NASA Technical Memorandum 101559

Charge Exchange Transition Probability for Collisions Between Unlike Ions and Atoms Within the Adiabatic Approximation

Y. J. Xu
G. S. Khandelwal
J. W. Wilson

(NASA-TM-101559) CHARGE EXCHANGE TRANSITION PROBABILITY FOR COLLISIONS BETWEEN UNLIKE IONS AND ATOMS WITHIN THE ADIABATIC APPROXIMATION (NASA. Langley Research Center) 43 p
N89-25104
CSCL 03B G3/93
Unclas
0211549

April 1989

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665-5225

CHARGE EXCHANGE TRANSITION PROBABILITY FOR COLLISIONS BETWEEN UNLIKE IONS AND ATOMS WITHIN THE ADIABATIC APPROXIMATION

Y. J. Xu and G. S. Khandelwal
Department of Physics, Old Dominion University
Norfolk, Virginia 23508

and

J. W. Wilson
Langley Research Center
National Aeronautics and Space Administration
Hampton, Virginia 23665-5225

ABSTRACT

A simple formula for the transition probability for electron exchange between unlike ions and atoms is established within the adiabatic approximation by employing the Linear Combination of Atomic Orbitals (LCAO) method. The formula also involves an adiabatic parameter, introduced by Massey, and thus the difficulties arising from the internal energy defect and the adiabatic approximation are avoided. Specific reactions $Li^{3+} + H \rightarrow Li^{++} + H^{+}$ and $Be^{4+} + H \rightarrow Be^{3+} + H^{+}$ are considered as examples. The calculated capture cross section results of the present work are compared with the experimental data and with the calculations of other authors over the velocity range of 10^{7}cm/sec to 10^{8}cm/sec.

I. INTRODUCTION

Charge transfer collisions provide an interesting three-body system which is amenable to theoretical analysis in addition to their importance in the studies of fusion plasmas, astrophysical processes, and more recent studies of short wavelength lasers. Traditional interest still looms as important applications in heavy ion accelerators and radiation-induced chemistry as well as charged particle transports in matter.

In the past, the perturbed stationary state (PSS) method has been applied to study a symmetric resonance process such as $A^+ + A \rightarrow A + A^+$. Various theoretical approaches rest on obtaining stationary molecular states (refs. 1-3). These results are usually in good agreement with their experimental counterparts. Encouraged with this success, in the above resonant process, extending these calculations to the collisions between unlike ions and atoms is presently studied. In this context, the reaction of the type

$$A^Z + B \rightarrow A^{Z-q} + B^q + \Delta E \tag{1.1}$$

in which ΔE is the internal energy defect would be of great interest.

Unfortunately, the formulation of the problem of the non-symmetrical charge transfer collisions of equation (1.1) is rather difficult using the procedures similar to the ones applied to the symmetric case. The correct procedure should involve the expansion of the wave function in terms of molecular wave functions. Rapp and Francis (ref. 4) have pointed out that the connection between the molecular and atomic approach in non-symmetrical charge transfer is not easily obtained. These authors in their work abandoned the molecular expansion, and instead, within the lowest order approximation, they replaced the molecular wave functions and energies by atomic orbitals and atomic energies.

In this paper, we adopt a correct molecular expansion procedure by employing the Linear Combination of Atomic Orbitals (LCAO) method. The non-symmetrical charge transfer process of equation (1.1) is calculated for low and intermediate energies using an adiabatic approximation together with Massey's (refs. 5 and 6) adiabatic criterion resulting in a limited collision range. A simple formula for the transition probability is obtained under the two-state approximation. The formula is expressed in terms of overlap integrals, exchange integrals, and Coulomb integrals. The internal energy defect ΔE and the collision range R_c also appear in these formulas.

Specific reactions $Li^{3+} + H \rightarrow Li^{++} + H^{+}$ and $Be^{4+} + H \rightarrow Be^{3+} + H^{+}$ are considered as examples. The results are compared with the experimental data and with the calculations of other authors, and a brief discussion is presented. All these overlap integrals, exchange intergrals, and the Coulomb integrals can be calculated analytically by employing the hydrogenic wave functions. The simplified picture presented in this paper gives insight into the essential nature of the charge transfer process.

II. QUASI-CLASSICAL APPROXIMATION

As is known, the passage from quantum mechanics to the limit of classical mechanics is similar to the passage from wave optics to geometric optics (ref. 7). The field components U in the electromagnetic wave can be written as $U = ae^{i\phi}$, where a is the amplitude, ϕ is the phase and i is the square root of minus one. The limiting case of geometric optics corresponds to a short wavelength i.e., to a large value of the phase ϕ. Similarly, in the limiting case of classical mechanics, one writes the electronic wave function as

$\Psi = a\ e^{iS/h}$ where a is a slowly varying function, S is the action which takes on large values, and h is the Planck constant divided by 2π. Henceforth, we will use atomic units in which h = 1. This use of the action variable is determined after considering the analogy of the principle of least action in classical mechanics and Fermat's principle in optics. As is known, the action function is given by

$$S = -\ Et + \Sigma \int p_i dq_i$$

$$\sim -\frac{ER}{\upsilon} + \Sigma \int p_i dq_i \tag{2.1}$$

and becomes large for small velocity υ. Thus, Landau (ref. 7) stated that $\psi = ae^{iS}$ is the wave function of an "almost classical" or "quasi-classical" physical system. Furthermore, by absorbing the second term of the above equations into the quantity a' and retaining the adiabatic approximation (i. e., υ extremely small), the wave function ψ becomes

$$\psi = a'\ e^{i\int_{to}^{t} Edt} \tag{2.2}$$

where a' is a slowly varying function of time t. Let us now apply the above to the capture process of present interest.

Consider the situation in which the projectile captures an electron from the target. Then ψ_1 is the wave function of the electron long before the collision and is essentially the electronic wave function of the target. On the other hand, after the collision the wave function of the electron would be the electronic wave function ψ_2 of the projectile. These states are not stationary states in the sense that $S \sim Et$ is an extremum along the trajectory. The stationary states of this system are the two molecular states denoted by ψ_g and ψ_u. (In a symmetric case, g refers to a gerade state and u to ungerade state.) Thus, according to equation (2.2), within the adiabatic approximation, the wave function at anytime t can be expanded as

$$\psi = A(t)\,\psi_g \exp(-i \int_{-to}^{t} E_g dt) + B(t)\,\psi_u \exp(-i \int_{-to}^{t} E_u dt) \qquad (2.3)$$

where E_g and E_u are eigen energies; ψ_g and ψ_u are the corresponding two eigen functions. (Two-state approximation is employed.) Equation (2.3) is similar to the one usually derived under the PSS method (ref. 8).

The quantities A(t), B(t), ψ_g, and ψ_u are slowly varying functions of time. The conditions under which A(t) and B(t) can be treated as time independent are discussed in the appendix. Under the adiabatic approximation, one can ignore the terms $\dot{\psi}_g$ and $\dot{\psi}_u$ relative to the other terms in the pertinent equations. This leads to the conclusion that the quantities A(t) and B(t) are independent of time.

For simplicity, consider a fully stripped ion of atomic number Z, moving slowly through the target hydrogen atoms. Let r_1 be the distance of the electron to the target nucleus and r_2 the distance from the projectile nucleus (fig. 1). The internuclear distance of the projectile and the target is denoted by R. The Hamiltonian of the system with the electron and two nuclei in atomic units is

$$H = \frac{Z}{R} - \frac{1}{2}\nabla^2 - \frac{Z}{r_2} - \frac{1}{r_1} . \qquad (2.4)$$

Wave functions of interest are

$$\psi_1 = \frac{1}{\sqrt{\pi}} \exp(-r_1) \qquad (2.5)$$

$$\psi_2 = A_n Z^{n-1} r_2^{n-1} \exp(-Zr_2/n) \qquad (2.6)$$

with

$$A_n = \frac{Z^{3/2}}{\sqrt{\pi}} \frac{2^{2n-1}}{(2n)!\, n^{2n+1}} \qquad (2.7)$$

The ψ_1 is the wave function of the electron when it is localized near the first nucleus (target), ignoring the presence of the fully stripped projectile ion. On the other hand, ψ_2 is the wave function of the electron when it is localized near the projectile nucleus, ignoring the presence of the target nucleus.

As noted earlier, in arriving at equation (2.3), the wave function at any time is given by the linear combination of two quasi-molecular stationary states ψ_g and ψ_u . These states are determined by the variational method by employing the Hamiltonian H with their form given as

$$\psi_g = \frac{1}{\sqrt{2 + 2S}} (\psi_1 + \psi_2) \qquad (2.8)$$

$$\psi_u = \frac{1}{\sqrt{2 + 2S}} (\psi_1 - \psi_2) \qquad (2.9)$$

where $S = \int \psi_1 \psi_2 \, d\tau$ is the well known overlap integral. The eigen value of the Hamiltonian is the potential function for the nuclear motion in the Born-Oppenheimer approximation. We note that the charge transfer problem is similar to the usual potential crossing problem.

The quantities A(t) and B(t) in equation (2.3) are determined from the initial condition $\psi \to \psi_1$ as $t \to -t_0$ to be satisfied by the value

$$A = \frac{1}{2}\sqrt{2 + 2S} \tag{2.10}$$

$$B = \frac{1}{2}\sqrt{2 - 2S} \tag{2.11}$$

Letting $t \to \infty$, using equation (2.3), we obtain

$$\psi = C_1'' \psi_1 + C_2'' \psi_2 \tag{2.12}$$

where

$$C_2'' = \frac{1}{2}\left[e^{-i\int_{-\infty}^{+\infty} E_g dt} \quad e^{-i\int_{-\infty}^{+\infty} E_u dt}\right] \tag{2.13}$$

Hence, the transition probability is given by

$$W_{12} = \left|C_2''\right|^2 = \sin^2\eta \tag{2.14}$$

where
$$\eta = \frac{1}{2}\int_{-\infty}^{+\infty} (E_g - E_u)\, dt \tag{2.15}$$

For any symmetric resonance process, the quantity $\Delta E = E_g - E_u$ plays the key role in determining the transition probability. We will determine it by the variational method. We note that the molecular wave function ϕ can be obtained by the LCAO method as

$$\phi = C_1\psi_1 + C_2\psi_2$$

The expectation value of the Hamiltonian H is

$$\varepsilon = \frac{\int \phi \, H\phi \, d\tau}{\int \phi^2 d\tau} = \frac{C_1^2 H_{11} + C_1 C_2 (H_{12} + H_{21}) + C_2^2 H_{22}}{C_1^2 + C_2^2 + 2 C_1 C_2 S} \tag{2.16}$$

where

$$H_{ij} = \int \psi_i^* H \psi_j d\tau \tag{2.17}$$

The stationary states are obtained by the stability condition

$$\frac{\partial \varepsilon}{\partial C_1} = \frac{\partial \varepsilon}{\partial C_2} = 0 \tag{2.18}$$

which leads to

$$C_1(H_{11} - \varepsilon) + C_2 (H_{12} - \varepsilon S) = 0 \tag{2.19}$$

$$C_1(H_{21} - \varepsilon S) + C_2(H_{22} - \varepsilon) = 0 \tag{2.20}$$

For the symmetric case (Z=n=1) we have $H_{11} = H_{22} = H$. Since H is a Hermitian operator, ψ_1 and ψ_2 are real functions, thus $H_{12} = H_{21}$. The secular equation of equations (2.19) and (2.20) is

$$(H - \varepsilon)(H - \varepsilon) = (H_{12} - \varepsilon S)^2 \tag{2.21}$$

which leads to two eigen energies

$$\varepsilon_1 = \frac{H - H_{12}}{1 - S} \tag{2.22}$$

$$\varepsilon_2 = \frac{H + H_{12}}{1 + S} \tag{2.23}$$

from which

$$\varepsilon_2 - \varepsilon_1 = 2\,\frac{(H_{12} - HS)}{1 - S^2} \tag{2.24}$$

Using the Hamiltonian and the wave functions ($Z=n=1$) results in

$$H = E_{1,0} + J \tag{2.25}$$

$$H_{12} = E_{2,0}S + K \tag{2.26}$$

where $E_{1,0}$ and $E_{2,0}$ are the atomic ground state energies of the electron in the target and projectile orbitals, respectively. The S is the overlap integral given (ref. 9) as

$$\begin{aligned} S &= \int \psi_2^* \psi_1 \, d\tau \\ &= (1 + R + \frac{R^2}{3})\, e^{-R} \end{aligned} \tag{2.27}$$

and K is the exchange integral given (ref. 9) as

$$\begin{aligned} K &= \frac{S}{R} - \int \frac{\psi_1 \psi_2}{r_1} \, d\tau \\ &= (\frac{1}{R} - \frac{2}{3} R)\, e^{-R} \end{aligned} \tag{2.28}$$

and J is the coulomb integral given (ref. 9) as

$$J = \frac{1}{R} - \int \frac{\psi_1^2}{r_2} d\tau$$

$$= (1 + \frac{1}{R}) e^{-2R} \tag{2.29}$$

Thus,

$$H_{12} - HS = K - JS \tag{2.30}$$

so that,

$$\varepsilon_2 - \varepsilon_1 = \frac{(\frac{2}{R} - \frac{4R}{3}) \exp(-R) - (\frac{2}{R} + 4 + \frac{8R}{3} + \frac{2R^2}{3}) \exp(-3R)}{1 - (1 + R + \frac{R^2}{3})^2 \exp(-2R)} \tag{2.31}$$

For, R >> 1, we have from the above:

$$\varepsilon_2 - \varepsilon_1 \approx -\frac{4}{3} Re^{-R} \tag{2.32}$$

which is on the order of the result given by Firsov, Landau, and Herring (see discussion in ref. 10) of $-4R\exp(-R-1)$. We now consider the extension of these results for symmetric resonance transfer to non-symmetric resonance transfer.

III. NON-SYMMETRICAL RESONANCE TRANSFER

In recent years, because of its usefulness in many areas of physics, the reaction $A^Z + B \rightarrow A^{Z-q} + B^q + \Delta E$ and, in particular, the fully stripped ion charge transfer process have received great attention. Considerable progress has been made in both the experimental and theoretical studies of this problem. The unitarized Distorted Wave Approximation (UDWA) of ref. 11 has been a successful numerical method, since it covers a wide energy region. For extremely low energies, the classical Barrier model of ref. 12 and the absorbing sphere model of ref. 13 have been of interest to experimental physicists because of their considerable simplicity. The other numerical models, on the other hand, involve complicated calculations. Still, the early Landau-Zener formula is widely used by many authors, since it has been studied fully for a long time (refs. 14-17). However, the Landau-Zener formula has its limitations. In this model the transition is assumed to be limited to a narrow region around the crossing point R_{cp}. The potential energy separation varies linearly with the internuclear distance in the narrow region, namely,

$$(H_i - H_f) \cong \gamma \; (R - R_{cp})$$

The coupling matrix element H_{if} has a constant value β.

In 1962, Rapp and Francis (ref. 4) studied the charge exchange between unlike atoms. They pointed out that the connection between the molecular states and the atomic orbitals is not easily obtained. Therefore, as a lowest order approximation, they replaced the wave functions of the stationary molecular states by the atomic orbitals. This connection was found by employing the LCAO method. The physical difficulties arise when one simultaneously retains the internal energy defect and the infinite interaction range within an adiabatic approximation or a quasi-classical approximation, because such a situation renders transition probabilities small. Actually, the infinite interaction time does not exist at all, since there are so many target atoms in the material that the average interatomic distance probably will be a suitable estimate of the upper limit of the effective interaction range. After such an interaction time, the projectile undergoes another collision process. Massey (refs. 5 and 6) introduced an adiabatic criterion based on the following argument. Classically, the transition probability is proportional to the ratio of transition time and the collision time. Since now there exists an energy defect, ΔE, the transition time can be estimated as $1/\Delta E$. Meanwhile, the collision time is proportional to an adiabatic parameter divided by the velocity of the projectile. Only when the transition time can be comparable to the collision time does there exist a significant transition probability. The adiabatic parameter thus cuts off the interaction time. This parameter is of the order of the atomic dimension. Hasted pointed out in ref. 6, that "the analysis of a large volume of experimental data leads to surprisingly small probable errors (10-20 percent) with a value $R_c = 7Å$ common to different types of reactions." This adiabatic parameter of 7Å is the range of internuclear separation over which the charge transfer is deemed possible (ref. 11). Actually, the cross sections were measured as functions of projectile velocities. Surprisingly, the velocities corresponding to maximum cross sections v_m were almost a linear function of ΔE. The slope leads to an adiabatic parameter $R_c = 7Å$. We apply this adiabatic parameter as a "cut-off" range in our calculations.

The capture cross section is thus determined in terms of the adiabatic parameter R_c, the energy defect ΔE, and the velocity of the projectile. It also depends on the atomic wave functions of both the projectile and the target and the interaction between them. In the non-symmetrical case, the two stationary molecular states are still denoted by ψ_g and ψ_u, where the subscripts g and u are used here only for convenience. These states assume a more general form than the corresponding symmetric resonance case. These more general states are defined as

$$\psi_g = C_1(\psi_1 + f_1\psi_2) \qquad (3.1)$$

and

$$\psi_u = C_1' \ (\psi_1 + f_2\psi_2) \qquad (3.2)$$

where C_1 and $C_{1'}$ are determined by the normalization condition

$$1 = C_1^2 \{\int \psi_1^2 \, d\tau + 2f_1 \int \psi_1\psi_2 \, d\tau + f_1^2 \int \psi_2^2 \, d\tau\} \qquad (3.3)$$

so that

$$C_1 = \frac{1}{(1 + 2Sf_1 + f_1 2)^{1/2}} \qquad (3.4)$$

Similarly,

$$C_1' = \frac{1}{(1 + 2Sf_2 + f_2 2)^{1/2}} \qquad (3.5)$$

The quantities S, f_1, and f_2 are functions of internuclear distance R.

Under the adiabatic or quasi-classical approximation, the quantites A(t) and B(t) in equation (2.3) can be treated as time independent. Thus, equation (2.3) with equations (3.1) and (3.2) becomes

$$\psi = A \, C_1(\psi_1 + f_1\psi_2) \exp \left(-i \int_{-t_0}^{t} E_g \, dt\right)$$

$$+ B \, C_1' \ (\psi_1 + f_2\psi_2) \exp \left(-i \int_{-t_0}^{t} E_u \, dt\right) \qquad (3.6)$$

Since ψ must tend to ψ_1 when $t \rightarrow -t_o$, we obtain from (3.6):

$$A' = \left. \frac{f_2}{f_2 - f_1} \right|_{-t_o} \tag{3.7}$$

and

$$B' = - \left. \frac{f_1}{f_2 - f_1} \right|_{-t_o} \tag{3.8}$$

with $A' = A\, C_1$ and $B' = C'_1$

The quantities A', B', f_1, and f_2 are all functions of internuclear distance R. Also, these quantities should be symmetric. Thus, $A'(-t_o) = A'(t_o)$, $B'(-t_o) = B'(t_o)$, $f_1(-t_o) = f_1(t_o)$, and $f_2(-t_o) = f_2(t_o)$, since the variational method is invoked, by which they depend only on the distances between the projectile and target nuclei. Also, since the quantities A and B can be deemed to be time independent

$$A'f_1 \Big|_{t_o} = A'f_1 \Big|_{-t_o} \tag{3.9}$$

Equation (3.6) can now be written in a general form as

$$\psi = C''_1\, \psi_1 + C''_2\, \psi_2 \tag{3.10}$$

where,

$$C_2'' = A' f_1 \exp(-i \int_{-t_o}^{t} E_g dt) + B' f_2 \exp(-i \int_{-t_o}^{t} E_u dt)$$
$$= \frac{f_2 f_1}{f_2 - f_1} \{\exp(-i \int_{-t_o}^{t} E_g\, dt) - \exp(-i \int_{-t_o}^{t} E_u\, dt)\} \tag{3.11}$$

where the coefficients are to be determined by the stationary phase method applied to the expectation value of the Hamiltonian. Hence, the transition probability is given by

$$W_{12} = 4 \left(\frac{f_2 f_1}{f_2 - f_1}\right)^2 \sin^2 \eta \tag{3.12}$$

where

$$\eta = \frac{1}{2} \int_{-t_o}^{t} (E_g - E_u)\, dt \tag{3.13}$$

Notice that the transition probability of (3.12) differs from the symmetric case by an additional factor $4 \left(\frac{f_2 f_1}{f_2 - f_1}\right)^2$. This factor is determined by the LCAO method, i.e., by the solutions of the basic equations (2.19).

$$C_1'' (H_1 - \varepsilon) + C_2''(\beta - \varepsilon S) = 0 \tag{3.14}$$

and

$$C_1'' (\beta - \varepsilon S) + C_2'' (H_2 - \varepsilon) = 0 \tag{3.15}$$

where $\varepsilon = H_{12} = J_{21}$ because H is Hermitian and ψ_1 and ψ_2 are real; $H_1 = H_{11}$ and $H_2 = H_{22}$.

In order to obtain a simple and explicit solution for the transition probability, the values of β, S, and ε will be discussed. When the internuclear distance is not too small, the quantities $-\beta$ and S are of the same order, whereas ε is about the order of -0.5. Thus, by replacing the quantity $\beta - \varepsilon S$ in equations (3.14) and (3.15) by $\frac{1}{2}\beta$, the problem is amply simplified. Later in this section, we will explain in detail the justification for this approximation. Thus, equations (3.14) and (3.15) can be written as

$$C_1'' (H_1 - \varepsilon) + C_2'' \frac{1}{2} \beta = 0 \tag{3.16}$$

and

$$C_1'' \frac{1}{2} \beta + C_2'' (H_2 - \varepsilon) = 0 \tag{3.17}$$

which give

$$(H_1 - \varepsilon)(H_2 - \varepsilon) = \left(\frac{1}{2} \beta\right)^2 \tag{3.18}$$

For the case $H_2 - H_1 > 0$, the above equation when solved for ε yields

$$\varepsilon = \frac{H_2 + H_1}{2} \pm \frac{(H_2 - H_1)}{2} \left(1 + \frac{B_1}{\Delta}\right) \tag{3.19}$$

where

$$\Delta = \frac{H_2 - H_1}{2} \tag{3.20}$$

$$B_1 = \{ \overline{1 - (\beta/2\Delta)^2} - 1 \} \Delta \tag{3.21}$$

When the internuclear distance is not too small, β is rather small. Also, in the non-symmetrical process, except for a resonant channel, H_1 and H_2 are usually not very close to each other. Thus,

$$\left| \frac{H_1 - H_2}{2} \right| \gg \left| \beta \right| \tag{3.22}$$

Hence, under the above condition, B_1 can be simplified as

$$B_1 \sim \frac{1}{4} \frac{\beta^2}{(H_2 - H_1)} \tag{3.23}$$

The equation (3.19) leads to

$$\varepsilon_1 = H_1 - B_1 \tag{3.24}$$

$$\varepsilon_2 = H_2 + B_1 \tag{3.25}$$

The equation (3.16) for $\varepsilon = \varepsilon_2$ becomes

$$C_1'' \, (H_1 - H_2 - B_1) + \frac{1}{2} C_2'' \beta = 0 \tag{3.26}$$

thus,

$$f_1 = \frac{C_2''}{C_1''} = - \frac{(H_1 - H_2 - B_1)}{\beta/2} \approx - \frac{H_1 - H_2}{\beta/2} \tag{3.27}$$

For $\varepsilon = \varepsilon_1$, the equation (3.17) becomes

$$\frac{C_1'' \beta}{2} + C_2''(H_2 - H_1 + B_1) = 0 \tag{3.28}$$

Thus,

$$f_2 = \frac{C''_2}{C''_1} = \frac{-\beta/2}{H_2 - H_1 + B_1} \sim \frac{-\beta/2}{H_2 - H_1} \tag{3.29}$$

Thus, the transition probability is

$$W_{12} = 4\left(\frac{1}{A}\right)^2 \sin^2 \eta \tag{3.30}$$

where

$$A = \frac{1}{f_1} - \frac{1}{f_2} = -\frac{\beta/2}{H_2 - H_1 - B_1} + \frac{H_2 - H_1 + B_1}{\beta/2} \tag{3.31}$$

and

$$\eta = \frac{1}{2}\int_{-t_0}^{t_0} \Delta E \, dt = \frac{1}{2}\int_{-t_0}^{t_0} \{(H_2 - H_1) + 2B_1\} \, dt \tag{3.32}$$

In the case $H_1 \neq H_2$, or where H_1 and H_2 are not close to the same value, applying (3.22), and remembering that B_1 is of the order of β^2, we have

$$A \simeq \frac{H_2 - H_1 + B_1}{\beta/2} \simeq \frac{H_2 - H_1}{\beta/2} \tag{3.33}$$

and the transition probability is

$$W_{12} = \frac{H_{12}^2}{(H_2 - H_1)^2} \sin^2 \eta \tag{3.34}$$

This is the required simple transition probability formula which is determined by H_{12}, $(H_2 - H_1)$, and the value of η. The quantity H_{12} is closely related to the overlap integral. Physically, it is reasonable to expect higher transition probability with more overlap. The quantity $H_2 - H_1$ is strongly related to the energy defect ΔE (at a large distance). Obviously there will be less transition probability with more energy defect.

For the case $H_1 = H_2$, we have from equation (3.18)

$$(H - \varepsilon)^2 = (\beta/2)^2 \tag{3.35}$$

which yields

$$\varepsilon = H \pm \beta/2 \tag{3.36}$$

$$f_1 = 1, \; f_2 = -1 \text{ and } A = 2 \tag{3.37}$$

The transition probability for this case is given by $W = \sin^2\eta$, which is the familiar formula (2.14) of the symmetric case obtained in Section II.

Let us now discuss the assumption of the replacement of the quantity $\beta - S\varepsilon$ by $\beta/2$ in equations (3.14) and (3.15). Initially, this approximation seems somewhat arbitrary. However, $\beta/2$ is not strictly equal to $\beta - S\varepsilon$ in equations (3.14) and (3.15). Recall that the equation (2.19) is derived from the variational principle, which implies that the LCAO molecular state function is made the most stable state at that particular interatomic separation. On the other hand, equations (3.14) and (3.15) were altered by the replacement $\beta - S\varepsilon \rightarrow \beta/2$, which implies that a set of molecular states are chosen that, although not the most stable, nevertheless approach the most stable states for large separation. In other words, a set of quasi-stationary molecular states are chosen. In this way we may refer to a quasi-stationary molecular state expansion procedure. Actually, in chemistry, at a large distance, the molecular states are not stable at all. However, we are more interested in looking for a set of mathematically permitted basis states.

Probably, this is one of the reasons why the atomic expansions are widely used (refs. 1, 2, 4, and 18). Thus, it is more important that these molecular states be orthogonal. Fortunately, our quasi-stationary molecular states approximately satisfy the requirement of orthogonality. In the following, we will explicitly show how the orthogonality requirement is approximately satisfied. Consider

$$\psi_g = C_1(\psi_1 + f_1\psi_2)$$
$$\psi_u = C_1' (\psi_1 + f_2\psi_2) \tag{3.38}$$

where

$$C_1 = \frac{1}{(1 + Sf_1 + f_1^2)^{1/2}} \text{ and } C_1' = \frac{1}{(1 + Sf_2 + {}^2f_2)^{1/2}}$$

and

$$f_1 = \frac{C_2''}{C_1''} \simeq - \frac{H_1 - H_2}{0.5\beta} \text{ and } f_2 = \frac{C_2'''}{C_1'''} \simeq - \frac{0.5\beta}{H_2 - H_1}$$

Now,

$$\int \psi_g\psi_u \, d\tau = C_1C_1' \int (\psi_1 + f_1\psi_2)\,(\psi_1 + f_2\psi_2)\, d\tau \tag{3.39}$$
$$= C_1C_1' \{\int (\psi_1^2 + f_1f_2\psi_2^2)\, d\tau + \int (f_1 + f_2)\, \psi_1\psi_2 \, d\tau\}$$

Remembering $f_1f_2 \simeq - 1$, we have

$$\int \psi_g\psi_u d\tau = C_1C_1' \int (f_1 + f_2)\, \psi_1\psi_2 \, d\tau \tag{3.40}$$

For the case $H_1 \neq H_2$, when the internuclear distance R is not too small, usually $|H_2 - H_1| >> |0.5\ \beta|$; thus $|f_1| >> 1$ and $|f_2| << 1$. Also, $f_1 + f_2 \rightarrow f_1$;

$$\frac{1}{(1 + 2Sf_1 + f_1^2)^{1/2}} \rightarrow \frac{1}{f_1} \text{ and } \frac{1}{(1 + 2Sf_2 + f_2^2)^{1/2}} \rightarrow 1$$

One sees from these that

$$\int \psi_g\psi_u d\tau \rightarrow \frac{f_1}{f_1} \int \psi_1\psi_2 d\tau = \int \psi_1\psi_2 d\tau = S$$

Now, the overlap integral of the two atomic orbitals between the projectile and the target is small except when the internuclear distance approaches zero. Thus, $\int \psi_g\psi_u d\tau \approx 0$.

For the case $H_1 = H_2$, we have $f_1 = 1$ and $f_2 = -1$. Thus,

$$\int \psi_g\psi_a d\tau = \frac{1}{(4-S^2)^{1/2}} \int (f_1 + f_2)\, \psi_1\psi_2 d\tau = 0$$

For the case $H_1 \sim H_2$, we have $f_1 \approx 1$ and $f_2 \approx -1$. Thus,

$$\int \psi_g\psi_u d\tau \sim (f_1 + f_2)\, S \approx 0$$

We observe that for the cases $H_1 = H_2$ and $H_1 \sim H_2$, because of the cancellation between f_1 and f_2, the orthogonality is preserved. From the orthogonality point of view, this expansion is at least not worse than the atomic expansion.

The capture cross section σ, according to the impact parameter method, is given by

$$\sigma = 2\pi \int P\big|_{t_0} b\,db \tag{3.41}$$

(see fig. 2) where b is the impact parameter, and P refers to the transition probability. Usually, P takes the value $P_{t\rightarrow\infty}$; but as discussed earlier, an adiabatic parameter will be employed to evaluate the cross section. The transition probability P is given by equation (3.34) as

$$P = \frac{H_{12}^2}{(H_2 - H_1)^2} \sin^2 n \tag{3.42}$$

where all the quantities appearing in this equation are functions of the internuclear distance $R = (b^2 + \frac{1}{4} R_c^2)^{1/2}$ in which R_c is the adiabatic parameter defined by $2 \upsilon t_o = R_c$. The value of the parameter R_c is chosen to be 7Å.

IV. CHARGE TRANSFER IN Li^{3+} + H

Let us evaluate the magnitude of the transition probability for the following reacton:

$$Li^{3+} + H \rightarrow Li^{2+}(n=3) + H^+$$

The magnitude of the transition probability is

$$P_o = \begin{cases} \dfrac{H_{12}^2}{(H_2 - H_1)} & (H_1 \neq H_2) \\ 4\left(\dfrac{1}{A}\right)^2 & (H_1 \sim H_2) \\ 1 & (H_1 = H_2) \end{cases} \tag{4.1}$$

where

$$A = \frac{-0.5\beta}{(H_1 - H_2 - B_1)} + \frac{(H_2 - H_1 + B_1)}{0.5\beta}$$

$$\begin{aligned} H_{12} &= \int \psi_1 H \psi_2 \, d\tau \\ &= \int \psi_1 \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r_2} - \frac{1}{r_1} + \frac{Z}{R}\right) \psi_2 \, d\tau \\ &= E_{2,n} S + \frac{SZ}{R} - K \end{aligned} \tag{4.2}$$

$$H_1 = \int \psi_1 \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{Z}{r_2} + \frac{Z}{R}\right) \psi_1 \, d\tau$$

$$= E_{1,0} - Z J_1 + \frac{Z}{R} \tag{4.3}$$

$$H_2 = \int \psi_2 \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r_2} - \frac{1}{r_1} + \frac{Z}{R}\right) \psi_2 \, d\tau$$

$$= E_{2,n} - J_2 + \frac{Z}{R} \tag{4.4}$$

The quantities β, H_1, H_2, and η are calculated by evaluating the overlap integral S, the exchange integral K, and the Coulomb integral J, defined as follows:

$$S = \int \psi_1 \psi_2 \, d\tau, \quad K = \int \frac{\psi_1 \psi_2 \, d\tau}{r_1}, \text{ and}$$

$$J_1 = \int \frac{\psi_1^2}{r_2} \, d\tau, \quad J_2 = \int \frac{\psi_2^2}{r_1} \, d\tau$$

The integrals S and K can be evaluated by introducing well known transformations of ref. 9 (fig. 3):

$$\lambda = \frac{1}{R}(r_2 + r_1); \; 1 < \lambda < \infty \tag{4.5}$$

$$\mu = \frac{1}{R}(r_2 - r_1); \; -1 < \mu < 1 \tag{4.6}$$

and

$$d\tau = \frac{R^3}{8}(\lambda^2 - \mu^2) \, d\phi. \tag{4.7}$$

For our special case, $Z_2 = 3$, $Z_1 = 1$, and $n = 3$, we have

$$S = \int \psi_1 \psi_2 \, d\tau$$

$$= 18 \, (\pi)^{1/2} A_3 \left(\frac{R}{2}\right)^3 \left(\frac{R}{2}\right)^2 \int (\lambda + \mu)^2 (\lambda^2 - \mu^2) \, e^{-R\lambda} \, d\lambda \, d\mu$$

Now, from table 1, the value of $A_3 = 0.013$; thus, we obtain

$$S = 0.013 \, (1.6 \, R^4 + 8R^3 + 24 \, R^2 + 48R + 48) \, e^{-R} \tag{4.8}$$

Similarly, the exchange integral is

$$K = 0.026 \, (4R^3 + 8R^2 + 12R + 12) \, e^{-R} \tag{4.9}$$

and

$$\beta = \int \Psi_1 \left(- \frac{1}{2} \nabla^2 - \frac{1}{r_1} - \frac{Z}{r_2} + \frac{Z}{R} \right) \Psi_2 \, d\tau$$

$$= E_{2,n} S + \frac{SZ}{R} - \int \frac{\Psi_1 \Psi_2}{r_1} \, d\tau$$

$$= -0.5S + \frac{3S}{R} - K$$

The calculations of the Coulomb integrals J_1 and J_2 are done in the following way. (See fig. 4.)

$$J_1 = \int \frac{\psi_1^2 \, d\tau}{r_2} = \frac{2\pi}{\pi} \int e^{-2r} \frac{\sin \theta \, d\theta \, r^2 dr}{(R^2 + r^2 - 2rR \cos \theta)^{1/2}}$$

$$= 2 \int e^{-2\rho R} \rho^2 R^2 \, d\rho \left[\frac{\rho + 1}{\rho} - \frac{\sqrt{1 + \rho^2 - 2\rho}}{\rho} \right] \tag{4.10}$$

where $\rho = r/R$. Finally, one obtains

$$\begin{aligned} J_1 &= 4R^2 \left\{ \int_0^1 e^{-2\rho R} \rho^2 \, d\rho + \int_1^\infty e^{-2\rho R} \rho \, d\rho \right\} \\ &= \frac{1}{R} - \left(1 + \frac{1}{R}\right) e^{-2R} \end{aligned} \tag{4.11}$$

One notes that $J_1 \rightarrow \frac{1}{R}$ $(R > 1)$ and $J_1 \rightarrow 1$ $(R \rightarrow 0)$. The quantity J_2 is calculated as follows (fig. 5):

$$\begin{aligned} J_2 &= \int \frac{\psi_2^2}{r_1} d\tau = 2\pi \, (A_3 \times 9)^2 \int e^{-2r} \frac{\sin\Theta \, d\Theta \, r^2 dr}{(R^2 + r^2 - 2rR\cos\Theta)^{1/2}} \\ &\cong \frac{1}{R} - \left\{0.043\,R^4 + 0.215R^3 + 0.645R^2 + 1.29R + 1.61 + \frac{1}{R}\right\} e^{-2R} \end{aligned} \tag{4.12}$$

For the calculation of η, one notes for the $Z = 3$ and $n = 3$ case (resonance) that

$$H_1 = -0.5 - 3J_1 + \frac{3}{R}$$

$$H_2 = -0.5 - J_2 + \frac{3}{R}$$

$$B_1 = \left(\sqrt{1 + \left(\frac{\beta}{2\Delta}\right)^2} - 1\right) \cdot \Delta \; ; \; 2\Delta = (H_2 - H_1)$$

Thus,

$$\eta = \frac{1}{2}\int_{-t_0}^{t_0} \Delta E\,(R')\,dt = \frac{1}{2}\int_{-t_0}^{t_0} (H_2 - H_1 + 2B_1)\,dt \tag{4.13}$$

where, $R' = \sqrt{b^2 + \upsilon^2 t^2}$

The capture cross section, σ, is given by

$$\sigma = \int_0^\infty P(R)\, 2\pi b\, db \tag{4.14}$$

where $P = P_0\,(R)\,\sin^2\eta$ in which P_0 is taken from equation (4.1) and H_{12}, $H_2 - H_1$, Δ, and B_1 are all functions of $R^2 = b^2 + \frac{1}{4}R_c^2$.

V. RESULTS AND DISCUSSIONS

The results of the calculations for the reactions $Li^{+++} + H \rightarrow Li^{++} + H^+$ are exhibited in figure 6. They are compared with the results based on the Unitarized Distorted-Wave Approximations of Ryufuku and Watanabe (ref. 18), the ten molecular-state calculations of Kimura and Torson (ref. 19), and the calculations of Stollberg and Hai-Woong Lee (ref. 17) based on the Landau-Zener formula. The results are also compared with the experimental data of Seim et al. (ref. 20). Also, the results of the calculations for the reaction $Be^{4+} + H \rightarrow Be^{3+} + H^+$ are exhibited in figure 7 and are compared with the UDWA approximation and Exponential Distorted-Wave Approximation calculations of Suzuki et al. (ref. 21) and with the molecular orbital close coupling calculation of Harel and Salin (ref. 22). No experimental data were available for this process.

In figure 6, both the results of our calculations as well as those based on the Landau-Zener formula do not appear to show the tendency of the cross section to increase toward the high-velocity region. This is partly due to the implied employment by us of the Born-Oppenheimer approximation in which the effect of the nuclear kinetic energy terms are ignored in the Hamiltonian. For a large projectile velocity ($\upsilon_2 > 10^8$cm/sec), the Born Oppenheimer approximation should break down. When nuclear motion is incorporated, there will appear an additional electron kinetic energy term because of the relative motion between the projectile and the target. This becomes more obvious when our coordinate system is set on the projectile. Then the kinetic energy of the electron becomes $\frac{1}{2} m_e(\bar{\upsilon}_2 + \bar{\upsilon}_0)^2$, where $\bar{\upsilon}_0$ is the velocity of the electron in the laboratory frame. Hence, the average kinetic energy becomes $\frac{1}{2} m_e(\upsilon_0^2 + \upsilon_2^2)$. A significant additional kinetic energy term is obtained when υ_2 is comparable to the electron velocity that is the first Bohr velocity. Also, if we choose the laboratory frame, the electron will receive an additional velocity from the momentum transfer. Thus, because of the above reasons, some higher states will be excited, causing a significant contribution to the total cross section.

Let us now discuss the general energy dependence of the cross section. One expects that toward the high velocity region, the cross section should decrease as a result of the increasing relative velocity between the projectile and the target. In the extremely low energy region, the cross section for these processes should not rapidly approach zero with a decrease in υ, but rather approach a not too small constant. The calculated cross section in the energy region of interest (below a few keV) approaches a constant value due to the term $H_2 - H_1$ in the argument of the sine function. This makes the value of the sine function very large, and the transition probability oscillates rapidly. The summation over the impact parameter approaches an average number, $\sin^2\eta \sim 0.5$. When ν becomes larger, there will be a slow oscillating behavior, but this velocity region is beyond our adiabatic approximation.

In the symmetric case, since $H_1 = H_2$, only when the impact parameter b is small does the transition probability exhibit the rapidly oscillating behavior different from the non-symmetric situation.

Finally, experimental physicists (refs. 23 and 24) have recently noticed that below a few keV, the capture cross section shows velocity independent behavior in helium and lithium materials. It is hoped that our results will help in classifying these and other relevant capture cross section observations.

CONCLUDING REMARKS

A semiclassical approach is used to derive a quasi-stationary state method to approximate the charge transfer cross section. The result is only slightly more complicated than the usual Landau-Zeuer formalism and greatly simpler than the coupled channel and various distorted wave formalisms. Unlike the Landau-Zener result, we predict nearly constant cross sections below a few KeV in agreement with recent experiments and the more complex formalisms.

REFERENCES

1. D. R. Bates and N. Lynn, Proc. Roy. Soc. (London) A253, 141 (1959).
2. E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237 (1957).
3. D. Rapp and I. B. Ortenburger, J. Chem. Phys. 33, 1230 (1960).
4. D. Rapp and W. E. Francis. J. Chem. Phys. 37, 2631 (1962).
5. H. S. W. Massey, Rept. Progr. Phys. 12, 248 (1949).
6. J. B. Hasted, Physics of Atomic Collisions (Butterworths, London, 1964), pp. 420-424.
7. L. D. Landau and E. M. Lifshitz, Quantum Mechanics Non-Relativisitic Theory (Pergamon Press, 1977), pp. 19-20.
8. D. R. Bates and R. McCarroll, Proc. Roy. Soc. A, 245, 175 (1958).
9. N. V. Riggs, Quantum Chemistry, (The Macmillan Company Collier-Macmillan Limited, London, 1969), pp. 72-75.
10. Reference 7, p. 313.
11. H. Ryufuku and T. Watanabe, Phys. Rev. A18, 2005 (1978).
12. H. Ryufuku, K. Sasaki and T. Watanabe, Phys. Rev. A21, 745 (1980).
13. R. E. Olson and A. Salop, Phys. Rev. A14, 579 (1976).
14. L. Landau, Z. Phys. Soviet, 2, 46 (1932).
15. C. Zener, Proc. Roy. Soc. A, 137, 696 (1932).
16. R. K. Janev, D. S. Belic and B. H. Bransden, Phys. Rev., A28, 1293 (1983).
17. M. T. Stollberg and Hai-Woong Lee, Phys. Rev. A29, 2448 (1984).
18. H. Ryufuku and T. Watanabe, Phys. Rev. A19, 1538 (1979).
19. M. Kimura and W. R. Torson, J. Phys. B16, 1471 (1983).
20. W. Seim, A. Muller, I. Wirkner-Bott and E. Salzborn, J. Phys. B, 14, 3475 (1981).

21. H. Suzuki, N. Toshima, T. Watanabe and H. Ryufuku, Phys. Rev. A29, 529 (1984).

22. C. Harel and A. Salin, Phys. Rev. B10, 3511 (1977).

23. E. Justiniano, C. L. Cocke, T. J. Gray, R. Dubois, C. Can, W. Waggoner, R. Schuch, H. Schmidt-Bocking and H. Ingwersen, Phys. Rev. A29, 1088 (1984).

24. W. Waggoner, C. L. Cocke, S. L. Varghes and M. Stockli, Phys. Rev. A29, 2457 (1984).

APPENDIX

In this appendix, the conditions under which the quantities A(t) and B(t) can be treated as time independent in the equation (2.3) are obtained. The central point in this treatment is the observation that when $\upsilon \to 0$, compared with the phase change, a is a slowly varying function in $\psi \sim a\, e^{iS}$. As discussed in Section II, this leads to

$$\psi = A(t)\, \psi_g e^{-i \int^t E_g\, dt} + B(t)\, \psi\, e_u^{-i \int^t E_u\, dt} \qquad (B.1)$$

We have shown previously that Ψ_g and Ψ_u are slowly varying functions and had assumed that A and B vary so slowly that they can be treated as time independent. Now, let us estimate how slowly Ψ_g and Ψ_u are varying and under what conditions A and B can be treated as time independent. Having done this, we will know the conditions under which our analytical model of this paper works.

The wave functions of the stationary states can be formed by linear combination of atomic wave functions, i.e.,

$$\psi_g = C_1 \psi_1 + C_2 \psi_2$$

and (B.2)

$$\psi_u = C_1' \psi_1 + C_2' \psi_2$$

where ψ_1 and ψ_2 are the atomic electronic wave functions of the projectile and the target, respectively. They are independent of the internuclear distance R. The coefficients C_1, C_2, C'_1, and C'_2 are determined by the normalization condition and the LCAO method to be

$$C_1 = \frac{1}{(1 + 2Sf_1 + f_1^2)^{1/2}} \; ; \quad C_2 = \frac{1}{(1 + 2Sf_1 + f_1^2)^{1/2}}$$

$$C_1' = \frac{1}{(1 + 2Sf_2 + f_2^2)^{1/2}} \; ; \quad C_2' = \frac{f_2}{(1 + 2Sf_2 + f_2^2)^{1/2}}$$

where f_1 and f_2 are solutions of equations (2.18) and (2.20) and are known functions of the internuclear distance R.

Now, first let us estimate how slowly the molecular eigen functions vary. For this consider

$$\dot{\psi}_g = \dot{C}_1\psi_1 + \dot{C}_2\psi_2$$

$$= \left(\frac{dC_1}{dR}\psi_1 + \frac{dC_2}{dR}\psi_2\right) \cdot \sqrt{1 - \left(\frac{b}{R}\right)^2} \cdot \upsilon_2$$

where b is the impact parameter and υ_2 is the velocity of the projectile. One notes that if υ_2 is small, then $\dot{\psi}_g$ and similarly $\dot{\psi}_u$ should be small. Now, consider the following

$$i\dot{\psi} = i\dot{A}\psi_g e^{-i\int^t E_g\,dt} + iA\dot{\psi}_g e^{-i\int^t E_g\,dt} + E_g A\psi_g e^{-i\int^t E_g\,dt}$$

$$+ i\dot{B}\psi_u e^{-i\int^t E_u\,dt} + iB\dot{\psi}_u e^{-i\int^t E_u\,dt} + E_u\psi_u B e^{-i\int^t E_u\,dt} \qquad \text{(B.3)}$$

In the above, the second term contains a factor υ_2 because of $\dot{\psi}_g$, and the third term contains a factor of E_g which is about the order of unity. Therefore, if $\upsilon_2 \ll 1$, compared to the terms containing E_g and E_u, we can neglect the terms $\dot{\psi}_g$ and $\dot{\psi}_u$.

Next, let us discuss the behavior of the quantities A(t) and B(t). For this we assume $\dot{\psi}_g = \dot{\psi}_u = 0$, then using the Schroedinger equation $i\dot{\psi} = H\psi$ and equations (B.1) and (B.2), we obtain

$$i\dot{A}\ (C_1 + C_2 S)\ e^{-\int^t E_g dt} + A\ \{C_1(E_g - H_{11}) + C_2(E_g S - H_{12})\}\ e^{-i\int^t E_g dt}$$

$$+\ i\dot{B}\ (C_1' + C_2' S)\ e^{-i\int^t E_u dt} + B\ \{C_1'(E_u - H_{11}) + C_2'\ (E_u S - H_{12})\}\ e^{-i\int^t E_u dt} = 0$$

Recall the basic equation of LCAO (eqs. (2.19) and (2.20))

$$C_1(H_{11} - \varepsilon) + C_2(H_{12} - \varepsilon S) = 0$$

$$C_1(H_{21} - \varepsilon S) + C_2(H_{22} - \varepsilon) = 0$$

and the two sets of solutions C_1, C_2 and C'_1, C'_2 corresponding to eigen energies E_g and E_u, respectively. Thus, the equations

$$C_1\ (E_g - H_{11}) + C_2(E_g S - H_{12}) = 0$$

$$C_1'\ (E_u - H_{11}) + C_2'(E_u S - H_{12}) = 0$$

lead to

$$i\ \dot{A}\ (C_1 + C_2 S)\ e^{-i\int^t E_g dt} + i\ \dot{B}\ (C_1' + C_2'\ S)\ e^{-i\int^t E_u dt} = 0 \qquad \text{(B.4)}$$

Similarly, starting again from the Schroedinger equation $i\dot{\psi} = H\psi$, we will obtain

$$i\,\dot{A}\,(C_2 + C_1 S)\,e^{-i\int^t E_g dt} + i\dot{B}\,(C'_2 + C'_1\,S)\,e^{-\int^t E_u dt} = 0$$

The above two equations can be written as

$$\dot{A}\,(C_1 + C_2\,S + \dot{B}\,(C'_1 + C'_2\,S)\,e^{-\,i\int^t (E_u - E_g)\,dt} = 0$$

and (B.5)

$$\dot{A}\,(C_2 + C_1 S) + \dot{B}\,(C'_2 + C'_1 S)\,e^{-\,i\int^t (E_u - E_g)\,dt} = 0 \tag{B.6}$$

Now, $\dot{A}$ and $\dot{B}$ have nonzero solutions if, and only if, the secular equation is equal to zero, as follows:

$$\begin{vmatrix} (C_1 + C_2 S) & (C'_1 + C'_2 S)\,e^{-\,i\int^t (E_u - E_g)\,dt} \\ (C_2 + C_1 S) & (C'_2 + C'_1 S)\,e^{-\,i\int^t (E_u - E_g)\,dt} \end{vmatrix} = 0$$

which leads to

$$f_2 - f_1 = (f_2 - f_1)S^2$$

where S is the overlap integral and is always less than unity except when $R = 0$ and $\psi_1 = \psi_2$, and where f_1 and f_2, defined by $f_1 = C_2/C_1$ and $f_2 = C'_2/C'_1$, are obviously not always equal. Thus, the secular equation cannot always be zero. Therefore, the only solution of equations (B.5) and (B.6) is $\dot{A} = \dot{B} = 0$.

Thus, if we assume $\dot{\psi}_g = \dot{\psi}_u = 0$, then A and B are independent of time. However, if $\upsilon \ll 1$, we can say that ψ_g, ψ_u, A(t), and B(t) are very slowly varying functions. In practice, if $\upsilon < 5 \cdot x\ 10^7$ cm/sec , i. e., in atomic units $\upsilon \ll 0.2$, the condition $\upsilon \ll 1$ is satisfied. It is noticed in figure 6 for values $\upsilon > 6 \times 10^7$ cm/sec, our results do not exhibit the increasing cross section as observed in experiment.

TABLE 1. A list of functions for the reaction of $Li^{3+} + H \rightarrow Li^{++} (n=3) + H^+$

FUNCTION	EXPRESSION
S	$0.013\ e^{-R}(1.6\ R^4 + 8R^3 + 24R^2 + 48R + 48)$
K	$0.026\ e^{-R}(4R^3 + 8R^2 + 12R + 12)$
J_1	$\frac{1}{R} - e^{-2R}\ (1 + \frac{1}{R})$
J_2	$\frac{1}{R} - (0.043\ R^4 + 0.215\ R^3 + 0.645R^2 + 1.29R + 1.61 + \frac{1}{R})\ e^{-2R}$
$\beta = H_{12}$	$-\ 0.5S + \frac{3S}{R} - K$
H_1	$-\ .05 - 3 \cdot J + \frac{3}{R}$
H_2	$-\ 0.5 - J_2 + \frac{3}{R}$
Δ	$\frac{1}{2}\ (H_2 - H_1)$
B_1	$\{ \sqrt{1 + (\frac{\beta}{2\Delta})^2} - 1\ \}\ \Delta$
$\Delta E(R)$	$(H_2 - H_1) + 2\ B_1$
Po	$\begin{cases} H_{12}^2/(H_2 - H_1)^2 & (H_1 \neq H_2) \\ 4\ A^{-2} \text{ where, } A = -\frac{0.5\ \beta}{H_1 - H_2 - B_1} + \frac{H_2 - H_1 + B_1}{0.5\ \beta} & (H_1 \sim H_2) \\ 1 \quad H_1 = H_2 & \end{cases}$
A_n	$\frac{Z\sqrt{Z}}{2\sqrt{\pi}} \sqrt{(\frac{2}{n})^{2n+1} \frac{1}{2n!}}$

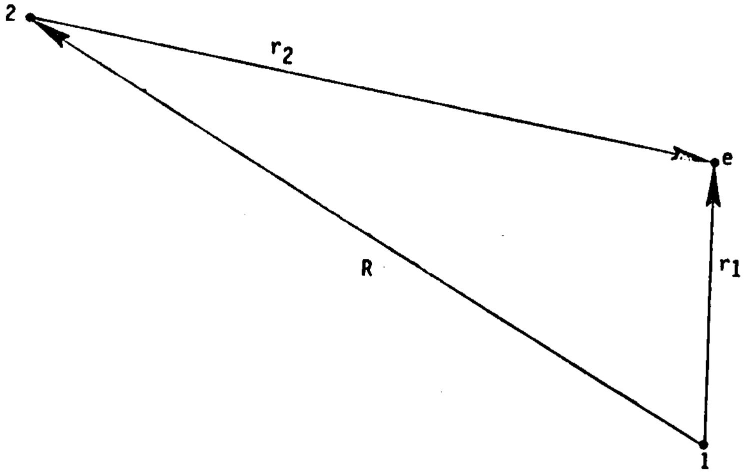

Figure 1. Coordinate vectors of the three-body system.

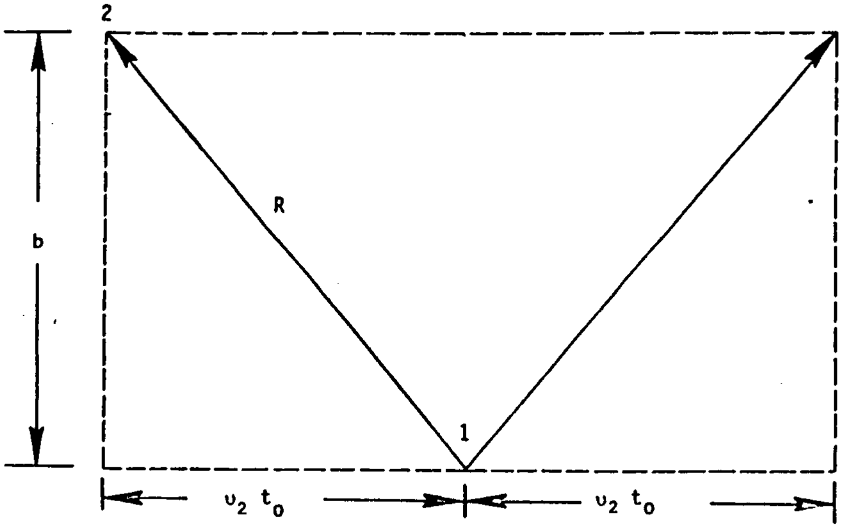

Figure 2. Domain of collision at impact parameter b over time domain $-t_0 < t < t_0$.

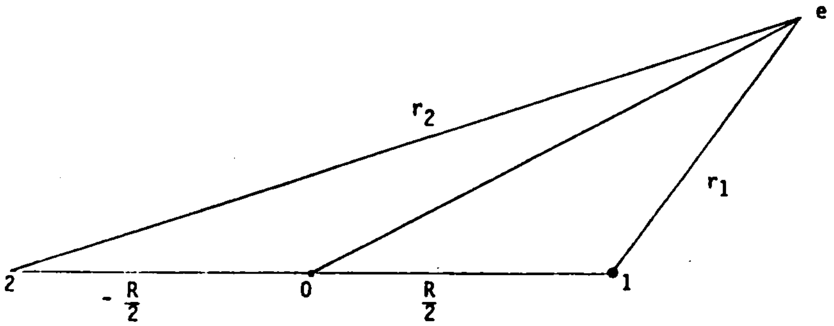

Figure 3. Coordinates used for transformation Equations (4.5) - (4.7).

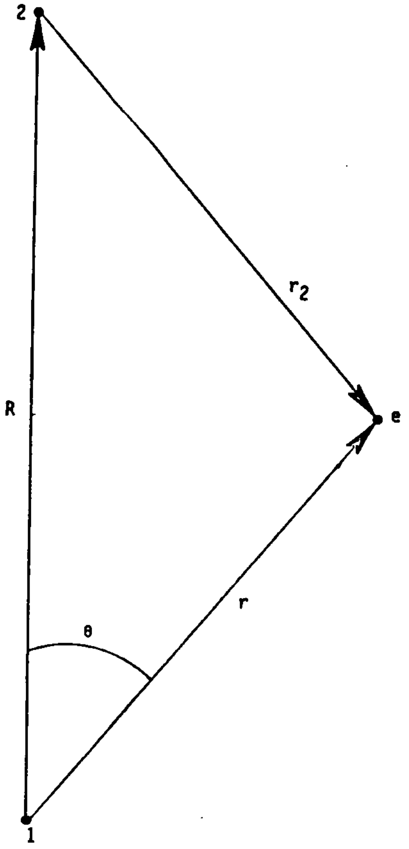

Figure 4. Coordinates used for evaluation of coulomb integral J_1.

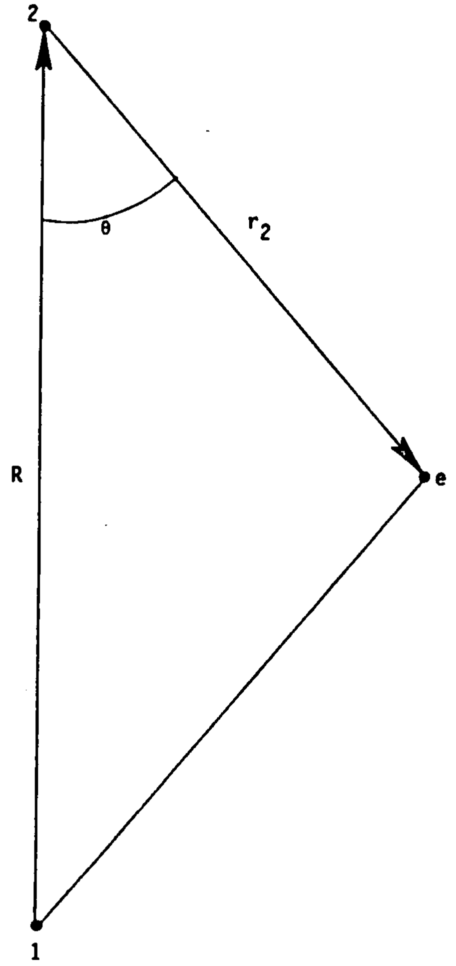

Figure 5. Coordinates used for evaluation of coulomb integral J_2.

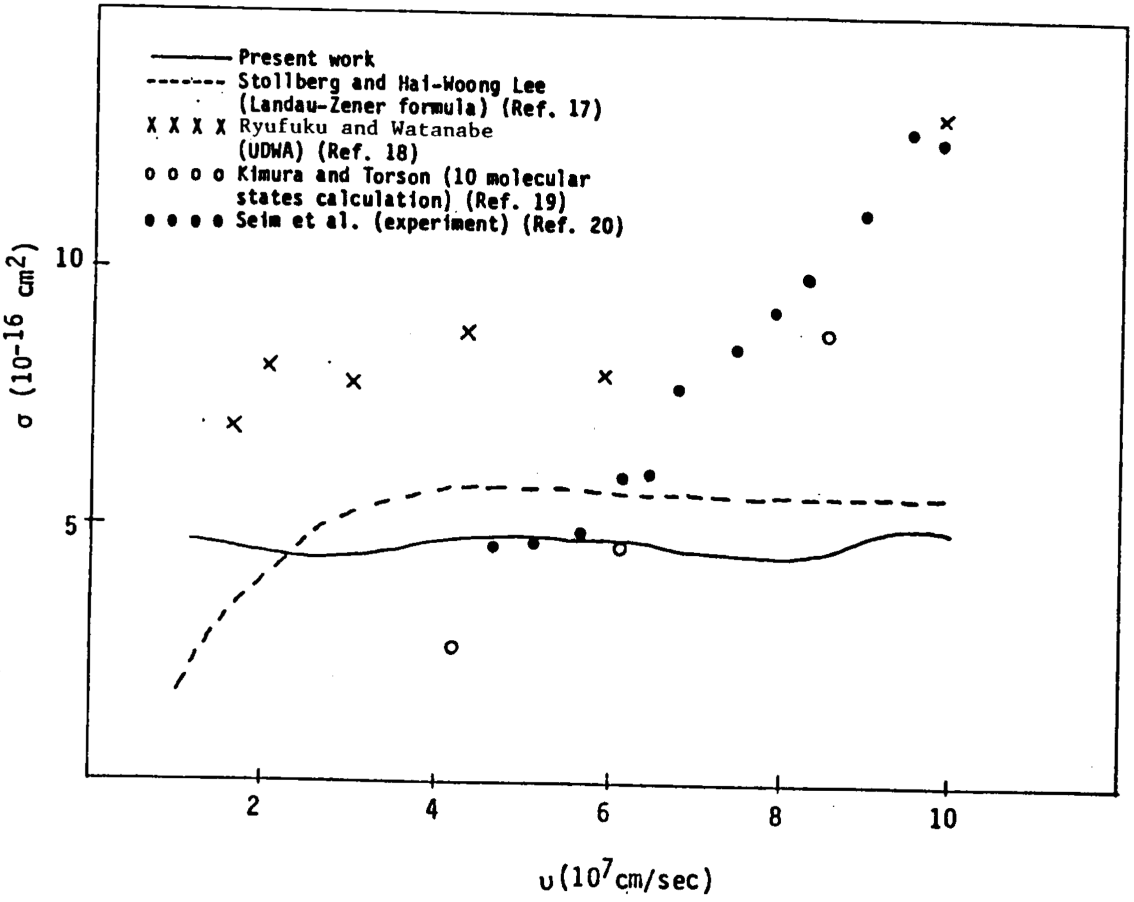

Figure 6. The total capture cross section as a function of the ion velocity υ for the reaction $Li^{+++} + H \rightarrow Li^{++} + H^{+}$.

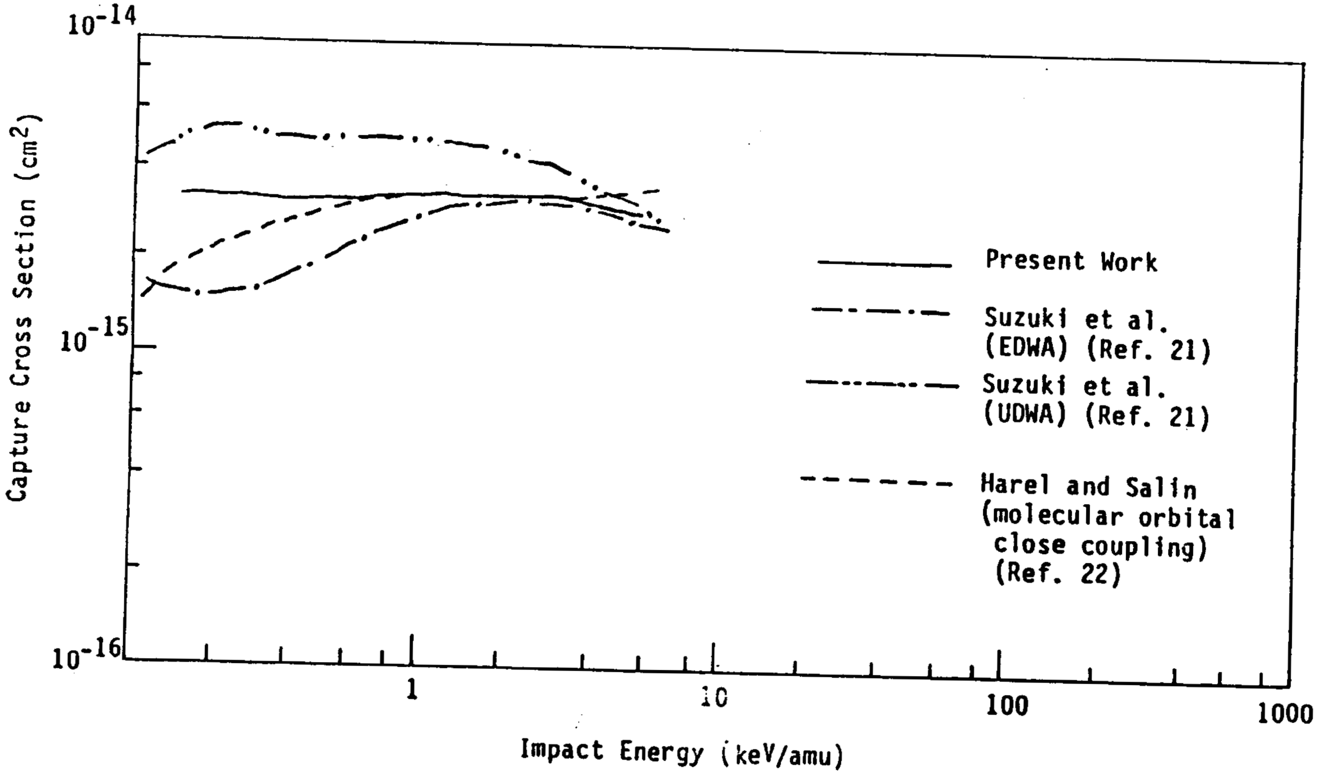

Figure 7. The total capture cross section as a function of the impact energy per nucleon for the reaction $Be^{4+} + H \rightarrow Be^{3+} + H^{+}$.

NASA
National Aeronautics and Space Administration

Report Documentation Page

1. Report No.
NASA TM-101559

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Charge Exchange Transition Probability for Collisions Between Unlike Ions and Atoms Within the Adiabatic Approximation

5. Report Date
April 1989

6. Performing Organization Code

7. Author(s)
Y. J. Xu, G. S. Khandelwal, J. W. Wilson

8. Performing Organization Report No.

9. Performing Organization Name and Address
NASA Langley Research Center
Hampton, VA 23665-5225

10. Work Unit No.
199-22-76-02

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546-0001

13. Type of Report and Period Covered
Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes

Y. J. Xu and G. S. Khandelwal: Old Dominion University, Norfolk, Virginia.
J. W. Wilson: Langley Research Center, Hampton, Virginia.

16. Abstract

A simple formula for the transition probability for electron exchange between unlike ions and atoms is established within the adiabatic approximation by employing the Linear Combination of Atomic Orbitals (LCAO) method. The formula also involves an adiabatic parameter, introduced by Massey, and thus the difficulties arising from the internal energy defect and the adiabatic approximation are avoided. Specific reaction $Li^{+++} + H \rightarrow Li^{++} + H^{+}$ and $Be^{4+} + H \rightarrow Be^{3+} + H^{+}$ are considered as examples. The calculated capture cross section results of the present work are compared with the experimental data and with the calculation of other authors over the velocity range of 10^{7} cm/sec to 10^{8} cm/sec.

17. Key Words (Suggested by Author(s))
Charge exchange
Ion reactions
Space Radiation

18. Distribution Statement
Unclassified-Unlimited

Subject Category - 93

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of pages
42

22. Price
A03

NASA FORM 1626 OCT 86