^{(1)}) \varphi_b^{(2)}(\vec{\zeta}_k^{(2)}) \prod_i^{(1)} dt_i^{(1)} \prod_k^{(2)} dt_k^{(2)}$$

$$U(a'b'/ab) = \int \varphi_{a'}^{(1)*}(\vec{r}_i^{(1)}) \varphi_{b'}^{(2)*}(\vec{\zeta}_k^{(2)}) U \varphi_a^{(1)} \varphi_b^{(2)}(\vec{\zeta}_k^{(2)}) \prod_i^{(1)} dt_i^{(1)} \prod_k^{(2)} dt_k^{(2)}$$

where

$$V_o = - \sum_i^{(1)} \frac{Z_1}{\zeta_i^{(1)}} - \sum_k^{(2)} \frac{Z_2}{r_k^{(2)}}$$

$$U = \sum_{ik} \frac{1}{r_{ik}} \quad (39a)$$

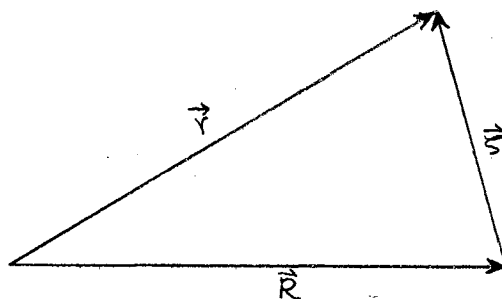
and where

$$\langle a'b' | V/\psi \rangle = \sum_{ab} V(a'b'/ab) F_{ab}(R) \quad (39b)$$

According to the "v" terms involved in the corresponding integrals, $V_o(a'b'/ab)$ and $U(a'b'/ab)$ are called the electron-nucleus and the electron-electron interaction terms respectively. Usually the

predominant term is the nucleus-electron interaction term, which will be discussed subsequently. The evaluation of the electron-electron interaction terms will be given in the next few sections.

For relatively light atoms where the hydrogenic wave functions are good approximations to their atomic wave functions, the introduction of elliptical coordinates will further reduce equation (39)



$$\begin{aligned}\xi &= (r + \zeta)/R \\ \eta &= (r - \zeta)/R \\ dt &= \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi\end{aligned}$$

Figure 3. The Elliptical Coordinate

In many cases the introduction of the elliptical coordinates will even enable one to integrate the interaction terms analytically. Some of the most common integrals involved in such an analytical integration are tabulated in Appendix B. As an example, let's consider the (00)→(11) transition in He + H⁺ collision. The hydrogenic wave functions are

$$\text{He: } U_{\text{He}}(r) = \frac{\alpha^{3/2}}{\pi^{1/2}} e^{-\alpha r}, \quad \alpha = 1.69 \quad (\text{Hylleraas wave function})$$

$$\text{He}^+ : U_{\text{He}^+}(r) = \frac{\beta^{3/2}}{\pi^{1/2}} e^{-\beta r}$$

$$\text{H} : W(r) = \frac{1}{\pi^{1/2}} e^{-r}$$

Since

$$V_0 = - \frac{2}{r_2} - \frac{1}{\zeta_1}$$

one writes for $V_o(R)$

$$V_o(00/11) = - U_1 - U_2$$

where

$$U_1 = 2\langle C^0 \rangle \quad \alpha = 1.69 \quad \beta = 2 \quad U_2 = \langle \frac{C^0}{\zeta} \rangle \quad \alpha = 1.69 \cdot \langle C^+ \rangle \quad \alpha = 1.69$$

$$\beta = 2 \quad \beta = 2 \quad \beta = 1$$

$$V_o(00/11) = 9.57e^{-R} - 4.16e^{-4R} - 2.46e^{-4.69R}$$

$$+ 2.69 \frac{e^{-R} - e^{-4R}}{R} + 1.59 \frac{e^{-1.69R} - e^{-4.69R}}{R}$$

$$- 14.28 \frac{e^{-4.69R} - e^{-4R}}{R} + 10.96 \frac{e^{-1.69R} - e^{-R}}{R}$$

$$+ 9.213 \frac{(1 - e^{-3R})(e^{-1.69R} - e^{-R})}{R^2}$$

$$\int V(00/11)dR = 3.92$$

2. THE INTERATOMIC ELECTRON-ELECTRON INTERACTION

The Coulomb interaction v_{ik} between the i^{th} electron of atom 1 and the k^{th} electron of atom 2 is

$$V_{ik} = \frac{1}{r_{ik}}$$

If the atomic wave functions of atom 1 and atom 2 are expressible in terms of Slater type wave functions, i.e., expressible in terms of single electron wave functions, then the electron-electron interaction term of equation (39) contains factors of the following general form:

$$V_{ik}(a'b'/ab) = \int \frac{U_i^{(1)*}(\vec{r}_i) U_k^{(2)}(\vec{r}_k) U_i(\vec{r}_i) U_k'(\vec{r}_k)}{r_{ik}} dt_i dt_k \quad (40)$$

where $U_i^{(1)}(\vec{r}_i)$ and $U_k^{(2)}(\vec{r}_k)$ are the single electron wave functions of the electrons i in atom 1 and k in atom 2 before the atomic impact. The primed functions are single electron wave functions after the atomic impact.

Provided that there is no ionization, the electrons can undergo the following transitions after the impact:

(1) Simple elastic collision

$$U^{(1)}(\vec{r}_i) \rightarrow U_1^{(1)}(\vec{r}_i)$$

$$U^{(2)}(\vec{r}_k) \rightarrow U^{(2)}(\vec{r}_k)$$

(2) Simple excitation

$$U^{(1)}(\vec{r}_i) \rightarrow U'^{(1)}(\vec{r}_i)$$

$$U^{(2)}(\vec{r}_k) \rightarrow U'^{(2)}(\vec{r}_k)$$

(3) Electron exchange without excitation

$$U^{(1)}(\vec{r}_i) \rightarrow U^{(2)}(\vec{r}_i)$$

$$U^{(2)}(\vec{r}_k) \rightarrow U^{(1)}(\vec{r}_k)$$

(4) Electron exchange with excitation

$$U^{(1)}(\vec{r}_i) \rightarrow U'^{(2)}(\vec{r}_i)$$

$$U^{(2)}(\vec{r}_k) \rightarrow U'^{(1)}(\vec{r}_k)$$

(5) Electron capture

$$U^{(1)}(\vec{r}_i) \rightarrow U'^{(1)}(\vec{r}_i)$$

$$a \quad U^{(2)}(\vec{r}_k) \rightarrow U'^{(1)}(\vec{r}_k)$$

$$U'^{(1)}(\vec{r}_i) \rightarrow U'^{(2)}(\vec{r}_i)$$

$$b \quad U^{(2)}(\vec{r}_k) \rightarrow U'^{(2)}(\vec{r}_k)$$

Furthermore, according to the l -values (angular momentum quantum number) of the single electron wave functions before and after the atomic impact, the transition may be classified as $ss \rightarrow ss$, $ss \rightarrow sp$, . . . etc., processes.

3. SPECIAL CASES

If some symmetries exist either around atom 1 or around atom 2, integral (40) can be greatly reduced by integrating over the polar angles of the atom with the symmetry property. For example, in cases of types (1), (2), and (5) a $ss \rightarrow ss$ transitions, the single electron wave functions in (14) are independent of r_k . Let $\theta_i = \widehat{r_i r_k}$ and express v_{ik} as

$$v_{ik} = (r_i^2 + r_k^2 - 2r_i r_k \cos \theta)^{-\frac{1}{2}}$$

$$dt_i = r_i^2 \sin \theta_i d\theta_i d\phi_i$$

After integrating over θ_i and ϕ_i , equation (14) becomes

$$V_{ik}(a'b'/ab) = \int U^{(1)*} U'^{(1)} U^{(2)*} U'^{(2)} V_{oo}(r_i r_k) r_i dr_i dt_k$$

where

$$V_{oo}(r_i r_k) = \int_0^{2\pi} d\phi_i \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_i^2 + r_k^2 - 2r_i r_k \cos \theta_i}}$$

$$= 4\pi \begin{cases} \frac{1}{r_i} & , \quad r_i < r_k \\ \frac{1}{r_k} & , \quad r_i > r_k \end{cases}$$

In general, if the single electron wave functions in integral (14) are independent of either one of the four variables r_i , r_k , ζ_i , ν_k , similar integrations about proper polar angles are always possible. For example, if ζ_i is the missing variable, then integral (14) is

reducible to the following form:

$$V_{em, e'm'}(a'b'/ab) = \int U^{(1)*} U'^{(1)} U^{(2)*} V_{em, e'm'}(r_i r_k) r_i dr_i dt_k$$

where

$$V_{em, e'm'}(r_i r_k) = \int \frac{y^{em}(\theta_i \varphi_i) y^{e'm'}(\theta_i \varphi_i) d\theta_i d\varphi_i}{(r_i^2 + r_k^2 - 2r_i r_k \cos \theta_i)^{\frac{1}{2}}}$$

where l, m, l', m' are the l -values of the single electron wave functions and $y^{em}, y^{e'm'}$ are the corresponding angular momentum eigenfunctions.

As an example, let's consider the $\text{He} + \text{H}^+ (00) \rightarrow (11)$ case"

$$U(00/11) = \int \frac{U_{\text{He}}(r_1) U_{\text{He}}(r_2) U_{\text{He}^+}(r_2) W(\zeta_1)}{r_{12}}$$

It can be seen that $V(00/11)$ involves a Type (5)a transition. By integrating over all the electronic coordinates, one has

$$U(00/11) = .1027e^{-5.38R} + 1.97e^{-R} + .087 (e^{-5.38R} - e^{-R})/R \\ + 1.78 (e^{-1.69R} - e^{-R})/R$$

Therefore,

$$\int V(00/11) dR = 0.63$$

APPENDIX B. SOME USEFUL INTEGRALS

$$u(r) = N_1 e^{-\alpha r}$$

$$N_1 = \frac{\alpha^{3/2}}{\pi^{1/2}}$$

$$v(r) = N_2 e^{-\beta r}$$

$$N_2 = \frac{\beta^{3/2}}{\pi^{1/2}}$$

$$1. \quad (c^0) = \int u(r)v(\rho) d\tau = \frac{8(\alpha\beta)^{3/2}}{(\alpha+\beta)}$$

$$2. \quad (c^+) = \int u(r)v(\rho) d\tau$$

$$= \frac{2^3(\alpha\beta)^{3/2}}{R(\alpha^2-\beta^2)} \left\{ e^{-\beta R} [(\alpha^2-\beta^2)\alpha R - 4\alpha\beta] \right. \\ \left. + e^{-\alpha R} [(\alpha^2-\beta^2)\beta R - 4\alpha\beta] \right\}$$

$$3. \quad (a^+) = \int u(r)u(\rho) d\tau$$

$$= e^{-\alpha R} \left[\frac{1}{3} \alpha^2 R^2 + \alpha R + 1 \right]$$

$$4. \quad (b^+) = \int v(\rho)v(r) d\tau = (a^+) \quad \alpha \rightarrow \beta$$

$$= e^{-\beta R} \left[\frac{1}{3} \beta^2 R^2 + \beta R + 1 \right]$$

$$5. \quad \left(\frac{a^+}{r}\right) = \int \frac{u(r)u(\rho)}{r} d\tau$$

$$= \alpha e^{-\alpha R} (1 + \alpha R) = 1.69 e^{-\alpha R} (1 + \alpha R)$$

$$6. \quad \left(\frac{a^0}{\rho}\right) = \int \frac{u^2(r)}{\rho} d\tau$$

$$= \frac{1}{R} [1 - e^{-2\alpha R} (\alpha R + 1)]$$

$$7. \quad \left(\frac{b^+}{r}\right) = \int \frac{v(r)v(\rho)}{r} d\tau$$

$$= \beta e^{-\beta R} (1 + \beta R)$$

$$8. \quad \left(\frac{b^+}{\rho}\right) = - \int \frac{v(r)v(\rho)}{\rho} d\tau$$

$$= \frac{1}{R} [1 - e^{-2\beta R} (\beta R + 1)]$$

$$9. \quad \left(\frac{c^0}{r}\right) = \int \frac{u(r)v(r)}{r} d\tau = \frac{4(\alpha\beta)^{3/2}}{(\alpha+\beta)^2}$$

$$\begin{aligned}
 10. \left(\frac{c^0}{\rho}\right) &= \int \frac{u(r)v(r)}{\rho} d\tau \\
 &= \frac{8(\alpha\beta)^{3/2}}{(\alpha+\beta)^3 R} \left\{ 1 - e^{-R(\alpha+\beta)} \left[\frac{R}{2}(\alpha+\beta) + 1 \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
 11. \left(\frac{c^+}{\rho}\right) &= \int \frac{u(r)v(\rho)}{\rho} d\tau \\
 &= \frac{2^3(\alpha\beta)^{3/2}}{(\alpha^2-\beta^2)^2 R} \left\{ \alpha e^{-\beta R} - e^{-\alpha R} \left[\frac{\alpha^2-\beta^2}{2} R + \alpha \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
 12. \left(\frac{c^+}{\rho}\right) &= \int \frac{u(r)v(\rho)}{r} d\tau \\
 &= \frac{2^3(\alpha\beta)^{3/2}}{(\alpha^2-\beta^2) R} \left\{ \beta e^{-\alpha R} - e^{-\beta R} \left[\frac{\beta^2-\alpha^2}{2} R + \beta \right] \right\}
 \end{aligned}$$

VITA

Loh-yi Chang

Candidate for the Degree of

Doctor of Philosophy

Thesis: ON THE THEORY OF ELECTRON CAPTURE IN $\text{He} + \text{H}^+$ COLLISIONS

Major Field: Physics

Biographical:

Personal Data: Born in Shantung Province, China, July 15, 1933,
the son of Major General and Mrs. Yung-shan Chang.

Education: Attended grade school in Hounan, Shanshi Provinces,
China; Graduated from Hsiangshu High School, Taipei, Taiwan,
China in 1950; Received the Bachelor of Science degree from
The National Taiwan University, with a major in physics, in
July, 1956; Completed requirements for the Doctor of
Philosophy degree in July, 1965.