

INTEGRAL EQUATION TREATMENT OF BOUND STATE ATOMIC SYSTEMS AND
COLLINEAR He - H₂⁺ PROTON TRANSFER REACTIVE COLLISIONS

A Dissertation

Submitted to the Department of Biophysical Sciences

and the Graduate Division of

The University of Houston

In Partial Fulfillment of the Requirements

for the

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by

W. Grant Cooper

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Dedicated to Hildegart

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FORWARD

Sophistication in more than one of the traditional disciplines of physics, biology, chemistry, and mathematics is required if research is to be conducted which utilizes the tools of physics, mathematics, and chemistry to explore those biological problems which are susceptible to such analysis. Investigations of this nature first require a relevant biological system which therefore demands biological insight and secondly, capable analytical "tools", i.e., skill in mathematics, chemistry, and physics. At the expense of not focusing on current researches in molecular biology, development of this latter aspect has been emphasized in the present graduate training. To this end, the dissertation topic was selected from an active area of theoretical chemistry and physics which involves the theory and computation of the properties of atomic systems and reactive scattering probabilities. The particular research discussed in this thesis involves the development and use of Green functions in order to employ recently developed techniques^{1,2} for noninteractively solving integral equations for atomic systems. In addition, three particle reactive collisions are investigated, using newly developed techniques³ for analyzing such processes.

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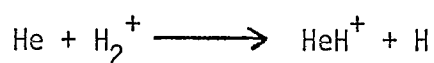
ABSTRACT

A unique prescription is given for obtaining the Green function for N free particles which can have different masses. The approach is systematic and straightforward. A coordinate transformation of the Fourier integral representation of the N -particle noninteracting Green function facilitates the integration over $3N-1$ angular variables of wave number space, using the orthogonal properties of Jacobi polynomials. A single radial integral can then be evaluated. The resulting Green function representation may be of use in applying the integral form of Schrödinger's equation to calculate the ground and excited states of atoms.

The Sams-Kouri method for noniteratively solving integral equations is used to solve the integral form of Schrödinger's equation for He such that the Hartree-Fock approximation is avoided and the inclusion of nuclear motion is straightforward. An exact formalism is presented which requires the solution to coupled integral equations, and the method for generalizing to many electron atoms is indicated. Calculations are reported for a single integral equation approximation to He which illustrates the essential features of the method. The energy value obtained is approximately 85% of the total binding energy. Calculations for the H atom are given so comparisons with an exactly soluble atomic problem can be made, and the energy values for the ground and first three excited states are in excellent agreement with

the exact values. Excited state calculations are found to be no more difficult than those for the ground state.

Reactive collision probabilities are calculated in the collinear approximation for the proton transfer scattering system of



where the cross derivative term in the kinetic energy operator is neglected. The total energy range of 0-3 e.v. includes the first four vibrational states of H_2^+ and the first three energy states of HeH^+ . The coupled channel $\mathcal{T}$ operator equations of Baer and Kouri are employed to execute the calculations and the flux conservation is consistently within the range of .92 - .99. The graphs of total reaction probability versus relative translational energy compare favorably with the experimental cross-section versus energy curves of Chaupka, Berkowitz, and Russell. Fermi's Golden Rule is one of two descriptive models used to interpret and discuss the data.

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CHAPTER I

N PARTICLE NONINTERACTING GREEN FUNCTION

For certain problems in quantum mechanics, it is advantageous to reduce the number of continuous variables, replacing them with sums over discrete variables. Many investigators⁴⁻⁹ have utilized some form of hyperspherical coordinates to express a $3N$ -dimensional ($N=2,3,4, \dots$) problem in terms of a single continuous radial variable with the remaining $3N-1$ coordinates being angles. Functions of the $3N$ coordinates may then be expanded in terms of a set of "generalized" spherical harmonics labeled by discrete indices. If N is one, ordinary spherical polar coordinates result.

In this chapter, a well known hyperspherical coordinate system is^{10,11} employed to obtain in the noninteracting Green function for $N + 1$ distinguishable particles. Although other forms of many-particle Green functions are available,^{12,13} the representation developed here permits one to employ the integral solution procedure of Sams and Kouri¹ which is a numerical method for noniteratively solving integral equations. It has been successfully used in carrying out numerous scattering calculations¹⁴ and bound states investigations for model potentials such as the Lennard-Jones (12,6). Since such integral equations are constructed using Green functions, their numerical method can be employed to calculate energy eigenstates of systems

composed of several particles if the relevant Green functions are known. The present representation for the N-particle Green function is computationally convenient for solving the integral form of Schrodinger's equation for atoms¹⁵ and it therefore may be of some benefit in analyzing other three or more body problems¹⁶.

In center of mass coordinates, $\underline{r}_1$ is the vector between particles 1 and 2 with masses m_1 and m_2 , respectively, $\underline{r}_2$ is the vector from their center of mass to a third particle and $\underline{r}_3$ is a vector from the center of mass of all three to a fourth particle. The i th vector $\underline{r}_i$ ($i=1,2,\dots, N$) is from the center of mass of all the particles 1,2,3, ..., i to the center of mass particle $i+1$. The i th reduced mass, μ_i , is

$$\mu_i = \frac{m_{i+1} \sum_{j=1}^i m_j}{\sum_{j=1}^{i+1} m_j}, \quad (1-1)$$

and η_i is defined by

$$\eta_i^2 = \mu_i. \quad (1-2)$$

The Green function $G(\underline{Q}|\underline{Q}')$ for N free particles having reduced masses η_i^2 satisfies the 3N-dimensional inhomogeneous differential equation

$$\left[\sum_{i=1}^N \left(\frac{1}{\eta_i^2} \right)^2 \nabla_i^2 + K^2 \right] G(\underline{Q}|\underline{Q}') = -\delta(\underline{r}_1 - \underline{r}_1') \delta(\underline{r}_2 - \underline{r}_2') \cdots \delta(\underline{r}_N - \underline{r}_N') \quad (1-3)$$

where the vector $\underline{\mathcal{R}}$ possesses $3N$ components and the right side of Eq. (1-3) is a product of N three-dimensional Dirac δ -functions. The Fourier integral representation of $G(\underline{\mathcal{R}}|\underline{\mathcal{R}}')$ may be written as

(1-4)

$$G(\underline{\mathcal{R}}|\underline{\mathcal{R}}') = \left(\frac{1}{2\pi}\right)^{3N} \int d\underline{u}_1 \int d\underline{u}_2 \cdots \int d\underline{u}_N \left[\frac{e^{i\underline{u}_1 \cdot (\underline{r}_1 - \underline{r}'_1)} e^{i\underline{u}_2 \cdot (\underline{r}_2 - \underline{r}'_2)} \cdots e^{i\underline{u}_N \cdot (\underline{r}_N - \underline{r}'_N)}}{\left(\frac{u_1}{\eta_1}\right)^2 + \left(\frac{u_2}{\eta_2}\right)^2 + \cdots + \left(\frac{u_N}{\eta_N}\right)^2 - K^2} \right],$$

using the Fourier representation of the Dirac δ -functions¹⁷. The method for treating the singularities in Eq. (1-4) follow from the boundary conditions imposed on $G(\underline{\mathcal{R}})$ as $\underline{\mathcal{R}} \rightarrow \infty$. It is convenient to let

(1-5)

$$\underline{g}_i = \frac{\underline{u}_i}{\eta_i}$$

and

(1-6)

$$\underline{R}_i = \eta_i \underline{r}_i$$

in order to obtain the equation

(1-7)

$$G(\underline{\mathcal{R}}|\underline{\mathcal{R}}') = \left(\frac{1}{2\pi}\right)^{3N} \int \eta_1 d\underline{g}_1 \int \eta_2 d\underline{g}_2 \cdots \int \eta_N d\underline{g}_N \left[\frac{e^{i\underline{g}_1 \cdot (\underline{R}_1 - \underline{R}'_1)} e^{i\underline{g}_2 \cdot (\underline{R}_2 - \underline{R}'_2)} \cdots e^{i\underline{g}_N \cdot (\underline{R}_N - \underline{R}'_N)}}{\underline{g}_1^2 + \underline{g}_2^2 + \cdots + \underline{g}_N^2 - K^2} \right].$$

By employing a partial wave decomposition¹⁸ and integrating Eq. (1-6) over the $2N$ spherical polar angles $\vartheta_{g_1}, \dots, \vartheta_{g_N}, \varphi_{g_1}, \dots, \varphi_{g_N}$, the expression for $G(\underline{R}|\underline{R}')$ becomes

$$\begin{aligned}
 G(\underline{R}|\underline{R}') &= \left(\frac{2}{\pi}\right)^N \int_0^\infty \eta_1^3 g_1^2 d g_1 \int_0^\infty \eta_2^3 g_2^2 d g_2 \cdots \int_0^\infty \eta_N^3 g_N^2 d g_N \sum_{\ell_1=0}^\infty \sum_{\ell_2=0}^\infty \cdots \sum_{\ell_N=0}^\infty \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} \cdots \sum_{m_N=-\ell_N}^{\ell_N} \\
 &\times \left\{ \frac{j_{\ell_1}(g_1 R_1) j_{\ell_1}(g_1 R'_1) j_{\ell_2}(g_2 R_2) j_{\ell_2}(g_2 R'_2) \cdots j_{\ell_N}(g_N R_N) j_{\ell_N}(g_N R'_N)}{g_1^2 + g_2^2 + \cdots + g_N^2 - K^2} \right. \\
 &\quad \times \left. Y_{\ell_1}^{m_1}(\hat{R}_1) Y_{\ell_1}^{m_1*}(\hat{R}'_1) Y_{\ell_2}^{m_2}(\hat{R}_2) Y_{\ell_2}^{m_2*}(\hat{R}'_2) \cdots Y_{\ell_N}^{m_N}(\hat{R}_N) Y_{\ell_N}^{m_N*}(\hat{R}'_N) \right\}
 \end{aligned} \tag{1-8}$$

where the orthonormality condition

$$\prod_{i=1}^N \int_0^{2\pi} d\varphi_{g_i} \int_0^\pi d\vartheta_{g_i} \sin \vartheta_{g_i} Y_{\ell_i}^{m_i}(\hat{g}_i) Y_{\ell'_i}^{m'_i*}(\hat{g}_i) = \prod_{i=1}^N \delta_{\ell_i \ell'_i} \delta_{m_i m'_i} \tag{1-9}$$

has been employed in performing the integration.

The orbital angular momentum of the i th particle ($i=1,2,\dots,N$) is designated ℓ_i and the z -component is m_i ; so, the spherical Bessel functions written in the form $j_{\ell_i}(g_i R_i)$ represent "single particle functions". The ℓ_i th spherical Bessel function, $j_{\ell_i}(g_i R_i)$, is

defined in terms of the cylindrical Bessel function, $J_{\ell_i + \frac{1}{2}}(q_i R_i)$, by the equation

(1-10)

$$j_{\ell_i}(q_i R_i) = \left(\frac{\pi}{2 q_i R_i} \right)^{\frac{1}{2}} J_{\ell_i + \frac{1}{2}}(q_i R_i)$$

and the $Y_{\ell_i}^{m_i}(\hat{R}_i)$ ($m_i = -\ell_i, -\ell_i+1, \dots, \ell_i$) are ordinary spherical harmonics defined by Edmonds¹⁹.

After Eq. (1-8) is expressed in hyperspherical coordinates, the many particle representation of the Green function will be explicitly given by executing the remaining integrals, which are tedious but not difficult. The hyperspherical coordinates include $4N$ spherical polar angles $\theta_i, \theta'_i, \phi_i, \phi'_i$ and hyperspherical distances ρ and ρ' defined by

(1-11)

$$\rho^2 = \sum_{i=1}^N (r_i)^2$$

and

$$\rho'^2 = \sum_{i=1}^N (r'_i)^2 \quad (1-12)$$

where r_i is the i th radial spherical polar coordinate for the observer; primes denote source coordinates. In addition there are $2N-2$ hyperspherical angles α_j and α'_j ($j = 1, 2, \dots, N-1$) given by the relations

$$r_1 = \rho \cos \alpha_1 \quad (1-13)$$

$$r_2 = \rho \sin \alpha_1 \cos \alpha_2$$

$$\cdot \quad \cdot \quad \cdot$$

$$r_{N-1} = \rho \sin \alpha_1 \sin \alpha_2 \cdots \cos \alpha_{N-1}$$

$$r_N = \rho \sin \alpha_1 \sin \alpha_2 \cdots \sin \alpha_{N-1} \quad (0 \leq \alpha_j \leq \frac{\pi}{2})$$

and

$$r'_1 = \rho' \cos \alpha'_1 \quad (1-14)$$

$$r'_2 = \rho' \sin \alpha'_1 \cos \alpha'_2$$

$$\cdot \quad \cdot \quad \cdot$$

$$r'_{N-1} = \rho' \sin \alpha'_1 \sin \alpha'_2 \cdots \cos \alpha'_{N-1}$$

$$r'_N = \rho' \sin \alpha'_1 \sin \alpha'_2 \cdots \sin \alpha'_{N-1} \quad (0 \leq \alpha'_j \leq \frac{\pi}{2})$$

Hyperspherical coordinates of wave number space have radius, Q , given by

$$Q^2 = \sum_{i=1}^N (q_i)^2, \quad (1-15)$$

and the hyperspherical angles β_j ($j = 1, 2, \cdots, N-1$) are introduced by the relations

$$\begin{aligned}
 q_1 &= Q \cos \beta_1 \\
 q_2 &= Q \sin \beta_1 \cos \beta_2 \\
 &\cdot \quad \cdot \quad \cdot \\
 q_{N-1} &= Q \sin \beta_1 \sin \beta_2 \cdot \cdot \cdot \cos \beta_{N-1} \\
 q_N &= Q \sin \beta_1 \sin \beta_2 \cdot \cdot \cdot \sin \beta_{N-1} \quad (0 \leq \beta_j \leq \frac{\pi}{2}).
 \end{aligned} \tag{1-16}$$

The other $2N$ coordinates, ϑ_{g_i} and φ_{g_i} , are the spherical polar angles over which integration was carried out to obtain Eq. (1-8).

With this choice of coordinates, the products of spherical Bessel functions $\prod_{i=1}^N j_{\ell_i}(g_i R_i)$ and $\prod_{i=1}^N j_{\ell_i}(g_i R'_i)$ in Eq. (1-8) can be separately coupled, using the product expansion relation ²⁰

$$\begin{aligned}
 J_\nu(z \sin \Theta \sin \Phi) J_\mu(z \cos \Theta \cos \Phi) &= 2z^{-1} \sum_{\lambda=0}^{\infty} J_{\nu+\mu+2\lambda+1}(z) \\
 &\quad {}_2F_1(-\lambda, \nu+\mu+\lambda+1; \nu+1; \sin^2 \Theta) {}_2F_1(-\lambda, \nu+\mu+\lambda+1; \nu+1; \sin^2 \Phi) \\
 &\quad {}_2F_1(-\lambda, \nu+\mu+\lambda+1; \nu+1; \sin^2 \Theta) {}_2F_1(-\lambda, \nu+\mu+\lambda+1; \nu+1; \sin^2 \Phi) \\
 &\quad (-1)^\lambda (\nu+\mu+2\lambda+1) \left[\frac{\Gamma(\nu+\mu+\lambda+1) \Gamma(\nu+\lambda+1)}{\lambda! [\Gamma(\nu+1)]^2 \Gamma(\mu+\lambda+1)} \right].
 \end{aligned} \tag{1-17}$$

The orders ν, μ of the Bessel functions can assume any value except negative integers, and λ is zero or a positive integer. Thus, ${}_2F_1$ is the Jacobi polynomial of $\lambda+1$ terms, and Γ is the usual gamma function. Equation (1-8) may be represented in hyperspherical coordinates exclusively

after $2(N-1)$ coupling operations are performed; however, a definite pattern is followed to implement this transformation. By using Eq. (1-17), the functions $j_{\ell_N}(g_N R_N)$ and $j_{\ell_{N-1}}(g_{N-1} R_{N-1})$ are initially coupled to yield a two particle "cluster function" where the hyperspherical variable ρ is a parameter. Likewise the functions $j_{\ell_N}(g_N R'_N)$ and $j_{\ell_{N-1}}(g_{N-1} R'_{N-1})$ are coupled, producing the two particle "cluster function" with ρ' entering as a parameter, i.e.,

(1-18)

$$\begin{aligned}
 j_{\ell_N}(g_N R_N) j_{\ell_{N-1}}(g_{N-1} R_{N-1}) &= \left[\left(\frac{\pi}{2 g_N R_N} \right) \left(\frac{\pi}{2 g_{N-1} R_{N-1}} \right) \right]^{\frac{1}{2}} J_{\ell_N + \frac{1}{2}}(g_N R_N) J_{\ell_{N-1} + \frac{1}{2}}(g_{N-1} R_{N-1}) \\
 &= \frac{\pi}{2 \phi \rho} \left[\frac{1}{\sin \beta_1 \cdots \sin \beta_{N-2} \sin \alpha_1 \cdots \sin \alpha_{N-2}} \right] \sum_{\lambda_i=0}^{\infty} \left(\frac{1}{\phi \rho} \right) J_{\ell_N + \ell_{N-1} + 2\lambda_i + 2}(\phi \rho \sin \beta_1 \cdots \sin \beta_{N-2} \\
 &\quad \times \sin \alpha_1 \cdots \sin \alpha_{N-2}) \cos^{\ell_{N-1}} \alpha_{N-1} \sin^{\ell_N} \alpha_{N-1} F(-\lambda_i, \ell_N + \ell_{N-1} + \lambda_i + 2; \ell_N + \frac{3}{2}; \sin^2 \alpha_{N-1}) \\
 &\quad \times \cos^{\ell_{N-1}} \beta_{N-1} \sin^{\ell_N} \beta_{N-1} F(-\lambda_i, \ell_N + \ell_{N-1} + \lambda_i + 2; \ell_N + \frac{3}{2}; \sin^2 \beta_{N-1}) (-1)^{\lambda_i} \eta_i^{-2}
 \end{aligned}$$

and

(1-19)

$$\begin{aligned}
 j_{\ell_N}(g_N R'_N) j_{\ell_{N-1}}(g_{N-1} R'_{N-1}) &= \left[\left(\frac{\pi}{2 g_N R'_N} \right) \left(\frac{\pi}{2 g_{N-1} R'_{N-1}} \right) \right]^{\frac{1}{2}} J_{\ell_N + \frac{1}{2}}(g_N R'_N) J_{\ell_{N-1} + \frac{1}{2}}(g_{N-1} R'_{N-1}) \\
 &= \frac{\pi}{2 \phi \rho'} \left[\frac{1}{\sin \beta_1 \cdots \sin \beta_{N-2} \sin \alpha'_1 \cdots \sin \alpha'_{N-2}} \right] \sum_{\lambda'_i=0}^{\infty} \left(\frac{1}{\phi \rho'} \right) J_{\ell_N + \ell_{N-1} + 2\lambda'_i + 2}(\phi \rho' \sin \beta_1 \cdots \sin \beta_{N-2} \\
 &\quad \times \sin \alpha'_1 \cdots \sin \alpha'_{N-2}) \cos^{\ell_{N-1}} \alpha'_{N-1} \sin^{\ell_N} \alpha'_{N-1} F(-\lambda'_i, \ell_N + \ell_{N-1} + \lambda'_i + 2; \ell_N + \frac{3}{2}; \sin^2 \alpha'_{N-1}) \\
 &\quad \times \cos^{\ell_{N-1}} \beta_{N-1} \sin^{\ell_N} \beta_{N-1} F(-\lambda'_i, \ell_N + \ell_{N-1} + \lambda'_i + 2; \ell_N + \frac{3}{2}; \sin^2 \beta_{N-1}) (-1)^{\lambda'_i} (\eta'_i)^{-2}
 \end{aligned}$$

where

$$\eta_1^2 = \frac{\lambda_1! [\Gamma(\ell_N + \frac{3}{2})]^2 \Gamma(\ell_{N-1} + \lambda_1 + \frac{3}{2})}{2[\ell_N + \ell_{N-1} + 2\lambda_1 + 2] \Gamma(\ell_N + \ell_{N-1} + \lambda_1 + 2) \Gamma(\ell_N + \lambda_1 + \frac{3}{2})} \quad (1-20)$$

and

$$\eta_1'^2 = \frac{\lambda_1'! [\Gamma(\ell_N + \frac{3}{2})]^2 \Gamma(\ell_{N-1} + \lambda_1' + \frac{3}{2})}{2[\ell_N + \ell_{N-1} + 2\lambda_1' + 2] \Gamma(\ell_N + \ell_{N-1} + \lambda_1' + 2) \Gamma(\ell_N + \lambda_1' + \frac{3}{2})} \quad (1-21)$$

Thus the two particle "cluster functions" are shown in Eqs. (1-18) and (1-19).

The second step in transforming the integrand of Eq. (1-8) entails coupling the single particle functions, $j_{\ell_{N-2}}(q_{N-2} R_{N-2})$ and $j_{\ell_{N-2}}(q_{N-2} R'_{N-2})$ to the 2 particle "cluster functions" of Eqs. (1-18) and (1-19) respectively, using the product expansion relation of Eq. (1-17). To these expanded results, the functions $j_{\ell_{N-3}}(q_{N-3} R_{N-3})$ and $j_{\ell_{N-3}}(q_{N-3} R'_{N-3})$ are respectively coupled which completes the third transformation step. Finally, the N-particle "cluster function" is formed by coupling the remaining single particle function, j_{ℓ_1} , to the (N-1)-particle "cluster function".

However, the integral representation for the noninteracting N-particle Green function $G(\mathcal{R}|\mathcal{R}')$ can be generated from a generalized expression for the product expansion operation that will couple M particles (M=2,3,4,---, N) within a hypersphere of 3 M-dimensions and will thus yield an M-particle "cluster function". The (M-1)th product expansion operation is now considered where an M_a -particle function is coupled to

an M_b -particle product expansion, and it follows that $M=M_a+M_b$. (Note that M_a is equal to one in the present treatment.) Using this coupling prescription with the hyperspherical coordinates introduced, the $(M-1)$ th expansion operation couples the $(N-M+1)$ th particle expression to the $(M-2)$ th M_b -particle expression. By identifying the relations

(1-22)

$$\tilde{Q}\tilde{p}\cos\beta_{N-M+1}\cos\alpha_{N-M+1} = Qp\sin\beta_1\cdots\sin\beta_{N-M}\cos\beta_{N-M+1}\sin\alpha_1\cdots\sin\alpha_{N-M}\cos\alpha_{N-M+1},$$

(1-23)

$$\tilde{Q}\tilde{p}\sin\alpha_{N-M+1}\sin\beta_{N-M+1} = Qp\sin\beta_1\cdots\sin\beta_{N-M}\sin\beta_{N-M+1}\sin\alpha_1\cdots\sin\alpha_{N-M}\sin\alpha_{N-M+1},$$

and

(1-24)

$$\sigma = N-M+1,$$

then the $(M-1)$ th product expansion in the sequence of $(N-1)$ expansions may be expressed as

(1-25)

$$\left(\frac{\pi}{2\tilde{Q}\tilde{p}\cos\beta_\sigma\cos\alpha_\sigma}\right)^{\frac{M_a}{2}} J_{\ell_\sigma+\frac{1}{2}}(\tilde{Q}\tilde{p}\cos\beta_\sigma\cos\alpha_\sigma)$$

$$\times \left(\frac{\pi}{2}\right)^{\frac{M_b}{2}} \left(\frac{1}{\tilde{Q}\tilde{p}\sin\beta_\sigma\sin\alpha_\sigma}\right)^{\left(\frac{3M_b}{2}-1\right)} J_{\nu_{M-2}}(\tilde{Q}\tilde{p}\sin\beta_\sigma\sin\alpha_\sigma)$$

$$\begin{aligned}
&= \left(\frac{\pi}{2}\right)^{\frac{M}{2}} \sum_{\lambda_{M-1}} \left[\left(\frac{1}{\tilde{\varphi} \tilde{\rho}}\right)^{\left(\frac{3M}{2}-1\right)} J_{\nu_{M-1}}(\tilde{\varphi} \tilde{\rho}) \cos^{\lambda_{\sigma}} \alpha_{\sigma} \sin^{\left\{\nu_{M-2}-\left(\frac{3M_b}{2}-1\right)\right\}} \alpha_{\sigma} \right. \\
&\quad \times F(-\lambda_{M-1}, \nu_{M-1}-\lambda_{M-1}; \nu_{M-2}+1; \sin^2 \alpha_{\sigma}) \cos^{\lambda_{\sigma}} \beta_{\sigma} \sin^{\left\{\nu_{M-2}-\left(\frac{3M_b}{2}-1\right)\right\}} \beta_{\sigma} \\
&\quad \left. \times F(-\lambda_{M-1}, \nu_{M-1}-\lambda_{M-1}; \nu_{M-2}+1; \sin^2 \beta_{\sigma}) (-1)^{\lambda_{M-1}} (\eta_{M-1})^{-2} \right] \\
&= \left(\frac{\pi}{2}\right)^{\frac{M}{2}} \left(\frac{1}{\tilde{\varphi} \tilde{\rho}}\right)^{\left(\frac{3M}{2}-1\right)} \sum_{\lambda_{M-1}=0}^{\infty} \left\{ J_{\nu_{M-2}}(\tilde{\varphi} \tilde{\rho}) \cos^{\lambda_a(\sigma)} \alpha_{\sigma} \sin^{\lambda_b(M-2)} \alpha_{\sigma} \cos^{\lambda_a(\sigma)} \beta_{\sigma} \sin^{\lambda_b(M-2)} \beta_{\sigma} \right. \\
&\quad \left. \times F(-\lambda_{M-1}, \nu_{M-1}-\lambda_{M-1}; \nu_{M-2}+1; \sin^2 \alpha_{\sigma}) F(-\lambda_{M-1}, \nu_{M-1}-\lambda_{M-1}; \nu_{M-2}+1; \sin^2 \beta_{\sigma}) (-1)^{\lambda_{M-1}} \eta_{M-1}^{-2} \right\}
\end{aligned} \tag{1-25}$$

where

$$\eta_{M-1}^2 = \frac{(\lambda_{M-1})! [\Gamma(\nu_{M-2}+1)]^2 \Gamma(\lambda_{M-1} + \lambda_a(\sigma) + \frac{3M_a}{2})}{2(\nu_{M-1}) \Gamma(\nu_{M-1} - \lambda_{M-1}) \Gamma(\lambda_{M-1} + \lambda_b(M-2) + \frac{3M_b}{2})}.$$

(1-26)

The M-particle "cluster-functions" constructed in Eq. (1-25) by the (M-1) product expansion operation contains a cylindrical Bessel function order ν_{M-1} which is given by

$$\nu_{M-1} = \sum_{i=0}^{M-1} \ell_{N-i} + 2 \sum_{i=1}^{M-1} \lambda_i + \frac{3M}{2} - 1 \tag{1-27}$$

where the ℓ_{N-i} are individual particle orbital angular momentum

quantum numbers and the λ_i are defined in Eq. (1-17). The order of the cylindrical function belonging to the M_b -particle "cluster function" is obtained from the relation

$$\nu_{M-2} = \sum_{i=0}^{M-2} \ell_{N-i} + 2 \sum_{i=1}^{M-2} \lambda_i + \frac{3M_b}{2} - 1 \quad (1-28)$$

It is also apparent that the powers, $\lambda_a(\sigma)$, of the cosine functions produced by the $(M-1)$ th product expansion are numbers related to the number of particles M_a ; i.e., the $\lambda_a(\sigma)$ are quantum numbers given by

$$\lambda_a(\sigma) = \ell_{N-M+1} \quad (1-29)$$

Similarly the powers, $\lambda_b(M-2)$, of the sine functions are connected with the number of particles M_b included by the $(M-2)$ th product expansion. The relevant relation here is

$$\lambda_b(M-2) = \sum_{i=0}^{M-2} \ell_{N-i} + 2 \sum_{i=1}^{M-2} \lambda_i \quad (1-30)$$

It also may be seen that

$$\nu_{M-2} = \lambda_b(M-2) + \frac{3M_b}{2} - 1 \quad (1-31)$$

and

$$\nu_{M-1} = 2\lambda_{M-1} + \lambda_a(\sigma) + \lambda_b(M-2) + \frac{3M}{2} - 1 \quad (1-32)$$

Now hyperspherical coordinates and Eqs. (1-27) and (1-30) are used

in order to write the N-particle Green function integral of Eq. (1-8) as

$$G(Q|Q') = \prod_{i=1}^N (\eta_i) \left(\frac{1}{\rho \rho'} \right)^{\left(\frac{3N}{2} - 1 \right)} \int_0^\infty \frac{Q J_{\nu_{N-1}}(Q\rho) J_{\nu_{N-1}}(Q\rho') dQ}{Q^2 - K^2} \quad (1-33)$$

$$\times \int_0^{\pi/2} \sin^2 \beta_{N-1} \cos^2 \beta_{N-1} d\beta_{N-1} \int_0^{\pi/2} \sin^2 \beta_{N-2} \cos^2 \beta_{N-2} d\beta_{N-2} \cdots \int_0^{\pi/2} \sin^{3(N-1)-1} \beta_1 \cos^2 \beta_1 d\beta_1$$

$$\times \sum_{\ell_N} \sum_{\ell_{N-1}} \cdots \sum_{\ell_1} \sum_{m_N} \sum_{m_{N-1}} \cdots \sum_{m_1} \sum_{\lambda_1=0}^\infty \sum_{\lambda_2=0}^\infty \cdots \sum_{\lambda_{N-1}=0}^\infty \sum_{\lambda'_1=0}^\infty \sum_{\lambda'_2=0}^\infty \cdots \sum_{\lambda'_{N-1}=0}^\infty$$

$$\times \cos^{\ell_{N-1}} \alpha_{N-1} \sin^{\lambda_{N-1}(0)} \alpha_{N-1} F(-\lambda_1, \nu_1 - \lambda_1; \nu_0 + 1; \sin^2 \alpha_{N-1}) \cos^{\ell_{N-1}} \beta_{N-1} \sin^{\lambda_{N-1}(0)} \beta_{N-1} F(-\lambda_1, \nu_1 - \lambda_1; \nu_0 + 1; \sin^2 \beta_{N-1})$$

$$\times \cos^{\ell_{N-1}} \alpha'_{N-1} \sin^{\lambda_{N-1}(0)} \alpha'_{N-1} F(-\lambda'_1, \nu_1 - \lambda'_1; \nu_0 + 1; \sin^2 \alpha'_{N-1}) \cos^{\ell_{N-1}} \beta_{N-1} \sin^{\lambda_{N-1}(0)} \beta_{N-1} F(-\lambda'_1, \nu_1 - \lambda'_1; \nu_0 + 1; \sin^2 \beta_{N-1})$$

$$\times \cos^{\ell_{N-2}} \alpha_{N-2} \sin^{\lambda_{N-2}(1)} \alpha_{N-2} F(-\lambda_2, \nu_2 - \lambda_2; \nu_1 + 1; \sin^2 \alpha_{N-2}) \cos^{\ell_{N-2}} \beta_{N-2} \sin^{\lambda_{N-2}(1)} \beta_{N-2} F(-\lambda_2, \nu_2 - \lambda_2; \nu_1 + 1; \sin^2 \beta_{N-2})$$

$$\times \cos^{\ell_{N-2}} \alpha'_{N-2} \sin^{\lambda_{N-2}(1)} \alpha'_{N-2} F(-\lambda'_2, \nu_2 - \lambda'_2; \nu_1 + 1; \sin^2 \alpha'_{N-2}) \cos^{\ell_{N-2}} \beta_{N-2} \sin^{\lambda_{N-2}(1)} \beta_{N-2} F(-\lambda'_2, \nu_2 - \lambda'_2; \nu_1 + 1; \sin^2 \beta_{N-2})$$

$$\times (\eta_1)^{-2} (\eta'_1)^{-2} (\eta_2)^{-2} (\eta'_2)^{-2} (-1)^{\lambda_1 + \lambda'_1 + \lambda_2 + \lambda'_2} \cdots (\eta_{N-1})^{-2} (\eta'_{N-1})^{-2} (-1)^{\lambda_{N-1} + \lambda'_{N-1}}$$

$$\times \cos^{\ell_1} \alpha_1 \sin^{\lambda_1(N-2)} \alpha_1 F(-\lambda_{N-1}, \nu_{N-1} - \lambda_{N-1}; \nu_{N-2} + 1; \sin^2 \alpha_1) \cos^{\ell_1} \beta_1 \sin^{\lambda_1(N-2)} \beta_1 F(-\lambda_{N-1}, \nu_{N-1} - \lambda_{N-1}; \nu_{N-2} + 1; \sin^2 \beta_1)$$

$$\times \cos^{\ell_1} \alpha'_1 \sin^{\lambda_1(N-2)} \alpha'_1 F(-\lambda'_{N-1}, \nu_{N-1} - \lambda'_{N-1}; \nu_{N-2} + 1; \sin^2 \alpha'_1) \cos^{\ell_1} \beta_1 \sin^{\lambda_1(N-2)} \beta_1 F(-\lambda'_{N-1}, \nu_{N-1} - \lambda'_{N-1}; \nu_{N-2} + 1; \sin^2 \beta_1)$$

$$\times Y_{\ell_N}^{m_N}(\hat{R}_N) Y_{\ell_N}^{m_N^*}(\hat{R}'_N) Y_{\ell_{N-1}}^{m_{N-1}}(\hat{R}_{N-1}) Y_{\ell_{N-1}}^{m_{N-1}^*}(\hat{R}'_{N-1}) \cdots Y_{\ell_1}^{m_1}(\hat{R}_1) Y_{\ell_1}^{m_1^*}(\hat{R}'_1).$$

The orthogonality condition²¹

(1-34)

$$\begin{aligned} & \int_0^{\pi/2} \left\{ d\beta_\sigma (\sin \beta_\sigma)^{2\lambda_b(M-2)+3M_b-1} (\cos \beta_\sigma)^{2\lambda_a(\sigma)+3M_a-1} \right. \\ & \quad \times F(-\lambda_{M-1}, \nu_{M-1}-\lambda_{M-1}; \nu_{M-2}+1; \sin^2 \beta_\sigma) F(-\lambda'_{M-1}, \nu'_{M-1}-\lambda'_{M-1}; \nu'_{M-2}+1; \sin^2 \beta_\sigma) \Big\} \\ & = \left[\frac{(\lambda_{M-1})! [\Gamma(\nu_{M-2}+1)]^2 \Gamma(\lambda_{M-1} + \lambda_a(\sigma) + \frac{3M_a}{2})}{2 \nu_{M-1} \Gamma(\nu_{M-1}-\lambda_{M-1}) \Gamma(\lambda_{M-1} + \lambda_b(M-2) + \frac{3M_b}{2})} \right] \delta_{\lambda_{M-1}} \delta_{\lambda'_{M-1}} \end{aligned}$$

is utilized to perform the (N-1)-fold integration over the hyperspherical angles β_j ($j = 1, 2, \dots, N-1$) in Eq. (1-33), and the resulting expression is

(1-35)

$$\begin{aligned} G(\mathcal{Q}|\mathcal{Q}') &= \prod_{i=1}^N (\eta_i)^3 \left(\frac{1}{\rho \rho'} \right)^{\frac{(3N-1)}{2}} \sum_{\ell_N} \sum_{\ell_{N-1}} \cdots \sum_{\ell_1} \sum_{m_N} \sum_{m_{N-1}} \cdots \sum_{m_1} \sum_{\lambda_1} \sum_{\lambda_2} \cdots \sum_{\lambda_{N-1}} \\ & \times \int_0^\infty \frac{d\varphi \varphi J_{\nu_{N-1}}(\varphi \rho) J_{\nu'_{N-1}}(\varphi \rho')}{\varphi^2 - K^2} Y_{\ell_N}^{m_N}(\hat{R}_N) Y_{\ell_N}^{m_N^*}(\hat{R}'_N) Y_{\ell_{N-1}}^{m_{N-1}}(\hat{R}_{N-1}) Y_{\ell_{N-1}}^{m_{N-1}^*}(\hat{R}'_{N-1}) \cdots Y_{\ell_1}^{m_1}(\hat{R}_1) Y_{\ell_1}^{m_1^*}(\hat{R}'_1) \\ & \times \cos^{\ell_{N-1}} \alpha_{N-1} \sin^{\lambda_b(\alpha)} \alpha_{N-1} F(-\lambda_1, \nu_1-\lambda_1; \nu_0+1; \sin^2 \alpha_{N-1}) \cos^{\ell_{N-1}'} \alpha_{N-1}' \sin^{\lambda_b(\alpha')} \alpha_{N-1}' F(-\lambda_1', \nu_1'-\lambda_1'; \nu_0'+1; \sin^2 \alpha_{N-1}') \eta_1^{-2} \\ & \times \cos^{\ell_{N-2}} \alpha_{N-2} \sin^{\lambda_b(\alpha)} \alpha_{N-2} F(-\lambda_2, \nu_2-\lambda_2; \nu_1+1; \sin^2 \alpha_{N-2}) \cos^{\ell_{N-2}'} \alpha_{N-2}' \sin^{\lambda_b(\alpha')} \alpha_{N-2}' F(-\lambda_2', \nu_2'-\lambda_2'; \nu_1'+1; \sin^2 \alpha_{N-2}') \eta_2^{-2} \end{aligned}$$

$$\cos^{\lambda_1}_{\alpha_1} \sin^{\lambda_2(N-2)}_{\alpha_1} F(-\lambda_{N-1}, \nu_{N-1} - \lambda_{N-1}; \nu_{N-2} + 1; \sin^2 \alpha_1) \cos^{\lambda_1}_{\alpha_1'} \sin^{\lambda_2(N-2)}_{\alpha_1'} F(-\lambda_{N-1}, \nu_{N-1} - \lambda_{N-1}; \nu_{N-2} + 1; \sin^2 \alpha_1') n_{N-1}^{-2}.$$

The sums of Eq. (1-35) are finite for a fixed value of ν_{N-1} . Thus, only a finite number of terms are associated with any one hyper-radial Green function. The hyper-radial integral in Eq. (1-35) can be evaluated to yield¹²

$$\frac{\pi i}{2} J_{\nu_{N-1}}(k\rho_<) H_{\nu_{N-1}}^{(1)}(k\rho_>),$$

and the outgoing wave solution $G(\underline{Q} | \underline{Q}')$ of Eq. (1-2) is thus determined where $\rho_<, \rho_>$ are the lesser and greater respectively of ρ and ρ' . The cylindrical Hankel function of the first kind is designated $H^{(1)}$, and the η_j^{-2} ($j = 1, 2, \dots, N-1$) are obtained from Eq. (1-26).

This representation of the many-particle Green function appears to be useful in obtaining non Hartree-Fock wave functions and energy levels for many electron atoms¹⁵ as will be indicated in chapter II.

CHAPTER II

INTEGRAL EQUATION APPROACH TO BOUND STATE ATOMIC SYSTEMS.
PRELIMINARY STUDIES OF HELIUM AND HYDROGEN

A. INTRODUCTION

It is well known that bound state atomic systems are formally described by the appropriate Schrödinger equation. A study of Schrodinger's equation for a many electron atom reveals that extreme numerical difficulties are encountered due to the presence of non-separable terms in the many electron Hamiltonian. In fact, the exact eigenfunctions and eigenvalues of atomic systems containing two or more interacting electrons are not known²³. The atomic theory for many electron atoms has been therefore strongly dependent on the skillful use of approximate theories and solutions. In particular, a large number of the quantitative calculations of the states of many electron atoms have involved the Hartree-Fock approximation which employs wave functions constructed from a determinant of single electron wave functions. Hartree-Fock atomic wave functions allow for electron correlation due to the Pauli exclusion principle but do not completely account for the effects of electron-electron repulsion interactions in a many electron atom.

It is evident that for such an atomic system an alternative method for obtaining accurate numerical solutions of the Schrödinger

equation, including correlation effects, would be useful in understanding many electron bound states in atoms. One such approach may be based directly on the homogeneous integral solution technique of Sams and Kouri²⁴ which previously has been applied to the problem of determining vibrational wave functions and energy levels¹⁴. The formalism is employed here for helium, and the method of generalizing to other many electron atoms is indicated.

Different models for the He atom will be considered, and the first will use the symmetric center-of-mass coordinates shown in Fig. 1. The complete nonrelativistic Hamiltonian for this system may be written as

(2-1)

$$H = - \left(\frac{1}{\eta_1} \right)^2 \nabla_{\mathbf{r}_1}^2 - \left(\frac{1}{\eta_2} \right)^2 \nabla_{\mathbf{r}_2}^2 - \frac{2Z}{|\mathbf{r}_2 - \frac{1}{2}\mathbf{r}_1|} - \frac{2Z}{|\mathbf{r}_2 + \frac{1}{2}\mathbf{r}_1|} + \frac{2}{|\mathbf{r}_1|}$$

where atomic units are chosen to measure energy in rydbergs. The interelectronic vector is $\mathbf{r}_1$; $\mathbf{r}_2$ is the vector from the center of mass of the electrons to the Helium nucleus, and the value of Z is 2. The reduced mass, η_1^2 , for the electrons is

$$\eta_1^2 = \frac{m_e}{2} \quad (2-2)$$

and the reduced mass of the helium nucleus and the center of mass of the electrons is

$$\eta_2 = \frac{2 M_\alpha m_e}{2 m_e + M_\alpha} \quad (2-3)$$

where M_α and M_e are the alpha-particle and electron masses respectively

Since the present investigation deals with bound states for atomic systems, the energy E is negative, and the wave-number is given by

$$K = i\mathcal{H} \quad (\mathcal{H} > 0) \quad (2-4)$$

such that

$$E = -\mathcal{H}^2. \quad (2-5)$$

Hence, the Schrodinger equation for the He system is written as

(2-6)

$$\left[\left(\frac{1}{\eta_1} \right)^2 \nabla_{\underline{r}_1}^2 + \left(\frac{1}{\eta_2} \right)^2 \nabla_{\underline{r}_2}^2 + K^2 \right] \Psi(\underline{r}_1, \underline{r}_2) =$$

$$\left[\frac{4}{|\underline{r}_2 - \frac{1}{2} \underline{r}_1|} + \frac{4}{|\underline{r}_2 + \frac{1}{2} \underline{r}_1|} - \frac{2}{r_1} \right] \Psi(\underline{r}_1, \underline{r}_2),$$

and the solution $\Psi(r_1, r_2)$ can be written in the form

$$\Psi(r_1, r_2) = \quad (2-7)$$

$$\iint \left\{ G(r_1, r_2 | r'_1, r'_2) \left[\frac{4}{|r'_2 - \frac{1}{2} r'_1|} + \frac{4}{|r'_2 + \frac{1}{2} r'_1|} - \frac{2}{r'_1} \right] \right. \\ \left. \times \Psi(r'_1, r'_2) \right\} dr_1 dr_2$$

The function $G(r_1, r_2 | r'_1, r'_2)$ is a noninteracting Green function which satisfies the inhomogeneous differential equation

(2-8)

$$\left[\left(\frac{1}{\eta_1} \right)^2 \nabla_{r_1}^2 + \left(\frac{1}{\eta_2} \right)^2 \nabla_{r_2}^2 + K^2 \right] G(r_1, r_2 | r'_1, r'_2) = \\ -\delta(r_1 - r'_1) \delta(r_2 - r'_2)$$

where the right side of Eq. (2-8) is a product of a two 3-dimensional Dirac delta functions.

Integral equations have been used extensively^{25,26} to treat bound state systems. Weinberg²⁶ and Delves^{4,5} have considered in detail collisions of three or more particles. In the present chapter, Eq. (2-7) is expressed in terms of hyperspherical coordinates¹⁰ and several of the relations encountered herein have also been discussed

by Delves. Many of the studies of bound state systems have been devoted to nuclear problems and problems where the mass of one particle is infinite. The present treatment deals with atomic systems and enables the effects of finite nuclear mass to be studied.

The purpose of this paper is to present a numerical method of noniteratively solving Eq. (2-7) for the total wave function of the atomic system and the energy E of the corresponding atomic state. Thus, using He as an example atom, an approach for calculating bound state atomic wave functions and energy levels is presented which does not involve the Hartree-Fock approximation and which permits nuclear motion to be readily included.

In the next section, the Green function $G(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1', \mathbf{r}_2')$ defined in Eq. (2-8) is determined using the Fourier integral representation where the integrals are easily done using hyperspherical coordinates. Different model systems of He are constructed in Section C, and the interaction potentials for each are expressed in hyperspherical coordinates. Next (2-7) is written in terms of hyperspherical coordinates and transformed into a Volterra integral equation such that numerical integration can be performed noniteratively by use of the integral solution technique of Sams and Kouri²³. The coupled integral equation formalism is then developed in Section D. In order to get an idea of the accuracy of the integral equation method, H atom bound states have been studied. The calculated energy values for the ground and first three excited s-states are shown to be in

excellent agreement with the exact results. Next the numerical procedure is illustrated by treating different models of the He system with zero total angular momentum. This analysis is approximate and involves only a single radial integral eigenvalue equation so the calculated energy levels represent qualitative information concerning the model He systems. The models may then be classified into two groups: the fixed nucleus approximation and the He systems which allow nuclear motion. It is finally noted that calculations to yield excited state energies are no more difficult than ground state calculations. The method and its implications are discussed in terms of these example systems in the last section.

B. SYSTEMATIC DETERMINATION OF THE NONINTERACTING GREEN FUNCTION FOR TWO DISTINGUISHABLE PARTICLES

An explicit representation of the Green function is required for application of the integral solution procedure^{3,23}. Thus, the non-interacting Green function for two distinguishable particles is considered where a convenient form can be easily obtained from Eq. (2-8) by using a Fourier integral representation in hyperspherical coordinates¹⁰. These coordinates have been used by numerous other authors (see references 4-8 and 27-29, for example) to discuss the wave equation.

It is noted that this approach for obtaining the Green function is of greater generality than indicated by the present problem. That is, it is readily generalized to construct the noninteracting Green function for a system of $N(N=2,3,4\dots)$ distinguishable particles³⁰ such that the final representation may be used to calculate energy eigenvalues and eigenstates of many electron atoms. As a result, the integral equation formalism herein introduced allows a straightforward generalization to atoms with more than two electrons.

The two particle Green function given in Eq. (2-8) can be written as

(2-9)

$$G(r_1, r_2 | r'_1, r'_2) = \left(\frac{1}{2\pi}\right)^6 \int d\underline{u}_1 \int d\underline{u}_2 \left[\frac{e^{i\underline{u}_1 \cdot (r_1 - r'_1)}}{\left(\frac{u_1}{\eta_1}\right)^2} + \frac{e^{i\underline{u}_2 \cdot (r_2 - r'_2)}}{\left(\frac{u_2}{\eta_2}\right)^2 - K^2} \right],$$

using the relation

(2-10)

$$\left[\nabla_{\underline{r}_j}^2 + k_j^2 \right]^{-1} \delta(\underline{r}_j - \underline{r}'_j) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{u}_j \left[\frac{e^{i\underline{u}_j \cdot (\underline{r}_j - \underline{r}'_j)}}{u_j^2 - k_j^2} \right]$$

where j equals 1,2. By introducing into Eq. (2-9) the variables

$\underline{q}_1$ and $\underline{q}_2$ defined as

$$\underline{q}_1 = \frac{\underline{u}_1}{\eta_1}, \quad \underline{q}_2 = \frac{\underline{u}_2}{\eta_2} \quad (2-11)$$

and the variables $\underline{R}_1, \underline{R}'_1, \underline{R}_2$, and $\underline{R}'_2$ given by

(2-12)

$$\begin{aligned} \underline{R}_1 &= \eta_1 \underline{r}_1, & \underline{R}'_1 &= \eta_1 \underline{r}'_1 \\ \underline{R}_2 &= \eta_2 \underline{r}_2, & \underline{R}'_2 &= \eta_2 \underline{r}'_2, \end{aligned}$$

the function $G(\underline{r}_1, \underline{r}_2 | \underline{r}'_1, \underline{r}'_2)$ becomes

(2-13)

$$G(\underline{r}_1, \underline{r}_2 | \underline{r}'_1, \underline{r}'_2) = \left(\frac{1}{2\pi} \right)^6 \int \eta_1 d\underline{q}_1 \int \eta_2 d\underline{q}_2 \left[\frac{e^{i\underline{q}_1 \cdot (\underline{R}_1 - \underline{R}'_1)} e^{i\underline{q}_2 \cdot (\underline{R}_2 - \underline{R}'_2)}}{\underline{q}_1^2 + \underline{q}_2^2 - K^2} \right].$$

The Fourier integral representation of $G(\underline{r}_1, \underline{r}_2 | \underline{r}'_1, \underline{r}'_2)$ in Eq. (2-13) is the form required for the present approach of obtaining the Green function in hyperspherical coordinates. It is seen that Eq. (2-9) would be of this same form if the mass factors η_1^2 and η_2^2 were equal to one. In fact, normalized center-of-mass coordinates³¹ could have been employed in the original Hamiltonian to achieve this result; however, the change of variables which leads to Eq. (2-13) is adequate

for obtaining the relevant Green function and performing the subsequent calculations.

To begin the transformation to hyperspherical coordinates, regular spherical polar coordinates are employed in Eq. (1-13), and the multipole expansion¹⁸

$$\begin{aligned}
 & e^{i \underline{q}_j \cdot (\underline{R}_j - \underline{R}'_j)} \\
 &= (4\pi)^2 \sum_{l_j=0}^{\infty} \sum_{m_j=-l_j}^{l_j} \sum_{l'_j=0}^{\infty} \sum_{m'_j=-l'_j}^{l'_j} (i)^{l_j} (-i)^{l'_j} j_{l_j}(q_j R_j) j_{l'_j}(q_j R'_j) \\
 & \times Y_{l_j}^{m_j}(\hat{q}_j) Y_{l'_j}^{m'_j*}(\hat{q}_j) Y_{l_j}^{m_j}(\hat{R}_j) Y_{l'_j}^{m'_j*}(\hat{R}'_j)
 \end{aligned} \tag{2-14}$$

is used where the subscript j equals 1,2. It will be seen that spherical polar angles ϑ_j and φ_j also belong to the hyperspherical coordinate system of interest. Thus ordinary spherical polar coordinates of 6-dimensions are sufficient for performing a 4-fold integration of Eq. (2-13) over the angles ϑ_{q_j} and φ_{q_j} . The resulting expression is

$$\begin{aligned}
 G(\underline{r}_1, \underline{r}_2 | \underline{r}'_1, \underline{r}'_2) &= \left(\frac{2}{\pi}\right)^2 \int_0^\infty \eta_1^3 q_1^2 dq_1 \int_0^\infty \eta_2^3 q_2^2 dq_2 \sum_{l_1} \sum_{l_2} \sum_{m_1} \sum_{m_2} \\
 & \times \left(\frac{j_{l_1}(q_1 R_1) j_{l_1}(q_1 R'_1) j_{l_2}(q_2 R_2) j_{l_2}(q_2 R'_2)}{q_1^2 + q_2^2 - K^2} \right) Y_{l_1}^{m_1}(\hat{R}_1) Y_{l_1}^{m_1*}(\hat{R}'_1) \\
 & \times Y_{l_2}^{m_2}(\hat{R}_2) Y_{l_2}^{m_2*}(\hat{R}'_2)
 \end{aligned} \tag{2-15}$$

where the orthonormality condition

$$\frac{2}{\prod_{j=1}^2} \int_0^{2\pi} d\varphi_{q_j} \int_0^\pi \sin \vartheta_{q_j} d\vartheta_{q_j} Y_{\ell_j}^{m_j}(\hat{q}_j) Y_{\ell'_j}^{m'_j*}(\hat{q}_j) \quad (2-16)$$

$$= \frac{2}{\prod_{j=1}^2} \delta_{\ell_j \ell'_j} \delta_{m_j m'_j}$$

has been utilized.

The functions Y_{ℓ}^m are ordinary spherical harmonics as defined by Edmonds¹⁹. The index ℓ_j is the orbital angular momentum quantum number of the j th particle ($j=1,2$), whereas m_j is the z component angular momentum quantum number of ℓ_j . The $j_{\ell}(qR)$ are spherical Bessel functions, and the ℓ_j th spherical Bessel function is defined in terms of the cylindrical Bessel function $J_{\ell_j+\frac{1}{2}}(q_j R_j)$ by the equation

(2-17)

$$j_{\ell_j}(q_j R_j) = \left[\frac{\pi}{2 q_j R_j} \right]^{\frac{1}{2}} J_{\ell_j+\frac{1}{2}}(q_j R_j)$$

The hyperspherical coordinates of wave number space include the regular spherical polar angles ϑ_{q_1} , ϑ_{q_2} , φ_{q_1} , and φ_{q_2} over which integration was performed in obtaining Eq. (2-16). In addition, a hyperspherical radius Q is defined by

$$Q^2 = q_1^2 + q_2^2 \quad (2-18)$$

and a hyperspherical angle β is given by the relations

$$\begin{aligned} q_1 &= Q \cos \beta, \\ q_2 &= Q \sin \beta \quad (0 \leq \beta \leq \frac{\pi}{2}) \end{aligned} \quad (2-19)$$

The volume element of the spherical polar coordinates is related to the 6 dimensional hyperspherical coordinate volume element by

$$(2-20)$$

$$\begin{aligned} &(\eta_1 \eta_2)^3 q_1^2 dq_1 q_2^2 dq_2 \sin \nu_{q_1} \sin \nu_{q_2} d\nu_{q_1} d\nu_{q_2} d\varphi_1 d\varphi_2 \\ &= (\eta_1 \eta_2)^3 Q^5 dQ \sin^2 \beta \cos^2 \beta d\beta \sin \nu_{q_1} \sin \nu_{q_2} d\nu_{q_1} d\nu_{q_2} d\varphi_1 d\varphi_2 \end{aligned}$$

Hyperspherical variables of coordinate space are analogously defined with the hyperspherical distances ρ and ρ' being

$$(2-21)$$

$$\rho^2 = R_1^2 + R_2^2, \quad \rho'^2 = R_1'^2 + R_2'^2.$$

Hyperspherical angles α and α' are introduced by

$$\begin{aligned} R_1 &= \rho \cos \alpha, \quad R_2 = \rho \sin \alpha \quad (0 \leq \alpha \leq \frac{\pi}{2}) \\ R_1' &= \rho' \cos \alpha', \quad R_2' = \rho' \sin \alpha' \quad (0 \leq \alpha' \leq \frac{\pi}{2}) \end{aligned} \quad (2-22)$$

The remaining hyperspherical coordinates are the ordinary spherical polar angles ψ_j , ψ'_j , φ_j , and φ'_j ($j=1,2$).

It is seen from Eqs. (2-22) that the distances r_1 , r_1' , and r_2' can be expressed in terms of hyperspherical coordinates as

$$r_1 = \eta_1^{-1} \rho \cos \alpha, \quad r_2 = \eta_2^{-1} \rho \sin \alpha \quad (2-23)$$

$$r_1' = \eta_1^{-1} \rho' \cos \alpha', \quad r_2' = \eta_2^{-1} \rho' \sin \alpha',$$

and the volume element relation is then

$$\begin{aligned} & r_1^2 r_2^2 dr_1 dr_2 \sin \psi_1 \sin \psi_2 d\psi_1 d\psi_2 d\varphi_1 d\varphi_2 \\ &= (\eta_1 \eta_2)^{-3} \rho^5 d\rho \sin^2 \alpha \cos^2 \alpha d\alpha \sin \psi_1 \sin \psi_2 d\psi_1 d\psi_2 d\varphi_1 d\varphi_2 \end{aligned} \quad (2-24)$$

Equation (2-15) can now be written in terms of hyperspherical coordinates when the expression given in Eq. (2-17) is substituted for the spherical Bessel functions. By using the product expansion²⁰ relation

$$\begin{aligned}
& \bar{J}_\nu (z \sin \theta \cos \phi) \bar{J}_\mu (z \cos \theta \cos \phi) \\
&= \sum_{k=0}^{\infty} z^{-1} \bar{J}_{\nu+\mu+2k+1}(z) \cos^\mu \theta \sin^\nu \theta {}_2F_1(-k, \nu+\mu+k+1; \nu+1; \sin^2 \theta) \\
&\quad \times \cos^\mu \phi \sin^\nu \phi {}_2F_1(-k, \nu+\mu+k+1; \nu+1; \sin^2 \phi) (-1)^k 2^{\nu+\mu+2k+1} \\
&\quad \times \left[\frac{\Gamma(\nu+\mu+1) \Gamma(\nu+k+1)}{k! [\Gamma(\nu+1)]^2 \Gamma(\mu+k+1)} \right];
\end{aligned}$$

the Green function integral in term of hyperspherical coordinates becomes

(2-26)

$$\begin{aligned}
G(\xi|\xi') &= (\eta_1 \eta_2)^3 \left(\frac{1}{\rho \rho'} \right)^2 \\
&\times \sum_{\ell_1=0}^{\infty} \sum_{\ell_2=0}^{\infty} \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} \sum_{k=0}^{\infty} \sum_{k'=0}^{\infty} Y_{\ell_1}^{m_1}(\hat{R}_1) Y_{\ell_1}^{m_1}(\hat{R}_1') Y_{\ell_2}^{m_2}(\hat{R}_2) Y_{\ell_2}^{m_2}(\hat{R}_2') \\
&\times \int_0^\infty \left(\frac{Q \sqrt{\ell_1+\ell_2+2k+2} (QP) \sqrt{\ell_1+\ell_2+2k'+2} (Q\rho')}{Q^2 - K^2} \right) dQ \\
&\times \int_0^{\pi/2} \left[\sin^{2(\ell_2+1)} \beta \cos^{2(\ell_1+1)} \beta {}_2F_1(-k_1, \ell_1+\ell_2+k_1+2; \ell_2+\frac{3}{2}; \sin^2 \beta) \right.
\end{aligned}$$

$$\times {}_2F_1(-\lambda'_1, \ell_1 + \ell_2 + \lambda'_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \beta) d\beta \left(\frac{(-1)^{\lambda'_1}}{\eta_1^2} \right) \left(\frac{(-1)^{\lambda'_2}}{\eta_1'^2} \right)$$

$$\times \cos^{\ell_1} \alpha \sin^{\ell_2} \alpha {}_2F_1(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \alpha)$$

$$\times \cos^{\ell_1} \alpha' \sin^{\ell_2} \alpha' {}_2F_1(-\lambda'_1, \ell_1 + \ell_2 + \lambda'_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \alpha')$$

In Eq. (2-25) the orders ν and μ can not be negative integers, and

λ is zero or a positive integer. The functions ${}_2F_1$ are Jacobi polynomials of $\lambda+1$ terms, and Γ is the usual gamma function.

The orthogonality properties of Jacobi polynomials²¹ are used in evaluating the integral over the hyperspherical angle β in Eq. (2-26), i.e.,

$$\int_0^{\pi/2} \sin^{2\ell_2+2} \beta \cos^{2\ell_1+2} \beta F(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \beta) \times F(-\lambda'_1, \ell_1 + \ell_2 + \lambda'_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \beta) d\beta = \delta_{\lambda_1 \lambda'_1} \eta_1^2 \quad (2-27)$$

where

$$\eta_1^2 = \frac{\lambda_1! [\Gamma(\ell_2 + \frac{3}{2})]^2 \Gamma(\ell_1 + \lambda_1 + \frac{3}{2})}{2[\ell_1 + \ell_2 + 2\lambda_1 + 2] \Gamma(\ell_1 + \ell_2 + \lambda_1 + 2) \Gamma(\ell_2 + \lambda_1 + \frac{3}{2})} \quad (2-28)$$

The integral over the hyper-radius Q can be evaluated for outgoing wave boundary conditions to yield²²

$$\frac{\pi i}{2} J_{\ell_1 + \ell_2 + 2\lambda_1 + 2}(k\rho_<) H_{\ell_1 + \ell_2 + 2\lambda_1 + 2}^{(1)}(k\rho_>)$$

where $H^{(1)}$ is the cylindrical Hankel function of the first kind and

$\rho_<, \rho_>$ are the lesser and greater, respectively of ρ and ρ' .

Thus the Green function $G(\xi|\xi')$ is given explicitly in hyperspherical coordinates as

$$G(\xi|\xi') \quad (2-29)$$

$$= \left(\frac{i\pi}{2}\right)(\rho\rho')^{-2}(\eta_1\eta_2)^3 \sum_{\mathcal{J}} \sum_{\ell_1} \sum_{\ell_2} \sum_{\lambda_1} \sum_M J_{\ell_1 + \ell_2 + 2\lambda_1 + 2}(k\rho_<)$$

$$\times H_{\ell_1 + \ell_2 + 2\lambda_1 + 2}^{(1)}(k\rho_>) \cos^{\ell_1} \alpha \sin^{\ell_2} \alpha \mathcal{F}(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \alpha)$$

$$\times \cos^{\ell_1} \alpha' \sin^{\ell_2} \alpha' \mathcal{F}(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{3}{2}; \sin^2 \alpha') Y_{\mathcal{J}, \ell_1, \ell_2}^M(\hat{R}, \hat{R}_2) Y_{\mathcal{J}, \ell_1, \ell_2}^M(\hat{R}', \hat{R}_2')$$

where ξ represents the coordinates $\rho, \alpha, \nu_1, \nu_2, \varphi_1, \varphi_2$ and the normalized Jacobi polynomial $\mathcal{P}$ is defined by the equation

(2-30)

$$\begin{aligned} & \mathcal{P}(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{1}{2}, \sin^2 \alpha) \\ &= \eta_1^{-1} F(-\lambda_1, \ell_1 + \ell_2 + \lambda_1 + 2; \ell_2 + \frac{1}{2}, \sin^2 \alpha) \end{aligned}$$

The function $y_{\ell_1 \ell_2}(\hat{R}_1, \hat{R}_2)$ is a sum of products of spherical harmonics obtained with aid of the vector addition coefficients, and the triangular inequality

(2-31)

$$|\ell_2 - \ell_1| \leq \ell \leq \ell_1 + \ell_2$$

and the condition

(2-32)

$$M = m_1 + m_2$$

on the magnetic quantum number M must be satisfied.

C. MODELS FOR THE He ATOM

The interaction terms of the He atom Hamiltonian given by Eq. (2-1) must now be expressed in hyperspherical coordinates. By

substituting the appropriate hyperspherical coordinates of Eq. (2-23) into the interaction potential of Eq. (2-1), the Hamiltonian H_I may be written as

$$H_I = -\left(\frac{1}{\eta_1}\right)^2 \nabla_{\mathbf{r}_1}^2 - \left(\frac{1}{\eta_2}\right)^2 \nabla_{\mathbf{r}_2}^2 - \frac{8}{\rho} \quad (2-33)$$

$$\times \sum_{\ell=0}^{\infty} \chi_{2\ell}(\alpha) P_{2\ell}(\cos \nu_{12}) + \frac{2\eta_1}{\rho \cos \alpha}$$

where the multipole expansions of the attractive terms are given by

$$\frac{4}{|\mathbf{r}_2 \pm \frac{1}{2}\mathbf{r}_1|} = \frac{4}{\rho} \sum_{\ell=0}^{\infty} (\mp 1)^\ell \chi_\ell(\alpha) P_\ell(\cos \nu_{12}) \quad (2-34)$$

and

$$\chi_{2\ell}(\alpha) = \begin{cases} 2\eta_1 \left[\frac{2\eta_1}{\eta_2} \tan \alpha \right]^{2\ell} \sec \alpha & (0 \leq \alpha \leq \omega) \\ \eta_2 \left[\frac{\eta_2}{2\eta_1} \cot \alpha \right]^{2\ell} \csc \alpha & (\omega \leq \alpha \leq \frac{\pi}{2}) \end{cases} \quad (2-35)$$

$$\omega = \tan^{-1} \left(\frac{\eta_2}{2\eta_1} \right), \quad (2-36)$$

and $\tilde{\nu}_{12}$ is the angle between the vectors r_1, r_2 .

To examine the present approach as applied to the He atom, two other He systems will be considered. Thus, energy calculations of the moving nucleus He, model I, will be compared with results calculated using Model II, the infinitely massive nucleus model and Model III, the fixed nucleus model.

The second model is constructed as a limiting case of the first by allowing $M_\alpha \rightarrow \infty$ in Eq. (2-33). The significant change is that

(2-37)

$$\text{Limit}_{M_\alpha \rightarrow \infty} \eta_2^2 = \eta_3^2 = 2m_e.$$

The Hamiltonian, H_{II} , for this system is then constructed by replacing η_2^2 in Eq. (2-33) with η_3^2 , i.e.,

(2-38)

$$H_{II} = -\left(\frac{1}{\eta_1}\right)^2 \nabla_{\underline{r}_1}^2 - \left(\frac{1}{\eta_3}\right)^2 \nabla_{\underline{r}_2}^2 - \frac{8}{\rho} \\ \times \sum_{l=0}^{\infty} \tilde{\chi}_{2l}(\alpha) P_{2l}(\cos \tilde{\nu}_{12}) + \frac{2\eta_1}{\rho \cos \alpha}$$

$$\tilde{\chi}_{2l}(\alpha) = \begin{cases} 2\eta_1 \left[\frac{2\eta_1}{\eta_3} \tan \alpha \right]^{2l} \sec \alpha & (0 \leq \alpha \leq \tilde{\omega}) \\ \eta_3 \left[\frac{\eta_3}{2\eta_1} \cot \alpha \right]^{2l} \csc \alpha & (\omega \leq \alpha \leq \frac{\pi}{2}), \end{cases} \quad (2-39)$$

(2-40)

$$\tilde{\omega} = \tan^{-1} \left(\frac{\eta_3}{2\eta_1} \right),$$

and $\tilde{\varphi}_{12}$ is the angle between the vectors $\underline{r}_1$, $\underline{r}_2$. The distance r_2 for this system is

(2-41)

$$r_2 = \eta_3^{-1} \rho \sin \alpha$$

The calculated energy differences for the systems given by Eqs. (2-33) and (2-38) of course indicate the manner in which nuclear motion affects the total energy of a He system.

In addition, the fixed nucleus approximation will be considered, and the initial Hamiltonian is given by

(2-42)

$$H = -\frac{1}{m_e} \nabla_{\underline{r}_1}^2 - \frac{1}{m_e} \nabla_{\underline{r}_2}^2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{2}{|\underline{r}_1 - \underline{r}_2|}$$

where the vectors $\underline{r}_1$, $\underline{r}_2$ locate the electrons relative to the nucleus and the electron mass m_e equals one. Thus the relations

$$r_1 = \rho \cos \alpha , \quad (2-43)$$

$$r_2 = \rho \sin \alpha$$

define the hyperspherical coordinates, and the Hamiltonian H_{III} is written as

(2-44)

$$H_{III} = -\nabla_{r_1}^2 - \nabla_{r_2}^2 - \frac{4}{\rho \cos \alpha} - \frac{4}{\rho \sin \alpha} \\ + \frac{2}{\rho} \sum_{\ell=0}^{\infty} \Omega_{\ell}(\alpha) P_{\ell}(\cos \theta_{12}).$$

Here the electron-electron interaction is expressed by the multipole expansion

(2-45)

$$\frac{2}{|r_1 - r_2|} = \frac{2}{\rho} \sum_{\ell=0}^{\infty} \Omega_{\ell}(\alpha) P_{\ell}(\cos \theta_{12})$$

where

$$\Omega_{\ell}(\alpha) = \begin{cases} \tan^{\ell} \alpha \sec \alpha & (0 \leq \alpha \leq \frac{\pi}{4}) \\ \cot^{\ell} \alpha \csc \alpha & (\frac{\pi}{4} \leq \alpha \leq \frac{\pi}{2}) \end{cases} \quad (2-46)$$

and Θ_{12} is the angle between the vectors $\underline{r}_1$, $\underline{r}_2$. The calculations performed for these three systems are presented in Sec. E.

D. COUPLED INTEGRAL EQUATIONS FOR He

The coupled integral equations are developed for the He system taking into account the motion of all particles. By substituting into Eq. (2-7) the Green function $G(\xi|\xi')$ given by Eq. (2-29) and the interaction potential expressed in Eq. (2-33), the bound state He system is formally described by the integral form of the Schrödinger equation

$$\begin{aligned}
 \Psi_I(\chi|\xi) &= \frac{i\pi}{2\rho^2} \int_0^\infty \rho'^3 d\rho' \int_0^{\pi/2} \sin^2\alpha' \cos^2\alpha' d\alpha' \\
 &\times \int_0^{2\pi} d\varphi'_1 \int_0^{2\pi} d\varphi'_2 \int_0^\pi \sin\varphi'_1 d\varphi'_1 \int_0^\pi \sin\varphi'_2 d\varphi'_2 \\
 &\times \sum_j \sum_{l_1} \sum_{l_2} \sum_{\lambda_1} \sum_M J_{l_1+l_2+2\lambda_1+2} (i\mathcal{H}\rho_2) H_{l_1+l_2+2\lambda_1+2}^{(1)} (i\mathcal{H}\rho) \\
 &\times Y_{j l_1 l_2}^M(\hat{r}_1 \hat{r}_2) Y_{j l_1 l_2}^{M*}(\hat{r}'_1 \hat{r}'_2) \cos^{l_1}\alpha \sin^{l_2}\alpha \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2\alpha) \\
 &\times \cos^{l_1}\alpha' \sin^{l_2}\alpha' \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2\alpha') \\
 &\times \left[\frac{8}{\rho'} \sum_{\ell=0}^{\infty} \chi_{2\ell}(\alpha') P_{2\ell}(\cos\varphi_{12}) - \frac{2\eta_1}{\rho' \cos\alpha'} \right] \Psi(\chi|\xi')
 \end{aligned} \tag{2-47}$$

We note that the mass factor $(\gamma_1, \gamma_2)^3$ in the Green function was canceled by the inverse factor $(\gamma_1, \gamma_2)^{-3}$ generated by the volume element given in Eq. (2-24).

It follows from Eq. (2-27) that the Jacobi polynomials satisfy the orthonormality condition

$$\int_0^{\pi/2} \sin^{2l_2+2} \alpha \cos^{2l_1+2} \alpha \mathcal{F}(-\lambda', l_1+l_2+\lambda'+2; l_2+\frac{3}{2}; \sin^2 \alpha) \times \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2 \alpha) d\alpha = \delta_{\lambda_1' \lambda_1}, \quad (2-48)$$

whereas the functions $y_{l_1, l_2}^M(\hat{r}_1, \hat{r}_2)$ satisfy

$$(2-49)$$

$$\int d\hat{r}_1 d\hat{r}_2 y_{l_1, l_2}^M(\hat{r}_1, \hat{r}_2) y_{l_1', l_2'}^{M'}(\hat{r}_1, \hat{r}_2) = \delta_{ll'} \delta_{l_1 l_1'} \delta_{l_2 l_2'} \delta_{MM'}$$

The wave function $\Psi(\chi|\xi)$ in Eq. (2-47) can therefore be expanded in terms of these orthogonal functions as

$$\Psi(\chi|\xi) = \sum_{\mathcal{J}} \sum_{l_1} \sum_{l_2} \sum_{\lambda_1} \sum_M \cos^{l_1} \alpha \sin^{l_2} \alpha \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2 \alpha) \times y_{l_1, l_2}^M(\hat{r}_1, \hat{r}_2) \Psi(\chi|\mathcal{J}, l_1, l_2, \lambda_1, M|\rho) \quad (2-50)$$

to yield the set of coupled integral equations

$$\begin{aligned}
 \Psi(K|l_1, l_2, \lambda, M|\rho) &= \frac{i\pi}{2} \int_0^\infty \rho'^2 d\rho' \int_0^{\pi/2} \sin^2 \alpha' \cos \alpha' d\alpha' \quad (2-51) \\
 &\times \int_0^{2\pi} d\varphi'_1 \int_0^{2\pi} d\varphi'_2 \int_0^\pi \sin \varphi'_1 d\varphi'_1 \int_0^\pi \sin \varphi'_2 d\varphi'_2 \\
 &\times J_{l_1+l_2+2\lambda+2}(i\mathcal{H}(\rho)) H_{l_1+l_2+2\lambda+2}^{(0)}(i\mathcal{H}(\rho)) Y_{l_1 l_2}^M(\hat{r}_1 \hat{r}_2) \\
 &\times \cos^{l_1} \alpha' \sin^{l_2} \alpha' \mathcal{F}(-\lambda, l_1+l_2+\lambda+2; l_2+\frac{3}{2}; \sin^2 \alpha') \\
 &\times \left[4 \sum_{\ell=0}^{\infty} \chi_{2\ell}(\alpha') P_{2\ell}(\cos \varphi'_{12}) - \frac{\eta_1}{\cos \alpha'} \right] \\
 &\times \sum_{\ell'} \sum_{\ell'_1} \sum_{\ell'_2} \sum_{\lambda'} \sum_{M'} Y_{\ell' \ell'_1 \ell'_2}^{M'}(\hat{r}_1 \hat{r}_2) \cos^{l'_1} \alpha' \sin^{l'_2} \alpha' \\
 &\times \mathcal{F}(-\lambda', \ell'_1+\ell'_2+\lambda'+2; \ell'_2+\frac{3}{2}; \sin^2 \alpha') \\
 &\times 2\Psi(K|l'_1, l'_2, \lambda', M'|\rho).
 \end{aligned}$$

A more convenient form of Eq. (2-51) is obtained by factoring the terms independent of ρ . Thus C and D are defined as

$$\begin{aligned}
 C(l_1, l_2, \lambda, M|l'_1, l'_2, \lambda', M') & \quad (2-52) \\
 &= -\pi \eta_1 \delta_{l'_1 l_1} \delta_{l'_2 l_2} \delta_{\lambda' \lambda} \delta_{M' M}
 \end{aligned}$$

$$\times \int_0^{\pi/2} d\alpha' \sin^{2l_2+2} \alpha' \cos^{2l_1+1} \alpha'$$

$$\times \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2 \alpha')$$

$$\times \mathcal{F}(-\lambda'_1, l'_1+l'_2+\lambda'_1+2; l'_2+\frac{3}{2}; \sin^2 \alpha')$$

and

(2-53)

$$D_2(l_1, l_2, \lambda_1, M | l'_1, l'_2, \lambda'_1, M') = 4\pi f_{2\ell}(l_1, l_2 | l'_1, l'_2 | f) \\ \times \int_0^{\pi/2} d\alpha' \sin^{l_2+l'_2+2} \alpha' \cos^{l_1+l'_1+2} \alpha' \chi_{2\ell}(\alpha')$$

$$\times \mathcal{F}(-\lambda_1, l_1+l_2+\lambda_1+2; l_2+\frac{3}{2}; \sin^2 \alpha)$$

$$\times \mathcal{F}(-\lambda'_1, l'_1+l'_2+\lambda'_1+2; l'_2+\frac{3}{2}; \sin^2 \alpha').$$

where $\chi_{2\ell}(\alpha)$ is defined in Eq. (2-35). The functions

$$f_{2\ell}(l_1, l_2 | l'_1, l'_2 | f) \text{ are given by }^{32}$$

(2-54)

$$f_{2\ell}(l_1, l_2 | l'_1, l'_2 | f) = \int d\hat{r}_1 d\hat{r}_2 Y_{f, l_1, l_2}^{M*}(\hat{r}_1, \hat{r}_2)$$

$$\times P_{2\ell}(\cos \vartheta_{12}) Y_{f, l_1, l_2}^{M'}(\hat{r}_1, \hat{r}_2).$$

In terms of these constants, Eq. (2-51) becomes

$$\Psi(\mathcal{H}|f, l_2, t, M|P) = \frac{i}{\rho^2} \int_0^\infty \rho'^2 d\rho' \quad (2-55)$$

$$\begin{aligned} & \times J_{l_1+l_2+2t_1+2}(i\mathcal{H}\rho_<) H_{l_1+l_2+2t_1+2}^{(1)}(i\mathcal{H}\rho_>) \sum_{j'} \sum_{l'_1} \sum_{l'_2} \sum_{t'_1} \sum_{M'} \\ & \times \left\{ \sum_{\ell=c}^{\infty} D_\ell(f, l_2, t, M|f', l'_1, l'_2, t'_1, M') + C(f, l_2, t, M|f', l'_1, l'_2, t'_1, M') \right\} \\ & \times \Psi(\mathcal{H}|f', l'_1, l'_2, t'_1, M'|P'). \end{aligned}$$

It is convenient to define a function $U(\mathcal{H}|f, l_2, t, M|P)$ by the equation

$$U(\mathcal{H}|f, l_2, t, M|P) = \rho^2 \Psi(\mathcal{H}|f, l_2, t, M|P) \quad (2-56)$$

and write Eq. (2-55) in the form

$$\begin{aligned} U(\mathcal{H}|f, l_2, t, M|P) &= i \int_0^\infty d\rho' J_{l_1+l_2+2t_1+2}(i\mathcal{H}\rho_<) \quad (2-57) \\ & \times H_{l_1+l_2+2t_1+2}^{(1)}(i\mathcal{H}\rho_>) \sum_{j'} \sum_{l'_1} \sum_{l'_2} \sum_{t'_1} \sum_{M'} \left[\sum_{\ell=c}^{\infty} C_\ell(f, l_2, t, M|f', l'_1, l'_2, t'_1, M') \right] \\ & \times U(\mathcal{H}|f', l'_1, l'_2, t'_1, M'|P') \end{aligned}$$

where the definition of $C_2(j, l, l_2, k, M | j', l', l'_2, k', M')$ is obvious from a comparison of Eqs. (2-57) and (2-55). By letting the single index σ represent the five indices, j, l, l_2, k, M , and removing the variables $\rho_<$ and $\rho_>$, Eq. (2-57) can be written as

$$\begin{aligned}
 U(\chi | \sigma | \rho) &= i H_{l, l_2 + 2k_1 + 2}^{(1)}(i\chi\rho) \int_0^\rho d\rho' \\
 &\times J_{l, l_2 + 2k_1 + 2}(i\chi\rho') \sum_{\sigma'} \sum_{\ell=0}^{\infty} C_\ell(\sigma | \sigma') U(\chi | \sigma' | \rho') \\
 &+ i J_{l, l_2 + 2k_1 + 2}(i\chi\rho) \left\{ A(\sigma) - \int_0^\rho d\rho' H_{l, l_2 + 2k_1 + 2}^{(1)}(i\chi\rho') \right. \\
 &\times \sum_{\sigma'} \sum_{\ell=0}^{\infty} C_\ell(\sigma | \sigma') U(\chi | \sigma' | \rho') \left. \right\}
 \end{aligned} \tag{2-58}$$

where

$$\begin{aligned}
 A(\sigma) &= \int_0^\rho d\rho' H_{l, l_2 + 2k_1 + 2}^{(1)}(i\chi\rho') \sum_{\sigma'} \sum_{\ell=0}^{\infty} C_\ell(\sigma | \sigma') U(\chi | \sigma' | \rho')
 \end{aligned} \tag{2-59}$$

The solution form of Eq. (2-58) is written as

$$U(\chi | \sigma | \rho) = \sum_{\sigma'} \mathcal{W}(\chi | \sigma; \sigma' | \rho) A(\sigma) \tag{2-60}$$

so that the matrix representation of the above is

$$\underline{\underline{U}}(\rho) = \underline{\underline{W}}(\rho) \cdot \underline{\underline{A}}. \quad (2-61)$$

The matrix $\underline{\underline{A}}$ satisfies the eigenvalue equation

$$\int_0^\infty H''(\rho') \cdot \left\{ \sum_{\ell=0}^{\infty} \underline{\underline{C}}_{\ell} \right\} \cdot \underline{\underline{W}}(\rho') \cdot \underline{\underline{A}} d\rho' = \epsilon \underline{\underline{A}}, \quad (2-62)$$

and the matrix function $\underline{\underline{W}}(\rho)$ satisfies the Volterra integral equation given by

$$\begin{aligned} \underline{\underline{W}}(\rho) = & i \underline{\underline{H}}''(\rho) \cdot \int_0^\rho \underline{\underline{J}}(\rho') \cdot \left\{ \sum_{\ell=0}^{\infty} \underline{\underline{C}}_{\ell} \right\} \cdot \underline{\underline{W}}(\rho') d\rho' \\ & - i \underline{\underline{J}}(\rho) \cdot \int_0^\rho \underline{\underline{H}}''(\rho') \cdot \left\{ \sum_{\ell=0}^{\infty} \underline{\underline{C}}_{\ell} \right\} \cdot \underline{\underline{W}}(\rho') d\rho' + i \underline{\underline{J}}(\rho) \end{aligned} \quad (2-63)$$

where the elements in the arrays $\underline{\underline{J}}(\rho)$ and $\underline{\underline{H}}(\rho)$ are given by

(2-64)

$$[\underline{\underline{J}}(\rho)]_{\sigma, \sigma'} = \delta_{\sigma \sigma'} J_2(\ell, \ell_2, \tau_1 | \rho)$$

and

$$[\underline{H}(\rho)]_{\ell, \ell'} = \delta_{\ell, \ell'} H_{\ell}(\ell, \ell, A_1 | \ell, \ell'). \quad (2-65)$$

A solution to Eq. (2-61) is obtained for an energy $E = -\mathcal{K}^2$ if the eigenvalue ϵ in Eq. (2-62) equals one. Thus, initial and corrected estimates for $\mathcal{K}$ are used in noniteratively solving Eq. (2-63) for $\underline{V}(\rho)$, and the eigenvalues of the matrix $\int_0^{\epsilon} \underline{H}'(\rho) \cdot \left\{ \sum_{\ell=0}^{\infty} \underline{C}_{\ell} \right\} \cdot \underline{V}(\rho) d(\rho)$ are calculated for each $\mathcal{K}$ with an eigenvalue equal one. The eigenvector $\underline{A}$ for that eigenvalue is then determined from Eq. (2-62) and the normalization condition

$$\int_0^{\infty} \underline{U}^{\dagger}(\rho') \cdot \underline{U}(\rho') d\rho' = 1, \quad (2-66)$$

and the normalized solution is given by Eq. (2-61).

E. SINGLE INTEGRAL EQUATION CALCULATIONS

1. H atom: Calculations of the Ground and First Three Excited S-States

In order to develop an understanding of the integral equation procedure, it was deemed desirable to initiate the numerical studies

using only a single integral equation. To illustrate this approach with an exact calculation, the s-state H atom is considered where the total angular momentum is zero. Energy values are calculated for the ground and first three excited states, and the results are in excellent agreement with the exact value as shown in Table 1. Since the average electron-nucleus separation is greater in the excited states, the radial integral from the origin to a point $R_{\max}$ must also be greater to yield accurate calculations for excited states. Other than the increased $R_{\max}$, the excited and ground state calculations are performed with equal ease.

The noninteracting single particle Green function $G(\underline{r}|\underline{r}')$ for an H atom is well known and can be obtained from Eq. (2-6) and expanded as ¹⁹

$$G(\underline{r}|\underline{r}') = \frac{e^{ik|\underline{r}-\underline{r}'|}}{4\pi|\underline{r}-\underline{r}'|} \quad (2-67)$$

$$= -k \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} j_{\ell}(kr_{<}) h_{\ell}^{(1)}(kr_{>}) Y_{\ell}^m(\hat{r}) Y_{\ell}^{m*}(\hat{r}').$$

For the H atom Eq. (2-7) becomes

$$\Psi(\underline{r}) = \int G(\underline{r}|\underline{r}') \left(\frac{\nabla^2}{2} \right) \Psi(\underline{r}') d\underline{r}' \quad (2-68)$$

and the wave function $\Psi(r)$ is expanded in terms of the $Y_\ell^m(\hat{r})$. The radial equation for the ℓ th partial wave is obtained by multiplying Eq. (2-68) through with a particular $Y_\ell^m(\hat{r})$ and integrating over the solid angle $\hat{r}$ to give

$$\Psi_\ell^m(r) = k \int_0^\infty j_\ell(kr_2) h_\ell^{(1)}(kr_1) \left(\frac{r_2}{r_1}\right) \Psi_\ell^m(r') dr' \quad (2-69)$$

where $h_\ell^{(1)}$ is the spherical Hankel function of the first kind. The total energy E is measured in rydbergs and

$$(2-70)$$

$$k = i\kappa$$

so that

$$(2-71)$$

$$E = -\kappa^2$$

where $i\kappa$ ($\kappa > 0$) is the pure imaginary wave number. Thus, from Eq. (2-69), the bound s-state solutions of Schrödinger's equation for the H atom may be written in integral form as

$$\begin{aligned} \Psi_0(\kappa|0|r) &= \frac{2}{\kappa} \int_0^\infty \sin \kappa(kr_2) e^{-\kappa r_2} \left(\frac{1}{r'}\right) \\ &\times \Psi_0(\kappa|0|r') dr', \end{aligned} \quad (2-72)$$

$$\text{and } \mathcal{J}_0(\kappa|0|r) = \frac{2e^{-\kappa r}}{\kappa} \int_0^r \left(\frac{1}{r'}\right) \sinh(\kappa r') \mathcal{J}_0(\kappa|0|r') dr' \\ + \frac{2\sinh(\kappa r)}{\kappa} - \frac{2\sinh(\kappa r)}{\kappa} \quad (2-73)$$

$$\times \int_0^r \left(\frac{1}{r'}\right) e^{-\kappa r'} \mathcal{J}_0(\kappa|0|r') dr'.$$

Here

$$\Psi_0(\kappa|0|r) = \mathcal{J}_0(\kappa|0|r) B \quad (2-74)$$

and

$$\int_0^\infty e^{-\kappa r'} \left(\frac{1}{r'}\right) \mathcal{J}_0(\kappa|0|r') dr' B = \epsilon B. \quad (2-75)$$

A solution to Eq. (2-74) is obtained for an energy $E = -\kappa^2$ where ϵ in Eq. (2-75) is one. The wave function $\Psi_0(\kappa|0|r)$ is then absolute square integrable.

2. He Models: Ground S-State Approximations

The single integral equation approximation to He requires that, only the term $\mathcal{L}_1 = \mathcal{L}_2 = \mathcal{L}_3 = 0$ be included in the wave function expansion, Eq. (2-51). This is tantamount to examining the first

element in the matrix, and is, of course, a rather crude approximation. However, the wave function may be improved by including higher order terms, i.e., $\ell_1, \ell_2, \ell_3 \neq 0$. Coupled equations are then encountered, and the calculated energy value will become correspondingly more accurate. Nevertheless, the present single term calculations will be shown to account for approximately 85% of the total binding energy of He.

With the imposition of specialized conditions that $\ell_1 = \ell_2 = \ell_3 = 0$, Eq. (2-51) becomes a single integral equation of the form

$$\begin{aligned} \Psi_{\pm c}(\mathbf{r}|\mathbf{0}|\rho) &= \frac{16\pi}{\rho^2} \int_0^\infty d\rho' \rho'^2 \\ &\times J_2(\lambda \lambda' \rho_\perp) H_2^{(0)}(\lambda \lambda' \rho_\parallel) \int_0^{\pi/2} \sin^2 \alpha' \cos^2 \alpha' \\ &\times U(\alpha') d\alpha' \Psi_{\pm c}(\mathbf{r}|\mathbf{0}|\rho') \end{aligned} \quad (2-76)$$

where $U(\alpha)$ represents an interaction potential for any one of the particular He systems. Certain interrelations of the model He systems may be made apparent by considering, for each system, the $U(\alpha)$ integral in Eq. (2-76); so these integrals are now evaluated.

The interaction $U_{\pm}(\alpha)$ associated with Hamiltonian H_I of Eq. (2-33) is first analyzed. It is recalled that the Hamiltonian H_I describes a He atom which takes into account the motion of both electrons and the nucleus, using the symmetric center of mass coordinates shown in Fig. 1a. However, if the asymmetric coordinates of Fig. 1b,

are employed, the results of the following analysis can be shown to remain unchanged.

From Eqs. (2-76) and (2-33), the expression for the integral over $\mathcal{U}_I(\alpha)$ is

$$\mathcal{E}_I = \int_0^{\pi/2} \sin^2 \alpha' \cos^2 \alpha' \left\{ 4 \chi_0(\alpha') - \frac{\eta_1}{\cos \alpha'} \right\} d\alpha', \quad (2-77)$$

and the evaluation yields

$$\mathcal{E}_I = \frac{\sqrt{2}}{6} \left\{ 4 \left(\frac{2M_\alpha}{M_\alpha + m_e} \right)^{1/2} - 1 \right\} \quad (2-78)$$

where use is made of Eq. (2-36). It is of interest to let $M_\alpha \rightarrow \infty$ in Eq. (2-78), so that one obtains

$$\text{Limit}_{M_\alpha \rightarrow \infty} \mathcal{E}_I = \frac{\sqrt{2}}{6} \{ 4\sqrt{2} - 1 \}. \quad (2-79)$$

The interaction potentials $\mathcal{U}_{II}(\alpha)$ and $\mathcal{U}_{III}(\alpha)$ are associated with the He atom Hamiltonians given by Eqs. (2-38) and (2-44) respectively. System III is the fixed nucleus approximation, whereas system II is considered a limiting case of system I since

$$\text{Limit}_{M_\alpha \rightarrow \infty} H_I = H_{II}. \quad (2-80)$$

Now Eqs. (2-38), (2-44), and (2-78) are used to construct the integrals

$\mathcal{E}_{II}$ and $\mathcal{E}_{III}$ which are given as

$$\mathcal{E}_{II} = \int_0^{\pi/2} \sin^2 \alpha' \cos^2 \alpha' \left\{ 4 \tilde{\chi}_0(\alpha') - \frac{\eta_1}{\cos \alpha'} \right\} d\alpha' \quad (2-81)$$

and

$$\mathcal{E}_{III} = \int_0^{\pi/2} \sin^2 \alpha' \cos^2 \alpha' \left\{ \frac{2}{\cos \alpha'} + \frac{2}{\sin \alpha'} - \Omega_0(\alpha') \right\} d\alpha'. \quad (2-82)$$

It can be shown that the result given in Eq. (2-79) is the value for both integrals $\mathcal{E}_{II}$ and $\mathcal{E}_{III}$. Therefore, when the interaction potentials are integrated over all angular variables, systems II and III manifest identical behavior. The inclusion of higher order terms could alter these conclusions.

Continuing the single equation integral solution treatment of He, we let $\mathcal{R}$ represent $\mathcal{E}_I$ and $\mathcal{E}_{II}$, $\mathcal{E}_{III}$, and use the relations³³

(2-83)

$$J_2(\vec{r}) = -I_2(\vec{r})$$

and

$$H_2^{(1)}(iz) = \frac{2i}{\pi} K_2(z) \quad (2-84)$$

in order to obtain

$$\Psi_0(\kappa|0|\rho) = \frac{32R}{\pi \rho^2} \int_0^\infty \rho'^2 I_2(\kappa \rho_2) K_2(\kappa \rho_2) \quad (2-85)$$

$$\times \Psi_0(\kappa|0|\rho') d\rho'$$

from Eq. (2-76).

The functions $I_2(z)$ and $K_2(z)$ are the modified Bessel and Hankel functions, respectively. Then the function $\tilde{\Psi}_0(\kappa|0|\rho)$ defined by

$$\Psi_0(\kappa|0|\rho) = \rho^{-2} g \tilde{\Psi}_0(\kappa|0|\rho) \quad (2-86)$$

may be shown to obey the Volterra integral equation

$$\begin{aligned} \tilde{\Psi}_0(\kappa|0|\rho) &= \gamma K_2(\kappa \rho) \int_0^\rho I_2(\kappa \rho') d\rho' \\ &+ \gamma I_2(\kappa \rho) - \gamma I_2(\kappa \rho) \int_0^\rho K_2(\kappa \rho') \\ &\times \tilde{\Psi}_0(\kappa|0|\rho') d\rho' \end{aligned} \quad (2-87)$$

where $\gamma = \frac{32R}{\pi}$ (2-88)

and $\int_0^\infty K_2(\kappa \rho') \tilde{\Psi}_0(\kappa | 0 | \rho') d\rho' g$ (2-89)

$$= \epsilon g.$$

Thus when (2-90)

$$\int_0^\infty K_2(\kappa \rho') \tilde{\Psi}_0(\kappa | 0 | \rho') d\rho' = 1,$$

the eigenvalue and associated eigenfunctions are determined, and the resulting wave function is the best angular independent single term representation possible for the ground state He atom. As shown in Table 3, the results of ground state energy calculations for He systems I and II, III are given by

(2-91)

$$- \epsilon_I^2 = -4.4457862 \text{ rydbergs}$$

and

(2-92)

$$-M_{II,III}^2 = -5.0000450 \text{ rydbergs.}$$

The He system in which nuclear motion is allowed is seen to be less tightly bound (by $\sim 2.59 \times 10^{-4}$ rydberg) than the systems which assume a fixed or infinitely massive nucleus. This energy difference is reasonable in view of the fact that nuclear motion contributes to the kinetic energy of the He atom.

F. DISCUSSION

In spite of the single equation approximation for He, comparative analysis of the different He models yields results which one would expect so far as the effect of nuclear motion. This suggests that the integral equation approach should be useful for studying quantum mechanical states of He and, therefore, other two electron atomic systems. In addition, the formalism allows a straightforward generalization to systems of more than three particles since the relevant Green functions are available³⁰. The non Born-Oppenheimer nature of the method is illustrated in the treatment of model I for He, and the present method could be used to study the electron correlation problem³⁴. Further, unlike methods which involve

expansions of atomic states in a hydrogenic basis, all expansion functions in the present analysis possess purely discrete indices so the present formalism avoids difficulties associated with the continuum contributions in expansions.

To obtain more accurate calculations, a formalism for coupled integral equations has been developed such that higher order terms may be included in the expansion basis. In this case, the accuracy attainable by the integral equation method could be competitive with other procedures. However, the rate of convergence and therefore the number of terms required in the expansions will determine its practicality. Thus far, it is not clear how large a number of particles can be considered in an atomic system where the present "total" wave function approach is employed. Here, "total" wave function is used to distinguish the wave functions constructed for the total system from the Hartree-Fock type of wave function.

Finally, an interesting facet of the method is revealed by the H atom treatment in that accurate results are obtained for excited state calculations without excess effort compared to the ground state calculation. This is a very desirable property for any formalism to possess which is used to calculate energy states of atomic systems. Calculations for coupled integral equations will be reported in a later communication.

CHAPTER III

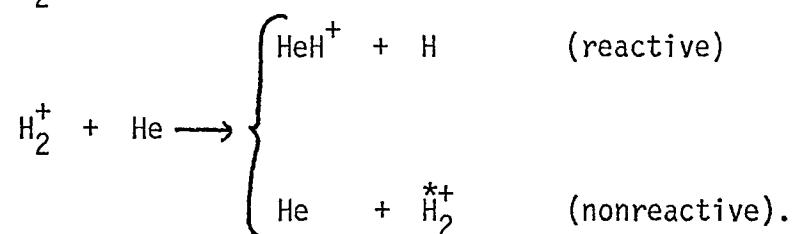
A. INTRODUCTION

Insight into the behavior of three body systems can be gained by employing approximate methods to obtain numerical results from which reliable theoretical models can then be constructed. One such model is the London-Eyring-Polanyi^{35,36} potential energy surface which has been widely used in studying energy transfer reactions resulting from atom-diatom collisions³⁷⁻⁴³. These collisions are considered to be collinear and electronically adiabatic; i.e., the surface is constructed from the electronic energy plus the nuclear repulsion potential so that the motion of the model particles sliding on the frictionless surface simulates that of the reactive system. These approximations render the problem mathematically tractable and seem to be qualitatively reasonable.

Baer and Kouri^{3,44} have recently introduced the channel $\mathcal{T}$ operator formalism which is an attractive technique for studying such atom-diatom reactive collisions^{45,46}. This approach differs from the more conventional wave function boundary matching procedures in that it can be generalized to include three dimensional effects in a straight forward manner and it has been successful in avoiding difficulties associated with nonconservation of flux^{46,47}. By treating the collinear atom-diatom collision with the coupled channel $\mathcal{T}$ operators, coupled integral equations are encountered and their solution yields

a set of coupled algebraic equations, the solutions of which are used to obtain the reactive probabilities.

The present chapter considers the collinear approximation to the reaction of $H_2^+ - He$ according to



The reaction probabilities are calculated using matrix elements of the channel $\mathcal{T}$ operators. This treatment neglects the cross terms in the kinetic energy operators in order to employ an L shaped potential energy surface.

The next section contains a description of the collision system and the relationship between the masses of the particles and the potential energy surface. In Section C the Hamiltonian is separated into perturbed and unperturbed parts. The eigenfunctions are obtained from the unperturbed Hamiltonian and the perturbations are defined. The coupled channel $\mathcal{T}$ operator equations are derived in Section D. The relevant algebraic equations are then obtained and the reflection (R_n) and transmission (T_n) coefficients are evaluated for the $H_2^+ - He$ collision. In the final section, qualitative models are employed to discuss the reaction and the numerical results are discussed and compared with other data.

B. DESCRIPTION OF THE COLLISION SYSTEM

The collinear atom-diatom collision system for $\text{H}_2^+ - \text{He}$ is shown in Fig. 2. Particles 1 and 2 (of mass m_{H_I} and $m_{\text{H}_{II}}$) represent the two proton masses; particle 3 is the He atom of mass m_{He} . The distance between particles 1 and 2 is R_α , whereas R_β is the distance from the "interior" proton to the H atom.

The initial stage of the scattering process, H_2^+ is vibrational in and energy eigenstate and is far from the incoming He atom. After the particle interact, the He atom is either reflected from the vibrating H_2^+ molecule or the "distal" H atom (particle 1) becomes freed and leaves the HeH^+ molecule vibrating in one of its accessible eigenstates. The possibility of a reaction yielding three free particles is not allowed.

The system is taken to be in the α configuration when H_2^+ is far from He and in the β configuration whe H is far from HeH^+ . For the α and β configurations, the vibrational coordinates are R_α and R_β respectively, and the complementary scattering coordinates are R_β and R_α . The subscript ρ is employed to indicate a general configuration, i.e., either α or β . By following the approach of Eyring and Polanyi³⁶ as modified by Hirschfelder⁴⁸, it can be shown that the shape of the potential energy surface for the collinear $\text{H}_2^+ - \text{He}$ system is obtained by diagonalizing the relative kinetic energy operators so the relative coordinates can be drawn at an angle which depends on the masses of particles.

In Fig. 2, the positions of the masses m_{H_I} , and $m_{H_{II}}$, and m_{He} are specified with respect to a reference point, using the vectors $\underline{r}_1$, $\underline{r}_2$, and $\underline{r}_3$, respectively. The relative coordinate, S , is a vector from the center of mass of m_{H_I} to the center of mass of the combined system, $m_{H_{II}}$ and m_{He} . The other relative coordinate, P , is a vector from the center of mass of m_{He} to the center of mass of $m_{H_{II}}$. For notational convenience, the masses m_{H_I} , $m_{H_{II}}$, and m_{He} will be denoted by m_1 , m_2 , and m_3 , respectively. The coordinates which render the internal kinetic energy operators diagonal can now be given by

(3-1)

$$P = \left[\frac{m_2 m_3}{m_2 + m_3} \right]^{\frac{1}{2}} (\underline{r}_2 - \underline{r}_3)$$

and

(3-2)

$$S = \left[\frac{m_1 (m_2 + m_3)}{M} \right]^{\frac{1}{2}} \left(\frac{m_2 \underline{r}_2 + m_3 \underline{r}_3}{m_2 + m_3} - \underline{r}_1 \right)$$

where

(3-3)

$$M = \sum_{i=1}^3 m_i .$$

Rearrangement of Eq. (3-2) yields

$$S = \left[\frac{m_1 (m_2 + m_3)}{M} \right]^{\frac{1}{2}} (r_3 - r_1) \quad (3-4)$$

$$+ \left[\frac{m_2 (m_1 + m_3)}{M} \right]^{\frac{1}{2}} \left[\frac{m_1 m_2}{(m_2 + m_3) (m_1 + m_3)} \right] (r_2 - r_3)$$

or

(3-5)

$$S = \gamma (r_3 - r_1) + \mu (r_2 - r_3) \cos \theta$$

where

(3-6)

$$\gamma = \left[\frac{m_1 (m_2 + m_3)}{M} \right]^{\frac{1}{2}},$$

(3-7)

$$\mu = \left[\frac{m_2 (m_1 + m_3)}{M} \right]^{\frac{1}{2}},$$

and

$$\cos \theta = \left[\frac{m_1 m_2}{(m_2 + m_3)(m_1 + m_3)} \right]^{\frac{1}{2}} \quad (3-8)$$

The expression for P becomes

$$P = \mu(r_2 - r_3) \sin \theta \quad (3-9)$$

where

$$\sin \theta = \left[\frac{M m_3}{(m_1 + m_3)(m_2 + m_3)} \right]^{\frac{1}{2}} \quad (3-10)$$

By displaying the relative coordinates S and P as shown in Fig. 3, the set of skewed coordinates $\mu(r_2 - r_3)$ and $r(r_3 - r_1)$ become apparent and the mass dependence of the angle θ is seen in Eq. (3-8) and (3-10). Note that as m_{He} becomes infinite, θ becomes $\pi/2$ to give an L shaped energy surface.

C. EIGENFUNCTIONS AND POTENTIAL ENERGY SURFACES

The full potential energy surface is shown in Fig. 4. The width, l_1 , of the entrance channel is taken to be $.37\text{\AA}$ with a potential of zero. The exit channel width, l_2 , is $.30\text{\AA}$ with an energy barrier of

.846 e.v. The rectangular corner region has a small potential well of -.20 e.v., and V_0 is 8.0 e.v.

In the α configuration, the potential energy surface felt by the unperturbed diatom is seen to be the $V_i(x,y)$ shown in Fig. 5a. The potential energy surface for the unperturbed diatom when the system is in the β configuration is $V_f(x,y)$ of Fig. 5b. The $V_i(x,y)$ and $V_f(x,y)$ are considered to be the effective diatom binding potentials for the α and β configurations respectively. Wave functions for these bound states are obtained from the Schrödinger equations given by

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial y^2} + V_i \right\} \phi(n_\alpha|y) = E_{n_\alpha} \phi(n_\alpha|y) \quad (3-11)$$

and

$$\left\{ -\frac{\hbar^2}{2\mu_\beta} \frac{\partial^2}{\partial x^2} + V_f \right\} \phi(n_\beta|x) = E_{n_\beta} \phi(n_\beta|x) \quad (3-12)$$

where μ_α and μ_β are the reduced masses for the two configurations. Thus the bound state wave functions, $\phi(n_\alpha|y)$ and $\phi(n_\beta|x)$, for the α and β configurations are given as

$$\phi(n_\alpha|y) = \begin{cases} A_{n_\alpha} \sin \lambda_{n_\alpha} y & 0 \leq y < l, \\ B_{n_\alpha} e^{-\tilde{T}_{n_\alpha} y} & y > l, \end{cases} \quad (3-13)$$

and

$$\phi(n_\beta | x) = \begin{cases} A_{n_\beta} \sin \lambda_{n_\beta} x & 0 \leq x < l_2 \\ B_{n_\beta} e^{-\tilde{\lambda}_{n_\beta} x} & x > l_2 \end{cases} \quad (3-14)$$

where

$$\lambda_{n_\alpha} = \left[\frac{2\mu_\alpha E_{n_\alpha}}{\hbar^2} \right]^{\frac{1}{2}}, \quad (3-15)$$

$$\tilde{\lambda}_{n_\alpha} = \left[\frac{2\mu_\alpha V_0}{\hbar^2} - \lambda_{n_\alpha}^2 \right]^{\frac{1}{2}}, \quad (3-16)$$

$$\lambda_{n_\beta} = \left[\frac{2\mu_\beta}{\hbar^2} (E_{n_\beta} - V_2) \right]^{\frac{1}{2}}, \quad (3-17)$$

and

$$\tilde{\lambda}_{n_\beta} = \left[\frac{2\mu_\beta}{\hbar^2} (V_0 - V_2) - \lambda_{n_\beta}^2 \right]^{\frac{1}{2}} \quad (3-18)$$

with the normalization constants given by

$$A_n = \left[\frac{2 \tilde{T}_n}{\tilde{T}_n l} \right] \quad (3-19)$$

and

$$B_n = A_n \sin(\lambda_n l) e^{\tilde{T}_n l} \quad (3-20)$$

The free particle eigenfunctions for the α and β configurations are taken to be

$$\tilde{\zeta}(n_\alpha | x) = \sin k_{n_\alpha} x \quad (3-21)$$

and

$$\tilde{\zeta}(n_\beta | y) = \sin k_{n_\beta} y \quad (3-22)$$

with the wave numbers k_{n_α} and k_{n_β} defined by

$$k_{n_\alpha}^2 = \frac{2\mu_\alpha E}{\hbar^2} - \lambda_{n_\alpha}^2 \quad (3-23)$$

and

$$k_{n_\beta}^2 = \frac{2\mu_\beta}{\hbar^2} (E - V_2) - \lambda_{n_\beta}^2. \quad (3-24)$$

Equations (3-10) and (3-11) are used in defining the unperturbed Hamiltonians, K_α and K_β , as

$$K_\alpha = -\frac{\hbar^2}{2\mu_\beta} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial y^2} + V_i \quad (3-25)$$

and

$$K_\beta = -\frac{\hbar^2}{2\mu_\beta} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial y^2} + V_f \quad (3-26)$$

so that the unperturbed eigenfunctions, $\Theta(n_\alpha|x,y)$ and $\Theta(n_\beta|x,y)$, are given by

$$\Theta(n_\alpha|x,y) = \bar{\zeta}(n_\alpha|x) \phi(n_\alpha|y) \quad (3-27)$$

and

$$\Theta(n_\beta|x,y) = \bar{\zeta}(n_\beta|y) \phi(n_\beta|x) \quad (3-28)$$

The K_α and K_β are related to the total Hamiltonian, H , by the equation

$$H = K_\alpha + V_\alpha = K_\beta + V_\beta. \quad (3-29)$$

The perturbations $V_\alpha(x, y)$ and $V_\beta(x, y)$ are then determined by

$$V_\alpha = H - K_\alpha = V_T(x, y) - V_i(x, y) \quad (3-30)$$

and

$$V_\beta = H - K_\beta = V_T(x, y) - V_f(x, y) \quad (3-31)$$

and are explicitly given by the relations

$$V_\alpha(x, y) = \begin{cases} V_1 & (0 \leq y < l_1) \\ V_2 - V_0 & y > l_1 \\ 0 & \end{cases} \quad \begin{matrix} 0 \leq x < l_2 \\ \\ x > l_2 \end{matrix} \quad (3-32)$$

and

$$V_{\rho}(x,y) = \begin{cases} V_1 - V_2 & (0 \leq x < l_2) \\ -V_0 & x > l_2 \end{cases} \quad \begin{matrix} 0 \leq y < l_1 \\ y > l_1 \end{matrix} \quad (3-33)$$

D. CHANNEL τ OPERATOR EQUATIONS

The channel operators are next obtained by considering the Lippman-Schwinger equation

$$|\tau\Psi^+\rangle = |\Theta_{\rho}\rangle + (E - K_{\rho} + i\epsilon)^{-1} V_{\rho} |\tau\Psi^+\rangle \quad (3-34)$$

where E is the total energy and $(E - K_{\rho} + i\epsilon)^{-1}$ is the operator form of the noninteracting ρ configuration Green function which assures that the scattering state $|\tau\Psi^+\rangle$ will satisfy casual boundary conditions. By letting $\rho = \alpha$, Eq. (3-34) can be written as

$$|\tau\Psi^+\rangle = |\Theta_{\alpha}\rangle + \{E - (K_{\alpha} + V_{\alpha}) + i\epsilon\}^{-1} V_{\alpha} |\Theta_{\alpha}\rangle \quad (3-35)$$

which becomes

$$|\Psi^+\rangle = |\Theta_\alpha\rangle + (E - K_\rho + i\epsilon)^{-1} \{V_\alpha + V_\rho (E - H + i\epsilon)^{-1} V_\alpha\} |\Theta_\alpha\rangle \quad (3-36)$$

by applying the identity

$$(E - H + i\epsilon)^{-1} = (E - K_\rho + i\epsilon)^{-1} \{1 + V_\rho (E - H + i\epsilon)^{-1}\}. \quad (3-37)$$

The channel operator, $\tilde{\zeta}_{\rho\alpha}$, is now identified in Eq. (3-36) as

$$\tilde{\zeta}_{\rho\alpha} = V_\alpha + V_\rho (E - H + i\epsilon)^{-1} V_\alpha \quad (3-38)$$

which, by using Eq. (3-37), can also be written as

$$\tilde{\zeta}_{\rho\alpha} = V_\alpha + V_\rho \{ (E - K_{\rho'} + i\epsilon)^{-1} [V_\alpha + V_{\rho'} (E - H + i\epsilon)^{-1} V_\alpha] \} \quad (3-39)$$

or

$$\tilde{\zeta}_{\rho\alpha} = V_\alpha + V_\rho (E - K_{\rho'} + i\epsilon)^{-1} \tilde{\zeta}_{\rho'\alpha}. \quad (3-40)$$

Since ρ and ρ' are independent, the operators $\tilde{\zeta}_{\alpha\alpha}$ and $\tilde{\zeta}_{\beta\alpha}$ can be expressed in terms of a set of coupled integral equations given by

$$\tilde{\zeta}_{\alpha\alpha} = V_\alpha + V_\alpha (E - K_\beta + i\epsilon)^{-1} \tilde{\zeta}_{\beta\alpha} \quad (3-41)$$

and

$$\tilde{\zeta}_{\beta\alpha} = V_{\alpha} + V_{\beta} (E - K_{\alpha} + i\epsilon)^{-1} \tilde{\zeta}_{\alpha\alpha}. \quad (3-42)$$

The channel operator matrix is given in the unperturbed representation as

$$\tilde{\zeta}_{\rho\alpha}(\theta'_{\rho} | \theta_{\alpha}) = \langle \theta'_{\rho} | \tilde{\zeta}_{\rho\alpha} | \theta_{\alpha} \rangle \quad (3-43)$$

and is related to the probability amplitude of the system going into a final configuration ρ and state θ' from an initial configuration α^0 and state θ .

By operating on the initial state, $\theta(n_{\alpha}^0 | x, y)$, with the channel operators, the amplitude density functions, $\chi(n_{\alpha} | x)$ and $\chi(n_{\beta} | y)$, are introduced and expanded in terms of the bound state functions as

$$\tilde{\zeta}_{\alpha\alpha} \theta(n_{\alpha}^0 | x, y) = \sum_{n_{\alpha}} \chi(n_{\alpha} | x) \phi(n_{\alpha} | y) \quad (3-44)$$

and

$$\tilde{\zeta}_{\beta\alpha} \theta(n_{\alpha}^0 | x, y) = \sum_{n_{\beta}} \chi(n_{\beta} | y) \phi(n_{\beta} | x). \quad (3-45)$$

The functions to be determined are the amplitude densities; so Eqs.

(3-41) and (3-42) are used to express Eqs. (3-44) and (3-45) as

(3-46)

$$\sum_{n_\alpha} \chi(n_\alpha|x) \phi(n_\alpha|y) = V_\alpha \theta(n_\alpha^o|x,y) \\ + V_\alpha (E - K_\beta + i\epsilon)^{-1} \sum_{n_\beta} \chi(n_\beta|y) \phi(n_\beta|x)$$

and

(3-47)

$$\sum_{n_\beta} \chi(n_\beta|y) \phi(n_\beta|x) = V_\alpha \theta(n_\alpha^o|x,y) \\ + V_\beta (E - K_\alpha + i\epsilon)^{-1} \sum_{n_\alpha} \chi(n_\alpha|x) \phi(n_\alpha|y).$$

Before integrals can be performed in Eq. (3-47), the integral operator must be obtained which will satisfy the equation

(3-48)

$$(E - K_\alpha + i\epsilon) G_\alpha(xy|x'y') = \delta(x-x') \delta(y-y').$$

By using the closure relation

(3-49)

$$\sum_{n_\alpha} \phi(n_\alpha|y) \phi(n_\alpha^*|y') = \delta(y-y')$$

and the fact that

$$\frac{2}{\pi} \int_0^{\infty} dk \sin kx \sin kx' = \delta(x-x'), \quad (3-50)$$

one may show that Eq. (3-48) is equivalent to

$$G_{\alpha}(xy|x'y') = \frac{1}{\pi} \sum_{n_{\alpha}} \int_{-\infty}^{\infty} dk_{n_{\alpha}} \frac{\sin(k_{n_{\alpha}}x) \sin(k_{n_{\alpha}}x') \phi(n_{\alpha}|y) \phi(n_{\alpha}|y')^*}{E - k_{n_{\alpha}}^2 - E_{n_{\alpha}} + i\epsilon}. \quad (3-51)$$

This integral is evaluated in the complex plane to yield

$$G_{\alpha}(xy|x'y') = - \sum_{n_{\alpha}} \frac{1}{k_{n_{\alpha}}} e^{i k_{n_{\alpha}} x_{>}} \sin(k_{n_{\alpha}} x_{<}) \phi(n_{\alpha}|y) \phi(n_{\alpha}|y')^* \quad (3-52)$$

where $x_{>}$, $x_{<}$ are the greater and lesser of x and x' . Since the α

and β configuration Green functions are symmetric in x and y ,

$G_{\beta}(xy|x'y')$ is given by

$$G_{\beta}(xy|x'y') = - \sum_{n_{\beta}} \frac{1}{k_{n_{\beta}}} e^{i k_{n_{\beta}} y_{>}} \sin(k_{n_{\beta}} y_{<}) \phi(n_{\beta}|x) \phi(n_{\beta}|x')^*. \quad (3-53)$$

By multiplying Eqs. (3-46) and (3-47) and by $\phi(m_\alpha|y)$ and $\phi(m_\beta|x)$ and integrating over the appropriate variables, these equations can now be expressed as

(3-54)

$$\begin{aligned} \chi(m_\alpha|x) &= \sin(k_{n_\alpha}x) \int dy \phi(m_\alpha|y) V_\alpha(x,y) \phi(n_\alpha|y) \\ &- \sum_{n_\beta} \frac{\phi(n_\beta|x)}{k_{n_\beta}} \int dy \phi(m_\alpha|y) V_\alpha(x,y) \int dy' e^{ik_{n_\beta}y'} \sin(k_{n_\beta}y') \chi(n_\beta|y') \end{aligned}$$

and

(3-55)

$$\begin{aligned} \chi(m_\beta|y) &= \phi(n_\alpha|y) \int dx \phi(m_\beta|x) V_\alpha(x,y) \sin(k_{n_\alpha}x) \\ &- \sum_{n_\alpha} \frac{\phi(n_\alpha|y)}{k_{n_\alpha}} \int dx \phi(m_\beta|x) V_\alpha(x,y) \int dx' e^{ik_{n_\alpha}x'} \sin(k_{n_\alpha}x') \chi(n_\alpha|x') \end{aligned}$$

To assist in evaluating the resulting integrals, the following definitions are convenient:

$$V_{m_{n_0}}(x) = \int_0^\infty dy \phi(m_\alpha|y) V_\alpha(x,y) \phi(n_\alpha|y), \quad (3-56)$$

$$\chi_{m_{n_0}}(y) = \int_0^\infty dx \phi(m_\beta|x) V_\alpha(x,y) \sin(k_{n_\alpha}x), \quad (3-57)$$

(3-58)

$$\alpha_{mn_\beta}(x) = \frac{1}{k_{n_\beta}} \int_0^\infty dy \phi(n_\alpha|y) V_\alpha(xy) \int_0^\infty dy' e^{ik_{n_\beta}y'} \sin(k_{n_\beta}y') \chi(n_\beta|y')$$

and

(3-59)

$$\beta_{mn_\alpha}(y) = \frac{1}{k_{n_\alpha}} \int_0^\infty dx \phi(m_\beta|x) V_\beta(xy) \int_0^\infty dx' e^{ik_{n_\alpha}x'} \sin(k_{n_\alpha}x') \chi(n_\alpha|x').$$

Thus Eqs. (3-54) and (3-55) become

(3-60)

$$\chi(m_\alpha|x) = V_{mn_0}(x) \sin(k_{n_\alpha}x) - \sum_{n_\beta} \alpha_{mn_\beta}(x) \phi(n_\beta|x)$$

and

(3-61)

$$\chi(m_\beta|y) = W_{mn_0}(y) \phi(n_\alpha|y) - \sum_{n_\alpha} \beta_{mn_\alpha}(y) \phi(n_\alpha|y).$$

The integrals given by Eqs. (3-56) through (3-59) are now evaluated by taking advantage of the piecewise constant nature of the $V_{mn_0}(x)$ and $W_{mn_0}(y)$. Thus,

(3-62)

$$V_{mn_0}(x) = \begin{cases} v_{mn_0} & 0 \leq x < l_z \\ 0 & x > l_z \end{cases}$$

where

(3-63)

$$v_{mn_0} = V_1 \Phi_{mn_0}(l_1, 0) + (V_2 - V_0) \Phi_{mn_0}(\infty, l_1)$$

and

(3-64)

$$\Phi_{mn_0}(a, b) = \int_b^a dy \phi(m_\alpha | y) \phi(n_\alpha | y).$$

Equation (3-57) is similarly evaluated to obtain

(3-65)

$$W_{mn_0}(y) = \begin{cases} W_{mn_0}^{(1)} & (0 \leq y < l_1) \\ W_{mn_0}^{(2)} & (l_1 \leq y < \infty) \end{cases}$$

where

(3-66)

$$W_{mn_0}^{(1)} = V_1 w_{mn_0}(l_2, 0)$$

and

(3-67)

$$W_{mn_0}^{(2)} = (V_2 - V_0) w_{mn_0}(l_2, 0)$$

with

(3-68)

$$w_{mn_0}(a, b) = \int_b^a dx \phi(m_\beta | x) \sin(k_{n_\alpha} x).$$

The quantity $\alpha_{mn\beta}(x)$ is expressed as

$$\alpha_{mn\beta}(x) = \begin{cases} \alpha_{mn\beta} & (0 \leq x < l_2) \\ 0 & (x > l_2) \end{cases} \quad (3-69)$$

where

$$\alpha_{mn\beta} = \frac{V_1}{k_{n\beta}} \mathcal{I}_{mn\beta}(l_1, 0) + \frac{(V_2 - V_0)}{k_{n\beta}} \mathcal{I}_{mn\beta}(\infty, l_1) \quad (3-70)$$

and

$$\mathcal{I}_{mn\beta}(a, b) = \int_b^a dy \phi(m_\alpha | y) \int_0^\infty dy' e^{ik_{n\beta} y'} \sin(k_{n\beta} y_2) \chi(n_\beta | y'). \quad (3-71)$$

The quantity $\beta_{mn\alpha}(y)$ is similarly expressed as

$$\beta_{mn\alpha}(y) = \begin{cases} \beta_{mn\alpha} & (0 \leq y < l_1) \\ 0 & (y > l_1) \end{cases} \quad (3-72)$$

where

$$\beta_{mn\alpha} = \frac{(V_1 - V_2)}{k_{n\alpha}} \tilde{\mathcal{I}}_{mn\alpha}(l_2, 0) - \frac{V_0}{k_{n\alpha}} \tilde{\mathcal{I}}_{mn\alpha}(\infty, l_2) \quad (3-73)$$

and

$$\tilde{I}_{m n_\alpha}(a, b) = \int_b^a dx \phi(m_\beta | x) \int_0^\infty dx' e^{i k_{n_\alpha} x'} \sin(k_{n_\alpha} x') \chi(n_\alpha | x'). \quad (3-74)$$

Equations (3-71) and (3-74) may be rewritten as

(3-75)

$$\begin{aligned} & I_{m n_\beta}(a, b) \\ &= \int_b^a dy \phi(m_\alpha | y) \left\{ e^{i k_{n_\beta} y} \int_0^y dy' \sin(k_{n_\beta} y') \chi(n_\beta | y') \right. \\ & \quad \left. + \sin(k_{n_\beta} y) \int_y^\infty dy' e^{i k_{n_\beta} y'} \chi(n_\beta | y') \right\} \end{aligned}$$

and

$$\begin{aligned} & \tilde{I}_{m n_\alpha}(a, b) \\ &= \int_b^a dx \phi(m_\beta | x) \left\{ e^{i k_{n_\alpha} x} \int_0^x dx' \sin(k_{n_\alpha} x') \chi(n_\alpha | x') \right. \\ & \quad \left. + \sin(k_{n_\alpha} x) \int_x^\infty dx' e^{i k_{n_\alpha} x'} \chi(n_\alpha | x') \right\} \end{aligned} \quad (3-76)$$

which, upon rearrangement, become

$$\begin{aligned} \mathcal{I}_{mn}(a, b) = & Q_{mn}(a, b, y) T_n \\ & + \int_b^a dy \phi(m|y) \int_y^\infty dy' \sin[k_n(y-y')] \chi(n|y') \end{aligned} \quad (3-77)$$

and

$$\begin{aligned} \tilde{\mathcal{I}}_{mn}(a, b) = & \tilde{Q}_{mn}(a, b, x) R_n \\ & + \int_b^a dx \phi(m|x) \int_x^\infty dx' \sin[k_n(x-x')] \chi(n|x'). \end{aligned} \quad (3-78)$$

Here,

$$Q_{mn}(a, b, r) = \int_b^a dr \phi(m|r) e^{-ik_n r}, \quad (3-79)$$

$$T_n = \int_0^\infty dy \chi(n|y) \sin(k_n y), \quad (3-80)$$

and

$$R_n = \int_0^\infty dx \chi(n|x) \sin(k_n x). \quad (3-81)$$

In order to further evaluate α_{mn} and β_{mn} , the functions $\chi(n|y)$ and $\chi(n|x)$ are required. These are given by

$$\chi(n|x) = \begin{cases} \sin(k_{n_0} x) u_{nn_0} - \sum_{n'} \alpha_{nn'} \phi(n'|x) & (0 \leq x < l_2) \\ 0 & (x > l_2) \end{cases} \quad (3-82)$$

and

$$\chi(n|y) = \begin{cases} \mathcal{W}_{nn_0}^{(1)} \phi(n_{\alpha_0}|y) - \sum_{n'} \beta_{nn'} \phi(n'|y) & (0 \leq y < l_1) \\ \mathcal{W}_{nn_0}^{(2)} \phi(n_{\alpha_0}|y) & (y > l_1) \end{cases} \quad (3-83)$$

Equations (3-70) and (3-73) are thus written as

$$\begin{aligned} \alpha_{mn} = & \frac{V_1}{k_n} \left\{ \Phi_{mn}(l_1, 0, y) T_n \right\} \\ & + \frac{V_1}{k_n} \left\{ \int_0^{l_1} dy \phi(m|y) \int_y^{\infty} dy' \sin[k_n(y-y')] \chi(n|y') \right\} \\ & + \frac{(V_2 - V_0)}{k_n} \left\{ \Phi_{mn}(\infty, l_1, y) T_n \right\} \\ & + \frac{(V_2 - V_0)}{k_n} \left\{ \int_{l_1}^{\infty} dy \phi(m|y) \int_y^{\infty} dy' \sin[k_n(y-y')] \chi(n|y') \right\} \end{aligned} \quad (3-84)$$

and

$$\begin{aligned}
\beta_{mn} = & \frac{(V_1 - V_2)}{k_n} \left\{ Q_{mn}(l_1, 0, x) R_n \right\} \\
& + \frac{(V_1 - V_2)}{k_n} \left\{ \int_0^{l_2} dx \phi(m|x) \int_x^\infty dx' \sin[k_n(x-x')] \chi(n|x') \right\} \\
& - \frac{V_0}{k_n} \left\{ Q_{mn}(\infty, l_2, x) R_n \right\} \\
& - \frac{V_0}{k_n} \left\{ \int_{l_2}^\infty dx \phi(m|x) \int_x^\infty dx' \sin[k_n(x-x')] \chi(n|x') \right\},
\end{aligned}$$

and can now be evaluated to yield

(3-86)

$$\begin{aligned}
\alpha_{mn} = & \frac{1}{k_n} \left\{ V_1 Q_{mn}(l_1, 0, y) + (V_2 - V_0) Q_{mn}(\infty, l_1, y) \right\} T_n \\
& + \frac{V_1}{k_n} \left\{ \mathcal{W}_{mn_0}^{(1)} Z_{mn n_0}(l_1, 0; l_1, y) + \mathcal{W}_{mn_0}^{(2)} Z_{mn n_0}(l_1, 0; \infty, l_1) \right\} \\
& - \frac{V_1}{k_n} \left\{ \sum_{n'_\alpha} \beta_n n'_\alpha Z_{mn n'_\alpha}(l_1, 0; l_1, y) \right\} \\
& + \frac{(V_2 - V_0)}{k_n} \mathcal{W}_{mn_0}^{(2)} Z_{mn n_0}(\infty, l_1; \infty, l_1)
\end{aligned}$$

and

(3-87)

$$\begin{aligned} \beta_{mn} = & \frac{(V_1 - V_2)}{k_n} \left\{ Q_{mn}(l_2, 0, x) R_n + U_{mn_0} S_{mn n_0}(l_2, 0; l_2, x) \right\} \\ & - \frac{(V_1 - V_2)}{k_n} \sum_{n'_\beta} \alpha_{nn'_\beta} Z_{mn n'_\beta}(l_2, 0; l_2, x) \\ & - \frac{V_0}{k_n} Q_{mn}(\omega, l_2; l_2, x) R_n \end{aligned}$$

where

(3-88)

$$\begin{aligned} Z_{mn n_0}(a, b; c, d) \\ = \int_b^a dq \phi(m|q) \int_d^c dq' \sin[k_n(q - q')] \phi(n_0|q') \end{aligned}$$

and

(3-89)

$$\begin{aligned} S_{mn n_0}(a, b; c, d) \\ = \int_b^a dq \phi(m|q) \int_d^c dq' \sin[k_n(q - q')] \sin(k_{n_0} q') \end{aligned}$$

with q being x or y .

Expressions for the values of the reaction or transmission coefficient, T_n , and the reflection coefficient, R_n , given in Eqs. (3-80) and (3-81) are now obtained by multiplying Eqs. (3-59) and (3-60) by the appropriate sine function and integrating; i.e., the equations

$$\int_0^{\infty} dx \chi(m_\alpha | x) \sin(k_m x) = \int_0^{\infty} dx V_{mn_0}(x) \sin(k_{n_0} x) \sin(k_m x) - \sum_{n_\beta} \int_0^{\infty} dx \alpha_{mn_\beta} \phi(n_\beta | x) \sin(k_m x) \quad (3-90)$$

and

$$\int_0^{\infty} dy \chi(m_\beta | y) \sin(k_m y) = \int_0^{\infty} dy W_{mn_0}(y) \phi(n_0 | y) \sin(k_m y) dy - \sum_{n_\alpha} \int_0^{\infty} dy \beta_{mn_\alpha} \phi(n_\alpha | y) \sin(k_m y) dy \quad (3-91)$$

become

$$R_{m_\alpha} = v_{mn_0} S_{n_0 m}(l_2, 0) - \sum_{n_\beta} \alpha_{mn_\beta} w_{n_\beta m}(l_2, 0) \quad (3-92)$$

and

$$T_{m_\beta} = W_{mn_0}^{(1)} w_{n_0 m}(l_1, 0) + W_{mn_0}^{(2)} w_{n_0 m}(l_1, \infty) - \sum_{n_\alpha} \beta_{mn_\alpha} w_{n_\alpha m}(l_1, 0) \quad (3-93)$$

respectively, where

$$S_{n_0 m}(l_2, 0) = \int_0^{l_2} dx S_{in}(k_{n_0} x) S_{in}(k_m x). \quad (3-94)$$

The probability amplitudes for reaction and reflection, T_m and R_m respectively, can now be calculated by solving simultaneously the algebraic Eqs. (3-86), (3-87), (3-92) and (3-93) for α_{mn} , β_{mn} , R_n , and T_m .

In appendix A the probability amplitudes T_n and R_n are shown to be related to the transition probability, P , by

$$P_{n_0 \rightarrow n_0}^{(R)} = |1 - 2i R_{n_0} / k_{n_0}|^2 \quad (3-95)$$

and

$$P_{n_0 \rightarrow n}^{(R)} = 4 |R_n|^2 / k_{n_0} k_n \quad (n \neq n_0) \quad (3-96)$$

for the nonreactive probabilities and by

$$P_{n_0 \rightarrow n}^{(T)} = 4 |T_n|^2 / k_{n_0} k_n \quad (3-97)$$

for the reactive probabilities.

E. RESULTS AND DISCUSSION

1. Descriptive Models

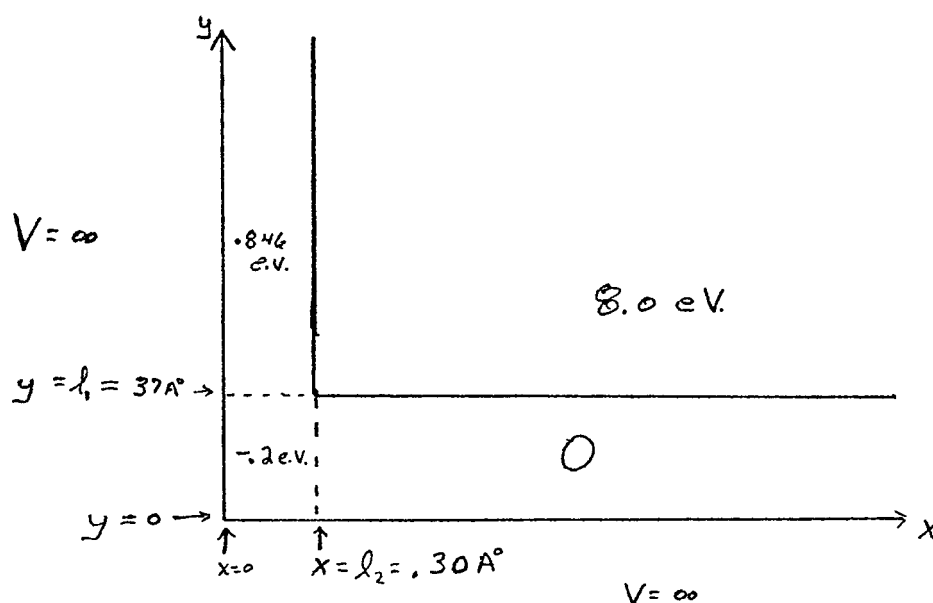
The reactive collision indicated by

(3-98)



will be qualitatively discussed from two different view points in order to seek additional insight into the scattering process and possibly construct a "physical picture". The first treatment considers the possibility of viewing the reaction probability as a product of the relevant reflection and transmission coefficients.

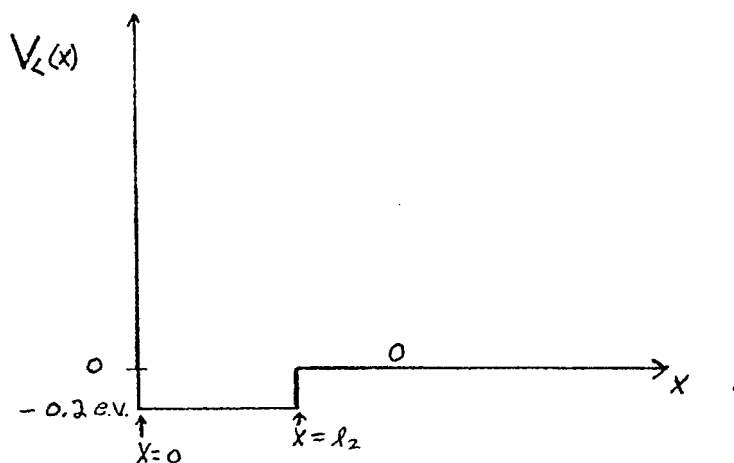
To illustrate this approach it is convenient to recall that the full potential energy surface (Fig. 4) is represented by



where, in the α configuration, the X motion on the energy surface is associated with the He atom and the y motion with the oscillating H atom. The motion of the reactant particles in Eq. (3-98) can therefore be represented on the energy surface by defining the position of the incoming He atom as X and the H atom position as y . The product particle motion is similarly given where x now defines the position of the oscillating atom associated with HeH^+ and y is the position of the free H atom. Since this problem is mathematically equivalent (except for non identical masses) to the motion of a single two dimensional particle moving in the x - y plane, the positions, x and y , of the two one dimensional particles can be viewed as the x and y components of a single two dimensional particle which moves in configuration space. The motion of the single point in configuration space which corresponds to the reaction given in Eq. (3-98) is a superposition of the motion of the two one dimensional particles displayed on the two dimensional plane. Thus the incoming point particle would be translated along the x coordinate in the direction of the origin and would oscillate in the y direction approximately within the region defined by $(0 \leq y \leq l_1 + \epsilon)$ where ϵ is the usual small number greater than zero. For some reactions, the point particle passes directly into the -0.2 e.v. "interaction region" defined by $\left\{ \begin{array}{l} 0 \leq y < l_1 \\ 0 \leq x < l_2 \end{array} \right\}$ and exits along the y coordinate with oscillatory motion now in the x direction. This path is referred to as the classical route. In other reactions, the point particle follows a nonclassical path in configura-

tion space which "cuts the corner" from the entrance channel into the exit channel such that the "interaction region" is never entered. For such "corner cutting" reactions, the point particle exhibits two dimensional tunneling. If the exchange reaction did not occur, the point particle could be reflected from the "interaction region" or a nonclassical region such that the direction of translational motion along the x coordinate would be reversed, i.e., away from the origin.

Thus, when the incoming He atom is not in the asymptotic region but is approaching the position λ_2 on the x coordinate, the potential energy surface felt by the He atom is a function of the position y of the H atom. The converse is also true; i.e., the energy surface for the oscillating H atom depends on the position x of He. One can see from the full potential energy surface that when the position y of the H atom is such that $(0 \leq y < \lambda_1)$, the potential energy surface, $V_{<}(x)$ [the symbol $<$ indicates the condition $y < \lambda_1$], seen by the He atom is given by

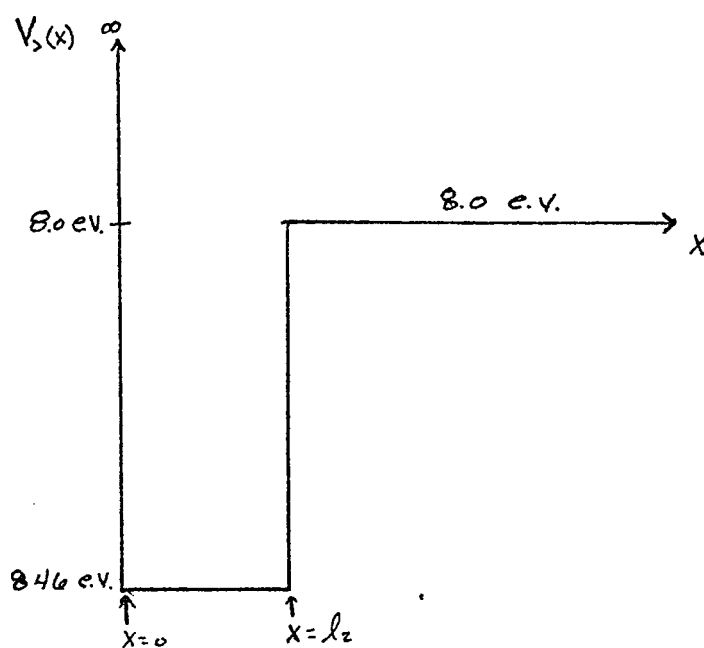


However, when the H atom penetrates into classically forbidden regions defined by

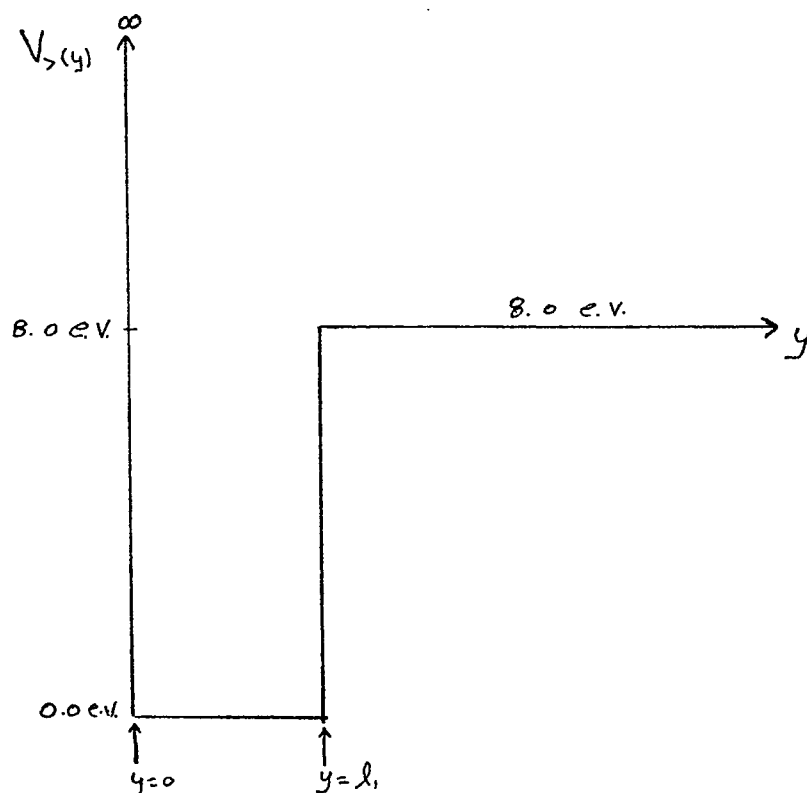
(3-99)

$$y = \lambda_1 + \epsilon \quad (\epsilon > 0),$$

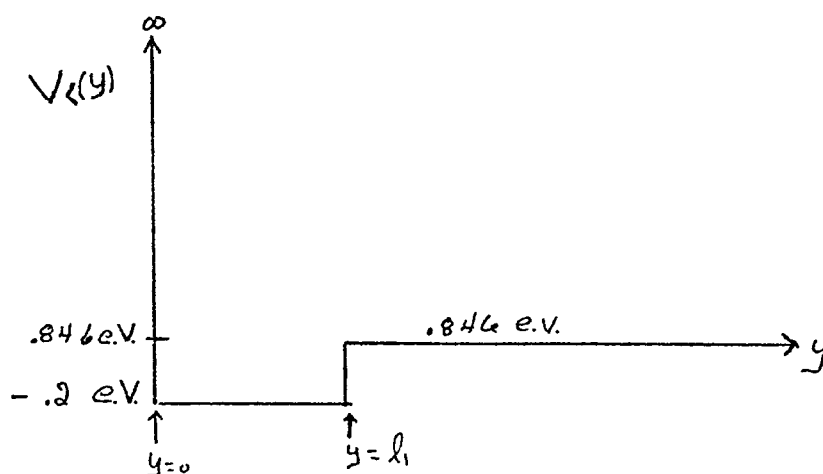
the He atom feels a potential energy surface $V_>(x)$ (i.e., $y > \lambda_1$) as indicated by



The potential energy surface $V_>(y)$ for the oscillating H_2^+ system is given by



where the position x of He satisfies the condition $x > l_2$. When the position x of He is within the region ($0 \leq x < l_2$), the H_2^+ system feels a potential energy surface $V_<(y)$ given by



The reaction given by Eq. (3-98) is now analyzed where the relative position of the oscillating H atom is considered to be, for case A, in a nonclassical ($y > \lambda_1$) region of the potential energy surface, or for case B, in the classical ($y < \lambda_1$) region of the surface. In both cases, A and B, the incoming He atoms are classified according to their relative transmission and reflection probabilities. Recall, however, that for H atom case A ($y > \lambda_1$), the potential energy surface for He is $V_>(x)$, whereas it is $V_<(x)$ for case B H atoms. The impinging He atoms are classified for each surface as (I) those which are initially reflected at $x = \lambda_2$ by the discontinuity in the potential, (II) those which are not initially reflected at $x = \lambda_2$ but maintain a localization within the region ($0 \leq x \leq \lambda_2 + \epsilon'$); this phenomenon could be considered as a type of standing wave or resonance, and (III) those which penetrate the initial discontinuity at $x = \lambda_2$, but compared to class II, the class III atoms remain only briefly within the region defined by ($0 \leq x \leq \lambda_2 + \epsilon'$); i.e., class III atoms could rebound several times between the positions $x=0$ and $x = \lambda_2$ before being transmitted back into the $x > \lambda_2$ region.

In case A, the H atom position is given by Eq. (3-99) and the potential energy surface seen by the incoming He atom is $V_>(x)$. The class I He gives rise to purely nonreactive scattering. Helium atoms of class II would enter the potential well over the region defined by ($0 \leq x \leq \lambda_2 + \epsilon'$) and exhibit standing wave or resonance properties. Therefore, the energy surface most likely to be seen by the nonclassical

H atom is $V_{<}(y)$, and it follows that impinging class II He atoms render the system reactive. Helium atoms classified as III can also lead to reaction since their effective position is that of II until the atoms are transmitted back into the $x > \lambda_2$ region. After this event, H atoms see the $V_{>}(y)$ surface and reaction is no longer possible.

In case A, collision the incident He atom is required to travel through classically forbidden regions in order to reach the well on the $V_{>}(x)$ surface. Since this same well binds the product oscillator, HeH^+ , and the wave function for such system would extend beyond the classical turning point ($x = \lambda_2$), it is suggested that wave functions of the class II He atoms "join on smoothly" to the HeH^+ wave functions in the nonclassical regions and that the class I and class III wave functions do not.

This case A H atom example is convenient for illustrating the "corner cutting" effect, using the point particle in configuration space picture. The H atom [Eq. (3-99)] position is $y = \lambda_1 + \epsilon$. If the incoming He atom were located by $x = \lambda_2 + \epsilon'$ and $\epsilon \gg \epsilon'$, it follows that the two dimensional point particle could pass into the exit channel (parallel to the y axis) from the entrance channel (parallel to the x axis) without ever entering the interaction region. This is possible since the particle motion in configuration space follows a path defined by the positions x and y of the two one dimensional particles.

In case B for the H atom, the position y is in the classical region and is given by

$$y = l_1 - \delta \quad (3-100)$$

where

$$\epsilon \leq \delta \leq l_1 \quad (\epsilon > 0). \quad (3-101)$$

The energy surface seen by the incoming He atoms (of classifications I, II, and III) is $V_L(x)$. Although the discontinuity at $x = l_2$ is smaller on the energy surface $V_L(x)$ than that on $V_S(x)$, incoming He atoms of class I are still nonreactive due to reflection at the initial discontinuity, $x = l_2$. Helium atoms classified as II are required to exhibit some type of "localization" behavior within the region defined by $(0 \leq x \leq l_2 + \epsilon)$ on the $V_L(x)$ surface. When the He atom is in this region, the H atom potential energy is such that reaction readily occurs. Atoms of class III can also be reactive provided the H atoms are not easily reflected by the $V_L(y)$ potential which they see when the class III He atoms are in the interaction region.

It is noted that the well depth for this problem is 0.2 e.v., whereas the energy difference between the top and bottom of the well of $V_S(x)$ for the same range of x is 7.154 e.v. At the kinetic energies considered for the incoming He atoms (i.e., 0-2.5 e.v.), it would

appear that the probability of localizing an incoming atom would be greater on the $V_>(x)$ surface than on the $V_<(x)$ energy surface. This, of course, implies that if the probability is increased for H atoms to penetrate into the classically forbidden regions, then the probability of yielding exchanged products per incident He atom is enhanced if such He atoms can penetrate into the $x < \lambda_2$ region.

Since the energy surfaces are functions of particle positions, the model surfaces actually felt by the two atoms change frequently, particularly for the He atom. It can be argued that for the lower energy states, the oscillating H atoms are of case B most of the time; so the incoming He sees the $V_<(x)$ surface the same percentage of the time. On this basis it seems reasonable to believe that the majority of exchange reactions occur with class III He - case B H atoms since relatively few class II He atoms would be expected due to the shallowness of the well and the kinetic energy range of He.

We can summarize He- H_2^+ collisions as follows: (a) for reaction, the incident He atom must be able to reach into region i ($0 \leq x < \lambda_2$) from region ii ($x > \lambda_2$) on either the surface $V_<(x)$ or $V_>(x)$, (b) for reaction, the energy of the reacting H atom must be sufficient to allow transmission from region i ($0 \leq y < \lambda_1$), on the $V_<(y)$ surface, into region ii ($y > \lambda_2$), (c) the He atom in region i ($0 \leq x < \lambda_2$) of $V_<(x)$ can be transmitted into region ii ($x > \lambda_2$), or reflected back into region i; He atoms in region i ($0 \leq x < \lambda_2$) of $V_>(x)$ are bound, and (d) H atoms are bound by $V_>(y)$. Statements (a), (b), and

(c) can be used to express the probability of exchanged products per collision as

(3-102)

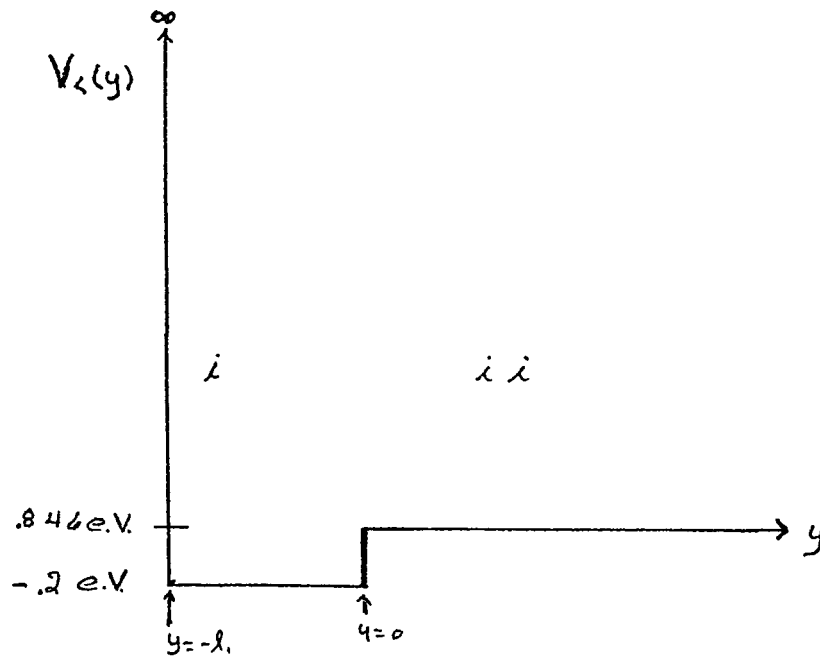
$$P = \left[T_{He}^{(E)} \right]_{i \rightarrow i} \left[T_H^{(E)} \right]_{i \rightarrow i} \left[R_{He}^{(E)} \right]_{i \rightarrow i}$$

where $T_{He}^{(E)} \big|_{i \rightarrow i}$ is the transmission coefficient associated with the $x = \ell_2$ discontinuity for the incident He atom on the surface $V_{<}(x)$ or $V_{>}(x)$, $T_H^{(E)} \big|_{i \rightarrow i}$ is the transmission coefficient for the reacting H atom at the discontinuity $y = \ell_1$ on the $V_{<}(y)$ surface, and $R_{He}^{(E)} \big|_{i \rightarrow i}$ is the reflection coefficient at $x = \ell_2$ for the He atom within region i of $V_{<}(x)$.

It is noted, however, that a H atom transition from region i ($0 \leq y < \ell_1$) into region ii ($y > \ell_1$) does not necessarily require a reflection of the incident He atom at $x = 0$ nor does it require a reflection at $x = \ell_1$ of the He atom which has been reflected at $x = 0$; i.e., the H atom transition could occur before the incident He atom is able to encounter the discontinuity at $x = 0$ or before the rebounded atom can reach the discontinuity at $x = \ell_2$. In either case, the barrier at $x = \ell_2$ would become 7.154 e.v., and the HeH^+ system would become bound without employing the reflection term in Eq. (3-102). If such initial conditions existed (e.g., high energy vibrational states of H_2^+ interacting with low kinetic energy He atoms), the contribution to the reaction probability from the term $R_{He}^{(E)} \big|_{i \rightarrow i}$ in Eq. (3-102) would be

small compared to the transmission coefficients.

We now develop expressions for the coefficients in the product of Eq. (3-102) for class III-case B. The transmission coefficient, $T_{H_{i \rightarrow ii}}$ for the H atom is obtained first where, for convenience, the $V_z(y)$ surface is now represented as



In region i, the solution of the Schrödinger equation can be given as

$$\Psi_i = A e^{ik_y y} + B e^{-ik_y y} \quad (3-103)$$

where

$$k^2 = \frac{2\mu_2 (E_v + .2 \text{ e.v.})}{\hbar^2} \quad (3-104)$$

and E_v is the internal energy of the oscillator before entering the 0.2 e.v. well. At $y = -l_1$, the boundary conditions is generally

(3-105)

$$\Psi_i = A e^{-ikl_1} + B e^{+ikl_1} = 0,$$

but for the present problem, this condition is not employed. Since the emitted H atoms travel only in the positive y direction, the solution to Schrödinger's equation in region ii is given by

(3-106)

$$\Psi_{ii} = C e^{iKy}$$

where

$$K^2 = \frac{2\mu_2(E - 1.046 \text{ e.v.})}{\hbar^2} \quad (3-107)$$

The boundary conditions at $y = 0$ require that

(3-108)

$$A + B = C$$

and

(3-109)

$$ik(A - B) = iK C.$$

The relative amplitude of the transmitted wave, C of Eq. (3-106), is expressed in terms of the amplitude of the incident wave, A, by the equation

(3-110)

$$C = \frac{2Ak}{K+k}.$$

The formula

$$J = \frac{e\hbar}{2mi} [\psi^* \nabla \psi - \psi \nabla \psi^*] \quad (3-111)$$

is then used to obtain the relative current densities, J_T for the transmitted waves and J_I for the incident waves, and the transmission coefficient is given by

$$T_{i \rightarrow ii} = \frac{J_T}{J_I} = \frac{4kK}{(K+k)^2} \quad (3-112)$$

where the kinetic energy, E , of the incident H atom must be such that is $E \geq 1.046$ e.v. Since the energy of the ground and first vibrational state of H_2^+ is less than 1.046 e.v., the product H atoms from these initial states must acquire sufficient energy for transmission by an energy transfer collision. The kinetic energy E of the H atom in the second excited state is given by (in region i)

(3-113)

$$\begin{aligned} E &= E_v + .2 = 1.22 + .2 \\ &= 1.42 \text{ e.v.}, \end{aligned}$$

and the corresponding transmission coefficient is obtained from Eq.

(3-112) as

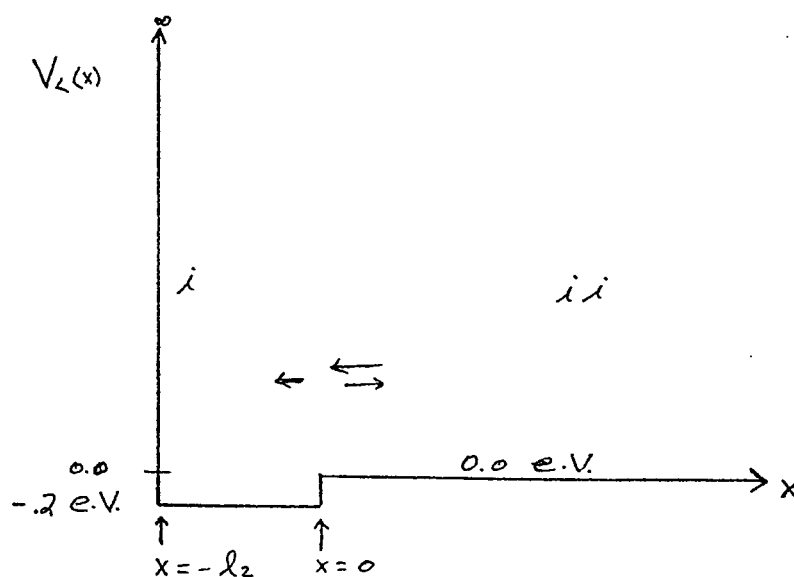
(3-114)

$$T_{H \atop i \rightarrow ii} = \frac{4 \sqrt{1.42} \sqrt{1.42 - 1.046}}{(\sqrt{1.42} + \sqrt{1.42 - 1.046})^2}$$

$$= 0.897$$

which suggests that the initial H_2^+ states of higher vibrational energies are more likely to react unless there is a very high probability of energy transfer between He and H atoms in the collision so that non-reactive inelastic collisions dominate.

The energy surface $V_L(x)$ for obtaining the transmission coefficients for the He atom can be represented by



and the solutions to Schrödinger's equation are, for the transmission

coefficient, given as

$$\psi_i = c e^{-i\alpha x} \quad (3-115)$$

for region i and as

$$\psi_{ii} = a e^{-\beta x} + b e^{+\beta x} \quad (3-116)$$

in region ii. The wave numbers are defined by

$$\alpha^2 = \frac{2\mu_1(E + 2 \text{ e.v.})}{\hbar^2} \quad (3-117)$$

and

$$\beta^2 = \frac{2\mu_1 E}{\hbar^2} \quad (3-118)$$

where E is the kinetic energy of the He atom in region ii. From the boundary conditions at $x = 0$ given by

$$(3-119)$$

$$a + b = c$$

and

$$(3-120)$$

$$-i\beta(a - b) = -i\alpha c,$$

the relationship

(3-121)

$$b = \left[\frac{g - \mathcal{H}}{g + \mathcal{H}} \right] a$$

can be obtained. By using Eq. (3-111), the reflection coefficient, "

$R_{ii \rightarrow ii}$, can be given as

(3-122)

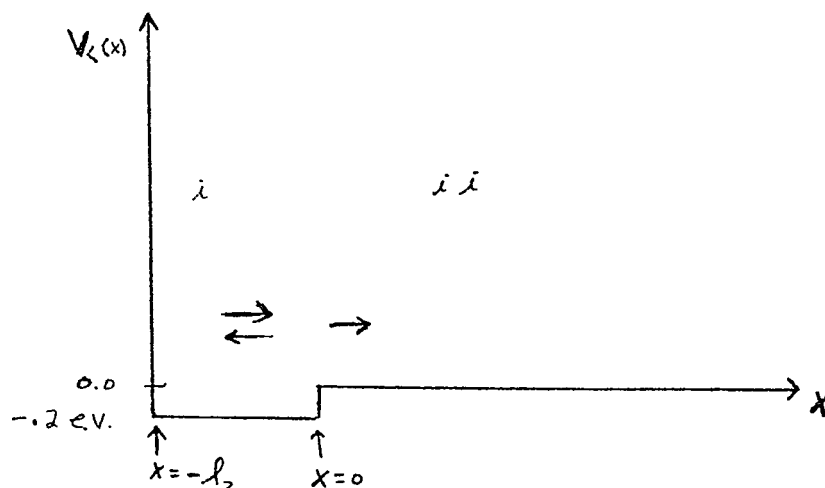
$$R_{ii \rightarrow ii} = \frac{J_R}{J_I} = \left[\frac{g - \mathcal{H}}{g + \mathcal{H}} \right]^2,$$

and the transmission coefficient is expressed as

(3-123)

$$T_{ii \rightarrow ii} = 1 - R_{ii \rightarrow ii}.$$

However, the reflection coefficient, $R_{He_{ii \rightarrow ii}}$, is obtained by representing the $V_L(x)$ surface as



where the wave functions are given by

$$\Psi_i = a' e^{i\mathcal{H}x} + b' e^{-i\mathcal{H}x} \quad (3-124)$$

and

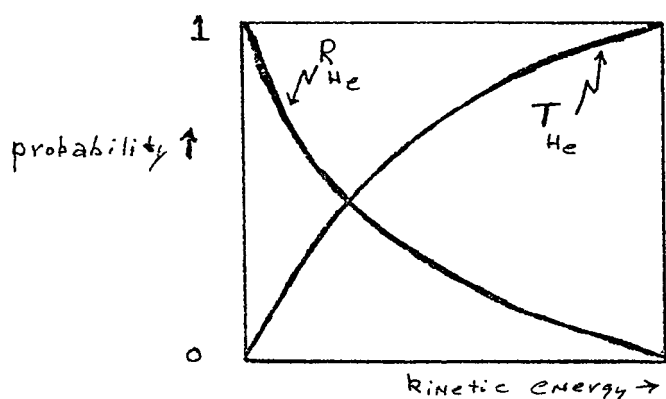
$$\Psi_{ii} = c' e^{i\mathcal{H}x} . \quad (3-125)$$

Since this form is the same as that employed to obtain the transmission coefficient of H [Eq. (3-112)], the reflection coefficient is given by

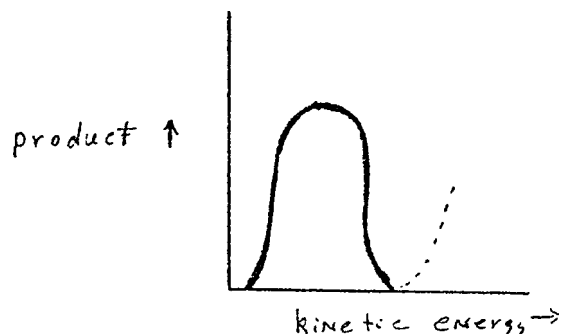
$$R_{\text{He}}^{i \rightarrow i} = 1 - \frac{4\mathcal{H}g}{(\mathcal{H} + g)^2} . \quad (3-126)$$

The graphs of the calculated reaction probabilities show considerable structure. In terms of this model, the reaction conditions for the lower energy states of H_2^+ are H atom case B-class III He. Although the energy exchange required for reaction of the ground and first vibrational state is not explicitly included by this model, the reaction probability curves can be viewed as products of the transmission coefficients, $T_{\text{H } i \rightarrow i}$ for H and $T_{\text{He } i \rightarrow i}$ for He, and the reflection coefficient $R_{\text{He } i \rightarrow i}$ of He. At the higher kinetic energy required of He to react with the ground and first excited state of H_2^+ , the coefficient, $T_{\text{He } i \rightarrow i}$, is effectively equal to one; however, the low kinetic energy He reactions

involving the second and third excited states of H_2^+ indicate that $T_{He_{ii \rightarrow i}}$ is less than one. The plot (Fig. 11) of total reaction probabilities versus kinetic energy of He can be used to illustrate the $T_{He_{ii \rightarrow i}} < 1$ behavior. The curve for the second excited state of H_2^+ peaks quickly, turns downward to a minimum, and rises sharply to a maximum. The initial peak which drops to a minimum can be explained by the case B H-class III He mechanism which assumes that $T_{H_{i \rightarrow ii}}$ remains constant. The transmission and reflection coefficients, T_{He} and R_{He} , as a function of kinetic energy can be graphically represented as



The product $R_{He} \times T_{He}$ is then given by the solid line as



which is the form of the initial total reaction probability peak for the second excited state of H_2^+ . The dashed line represents the sharp increase observed in reaction probability and can be explained as case A H-class II He effects. Such behavior (i.e., the dip) was not observed for the third excited state of H_2^+ due to contributions from the class II and III He-case A H atoms. The increase in probabilities which occurs immediately after the opening of a new reactive channel can be attributed to a "smooth joining" of the He atom scattering wave function to the wave functions of the product oscillator. This corresponds to "resonant" type reaction associated with class II He-case A H atom collisions.

We now discuss an alternative approach for treating the reactive system [(Eq. (3-38)]. This discussion employs a noninteracting state $|i\rangle$ to describe the initial system as that of free He-bound H atom (as H_2^+), whereas $\langle f|$ is the noninteracting final state for the bound He atom (as HeH^+)- free H atom system. The full potential energy surface $V(xy)$ is decomposed into a form given by

(3-127)

$$V(xy) = V(x)^i + V(y)^i + \Delta V(xy) = V(x)^f + V(y)^f + \Delta V(xy)$$

which enables one to write the full Hamiltonian H as

(3-128)

$$H = H_o^i + \Delta V(xy) = H_o^f + \Delta V(xy).$$

The states $|i\rangle$ and $|f\rangle$ are constructed to satisfy the equations

(3-129)

$$H_o^i |i\rangle = \epsilon_i |i\rangle$$

and

(3-130)

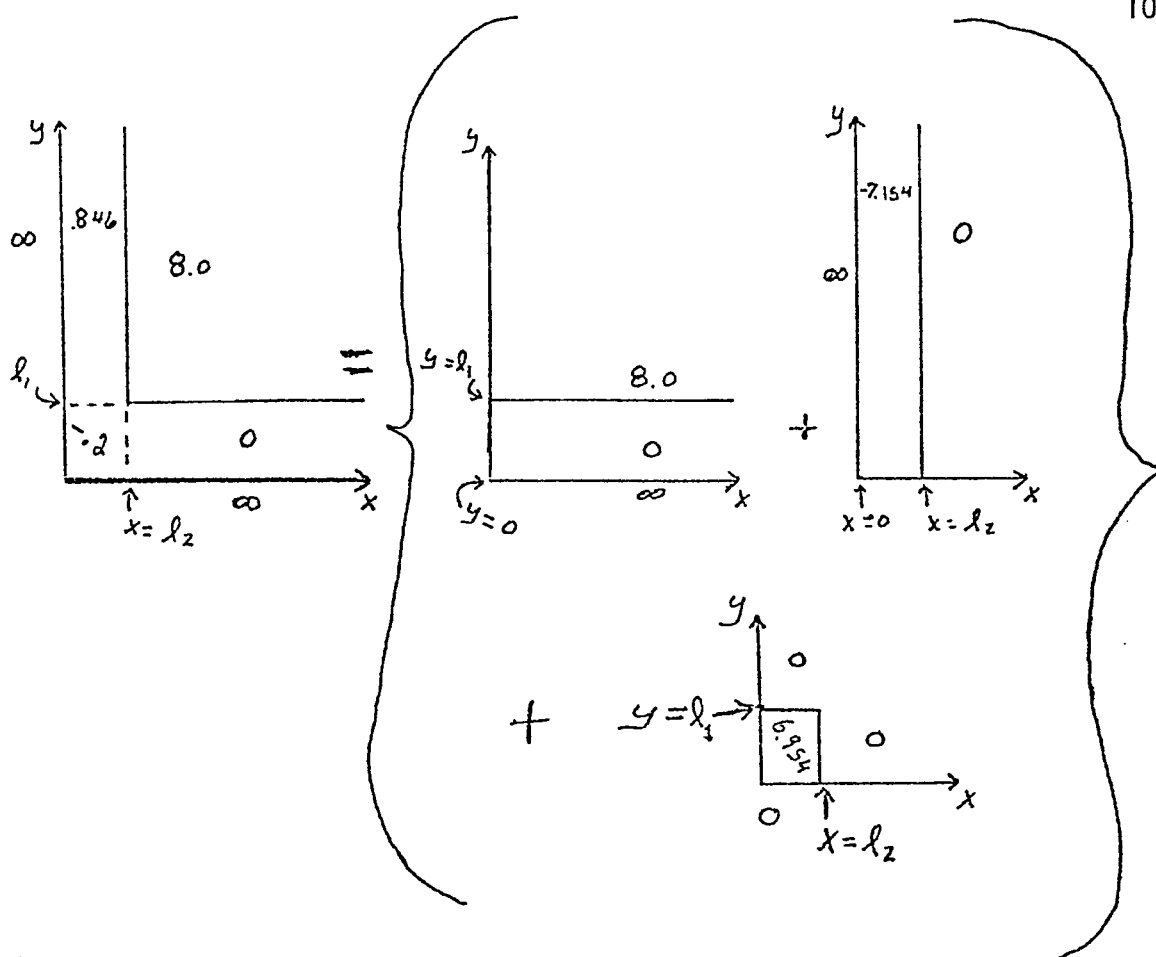
$$H_o^f |f\rangle = \epsilon_f |f\rangle$$

and the first order transition rate, $\mathcal{W}_{if}^{(1)}$, is then expressed by Fermi's Golden Rule,⁴⁹ as

(3-131)

$$\mathcal{W}_{if}^{(1)} = \frac{2\pi}{\hbar} |\langle f | \Delta V | i \rangle|^2 \delta(\epsilon_f - \epsilon_i)$$

where $\Delta V(xy)$ is a perturbation and the δ -function ensures energy conservation. The perturbation, $\Delta V(xy)$, is the portion of the full potential energy surface which is responsible for reaction. Thus, in the state $|i\rangle$, the system is nonreactive, translational motion of the free He atom is measured by the x coordinate, and the displacement from the origin of the oscillating H atom is measured by y. In the state $|f\rangle$, the free nonreactive H atom is allowed translational motion along the y coordinate, whereas the bound He atom oscillates in the x direction without reacting. The full potential energy surface may be decomposed as



where

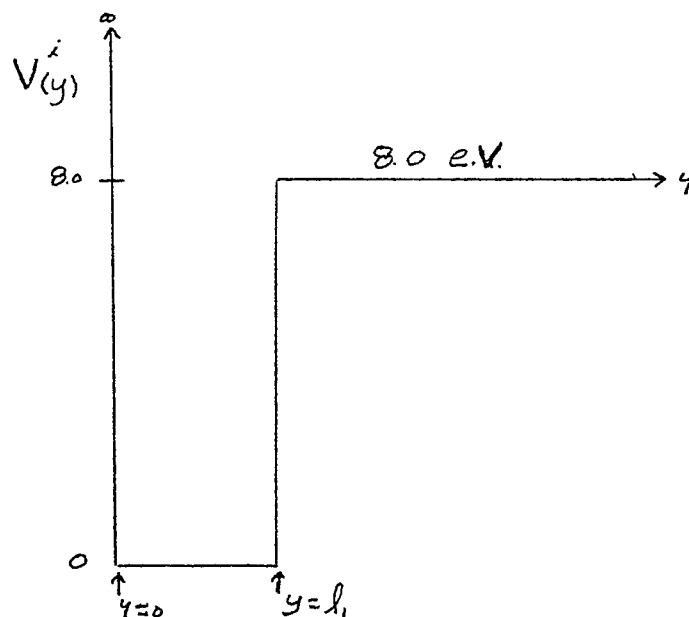
$$V(y) = \begin{cases} 8.0 \text{ e.V.} & (y > l_1) \\ 0 & (0 \leq y < l_1) \\ \infty & (y < 0), \end{cases} \quad (3-132)$$

$$V(x) = \begin{cases} \infty & (x < 0) \\ -7.154 \text{ e.V.} & (0 \leq x < l_2) \\ 0 & (x > l_2) \end{cases} \quad (3-133)$$

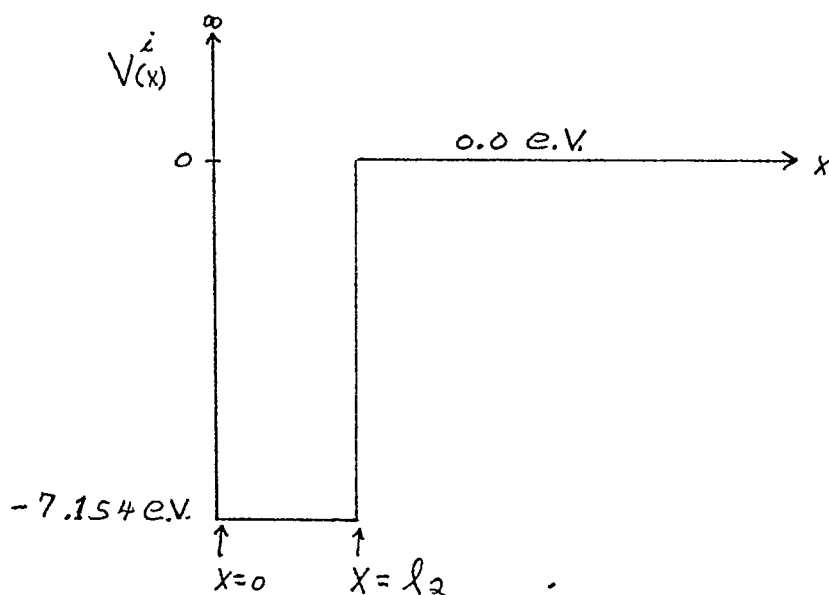
and

$$\Delta V(xy) = \begin{cases} 0 & (\text{elsewhere}) \\ 6.954 \text{ e.V.} & \begin{cases} (0 \leq y < l_1) \\ (0 \leq x < l_2) \end{cases} \end{cases} \quad (3-134)$$

The H_2^+ oscillator potential can be represented as



and the potential for the free He atom is schematically represented by



In order to obtain the initial state $|i\rangle$ of Eq. (3-131), it is necessary to solve the Schrödinger equation

$$H_o^i \Psi_i(xy) = E_i \Psi_i(xy) . \quad (3-135)$$

The Hamiltonian H_o^i is related to the full Hamiltonian by Eq. (3-128) and H_o^i is given by

$$H_o^i = T_{H_2^+} + T_{He} + V(x) + V(y) \quad (3-136)$$

and $T_{H_2^+}$ and T_{He} are the kinetic energy operators of the H and He atoms respectively. By letting

$$\Psi_i(xy) = \xi(x) \phi(y), \quad (3-137)$$

Eq. (3-135) is separable and can be expressed as

$$-\frac{1}{\xi_i} \frac{\partial^2 \xi_{ni}}{\partial x^2} + V(x) = - \left\{ -\frac{1}{\phi_{ni}} \frac{\partial^2 \phi_{ni}}{\partial y^2} + V(y) - E_{ni} \right\} = \lambda_{ni}^2 \quad (3-138)$$

where units are chosen such that $\hbar$ equals one. The solutions $\phi(y)$ are given by

$$\phi_{ni}(y) = a \sin(K_{ni} y) \quad (0 \leq y < l_1) \quad (3-139)$$

and

$$\phi_{ni}(y) = b e^{-\lambda_{ni} y} \quad (y > l_1) \quad (3-140)$$

where

$$K_{ni}^2 = 2\mu_z [E_{ni} - \mathcal{H}_{ni}^z] \quad (3-141)$$

and

$$\lambda_{ni}^2 = K_{ni}^2 - 2\mu_z V(y). \quad (3-142)$$

However, in order to simplify this calculation, we make the approximation that the wave function ϕ vanishes at $y = l_1$; therefore,

$$K_{ni} = \left\{ 2\mu_z [E_{ni} - \mathcal{H}_{ni}^z] \right\}^{\frac{1}{2}} = \frac{n_i \pi}{l_1} \quad (n_i = 1, 2, 3, \dots) \quad (3-143)$$

and

$$\phi_{ni}(y) = a \sin\left(\frac{n_i \pi}{l_1} y\right) \quad (0 \leq y < l_1). \quad (3-144)$$

The x dependent solutions of Eq. (3-138) are given as

$$\xi_{ni}(x) = A_{ni} e^{i \phi_{ni} x} + B_{ni} e^{-i \phi_{ni} x} \quad (x > l_2) \quad (3-145)$$

and

(3-146)

$$\sum_{ni}(x) = C_{ni} \sin(\nu_{ni}x) \quad (0 \leq x < l_2)$$

where

(3-147)

$$\nu_{ni}^2 = 2\mu_1 [\mathcal{H}_{ni}^2 - V'(x)]$$

and

(3-148)

$$\phi_{ni}^2 = 2\mu_1 \mathcal{H}_{ni}^2.$$

The conditions on Eqs. (3-145) and (3-146) at $x = l_2$ are that

(3-149)

$$A_{ni} e^{i\phi_{ni}l_2} + B_{ni} e^{-i\phi_{ni}l_2} = C_{ni} \sin(\nu_{ni}l_2)$$

and

(3-150)

$$i\phi_{ni} [A_{ni} e^{i\phi_{ni}l_2} - B_{ni} e^{-i\phi_{ni}l_2}] = \{C_{ni} \cos(\nu_{ni}l_2)\} \nu_{ni}.$$

The constant C_{ni} can be determined in terms of B_{ni} , and the He atom wave function in the region ($0 \leq x < l_2$) is expressed as

(3-151)

$$\sum_{ni}(x) = \left\{ \frac{2\phi_{ni}}{\phi_{ni} \sin(\nu_{ni}l_2) + i\nu_{ni} \cos(\nu_{ni}l_2)} \right\} e^{-i\phi_{ni}l_2} \sin(\nu_{ni}x)$$

where the constant B_{ni} in Eq. (3-145) has been assigned the value of one. The normalization constant, a , of Eq. (3-144) is given by

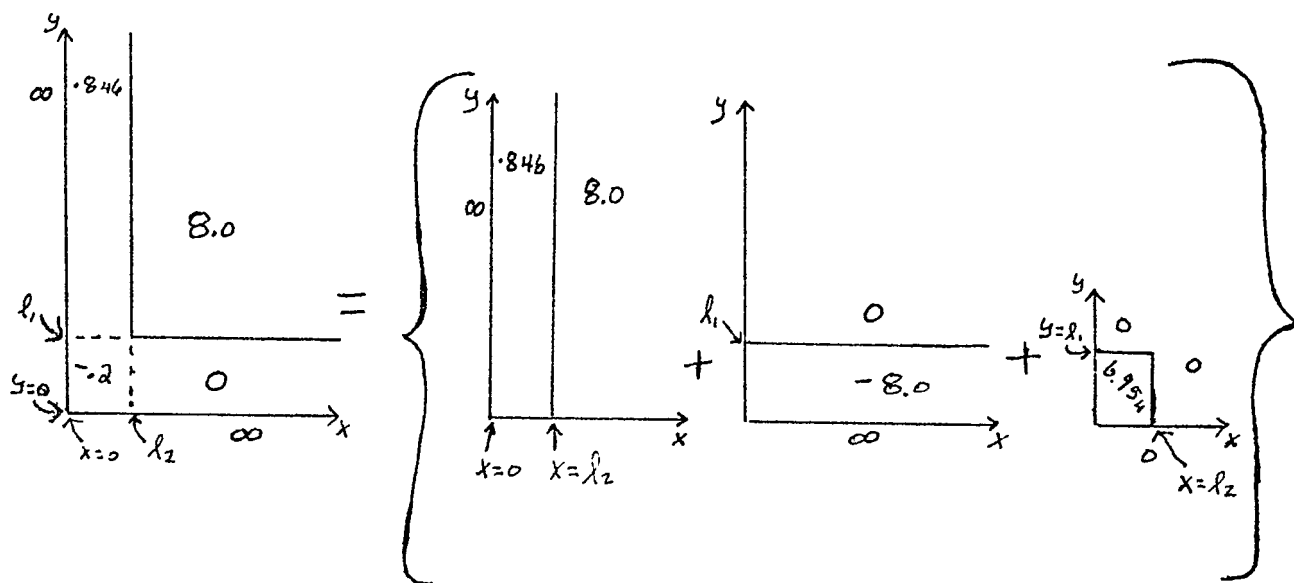
$$a = \left[\frac{2}{l_1} \right]^{\frac{1}{2}}, \quad (3-152)$$

and the initial state $|i\rangle$ can now be written as

$$(3-153)$$

$$|i\rangle = \sqrt{\frac{2}{l_1}} \left[\frac{2\phi_{ni}}{\phi_{ni} \sin(\alpha_{ni} l_2) + i \alpha_{ni} \cos(\alpha_{ni} l_2)} \right] e^{-i\phi_{ni} l_2} \sin\left(\frac{n_i \pi y}{l_1}\right) \sin(\alpha_{ni} x).$$

The state $\langle f|$ is constructed such that y denotes the displacement of the free H atom (of mass μ_2) and the position of the oscillating He atom (of mass μ_1) is designated by x . The complete potential energy surface of Fig. 4 is decomposed into the components $V^f(x)$, $V^f(y)$, and $\Delta V(xy)$ as

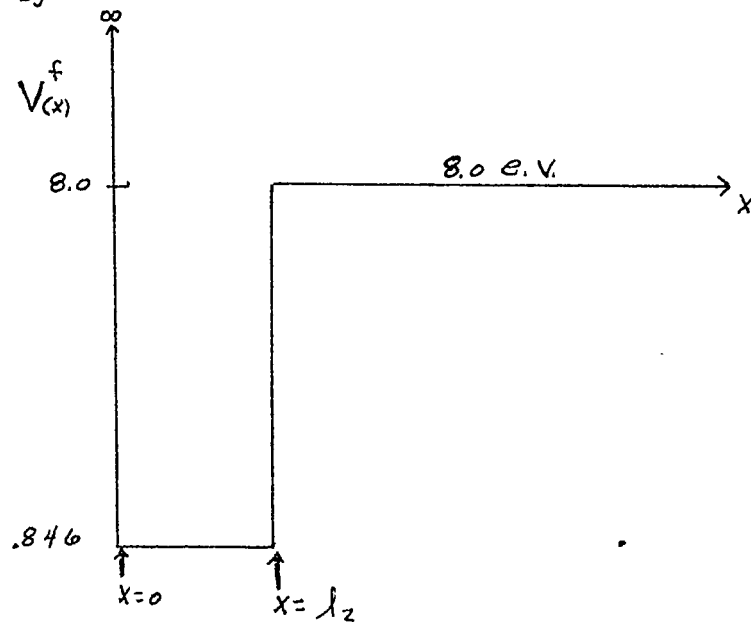


where

(3-154)

$$V_{(x)}^f = \begin{cases} \infty & (x < 0) \\ .846 \text{ e.v.} & (0 \leq x < l_2) \\ 8.0 \text{ e.v.} & (x > l_2) \end{cases}$$

and the energy surface containing the well for the HeH^+ oscillator can be represented by

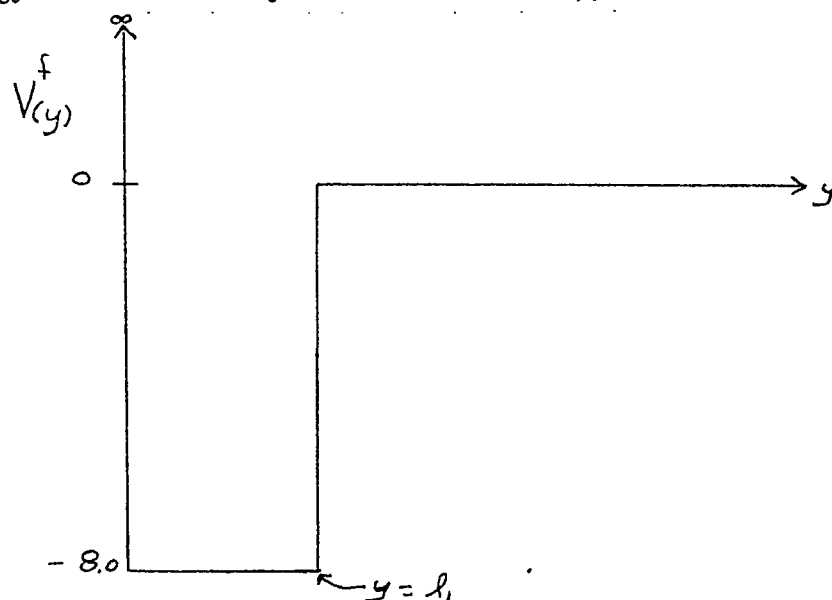


The $V(y)^f$ segment is given as

(3-155)

$$V_{(y)}^f = \begin{cases} \infty & (y < 0) \\ -8.0 \text{ e.v.} & (0 \leq y < l_1) \\ 0 & (y > l_1) \end{cases}$$

and the energy surface seen by the free H atom appears as



The remaining contribution to the full potential energy surface is $\Delta V(xy)$ and has been defined by Eq. (3-134).

The Hamiltonian H_o^f is given by

(3-156)

$$H_o^f = T_H + T_{HeH^+} + V(x) + V(y)$$

where T_H and T_{HeH^+} are the kinetic energy operators for the free H atom and the HeH^+ oscillator. The solutions $\Psi_f(xy)$ of the Schrödinger equation

(3-157)

$$H_o^f \Psi_f(xy) = E_{n_f} \Psi_f(xy)$$

are now required in order to obtain the state $\langle f|$. Equation (3-157) can be written in separable form as

$$-\frac{1}{\tilde{\epsilon}_{nf}} \frac{\partial^2 \tilde{\Sigma}_{nf}}{2\mu_2 \partial y^2} + V(y) = -\left\{ \frac{1}{\tilde{\epsilon}_{nf}} \frac{\partial^2 \phi_{nf}}{2\mu_1 \partial x^2} \quad V(x) - E_{nf} \right\} = \tilde{\mathcal{K}}_{nf}^2 \quad (3-158)$$

and the solutions to the oscillator problem are given, as before, by

$$\phi_{nf}(x) = D \sin\left(\frac{n_f \pi}{l_2} x\right) \quad (0 \leq x < l_2) \quad (3-159)$$

where

$$\tilde{\mathcal{K}}_{nf} = \left\{ 2\mu_1 (E_{nf} - \tilde{\mathcal{K}}_{nf}^2 - .844 \text{ e.V.}) \right\}^{1/2} = \frac{n_f \pi}{l_2} \quad (n_f = 1, 2, 3, \dots) \quad (3-160)$$

and

$$D = \left(\frac{2}{l_2}\right)^{1/2}. \quad (3-161)$$

The free H atom solutions from Eq. (3-157) are given by

$$\tilde{\Sigma}_{nf}(y) = A_{nf} e^{i \tilde{\Phi}_{nf} y} + B_{nf} e^{-i \tilde{\Phi}_{nf} y} \quad (y > l_1) \quad (3-162)$$

and

(3-163)

$$\xi_{nf}(y) = C_{nf} \sin(\theta_{nf} y) \quad (0 \leq y < l_1)$$

where

(3-164)

$$\tilde{\phi}_{nf}^2 = 2\mu_2 \tilde{\mathcal{H}}_{nf}^2$$

and

(3-165)

$$\theta_{nf}^2 = 2\mu_2 \left[\tilde{\mathcal{H}}_{nf}^2 + 8.0 \text{ e.v.} \right],$$

By requiring the continuity conditions on $\xi_{nf}(y)$ at $y = l_1$, the constant C_{nf} in Eq. (3-163) can be given in terms of B_{nf} , of Eq. (3-162), as

$$C_{nf} = \left[\frac{2 \tilde{\phi}_{nf}}{\tilde{\phi}_{nf} \sin(\theta_{nf} l_1) + i \theta_{nf} \cos(\theta_{nf} l_1)} \right] e^{-i \tilde{\phi}_{nf} l_1}, \quad (3-166)$$

and for the region ($0 \leq y < l_1$), the wave function $\xi_{nf}(y)$ is given by

(3-167)

$$\xi_{nf}(y) = \left[\frac{2 \tilde{\phi}_{nf}}{\tilde{\phi}_{nf} \sin(\theta_{nf} l_1) + i \theta_{nf} \cos(\theta_{nf} l_1)} \right] e^{-i \tilde{\phi}_{nf} l_1} \sin(\theta_{nf} y)$$

The final state $\langle f |$ is thus given as

(3-168)

$$\langle f | = \left\{ \sqrt{\frac{2}{l_2}} \left[\frac{2 \tilde{\phi}_{nf}}{\tilde{\phi}_{nf} \sin(\theta_{nf} l_1) + i \theta_{nf} \cos(\theta_{nf} l_1)} \right] e^{-i \tilde{\phi}_{nf} l_1} \sin\left(\frac{n_f \pi x}{l_2}\right) \sin(\theta_{nf} y) \right\}^*$$

Equation (3-131), now given by

(3-169a)

$$\mathcal{W}_{if}^{(1)} = 2\pi(\Delta V)^2 \left| \sqrt{\frac{4}{l_1 l_2}} \left(\frac{2 \tilde{\phi}_{nf}}{\tilde{\phi}_{nf} \sin(\theta_{nf} l_1) - i \theta_{nf} \cos(\theta_{nf} l_1)} \right) e^{i(\tilde{\phi}_{nf} l_1 - \phi_{ni} l_2)} \right. \\ \left. \times \left(\frac{2 \phi_{ni}}{\phi_{ni} \sin(\varphi_{ni} l_2) + i \varphi_{ni} \cos(\varphi_{ni} l_2)} \right) \int_0^{l_1} \int_0^{l_2} dy dx \sin\left(\frac{n_f \pi x}{l_2}\right) \sin(\varphi_{ni} x) \sin\left(\frac{n_i \pi y}{l_1}\right) \sin(\theta_{nf} y) \right|^2$$

(3-169b)

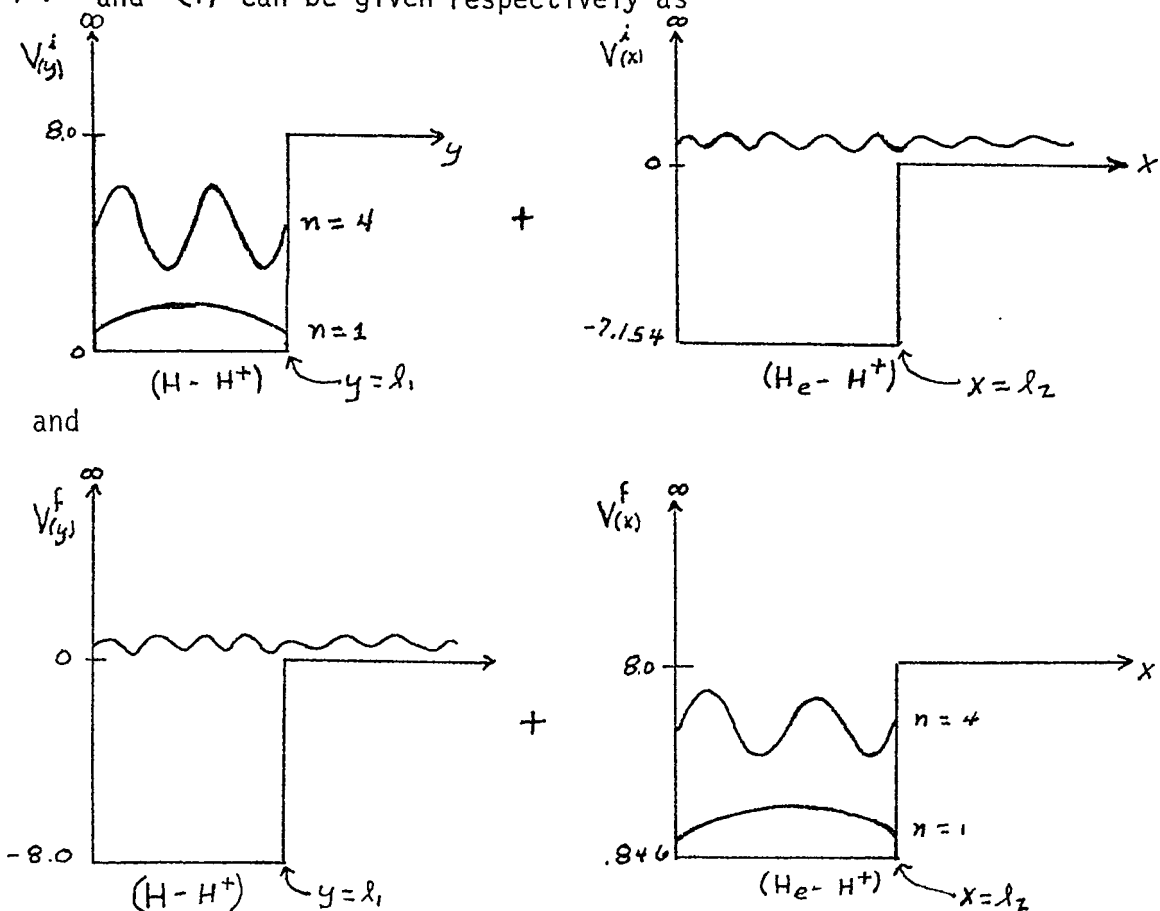
$$= \left\{ \left[\frac{4 \tilde{\phi}_{nf}^2}{\tilde{\phi}_{nf}^2 \sin^2(\theta_{nf} l_1) + \theta_{nf}^2 \cos^2(\theta_{nf} l_1)} \right] \left[\frac{4 \phi_{ni}^2}{\phi_{ni}^2 \sin^2(\varphi_{ni} l_2) + \varphi_{ni}^2 \cos^2(\varphi_{ni} l_2)} \right] \right\} \frac{(\Delta V)^2 8\pi}{l_1 l_2}$$

$$\left| \left(\frac{\sin\left[\left(\frac{n_f \pi}{l_2} - \varphi_{ni}\right) l_2\right]}{2\left(\frac{n_f \pi}{l_2} - \varphi_{ni}\right)} - \frac{\sin\left[\left(\frac{n_f \pi}{l_2} + \varphi_{ni}\right) l_2\right]}{2\left(\frac{n_f \pi}{l_2} + \varphi_{ni}\right)} \right) \left(\frac{\sin\left[\left(\frac{n_i \pi}{l_1} - \theta_{nf}\right) l_1\right]}{2\left(\frac{n_i \pi}{l_1} - \theta_{nf}\right)} - \frac{\sin\left[\left(\frac{n_i \pi}{l_1} + \theta_{nf}\right) l_1\right]}{2\left(\frac{n_i \pi}{l_1} + \theta_{nf}\right)} \right) \right|^2$$

can be employed to obtain first order perturbation theoretic calculations of the transition rates from the various vibrational states of $|i\rangle$ into the vibrational states of $\langle f|$.

Note that in both states, $|i\rangle$ and $\langle f|$, $\Delta V(xy)$ can be associated with the He-H interaction and that the attractive potentials of $\text{H}-\text{H}^+$ and $\text{He}-\text{H}^+$ are represented respectively by $V(y)$ and $V(x)$. The state $\langle f|$ is thus obtained from the state $|i\rangle$ by allowing the free He atom to interact with the bound H atom through the perturbation $\Delta V(xy)$. The bound H atom must acquire sufficient energy to become free at the expense of an energy loss for He, which is then rendered bound as HeH^+ .

The potentials with representative wave functions for the states $|i\rangle$ and $\langle f|$ can be given respectively as



where the wave functions for the oscillators correspond to the ground and third excited states. Note that the wave functions for bound particles approach the form of that given for the free particle as the energy state of the oscillator is increased, i.e., shorter wavelengths. Thus smaller amounts of energy exchange are required to produce a reaction if the initial oscillator is in a higher energy state. In such cases, the state of the final oscillator is more likely to be one of higher energy than if the initial oscillator were in the ground state. This is consistent with the $\mathcal{T}$ operator calculations for He-H_2^+ (Fig. 11) in that the reaction probabilities increase as the energy of the initial oscillator is increased and the higher energy states of the final oscillator (HeH^+) occurred most frequently when the initial oscillator was in an excited state.

These conclusions are also embedded in the transition rate equation, (3-169) which is rewritten here as

$$\mathcal{W}_{if}^{oi} = \frac{8\pi(\Delta V)^2}{\lambda_1 \lambda_2} \left\{ |C_{ni} C_{nf} F(\lambda_2) F(\lambda_1)|^2 \right\} \quad (3-170)$$

where the terms outside the brackets, $\{ \}$, are constants. The probability amplitudes, C_{ni} and C_{nf} , are given respectively, in Eqs. (3-151) and (3-166), and the definitions for $F(\lambda_1)$ and $F(\lambda_2)$ are given as

$$F(\lambda) = \int_0^{\lambda} dy \sin\left(\frac{n_i \pi y}{\lambda_1}\right) \sin(\theta_{nf} y)$$

and

$$F(\ell_2) = \int_0^{\ell_2} dx \sin\left(\frac{n_f \pi x}{\ell_2}\right) \sin(\nu_{ni} x) \quad (3-172)$$

In Eq. (3-169b), the integrated form of $F(\ell_2)$ is given as

$$F(\ell_2) = \left\{ \frac{\sin\left[\left(\frac{n_f \pi}{\ell_2} - \nu_{ni}\right)\ell_2\right]}{2\left(\frac{n_f \pi}{\ell_2} - \nu_{ni}\right)} - \frac{\sin\left[\left(\frac{n_f \pi}{\ell_2} + \nu_{ni}\right)\ell_2\right]}{2\left(\frac{n_f \pi}{\ell_2} + \nu_{ni}\right)} \right\} \quad (3-173)$$

and can be expressed as

$$\begin{aligned} F(\ell_2) &= \frac{\sin(\nu_{ni} \ell_2)}{2} \left[\frac{1}{\nu_{ni} - \frac{n_f \pi}{\ell_2}} - \frac{1}{\nu_{ni} + \frac{n_f \pi}{\ell_2}} \right] \\ &= \sin(\nu_{ni} \ell_2) \left[\frac{\mathcal{K}_{n_f}^2}{\nu_{ni}^2 - \mathcal{K}_{n_f}^2} \right], \end{aligned} \quad (3-174)$$

using the identity

$$\sin(a \pm b) = \sin a \cos b \pm \sin b \cos a. \quad (3-175)$$

Since ν_{ni} is the wave number of free He (state $|i\rangle$) over the region

$x < \ell_2$ [Eq. (3-145)] and $\mathcal{K}_{n_f}$ is the wave number of bound He

[state $\langle f|$; given in Eq.(3-160)] that $\frac{n_f \pi}{\ell_2} = \mathcal{K}_{n_f}$, Eq. (3-174)

indicates that $F(\ell_2)$ makes larger contributions to $\mathcal{H}_{if}^{(n)}$ for smaller

differences, δ_{He} , in the initial and final wave numbers of He where

δ_{He} is given by

$$\begin{aligned}\delta_{He} &= \mathcal{V}_{ni}^2 - \cancel{\mathcal{K}_{nf}}^2 & (3-176) \\ &= 2\mu_1(\mathcal{H}_{ni}^2 - 7.154 \text{ e.v.}) - 2\mu_1(E_{nf} - \tilde{\mathcal{H}}_{nf}^2 - .846 \text{ e.v.})\end{aligned}$$

Recall that $\mathcal{H}_{ni}^2$ is the initial kinetic energy for regions $x > \lambda_2$, whereas $\tilde{\mathcal{H}}_{nf}^2$ is the kinetic energy of H over the regions $y > \lambda_1$, E_{nf} is the total energy, and .846 is the endogeneity requirement. The analogous equation for $F(\lambda_1)$ is given by

$$\begin{aligned}F(\lambda_1) &= \frac{\sin(\theta_{nf} \lambda_1)}{2} \left[\frac{1}{\theta_{nf} - \frac{\eta_i \pi}{\lambda_1}} - \frac{1}{\theta_{nf} + \frac{\eta_i \pi}{\lambda_1}} \right] & (3-177) \\ &= \sin(\theta_{nf} \lambda_1) \left\{ \frac{\cancel{\mathcal{K}_{ni}}}{\theta_{nf}^2 - \cancel{\mathcal{K}_{ni}}^2} \right\}\end{aligned}$$

and the same argument follows for smaller differences, δ_H , in the initial and final wave number of H given by

$$\begin{aligned}\delta_H &= \theta_{nf}^2 - \left(\frac{\eta_i \pi}{\lambda_1}\right)^2 = \theta_{nf}^2 - \cancel{\mathcal{K}_{ni}}^2 & (3-178) \\ &= 2\mu_2(\tilde{\mathcal{H}}_{nf}^2 + 8.0 \text{ e.v.}) - 2\mu_2(E_{ni} - \mathcal{H}_{ni}^2).\end{aligned}$$

The kinetic energies are expressed in terms of the total energy, E_T , and the oscillator energies, E_{H_2} and E_{HeH^+} , as

$$\mathcal{H}_{ni}^2 = E_T - E_{H_2^+} \quad (3-179)$$

and

(3-180)

$$\tilde{\mathcal{H}}_{\eta f}^2 = E_T - E_{\text{HeH}^+} - .846 \text{ e.v.}$$

in order to write δ_H and δ_{He} as

(3-181)

$$\frac{\delta_H}{2\mu_2} = \bar{\delta}_H = (E_T - E_{\text{HeH}^+} + 7.154 \text{ e.v.}) - E_{\text{H}_2^+}$$

and

(3-182)

$$\frac{\delta_{He}}{2\mu_1} = \bar{\delta}_{He} = (E_T - E_{\text{H}_2^+} + 7.154 \text{ e.v.}) - E_{\text{HeH}^+}.$$

Consistent with higher probabilities corresponding to smaller $\bar{\delta}_H$ and $\bar{\delta}_{He}$, Eqs. (3-181) and (3-182) indicate that the probability of yielding an excited state final oscillator is greater if the initial oscillator were in an excited state. For example, in Eq. (3-181) if the energy, $E_{\text{H}_2^+}$, of the initial oscillator were large, a smaller $\bar{\delta}_H$ would result if higher energy states, E_{HeH^+} , were allowed for the final HeH^+ oscillator. If the energy state, $E_{\text{H}_2^+}$, is low for the initial H_2^+ oscillator, excited state final HeH^+ oscillators could be obtained when sufficient total energy is available. However, the corresponding $\bar{\delta}_H$ is larger (due to the smaller $E_{\text{H}_2^+}$) and the $\mathcal{W}_{if}^{(1)}$ is comparatively smaller.

From Eqs. (3-146) and (3-151), C_{ni} can be interpreted as the amplitude for the state $|i\rangle$ He atom being in the $x < l_2$ region. The absolute square of the amplitude C_{ni} , given by

$$|C_{ni}|^2 = \frac{4 \phi_{ni}^2}{\phi_{ni}^2 \sin^2(\nu_{ni} l_2) + \nu_{ni}^2 \cos^2(\nu_{ni} l_2)}, \quad (3-183)$$

is not the probability per se of finding the He atom of $|i\rangle$ in the $x < l_2$ region, but $|C_{ni}|^2$ is proportional to this probability. The wave number ϕ_{ni} is related to the kinetic energy of the He atom in the $x < l_2$ region according to Eq. (3-143) given here as

$$\phi_{ni} = 2\mu_i \mathcal{H}_{ni}^2.$$

(3-184)

Since the interaction region of the first model is defined by $\begin{cases} 0 \leq y < l_1 \\ 0 \leq x < l_2 \end{cases}$, $|C_{ni}|^2$ of Eqs. (3-183) is related to the transition coefficient, $T_{\text{He}, i \rightarrow i}$ which appears in Eq. (3-102), and the reflection coefficient, $R_{\text{He}, i \rightarrow i}$ of the first model. Both $T_{\text{He}, i \rightarrow i}$ and $|C_{ni}|^2$ become vanishingly small as $\mathcal{H}_{ni}^2$ approaches zero, and in the limit of small ϕ_{ni} and/or small $\sin(\nu_{ni} l_2)$, the expression for $|C_{ni}|^2$ is given by

(3-185)

$$|C_{ni}|^2 = \frac{4 \phi_{ni}^2}{\nu_{ni}^2 \cos^2(\nu_{ni} l_2)} \quad (\cos(\nu_{ni} l_2) \neq 0)$$

where

$$\mathcal{V}_{ni}^2 = 2\mu_1(\mathcal{V}_{ni}^2 + 7.154 \text{ e.v.}) . \quad (3-186)$$

Equation (3-167) is similarly used to interpret C_{nf} as the amplitude for the H atom of $\langle f|$ being in the $y < l_1$ region, and the absolute square of C_{nf} , given as

$$|C_{nf}|^2 = \frac{4 \tilde{\Phi}_{nf}^2}{\tilde{\Phi}_{nf}^2 \sin^2(\theta_{nf} l_1) + \theta_{nf}^2 \cos^2(\theta_{nf} l_1)} , \quad (3-187)$$

is proportional to the probability that the $\langle f|$ state H atom be in the $y < l_1$ region. The kinetic energy, $\tilde{\mathcal{H}}_{nf}^2$, of the H atom in the $y < l_1$ region is related to the wave number $\tilde{\Phi}_{nf}$, by [Eq. (3-164)].

$$\phi_{nf}^2 = 2\mu_2 \tilde{\mathcal{H}}_{nf}^2 . \quad (3-188)$$

In the limit of small ϕ_{nf} and/or small $\sin(\theta_{nf} l_1)$, the equation for $|C_{nf}|^2$ is given by

$$|C_{nf}|^2 = \frac{4 \tilde{\Phi}_{nf}^2}{\theta_{nf}^2 \cos^2(\theta_{nf} l_1)} \quad (\cos(\theta_{nf} l_1) \neq 0) \quad (3-189)$$

which implies that the probability of the $\langle f |$ state H atom being in the $y < l_1$ region becomes smaller as the kinetic energy of the H atom decreases. Note, however, that the H atom must be in the $y < l_1$ region in order for the reaction to occur, i.e., for energy exchange purposes.

2. Data and Analysis

The $\text{He} - \text{H}_2^+$ reaction [Eq. (3-98)] has been investigated⁵⁰ experimentally over the relative translational energy range of 0-10 e.v. The calculated total reaction probability curves of Figs. 7-10 compare favorably with the experimentally obtained cross-sections over the 0-1.6 e.v. energy range; i.e., the general qualitative features of the experimental and theoretical curves are compatible over the RTE values specified. However the experimental cross-section curve using ground state H_2^+ does not display an initial downward slope as shown by the $1_\alpha \rightarrow 1_\beta$ curve of Fig. 10. The difference in the experimental and the theoretical curves is likely due to an oscillation, and calculations at lower RTE should drop back to zero. The 2_α , 3_α , and 4_α total

reaction probability curves [Figs. 8-10] agree in form over the whole energy range with the corresponding experimental curves for cross-sections. The most noticeable differences are the oscillations of the calculated probability curves compared to the smooth experimental cross-section curves. After reaching a maximum, the experimental cross-section curves generally approach zero at higher RTE values, i.e., 6-10 e.v. This effect is not a prominent in the calculated probability curves due to the more restricted RTE ranges employed in the latter. This comparison implies that the experimental and theoretical treatments of the reactive collision are in qualitative agreement at least over the RTE range considered. Of course, the experimental cross-sections reflect reactions of He-H_2^+ in three dimensional space which were not necessarily the result of collinear collisions. Furthermore the He-H_2^+ interaction potential is, of course, completely smooth.

The calculated reaction probabilities were obtained, however, by restricting the collisions to be collinear. Also, the potential surface is at best only qualitative since it possesses discontinuities. Finally, the cross derivate terms in the kinetic energy operator which result from our choice of relative coordinates were neglected. The neglected cross derivate, $\frac{\partial^2}{\partial x \cdot \partial y}$, corresponds classically to the dot product of the momenta for the two reacting particles, i.e., $\hat{p}_H \cdot \hat{p}_{He}$. If this interaction were included, it is not clear how the structure of the reaction probability curves would be altered. By neglecting the cross term, the kinetic energy operator of the

Hamiltonian is diagonalized. We then scale the He atom distance such that only the H atom mass appears in the coefficients of the kinetic energy operators. This scale change for the He atom distance results in a change in the width of the exit "trough" of the potential.

The potential energy surface shown in Fig.4 is employed for the calculations. The channel width ℓ_1 is chosen to be $.37 \text{ \AA}$ so that the initial H_2^+ molecule has the correct zero point energy. The channel width ℓ_2 is taken to be $.30 \text{ \AA}$ so that the bound state energy levels of HeH^+ are correct. The potential energy of 0.846 e.v. assigned to the exit channel is the endoergicity requirement for the reaction (where the endoergicity is the difference in the binding energies of H_2^+ and HeH^+). The interaction region is a potential well of -0.2 e.v. which is obtained from the ab initio energy surface for HeH_2^+ generated by Brown and Hayes⁵¹. The region designated as V_0 was assigned a value of 8.0 e.v. in order to obtain a sufficient number of bound HeH^+ states with the present version of the program. A value such as 2.4 e.v. which correspond more closely to the H_2^+ binding energy would produce a more realistic simulation of the He-H_2^+ energy surface. An important consequence of this is the fact that the perturbation, $\Delta V(xy)$ which is responsible for the reaction in the second descriptive model, would become $+ 1.354 \text{ e.v.}$ compared to the ΔV of $+ 6.954 \text{ e.v.}$ when $V_0 = 8.0 \text{ e.v.}$

The reaction probabilities computed with coupled $\mathcal{Z}$ operator equations can be discussed in a "physical sense", using the two qualitative models introduced in the previous section. The reactant

oscillator, H_2^+ , is in configuration α and notation 1_α , 2_α , 3_α , and 4_α is used to indicate respectively, the first four vibrational energy states of H_2^+ . In configuration β , HeH^+ is the oscillator and the first three vibrational energy states are denoted by 1_β , 2_β , and 3_β respectively. Thus, the notation $3_\alpha \rightarrow 1_\beta$ is used to represent the reactive collision of a third vibrational state H_2^+ with He yielding a ground state HeH^+ (1_β) and H.

In Figures 7-10, reaction probabilities versus relative translational energy of reactants are plotted for the first four vibrational energy states of H_2^+ where the first three energy states of HeH^+ are available as product oscillator. In Fig. 7, the initial oscillator, H_2^+ , is in the third vibrational energy state (3_α) with an internal energy of 1.22 e.v. The minimum energy required for a $3_\alpha \rightarrow 1_\beta$ reaction is 1.047 e.v. which is the sum of the HeH^+ ground state (.201 e.v.) and the endoergicity requirements (.846 e.v.). Since this energy requirement is less than the internal vibrational energy (1.22 e.v.), the $3_\alpha \rightarrow 1_\beta$ reaction probabilities are non zero at very low relative translational energies. Note, however, that the reaction probabilities decreases sharply as the relative translational energy, RTE, approaches zero and that such behavior is consistent with predictions of both qualitative models.

The reaction probability curves in Fig. 7 exhibit two characteristic features which are found in the other reaction probability curves corresponding to the calculations using the initial H_2^+ oscillator states of 1_α , 2_α , and 4_α . First, the individual reaction probability curves in Fig. 7 fluctuate considerably and the curve, $\sum R$, representing

the sum of reaction probabilities displays an oscillatory behavior as a function of translational energy. Second, increases in reaction probabilities are observed for the newly opened reactive channels compared to the reaction probabilities of those channels which opened at lower energies, i.e., $3_{\alpha} \rightarrow 2_{\beta}$ and $3_{\alpha} \rightarrow 3_{\beta}$ are the newly opened channels in Fig. 7.

The energies corresponding to the second and third vibrational states of HeH^+ are .804 e.v. and 1.80 e.v., respectively. The $3_{\alpha} \rightarrow 2_{\beta}$ channel requires a total energy of 1.65 e.v. (.846 e.v. + .804 e.v.) and opens at the threshold translational energy of .43 e.v. (=1.65 e.v. -1.22 e.v.). The ensuing reaction probabilities are enhanced for this newly opened channel compared to the probabilities of the $3_{\alpha} \rightarrow 1_{\beta}$ channel. Such behavior is predicted by Eq. (3-174), rewritten here as

(3-190)

$$F(\ell_2) = \sin(\nu_{ni}\ell_2) \left[\frac{\kappa'_{nf}}{\nu_{ni}^2 - \kappa_{nf}^2} \right]$$

which indicates that $F(\ell_2)$ becomes larger for smaller differences in the initial and final wave numbers for the He atom. Since κ'_{nf} is given by

(3-191)

$$\kappa_{nf}^2 = 2\mu_1(E_{\text{HeH}^+})$$

where E_{HeH^+} is the HeH^+ oscillator energy, the difference in the wave number, $\mathcal{Z}_{ni}$, of free He and the wave number, $\mathcal{K}_{nf}$, of bound He is less when $\mathcal{K}_{nf}$ is the He atom wave number for the second vibrational state rather than the ground state of HeH^+ . The contribution of to $\mathcal{W}_{if}^{(1)}$ [Eq. (3-170)] is accordingly larger for the smaller differences in wave numbers, and since the reaction probability is proportional to $\mathcal{W}_{if}^{(1)}$, the probability curve of the newly opened $3_\alpha \rightarrow 2_\beta$ channel is qualitatively consistent with the first order transition rate expression of Eq. (3-171).

The next reactive channel to open in Fig. 7 is $3_\alpha \rightarrow 3_\beta$ which requires a total energy of 2.646 e.v. (=1.80 e.v. + .846 e.v.) and the threshold energy is 1.42 e.v. (=2.64 e.v. - 1.22 e.v.). The reaction probabilities of the newly opened channel are seen to increase here as previously described, and the same argument applies to the newly opened $3_\alpha \rightarrow 3_\beta$ channel as was applied to the newly opened $3_\alpha \rightarrow 2_\beta$ channel. Thus with each opening of a new reactive channel, the difference in wave numbers between the free He atom and bound Helium is less since the bound atoms occupy higher energy states. Associated with this "likeness of wave number" is an enhancement of the reaction probabilities into the said channels. Recall that the transition rate expression $\mathcal{W}_{if}^{(1)}$ is the absolute square of a product of four quantities, the two integrals $F(\ell_1)$ and $F(\ell_2)$ and the two amplitudes C_{ni} and C_{nf} . The integral $F(\ell_2)$ is given on previous page by Eq. (3-190) and the absolute square of the amplitude C_{ni} is rewritten here for convenience

as

$$|C_{ni}|^2 = \frac{4 \phi_{ni}^2}{\phi_{ni}^2 \sin^2(\nu_{ni} l_2) + \nu_{ni}^2 \cos^2(\nu_{ni} l_2)} \quad (3-192)$$

The physical variables in Eqs. (3-190) and (3-192) are the wave numbers ν_{ni} , K_{nf} , and ϕ_{ni} respectively for free and bound He at $x < l_2$ and free He at $x > l_2$. Thus the quantity $\sin(\nu_{ni} l_2)$ in Eq. (3-190) would cause oscillation in the reaction probability curves for individual channels such as that demonstrated by the $3\alpha \longrightarrow 1\beta$ curve of Fig. 7. The sine function would also cause $\mathcal{N}_{if}^{(1)}$ to vanish, of course, when the product $\nu_{ni} l_2$ is equal to $n\pi$ ($n = 1, 2, 3, \dots$). The cosine and sine functions in the denominator of Eq. (3-192) also cause oscillatory behavior in $\mathcal{N}_{if}^{(1)}$, whereas $|C_{ni}|^2$ vanishes only if ϕ_{ni} vanishes. The analogous arguments apply to the quantities $F(l_i)$ and $|C_{nf}|^2$ given respectively by Eqs. (3-177) and (3-187) where the wave numbers θ_{nf} , K_{ni} , and $\tilde{\phi}_{nf}$ are for the H atom. Therefore, $\mathcal{N}_{if}^{(1)}$ expressed as a product of these four quantities as in Eq. (3-170) would be expected to demonstrate some type of oscillatory behavior as a function of relative translational energy.

In Fig. 8, the initial oscillator is in the fourth vibrational state (4α) at an energy level of 2.16 e.v. which is sufficient to open both of the first two reactive channels, i.e., $4\alpha \longrightarrow 1\beta$, which requires 1.047 e.v. ($= .201 \text{ e.v.} + .846 \text{ e.v.}$) and $4\alpha \longrightarrow 2\beta$, which

requires 1.65 e.v. ($=.804 \text{ e.v.} + .846 \text{ e.v.}$). These channels which are opened by the availability of sufficient vibrational energy are seen to exhibit similar reaction probabilities for low RTE (relative translational energy) values; e.g., the reaction probability curves for $4\alpha \rightarrow 1\beta$, $4\alpha \rightarrow 2\beta$, and $3\alpha \rightarrow 1\beta$ (Fig. 7) decline very rapidly as the RTE value converges toward zero. Such behavior appears to be independent of the particular channels available for reaction but dependent on the relative kinetic energy as discussed in the descriptive models. The large dip observed in the reaction probabilities of the $3\alpha \rightarrow 1\beta$ channel is also seen, to a lesser extent, in the $4\alpha \rightarrow 1\beta$ curve at approximately the same RTE value of .29 e.v. However the dip observed in the total probabilities for $3\alpha \text{ } H_2^+$ (Fig. 11) does not occur in $4\alpha \text{ } H_2^+$ (Fig. 8) since the open 2β channel is sufficiently reactive to mask the decrease in 1β reactivity.

After opening the $4\alpha \rightarrow 3\beta$ channel at a total energy of 2.646 e.v. ($=1.80 \text{ e.v.} + .846 \text{ e.v.}$) and a RTE value of 0.48 e.v. ($=2.160 \text{ e.v.}$), the 3β channel reaction probabilities increase rapidly as a function of RTE, which is the expected pattern for a newly opened channel. However, the characteristic high probability "peak" which usually accompanies the opening of a new channel (e.g., $3\alpha \rightarrow 3\beta$ of Fig. 7) is not seen in the $4\alpha \rightarrow 3\beta$ curve of Fig. 8 due to a lower maximum RTE value. This results from using the same maximum total energy for each of the different H_2^+ initial states. The range of relative translational energy is thus decreased (Figs. 11 and 12) as the energy level of the

initial H_2^+ oscillator increases from 1_α to 4_α .

The reaction probability curves for the second vibrational H_2^+ state (2_α) are shown in Fig. 9. The $2_\alpha \rightarrow 1_\beta$ channel opens at a total energy value of 1.047 e.v. ($= .201 \text{ e.v.} + .846 \text{ e.v.}$) with the threshold RTE being .505 e.v. ($= 1.047 \text{ e.v.} - .542 \text{ e.v.}$). The 1_β reaction probability curve then increases until the $2_\alpha \rightarrow 2_\beta$ channel opens at a total energy requirement of 1.65 e.v. ($= .804 \text{ e.v.} + .846 \text{ e.v.}$) and threshold RTE value of 1.118 e.v. ($= 1.650 \text{ e.v.} - .542 \text{ e.v.}$). The reaction probability for the 1_β channel then decreases more sharply than that of the 2_β channel, which is usual pattern. However at higher RTE values, the reaction probabilities display large oscillations and a "spike" in the 1_β curve is greater than a similar "spike" in the 2_β curve. The reaction probability curves for the $2_\alpha \rightarrow 3_\beta$ and $1_\alpha \rightarrow 3_\beta$ (Fig. 10) channels exhibit clearly the expected behavior associated with close matching of the wave number for the initially free He atom and the wave number for the He atom when it is bound.

The probability curves for the H_2^+ ground state (1_α) initial oscillator are given in Fig. 10. The total reaction probabilities shown by the curve, ΣR , are seen to be less for the 1_α H_2^+ compared to the total probabilities arising from the 2_α , 3_α , and 4_α initial H_2^+ states, as shown in Fig. 11. This pattern is consistent with the model prediction that when the bound H atom wave number and final free H atom wave number are close, reaction is enhanced. That is higher vibrational states of H_2^+ correspond to "more nearly free" H atoms.

APPENDIX A

TRANSITION PROBABILITIES FOR THE CHANNEL $\tilde{\tau}$ OPERATOR
EQUATIONS

The transition probabilities are obtained from the asymptotic form of the scattering wave function $\Psi^+(xy)$. For the nonreactive collision, Y remains finite as X approaches infinity and the scattering wave function is written as

$$\lim_{X \rightarrow \infty} \Psi^+(xy) = C \left[e^{-i k_{n_0} X} \phi(n|y) + \sum_{n=1}^N \rho_n e^{i k_n X} \phi(n|y) \right] \quad (\text{A-1})$$

where C is a constant and N is the number of open channels. The transition probabilities, $P_{n_0 \rightarrow n}^{(R)}$, for nonreactive collision are then given by

$$P_{n_0 \rightarrow n}^{(R)} = \left(k_n / k_{n_0} \right) \left| \rho_n \right|^2. \quad (\text{A-2})$$

From Eq. (3-36) the scattering state Ψ^+ can be written in terms of $\tilde{\tau}_{\alpha\alpha}$ as

$$\Psi^+(xy) = \Theta_\alpha + (E - K_\alpha + i\epsilon)^{-1} \tilde{\tau}_{\alpha\alpha} \Theta_\alpha \quad (\text{A-3})$$

which can also be expressed as

$$\sum_n \Psi(n|x) \phi(n|y) = \Theta_\alpha + (E - K_\alpha + i\epsilon)^{-1} \sum_n \chi(n|x) \phi(n|y) \quad (\text{A-4})$$

by using Eq. (3-44) and expanding the scattering state Ψ^+ as

$$\Psi^+ = \sum_n \Psi(n|x) \phi(n|y). \quad (\text{A-5})$$

Equation (A-4) can be multiplied by $\phi(l|y)$ and integrated with respect to y to yield

$$\begin{aligned} \Psi(l|x) &= \sin k_{n_0} x \int_0^\infty \phi(n_0|y) \phi(l|y) dy \\ &\quad - \frac{1}{k_l} \int_0^\infty e^{i k_l x} \sin(k_l x') \chi(l|x') dx'. \end{aligned} \quad (\text{A-6})$$

In the asymptotic limit of x , Eq. (A-6) becomes

$$\begin{aligned} \lim_{x \rightarrow \infty} \Psi(l|x) &= \sin(k_{n_0} x) \delta_{n_0, l} - \frac{e^{i k_l x}}{k_l} \int_0^\infty dx' \sin k_l x' \chi(l|x') \\ &= \sin k_{n_0} x \delta_{n_0, l} - \frac{e^{i k_l x}}{k_l} R_l. \end{aligned} \quad (\text{A-7})$$

Equation (A-7) can now be substituted into Eq. (A-5) to produce

$$\begin{aligned}
 \lim_{x \rightarrow \infty} \Psi^+(x, y) &= \sum_{n=1}^N \left\{ \sin k_n x \delta_{n_0 n} - \frac{e^{i k_n x}}{k_n} R_n \right\} \phi(n, y) \quad (\text{A-8}) \\
 &= \sin k_{n_0} x \phi(n_0, y) - \frac{e^{i k_{n_0} x}}{k_{n_0}} R_{n_0} \phi(n_0, y) \\
 &\quad - \sum_{n \neq n_0}^N \left(\frac{e^{i k_n x}}{k_n} \right) R_n \phi(n, y)
 \end{aligned}$$

which can be rewritten as

$$\begin{aligned}
 \lim_{x \rightarrow \infty} \Psi^+(x, y) &= \frac{-1}{2i} \left\{ e^{-i k_{n_0} x} \phi(n_0, y) - \left(1 - \frac{2i R_{n_0}}{k_{n_0}} \right) \right. \\
 &\quad \left. x e^{i k_{n_0} x} \phi(n_0, y) \right\} \quad (\text{A-9}) \\
 &\quad - \frac{1}{2i} \sum_{n \neq n_0} \left(\frac{2i e^{i k_n x}}{k_n} \right) R_n \phi(n, y).
 \end{aligned}$$

By equation Eqs. (A-1) and (A-9), the constant C can be identified with $-\frac{1}{2i}$ and it follows that

$$\rho_{n_0} = - \left[1 - \frac{2i R_{n_0}}{k_{n_0}} \right] \quad (\text{A-10})$$

and

$$\rho_n = \frac{2i R_n}{k_n} \quad (n \neq n_0). \quad (\text{A-11})$$

The nonreactive transition probabilities are therefore given as

$$P_{n_0 \rightarrow n}^{(R)} = \left| 1 - \frac{2i R_{n_0}}{R_{n_0}} \right|^2 \quad (\text{A-12})$$

and

$$P_{n_0 \rightarrow n_0}^{(R)} = \frac{4}{k_{n_0} k_n} |R_n|^2. \quad (\text{A-13})$$

A similar analysis can be used to show that the transition probability, $P_n(T)$, for the reactive channel are given by

$$P_{n_0 \rightarrow n}^{(T)} = \frac{4}{k_{n_0} k_n} |T_n|^2 \quad (\text{A-14})$$

APPENDIX B

CHANNEL $\tilde{\tau}$ OPERATOR FORMALISM FOR THREE BODY COLLISIONS
WITH SMOOTH INTERACTION POTENTIALS.

Baer and Kouri have generalized the $\tilde{\tau}$ operator formalism to treat non-collinear reactive collisions in three dimensions with angle dependent potential energy surfaces. A further refinement of the $\tilde{\tau}$ formalism would result if the piecewise constant potential were replaced with a "smooth" potential in order to more closely approximate the actual interaction potential of an atomic system. However, it is convenient if the functions employed to represent the "smooth" potential have the same separable qualities as the piecewise constant potentials. One possible function is the Morse potential⁵² which has been successfully used^{53,54} to approximate the potential energy of diatomic molecules.

The purpose of this chapter is to present the $\tilde{\tau}$ operator equations for treating the collinear reactive system of Li-HBr where the interactions are represented with Morse potentials.

The collision system can be schematically represented by Fig. 2 if the center atom, Br, is taken to be infinitely massive. When Li is far from Br, the scattering system is in the α configuration, whereas it is in the β configuration when the H atom is far from Br.

The total interaction potential $V_T(R_\alpha, R_\beta)$ is given by

(B-1)

$$V_T(R_\alpha, R_\beta) = V_{LiBr}(R_\alpha) + V_{HBr}(R_\beta) + V_{LiH}(R_\alpha + R_\beta)$$

where Morse potentials will be used to express the two particle interactions V_{LiBr} , V_{HBr} , and V_{LiH} . In the α configuration, R_α is large and the perturbation $V_\alpha(R_\alpha, R_\beta)$ is given by

$$V_\alpha(R_\alpha, R_\beta) = V_T(R_\alpha, R_\beta) - V_{\text{HBr}}(R_\beta) \quad (\text{B-2})$$

This can be written in a separable form as

$$V(R_\alpha, R_\beta) = \sum_{\lambda=1}^3 A_{\alpha\lambda}(R_\alpha) B_{\alpha\lambda}(R_\beta) \quad (\text{B-3})$$

where

$$A_{\alpha 1}(R_\alpha) = D_e^{(1)} e^{-a_1(R_\alpha - R_1^e)} \left[e^{-a_1(R_\alpha - R_1^e)} - 2 \right] \quad (\text{B-4})$$

$$B_{\alpha 1}(R_\beta) = 1.0, \quad (\text{B-5})$$

$$A_{\alpha 2}(R_\alpha) = \left[D_e^{(3)} \right]^{1/2} \left[e^{-2a_3(R_\alpha - R_3^e/2)} \right], \quad (\text{B-6})$$

$$B_{\alpha 2}(R_\beta) = \left[D_e^{(3)} \right]^{1/2} \left[e^{-2a_3(R_\beta - R_3^e/2)} \right], \quad (\text{B-7})$$

$$A_{\alpha 3}(R_\alpha) = \left[2 D_e^{(3)} \right]^{1/2} \left[e^{-a_3(R_\alpha - R_3^e/2)} \right], \quad (\text{B-8})$$

and

$$B_{\alpha 3}(R_\beta) = \left[2 D_e^{(3)} \right]^{1/2} \left[e^{-a_3(R_\beta - R_3^e/2)} \right]. \quad (\text{B-9})$$

We note that the $A_{\alpha i}$ ($i = 1, 2, 3$) are function of R_α only and the $B_{\alpha i}$ are functions of R_β . In equations (B-4) through (B-9), the constants $D_e^{(j)}$, a_j , and R_j^e occur in the Morse function representing the j th interaction potential where j is 1, 2, or 3 corresponding to the LiBr, HBr, or LiH interaction terms, respectively. The perturbation V_β is given as

(B-10)

$$V_\beta(R_\alpha, R_\beta) = V_\tau(R_\alpha, R_\beta) - V_{LiBr}(R_\alpha)$$

which has a separable form analogously expressed as

(B-11)

$$V_\beta(R_\alpha, R_\beta) = \sum_{i=1}^3 A_{\beta i}(R_\alpha) B_{\beta i}(R_\beta)$$

with

(B-12)

$$A_{\beta 1}(R_\alpha) = 1.0 ,$$

(B-13)

$$B_{\beta 1}(R_\beta) = D_e^{(2)} e^{-a_2(R_\beta - R_2^e)} \left[e^{-a_2(R_\beta - R_2^e)} - 2 \right],$$

(B-14)

$$A_{\beta 2}(R_\alpha) = \left[D_e^{(3)} \right]^{\frac{1}{2}} \left[e^{-2a_3(R_\alpha - R_3^e/2)} \right],$$

(B-15)

$$B_{\beta 2}(R_\beta) = \left[D_e^{(3)} \right]^{\frac{1}{2}} \left[e^{-2a_3(R_\beta - R_3^e/2)} \right],$$

(B-16)

$$A_{\beta 3}(R_\alpha) \quad \left[2 \mathcal{D}_e^{(3)} \right]^{\frac{1}{2}} \left[e^{-a_3(R_\alpha - R_3^e/2)} \right],$$

and

(B-17)

$$B_{\beta 3}(R_\beta) \quad \left[2 \mathcal{D}_e^{(3)} \right]^{\frac{1}{2}} \left[e^{-a_3(R_\beta - R_3^e/2)} \right].$$

It is recalled from Chapter III that the coupled equations for the channel operators are given as

(B-18)

$$\tilde{\tau}_{\alpha\alpha} = V_\alpha + V_\alpha (E - K_\beta + i\epsilon)^{-1} \tilde{\tau}_{\beta\alpha}$$

and

(B-19)

$$\tilde{\tau}_{\beta\alpha} = V_\alpha \quad V_\beta (E - K_\alpha + i\epsilon)^{-1} \tilde{\tau}_{\alpha\alpha}.$$

Operating with the channel operators on the eigenstate,

$\Theta(v_\alpha^\circ | R_\alpha R_\beta)$ of the unperturbed Hamiltonian K_α , the amplitude densities $\chi_\alpha(v_\alpha | R_\alpha)$ and $\chi_\beta(v_\beta | R_\beta)$ result which can be expanded in terms of the bound state vibrational functions, $u_\alpha(v_\alpha | R_\beta)$ and $u_\beta(v_\beta | R_\alpha)$, as

(B-20)

$$\tilde{\tau}_{\alpha\alpha} \Theta(v_\alpha^\circ | R_\alpha R_\beta) = \sum_{v_\alpha} \chi_\alpha(v_\alpha | R_\alpha) u_\alpha(v_\alpha | R_\beta)$$

and

(B-21)

$$\tilde{\tau}_{\beta\alpha} \Theta(\nu_\alpha^0 | R_\alpha R_\beta) = \sum_{\nu_\beta} \chi_\beta(\nu_\beta | R_\beta) U_\beta(\nu_\beta | R_\alpha).$$

The bound state function $U_\beta(\nu_\beta | R_\beta)$, are Morse eigenfunctions. The unperturbed eigenfunctions, $\Theta(\nu_\alpha^0 | R_\alpha R_\beta)$, are given by

(B-22)

$$\Theta(\nu_\alpha^0 | R_\alpha R_\beta) = U_\alpha(\nu_\alpha^0 | R_\beta) \sin(K_{\nu_\alpha^0} R_\alpha)$$

where K is the wave number, and ν is the vibrational quantum number.

By multiplying Eqs. (B-20) and (B-21) by $\Theta^*(\nu_\alpha | R_\alpha R_\beta)$ and integrating over the R_α and R_β , the transition amplitude matrix elements can then be expressed as

(B-23)

$$\langle \Theta(\nu_\alpha) | \tilde{\tau}_{\alpha\alpha} | \Theta(\nu_\alpha^0) \rangle = \int dR_\alpha \sin[K_{\nu_\alpha} R_\alpha] \chi_\alpha(\nu_\alpha | R_\alpha)$$

and

(B-24)

$$\langle \Theta(\nu_\beta) | \tilde{\tau}_{\beta\alpha} | \Theta(\nu_\alpha^0) \rangle = \int dR_\beta \sin(K_{\nu_\beta} R_\beta) \chi_\beta(\nu_\beta | R_\beta)$$

These $\tilde{\tau}$ elements can therefore be computed once the $\chi(\nu | R)$ are known.

Equations for the $\chi(\nu | R)$ can be obtained by employing Eqs.

(B-18) and (B-19) to rewrite Eqs. (B-20) and (B-21) as

(B-25)

$$\sum_{\nu_\alpha} \chi_\alpha(\nu_\alpha | R_\alpha) U_\alpha(\nu_\alpha | R_\beta) = V_\alpha(R_\alpha R_\beta) \Theta(\nu_\alpha^\circ | R_\alpha R_\beta)$$

$$+ V_\alpha(R_\alpha R_\beta) \int dR'_\alpha \int dR'_\beta G_\beta(R_\alpha R_\beta | R'_\alpha R'_\beta) \sum_{\nu_\beta} \chi_\beta(\nu_\beta | R'_\beta) U_\beta(\nu_\beta | R'_\alpha)$$

and

(B-26)

$$\sum_{\nu_\beta} \chi_\beta(\nu_\beta | R_\beta) U_\beta(\nu_\beta | R_\alpha) = V_\beta(R_\alpha R_\beta) \Theta(\nu_\beta^\circ | R_\alpha R_\beta)$$

$$+ V_\beta(R_\alpha R_\beta) \int dR'_\alpha \int dR'_\beta G_\alpha(R_\alpha R_\beta | R'_\alpha R'_\beta) \sum_{\nu_\alpha} \chi_\alpha(\nu_\alpha | R'_\alpha) U_\alpha(\nu_\alpha | R'_\beta)$$

By multiplying Eqs. (B-25) and (B-26) by $U_\alpha(\nu_\alpha | R_\beta)$ and $U_\beta(\nu_\beta | R_\alpha)$, respectively and integrating over the appropriate R , the $\chi(\nu | R)$ are found to satisfy coupled integral equations given by

(B-27)

$$\begin{aligned} \chi_\alpha(\nu_\alpha | R_\alpha) = & \int dR_\beta U_\alpha(\nu_\alpha | R_\beta) V_\alpha(R_\alpha R_\beta) U_\alpha(\nu_\alpha^\circ | R_\beta) \sin(k_{\nu_\alpha^\circ} R_\alpha) \\ & + \int dR_\alpha U_\beta(\nu_\beta | R_\alpha) V_\beta(R_\alpha R_\beta) \int dR'_\alpha \int dR'_\beta G_\alpha(R_\alpha R_\beta | R'_\alpha R'_\beta) \sum_{\nu_\alpha} \chi_\alpha(\nu_\alpha | R'_\alpha) U_\alpha(\nu_\alpha | R'_\beta) \end{aligned}$$

(B-28)

$$\begin{aligned} \chi_p(z_p|R_p) &= \int dR_\alpha U_p(z_p|R_\alpha) V_\alpha(R_\alpha R_p) U_\alpha(z_\alpha|R_p) \sin K_{z_\alpha} R_\alpha \\ &\int dR'_\alpha U_p(z_p|R_\alpha) V_\alpha(R_\alpha R_p) \int dR'_\alpha \int dR'_\beta G_\alpha(R_\alpha R_p | R'_\alpha R'_\beta) \sum_{\gamma_\alpha} \chi_\alpha(z_\alpha|R'_\alpha) U_\alpha(z_\alpha|R'_\beta). \end{aligned}$$

The Green function $G_p(R_\alpha R_p | R'_\alpha R'_\beta)$ was obtained in Chapter III and is given here as

(B-29)

$$G_p(R_\alpha R_p | R'_\alpha R'_\beta) = -i \sum_{\gamma_p} \frac{1}{K_{\gamma_p}} e^{i K_{\gamma_p} R_p} \sin K_{\gamma_p} R_\alpha U_p(z_p|R_p) U_p^*(z_p|R'_\beta)$$

where R_α and R_p are the lesser and greater respectively of R and R' . The resulting integrals in Eqs. (B-27) and (B-28) are now executed to give

(B-30)

$$\begin{aligned} \chi_\alpha(z_\alpha|R_\alpha) &= \sin K_{z_\alpha} R_\alpha \int_0^\infty dR_\beta U_\alpha(z_\alpha|R_\beta) V_\alpha(R_\alpha R_\beta) U'_\alpha(z_\alpha|R_\beta) \\ &- i \sum_{\gamma_p} U_p(z_p|R_\alpha) \int_0^\infty dR_\beta U_\alpha(z_\alpha|R_\beta) V_\alpha(R_\alpha R_\beta) F_p(z_p|R_\beta) \end{aligned}$$

and

(B-31)

$$\begin{aligned} \chi_p(z_p|R_p) &= U_\alpha(z_\alpha|R_p) \int_0^\infty dR_\alpha U_p(z_p|R_\alpha) V_\alpha(R_\alpha R_p) \sin K_{z_\alpha} R_\alpha \\ &- i \sum_{\gamma_\alpha} U_\alpha(z_\alpha|R_p) \int_0^\infty dR_\alpha U_p(z_p|R_\alpha) V_\alpha(R_\alpha R_p) F_\alpha(z_\alpha|R_\alpha) \end{aligned}$$

where

$$F_p(z_p|R_p) = \frac{1}{\kappa_{z_p}} \int_0^\infty dR'_p \chi_p(z_p|R'_p) J_p(R_{p<}|R_{p>}) \quad (\text{B-32})$$

and

$$J_p(R_{p<}|R_{p>}) = \sin \kappa_{z_p} R_{p<} e^{i \kappa_{z_p} R_{p>}}. \quad (\text{B-33})$$

It is now convenient to express Eqs. (B-30) and (B-31) in terms of the $F_p(z_p|R_p)$. Thus each equation is multiplied by the appropriate $J_p(R_{p<}|R_{p>})/\kappa_{z_p}$ and integrated over the corresponding R_p to yield

$$\begin{aligned} F_\alpha(z_\alpha|R_\alpha) &= \frac{1}{\kappa_{z_\alpha}} \int_0^\infty dR'_\alpha J_\alpha(R_{\alpha<}|R_{\alpha>}) \sin \kappa_{z_\alpha} R'_\alpha \int_0^\infty dR_\beta U_\alpha(z_\alpha|R_\beta) V_\alpha(R_\alpha R_\beta) U_\alpha(z_\alpha|R_\beta) \\ &\quad - \frac{i}{\kappa_{z_\alpha}} \sum_{\beta} \int_0^\infty dR'_\alpha J_\alpha(R_{\alpha<}|R_{\alpha>}) U_\beta(z_\beta|R'_\alpha) \int_0^\infty dR_\beta F_\beta(z_\beta|R_\beta) V_\alpha(R_\alpha R_\beta) U_\alpha(z_\alpha|R_\beta) \end{aligned} \quad (\text{B-34})$$

and

$$\begin{aligned} F_\beta(z_\beta|R_\beta) &= \frac{1}{\kappa_{z_\beta}} \int_0^\infty dR'_\beta J_\beta(R_{\beta<}|R_{\beta>}) U_\alpha(z_\alpha|R'_\beta) \int_0^\infty dR_\alpha U_\beta(z_\beta|R_\alpha) V_\alpha(R_\alpha R'_\beta) \sin \kappa_{z_\alpha} R_\alpha \\ &\quad - \frac{i}{\kappa_{z_\beta}} \sum_{\alpha} \int_0^\infty dR'_\beta J_\beta(R_{\beta<}|R_{\beta>}) U_\alpha(z_\alpha|R'_\beta) \int_0^\infty dR_\alpha F_\alpha(z_\alpha|R_\alpha) V_\beta(R_\alpha R'_\beta) U_\beta(z_\beta|R_\alpha). \end{aligned} \quad (\text{B-35})$$

Since the perturbations $V_\alpha(R_\alpha, R_\beta)$ and $V_\beta(R_\alpha, R_\beta)$ are separable in R_α and R_β as indicated by Eqs. (B-) and (B-11), the separable equations for $F_\alpha(v_\alpha | R_\alpha)$ and $F_\beta(v_\beta | R_\beta)$ are

$$\begin{aligned}
 F_\alpha(v_\alpha | R_\alpha) &= \frac{1}{K_{v_\alpha}} \sum_{i'=1}^3 \int_0^\infty dR'_\alpha J_\alpha(R_\alpha | R'_\alpha) \sin(K_{v_\alpha} R'_\alpha) A_{\alpha i'}(R'_\alpha) \\
 &\quad \times \int_0^\infty dR_\beta U_\alpha(v_\alpha | R_\beta) B_{\alpha i'}(R_\beta) U_\alpha(v_\alpha | R_\beta) \\
 &\quad - \frac{i}{K_{v_\alpha}} \sum_{v'_\beta} \sum_{i'=1}^3 \int_0^\infty dR_\beta F_\beta(v'_\beta | R_\beta) U_\alpha(v_\alpha | R_\beta) B_{\alpha i'}(R_\beta) \\
 &\quad \times \int_0^\infty dR'_\alpha J_\alpha(R_\alpha | R'_\alpha) A_{\alpha i'}(R'_\alpha) U_\beta(v'_\beta | R'_\alpha)
 \end{aligned} \tag{B-36}$$

or more compactly as

$$\begin{aligned}
 F_\alpha(v_\alpha | R_\alpha) & \\
 &= \frac{1}{K_{v_\alpha}} \left[\sum_{i'=1}^3 I_{\alpha 0}(v_\alpha | R_\alpha | i') - i \sum_{v'_\beta} \sum_{i'=1}^3 H_\alpha(v_\alpha | v'_\beta | i' | R_\alpha) F_\beta(v_\alpha | v'_\beta | i') \right];
 \end{aligned} \tag{B-37}$$

and

(B-38)

$$\begin{aligned}
F_{\beta}(v_{\beta}|R_{\beta}) &= \frac{1}{K_{v_{\beta}}} \sum_{i'=1}^3 \int_0^{\infty} dR'_{\beta} J_{\beta}(R'_{\beta}|R_{\beta}) B_{\beta i'}(R'_{\beta}) U_{\alpha}(v_{\alpha}|R'_{\beta}) \\
&\quad \times \int_0^{\infty} dR_{\alpha} U_{\beta}(v_{\beta}|R_{\alpha}) A_{\beta i'}(R_{\alpha}) \sin K_{v_{\alpha}} R_{\alpha} \\
&\quad - \frac{i}{K_{v_{\beta}}} \sum_{v'_{\alpha}} \sum_{i'=1}^3 \int_0^{\infty} dR_{\alpha} F_{\alpha}(v'_{\alpha}|R_{\alpha}) U_{\beta}(v_{\beta}|R_{\alpha}) A_{\beta i'}(R_{\alpha}) \\
&\quad \times \int_0^{\infty} dR'_{\beta} J_{\beta}(R'_{\beta}|R_{\beta}) B_{\beta i'}(R'_{\beta}) U_{\alpha}(v'_{\alpha}|R'_{\beta})
\end{aligned}$$

which in condensed notation becomes

(B-39)

$$\begin{aligned}
F_{\beta}(v_{\beta}|R_{\beta}) \\
= \frac{1}{K_{v_{\beta}}} \left[\sum_{i'=1}^3 I_{\beta o}(v_{\beta}|R_{\beta}|i') - i \sum_{v'_{\alpha}} \sum_{i'=1}^3 H_{\beta}(v_{\beta}|v'_{\alpha}|i'|R_{\beta}) F_{\alpha}(v'_{\alpha}|i') \right]
\end{aligned}$$

The quantities $I_{\beta o}(v_{\beta}|R_{\beta}|i)$, $H_{\beta}(v_{\beta}|v'_{\alpha}|i'|R_{\beta})$ and $F_{\alpha}(v'_{\alpha}|i)$ above are defined by

(B-40)

$$\begin{aligned}
I_{\alpha o}(v_{\alpha}|R_{\alpha}|i) &= \int_0^{\infty} dR'_{\alpha} J_{\alpha}(R'_{\alpha}|R_{\alpha}) \sin K_{v_{\alpha}} R'_{\alpha} A_{\alpha i}(R'_{\alpha}) \\
&\quad \times \int_0^{\infty} dR_{\beta} U_{\alpha}(v_{\alpha}|R_{\beta}) B_{\alpha i}(R_{\beta}) U_{\beta}(v_{\beta}|R_{\beta}),
\end{aligned}$$

(B-41)

$$I_{\beta_0}(v_{\beta}|R_{\beta}|i) = \int_0^{\infty} dR'_{\beta} J_{\beta}(R_{\beta_0}|R_{\beta_0}) B_{\beta i}(R'_{\beta}) U_{\alpha}(v_{\alpha_0}|R'_{\beta}) \\ \times \int_0^{\infty} dR_{\alpha} U_{\beta}(v_{\beta}|R_{\alpha}) A_{\beta i}(R_{\alpha}) \text{Sin}(\kappa_{\alpha} R_{\alpha}),$$

(B-42)

$$H_{\alpha}(v_{\alpha}|v_{\beta}|i|R_{\alpha}) = \int_0^{\infty} dR'_{\alpha} J_{\alpha}(R_{\alpha_0}|R_{\alpha_0}) A_{\alpha i}(R'_{\alpha}) U_{\beta}(v_{\beta}|R'_{\alpha}),$$

(B-43)

$$H_{\beta}(v_{\beta}|v_{\alpha}|i|R_{\beta}) = \int_0^{\infty} dR'_{\beta} J_{\beta}(R_{\beta_0}|R_{\beta_0}) B_{\beta i}(R'_{\beta}) U_{\alpha}(v_{\alpha}|R'_{\beta}),$$

(B-44)

$$F_{\alpha}(v_{\beta}|v_{\alpha}|i) = \int_0^{\infty} dR_{\alpha} F_{\alpha}(v_{\alpha}|R_{\alpha}) U_{\beta}(v_{\beta}|R_{\alpha}) A_{\beta i}(R_{\alpha}),$$

and

(B-45)

$$F_{\beta}(v_{\alpha}|v_{\beta}|i) = \int_0^{\infty} dR_{\beta} F_{\beta}(v_{\beta}|R_{\beta}) U_{\alpha}(v_{\alpha}|R_{\beta}) B_{\alpha i}(R_{\beta}).$$

Equations (B-37) and (B-49) can be substituted into the right hand sides of Eqs. (B-44) and (B-45), respectively to obtain equations for the constants $F_{\alpha}(v_{\beta}|v_{\alpha}|i)$ and $F_{\beta}(v_{\alpha}|v_{\beta}|i)$ given by

(B-46)

$$F_{\alpha}(v_{\beta}|v_{\alpha}|i) = \frac{1}{K_{v_{\alpha}}} \sum_{i'=1}^3 \int_0^{\infty} dR_{\alpha} I_{\alpha 0}(v_{\alpha}|R_{\alpha}|i') U_{\beta}(v_{\beta}|R_{\alpha}) A_{\beta i}(R_{\alpha})$$

$$- \frac{i}{K_{v_{\alpha}}} \sum_{v'_{\beta}} \sum_{i'=1}^3 F_{\beta}(v_{\alpha}|v'_{\beta}|i') \int_0^{\infty} dR_{\alpha} H_{\alpha}(v_{\alpha}|v'_{\beta}|i') U_{\beta}(v'_{\beta}|R_{\alpha}) A_{\beta i}(R_{\alpha})$$

and

(B-47)

$$F_{\beta}(v_{\alpha}|v_{\beta}|i) = \frac{1}{K_{v_{\beta}}} \sum_{i'=1}^3 \int_0^{\infty} dR_{\beta} I_{\beta 0}(v_{\beta}|R_{\beta}|i') U_{\alpha}(v_{\alpha}|R_{\beta}) B_{\alpha i}(R_{\beta})$$

$$- \frac{i}{K_{v_{\beta}}} \sum_{v'_{\alpha}} \sum_{i'=1}^3 F_{\alpha}(v_{\beta}|v'_{\alpha}|i') \int_0^{\infty} dR_{\beta} H_{\beta}(v_{\beta}|v'_{\alpha}|i') U_{\alpha}(v'_{\alpha}|R_{\beta}) B_{\alpha i}(R_{\beta});$$

and these are expressed more concisely as

(B-48)

$$F_{\alpha}(v_{\beta}|v_{\alpha}|i) = \frac{1}{K_{v_{\alpha}}} \tilde{I}_{\alpha 0}(v_{\alpha}|v_{\beta}|i)$$

$$- \frac{i}{K_{v_{\alpha}}} \sum_{v'_{\alpha}} \sum_{v'_{\beta}} \sum_{i'=1}^3 \mathcal{L}_{v_{\alpha} v'_{\alpha}} \tilde{H}_{\alpha}(i|v_{\alpha}|v'_{\beta}|i') F_{\beta}(v'_{\alpha}|v'_{\beta}|i')$$

and

(B-49)

$$F_{\beta}(v_{\alpha}|v_{\beta}|i) = \frac{1}{K_{v_{\beta}}} \tilde{I}_{\beta 0}(v_{\beta}|v_{\alpha}|i)$$

$$- \frac{i}{K_{v_{\beta}}} \sum_{v'_{\beta}} \sum_{v'_{\alpha}} \sum_{i'=1}^3 \mathcal{L}_{v_{\beta} v'_{\beta}} \tilde{H}_{\beta}(i|v'_{\beta}|v'_{\alpha}|i') F_{\alpha}(v'_{\beta}|v'_{\alpha}|i').$$

Equations (B-48) and (B-49) constitute members of a set of coupled algebraic equations which can be simultaneously solved for the $F_\alpha(\nu_\alpha|\nu_\alpha|i)$ and $F_\beta(\nu_\alpha|\nu_\beta|i)$, using a computer. After obtaining these quantities, the functions $F_\alpha(\nu_\alpha|R_\alpha)$ and $F_\beta(\nu_\beta|R_\beta)$ can be obtained from Eqs. (B-37) and (B-39).

The transition amplitudes given by Eqs. (B-23) and (B-24) can now be obtained by considering the asymptotic form of $F_\beta(\nu_\beta|R_\beta)$, i.e.,

(B-50)

$$\begin{aligned} \lim_{R_\alpha \rightarrow \infty} F_\alpha(\nu_\alpha|R_\alpha) = & \sum_{i=1}^3 \frac{e^{iK_{\nu_\alpha} R_\alpha}}{K} \int_0^\infty dR'_\alpha \sin(K_{\nu_\alpha} R'_\alpha) \sin(K_{\nu_\alpha} R'_\alpha) A_{\alpha i}(R'_\alpha) \\ & \times \int_0^\infty dR_\beta U_\alpha(\nu_\alpha|R_\beta) B_{\alpha i}(R_\beta) U_\alpha(\nu_\alpha|R_\beta) \\ & - \frac{i}{K_{\nu_\alpha}} \sum_{\nu_\beta} \sum_{i=1}^3 F_\beta(\nu_\alpha|\nu_\beta|i) e^{iK_{\nu_\alpha} R_\alpha} \int_0^\infty dR'_\alpha \sin K_{\nu_\alpha} R'_\alpha A_{\alpha i}(R'_\alpha) U_\beta(\nu_\beta|R_\alpha). \end{aligned}$$

(B-51)

$$\lim_{R_\alpha \rightarrow \infty} F_\alpha(\nu_\alpha|R_\alpha) = \frac{e^{iK_{\nu_\alpha} R_\alpha}}{K_{\nu_\alpha}} \langle \Theta(\nu_\alpha) | \tilde{U}_\alpha | \Theta(\nu_\alpha) \rangle.$$

Similarly

(B-52)

$$\lim_{R_\beta \rightarrow \infty} F_\beta(\nu_\beta|R_\beta) = \frac{e^{iK_{\nu_\beta} R_\beta}}{K_{\nu_\beta}} \langle \Theta(\nu_\beta) | \tilde{U}_\beta | \Theta(\nu_\beta) \rangle$$

and the transition matrix elements can be determined from these relations.

If Morse eigenfunctions are used as the bound state vibrational function $U_\alpha(\nu_\rho | R_\rho)$, it appears that a numerical evaluation is required of the integrals which define the $\tilde{I}_\rho$ and $\tilde{H}_\rho$ in Eqs. (B-48) and (B-49). However, if $U_\alpha(\nu_\rho | R_\rho)$ is expressed as a Slater function, i.e., as

(B-53)

$$U_\alpha(\nu_\rho | R_\rho) = \sum_n B_n(\nu_\rho) R_\rho^n e^{-\gamma_n R_\rho},$$

the integrals in question can be evaluated analytically once the constants $B_n(\nu_\rho)$ and γ_n for the Slater functions are known.

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TABLE 1. H atom: Comparison of Calculated and Exact
Energy Values in rydbergs for the Ground and
First Three Excited S-States

	Ground State 1 s	1st Excited State 2 s	2nd Excited State 3 s	3rd Excited State 4 s
Exact	-1.0	-0.25	-1/9	-0.0625
Calculation I ^a	-1.000000000000	-0.249999999988	-0.111111111102	-0.0624999996
Calculation II	-1.000000000001	-0.249999999990	-0.111111111106	-0.0624999997

^aFor calculations I and II, the radial component was
integrated to a maximum value of 75 in step sizes of 0.005
and 0.01, respectively.

TABLE 2. H atom: Calculated Energy Values in rydbergs
as a Function of the Upper Limit of Integration,
R max.

	Ground state 1 s	1st Excited state 2 s	2nd Excited state 3 s	3rd Excited state 4 s
$R_{\max}$				
25	-1.0000000000004	-0.24999999565	-0.110594711	-0.04594868
35	-0.999999999999	-0.24999999998	-0.111106206	-0.06079321
45	-0.999999999997	-0.24999999998	-0.111111085	-0.06239419
50	-0.999999999998	-0.24999999993	-0.111111109	-0.06247836
60	-0.999999999995	-0.24999999991	-0.111111111	-0.06249933
75	-1.0000000000011	-0.24999999990	-0.111111111	-0.06249999

^aThe step size was 0.01 for each case and the maximum
computer time required on the Univac 1108 was 20 seconds for

$R_{\max} = 75$.

TABLE 3. Comparison of the Helium Atom Calculations with the
Experimental Ground State Energy

Type of He system	total energy, rydbergs
experimental observation	-5.808
system I ^a (moving nucleus model)	-4.9957862
systems II & III (infinitely massive and fixed nucleus models)	-5.0000450

^aAn upper limit of integration of 35 and a step size
of 0.001 was employed to compute the energy values.

TABLE 4. Calculated Energy for the Ground State Helium Atom
as a Function of Step Size and Comparison of the
Results Obtained Using Numerical and Analytic
Techniques of Integration

Method of integration	total energy, rydbergs
analytic ^a	-5.0000456
numerical ^b ($\Delta=0.001$)	-5.0000450
numerical ($\Delta=0.005$)	-5.0002951
numerical ($\Delta=0.01$)	-5.001 0764

^aReference 11

^bThe upper limit of integration is 35 and the step size
is indicated by Δ .

FIGURE 1.

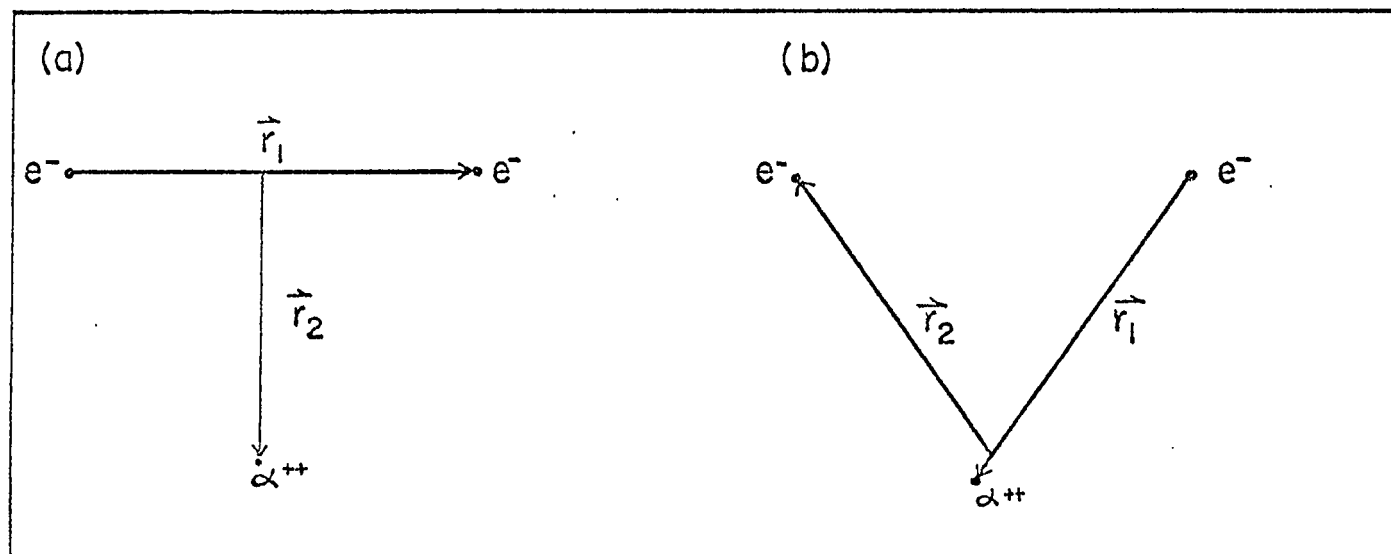


FIGURE 2

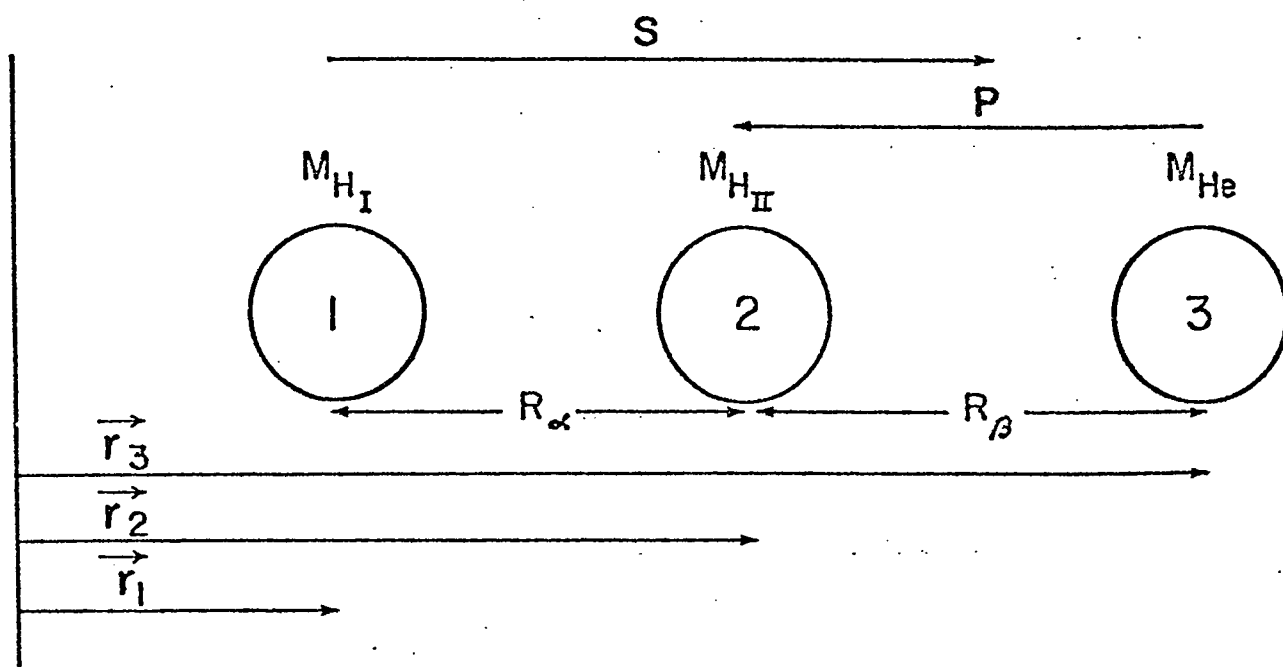


FIGURE 3

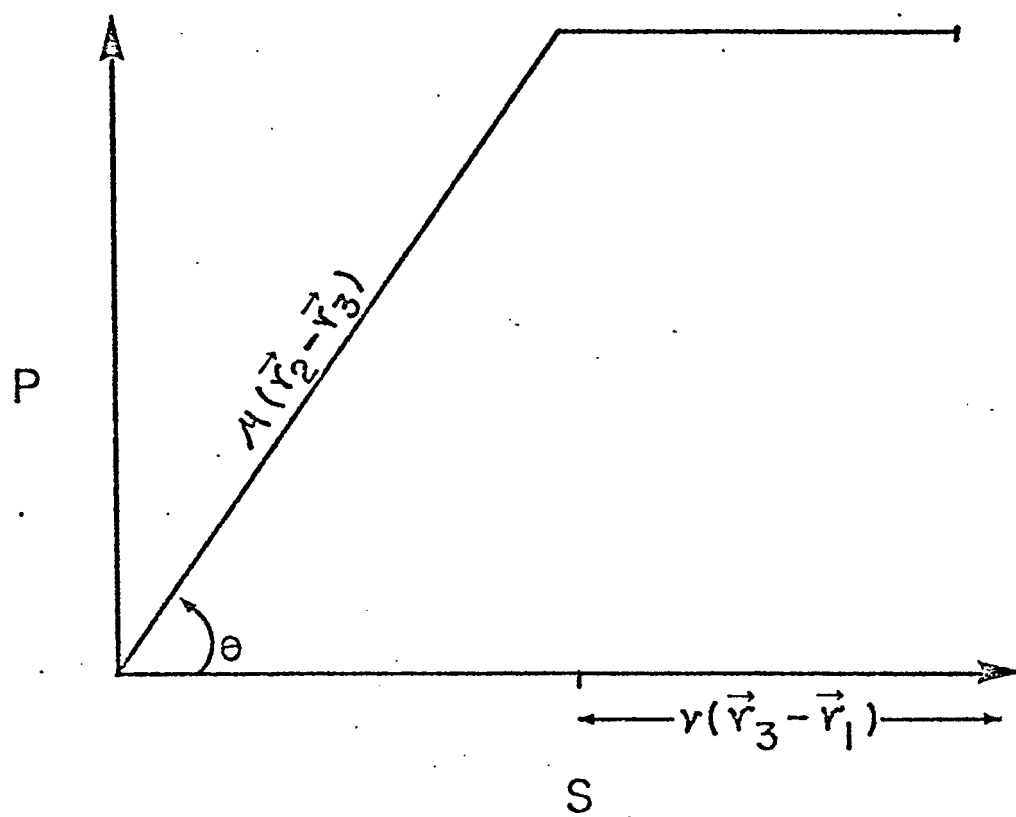
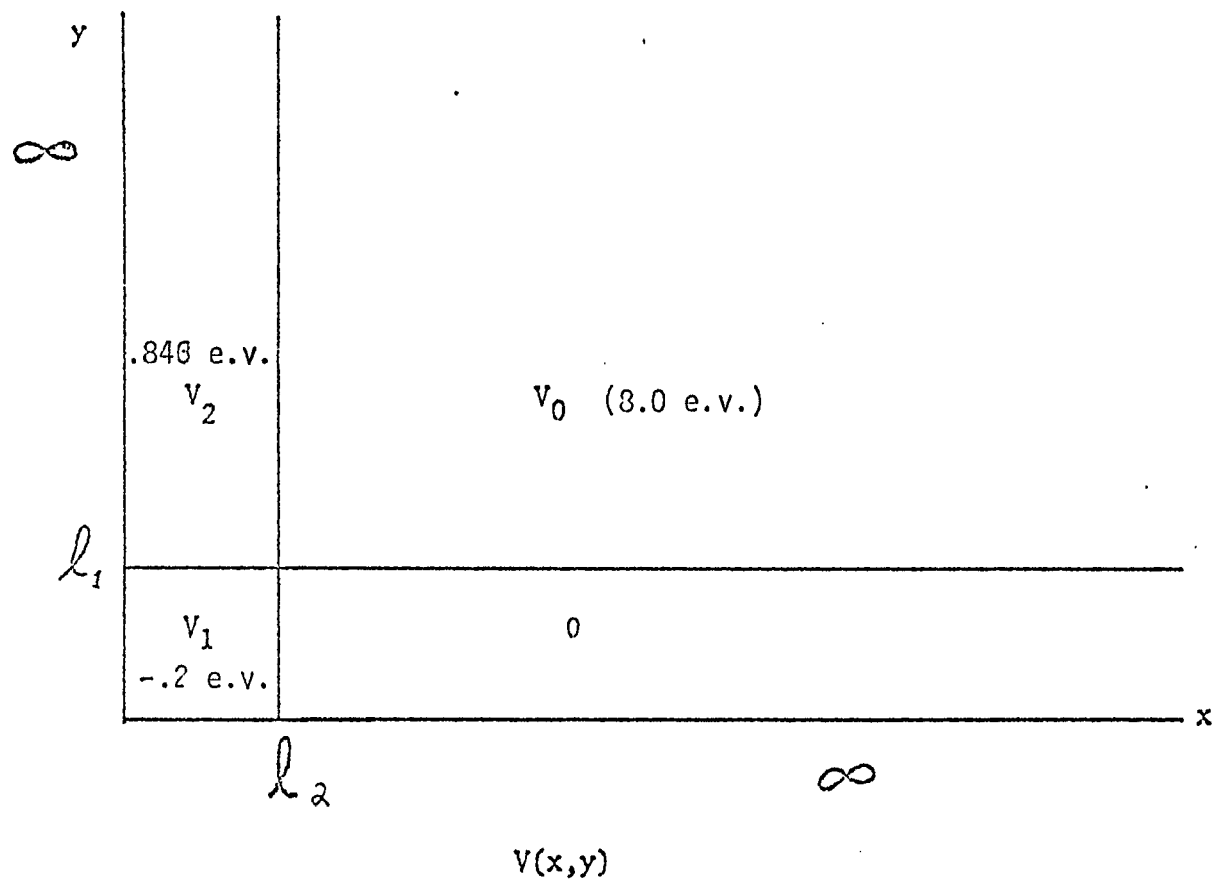


FIGURE 4



(a)

FIGURE 5

(b)

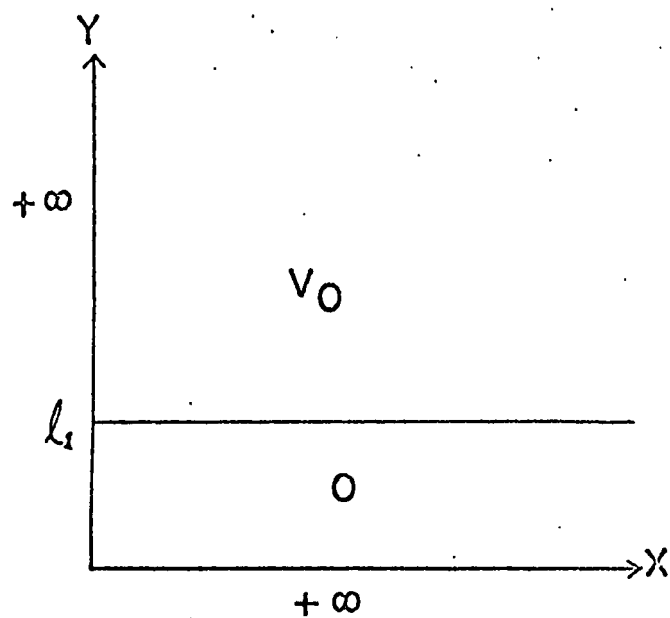
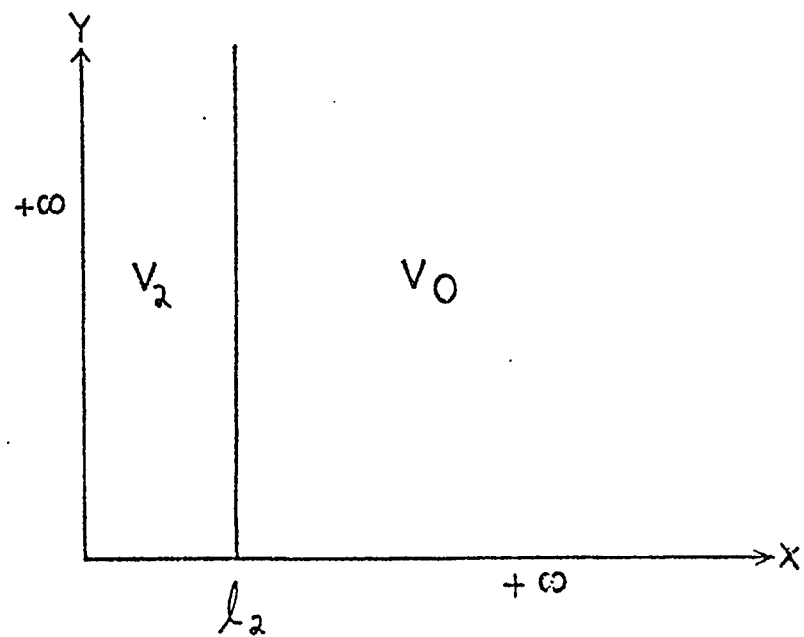
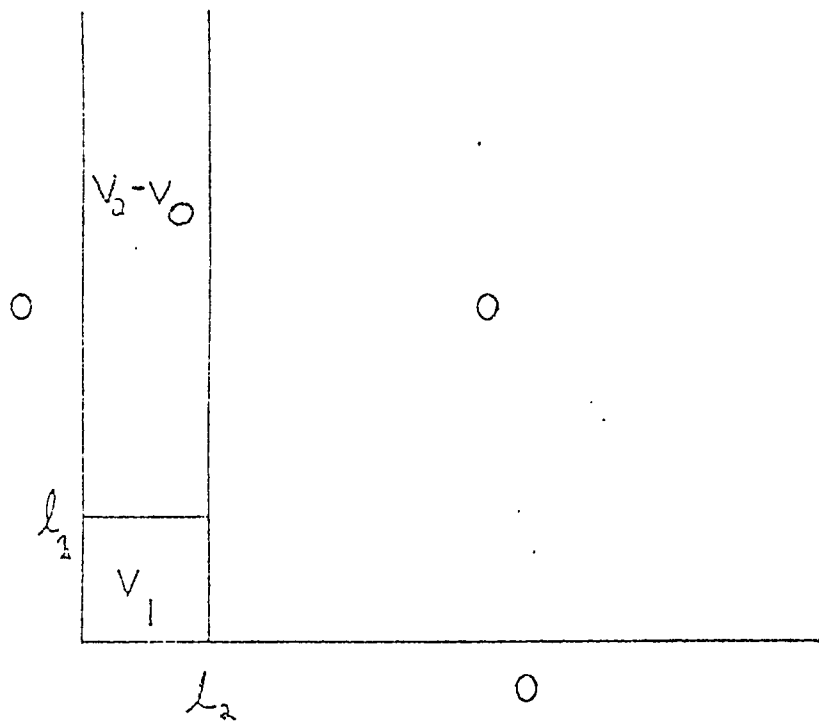
 $v_i(x, y)$  $v_f(x, y)$

FIGURE 6

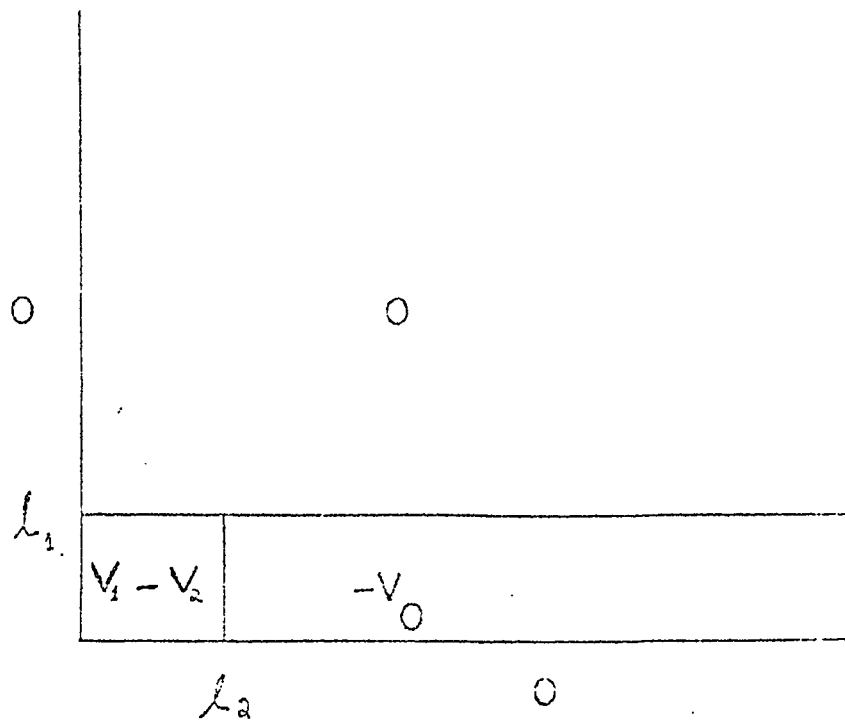
159

(a)



$V_\alpha(x, y)$

(b)



$V_\beta(x, y)$

Figure 7

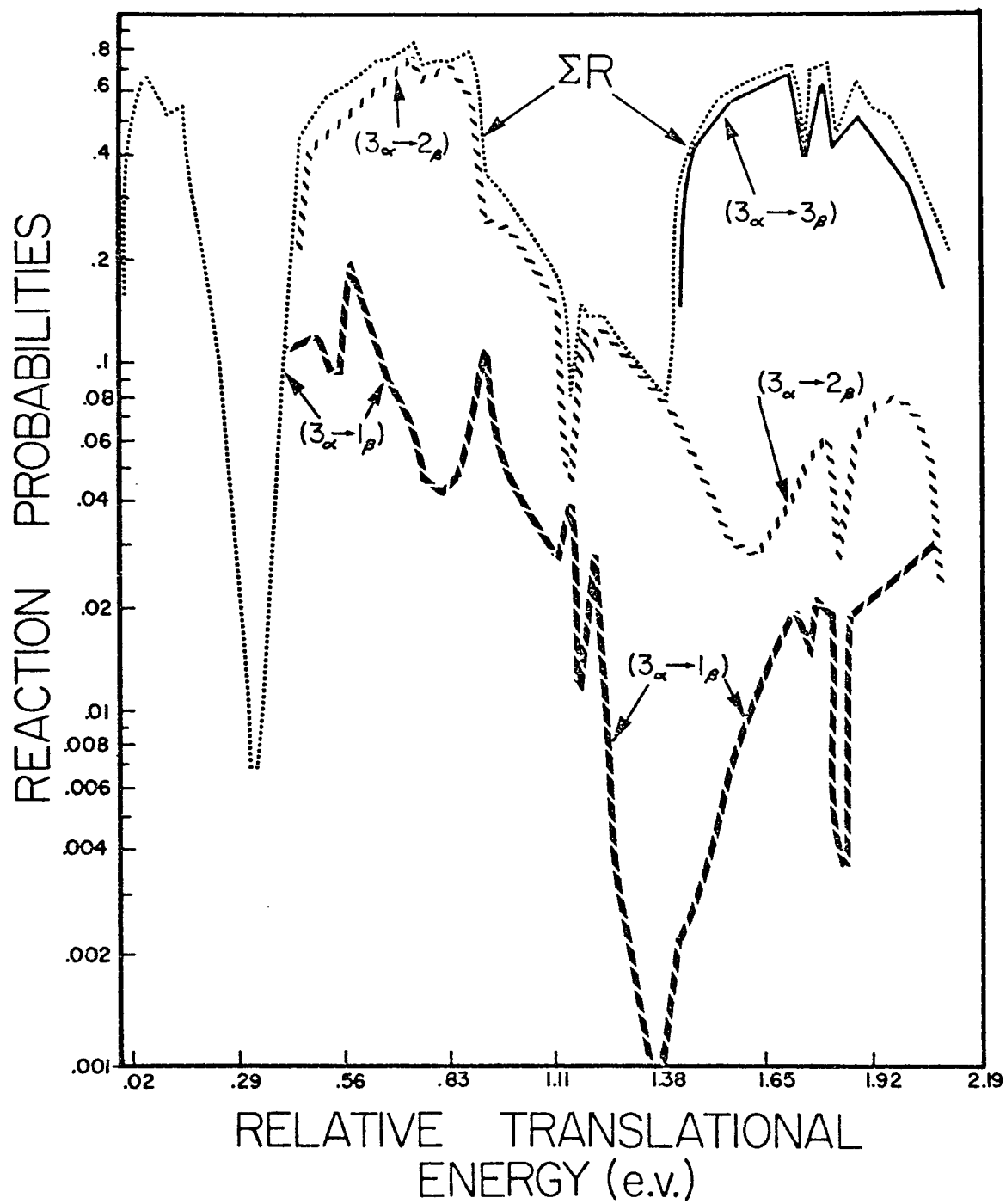
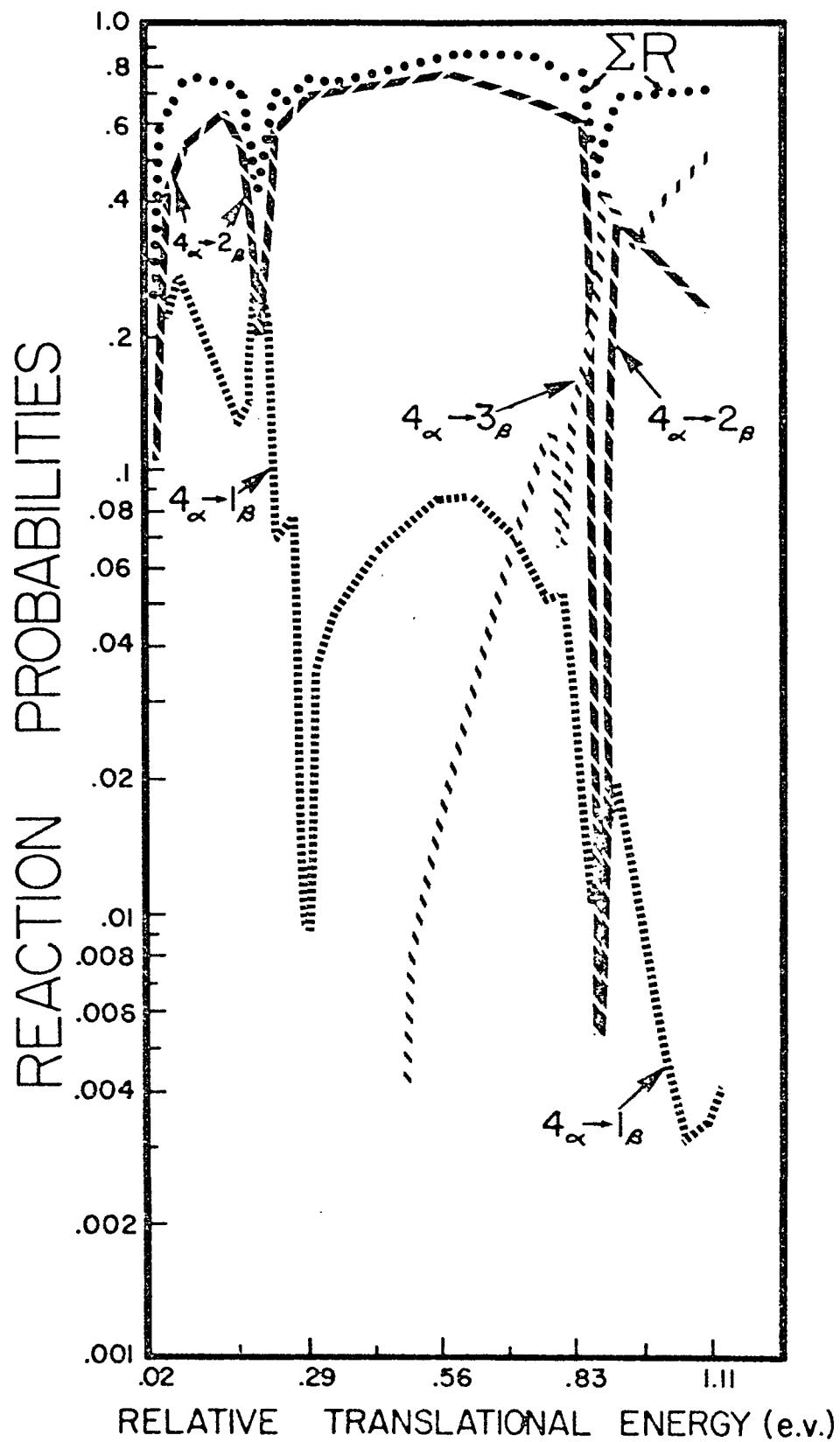


Figure 8

163



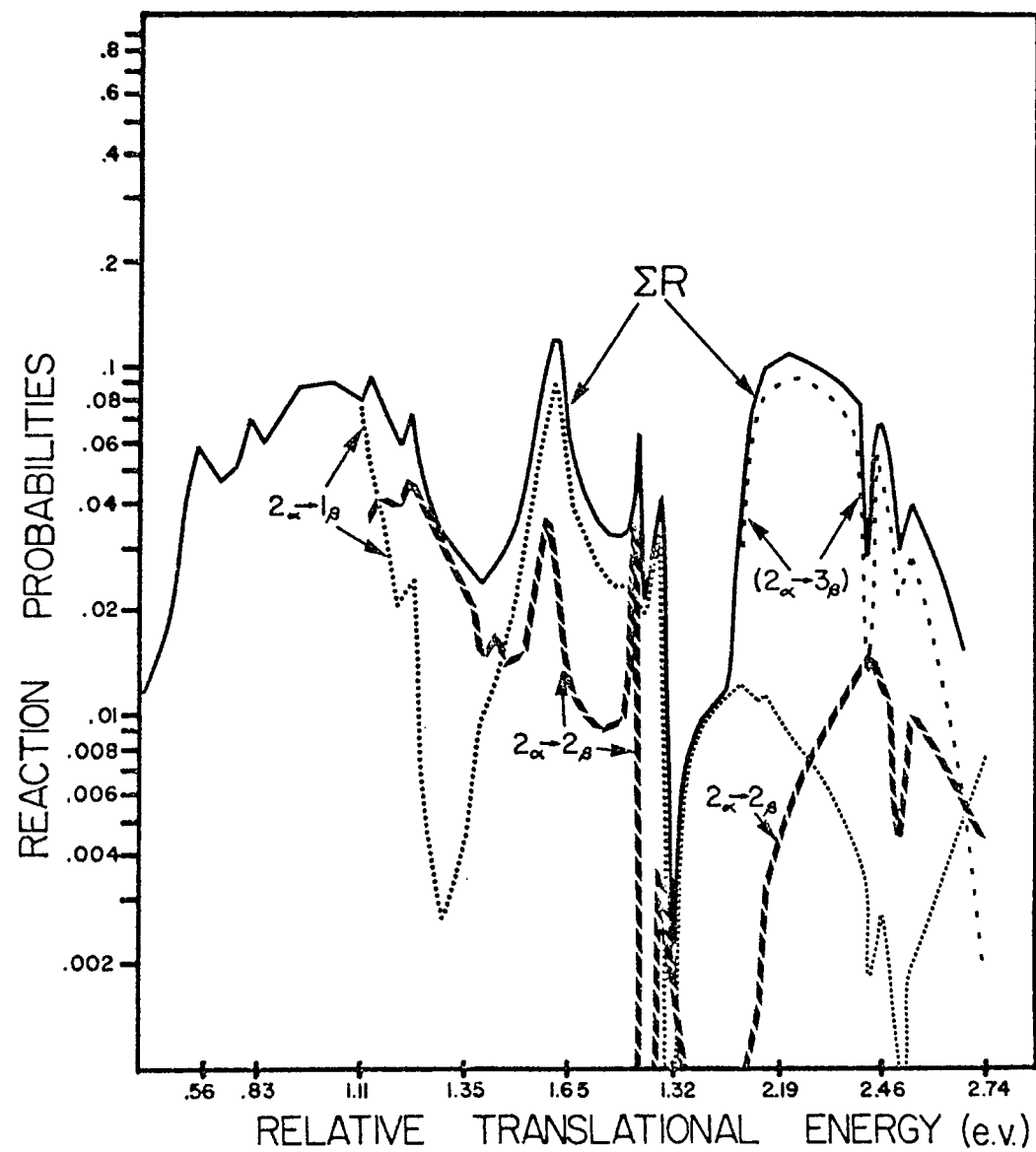
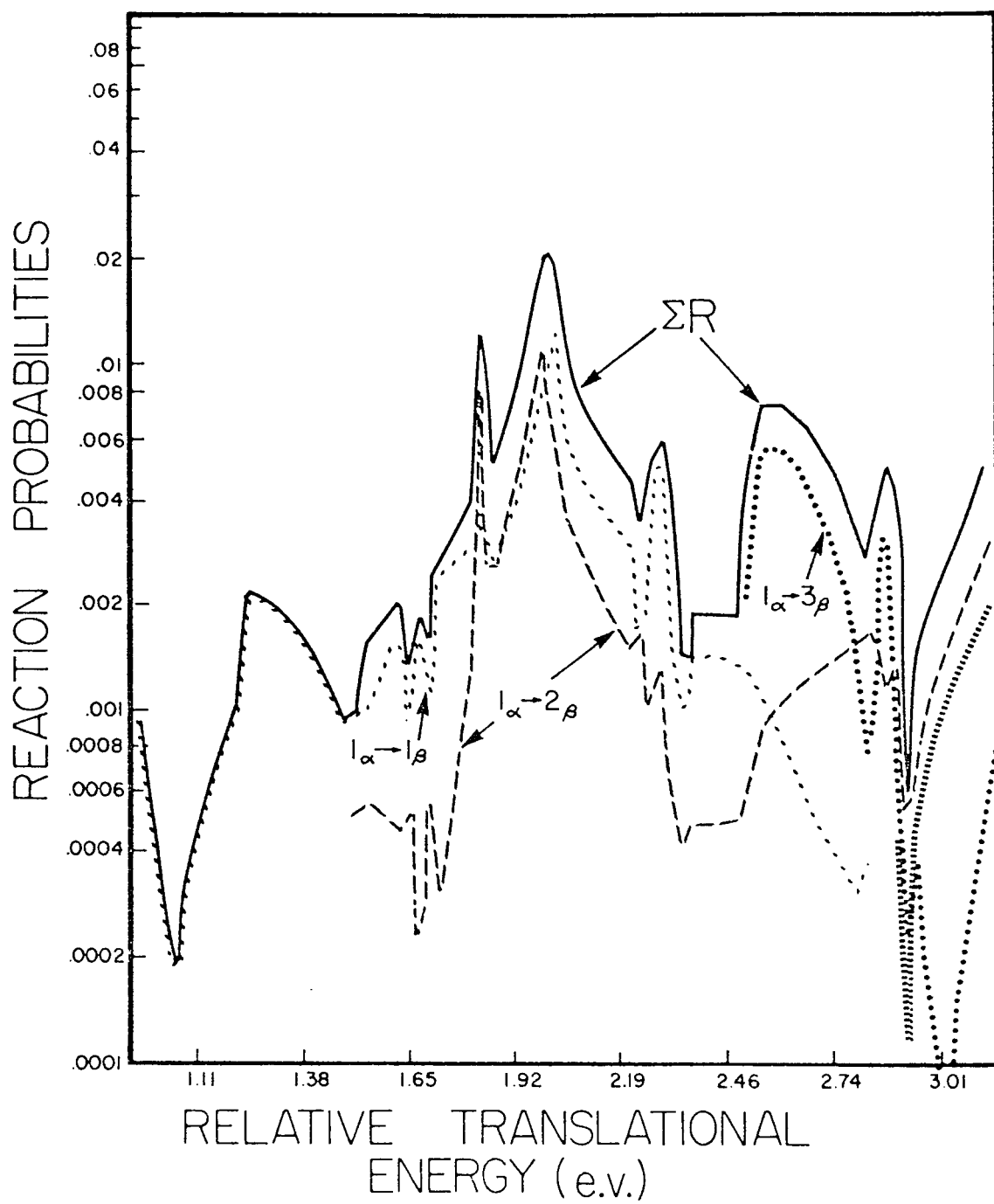


Figure 9

Figure 10



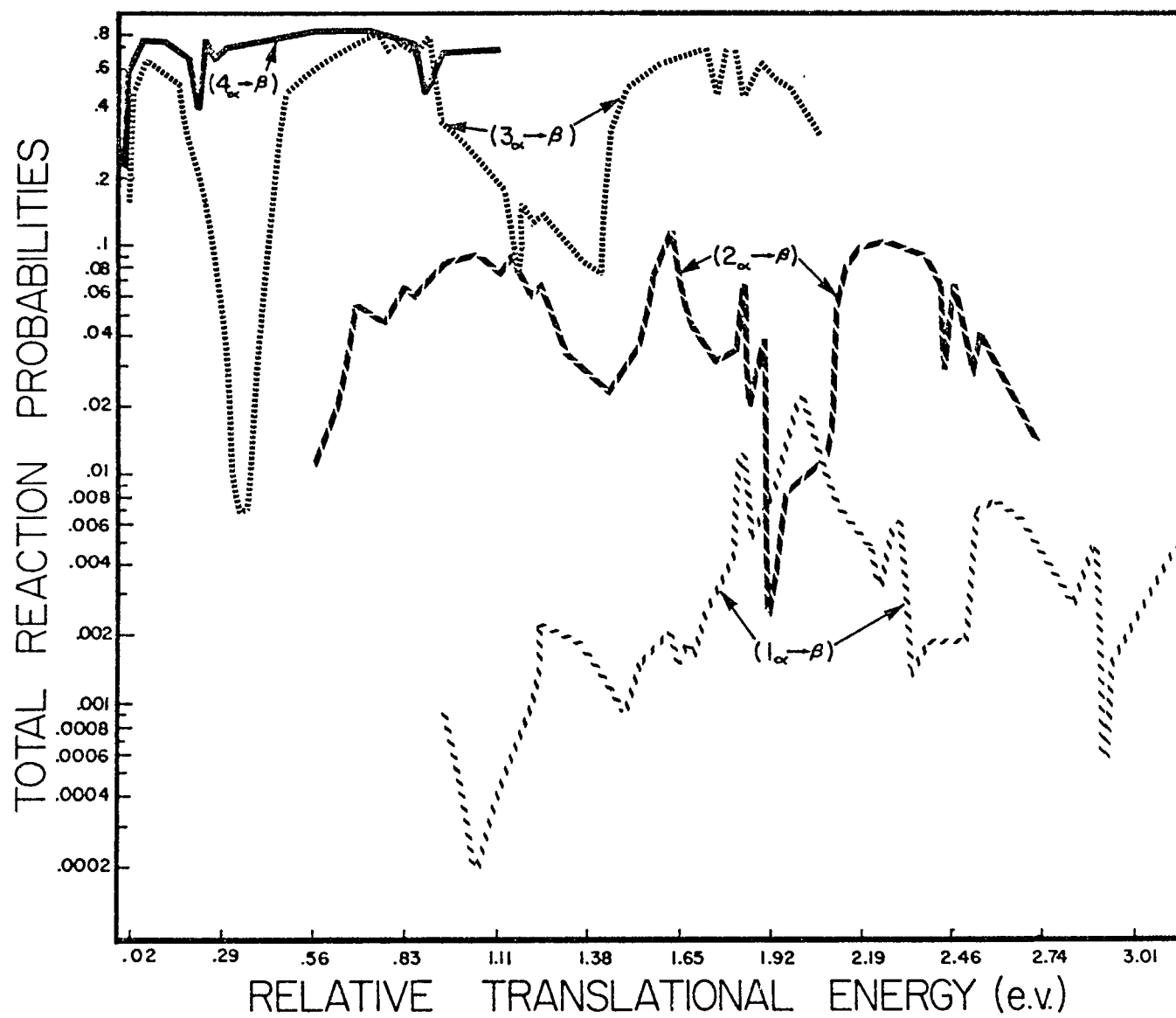


Figure 11

Figure 12

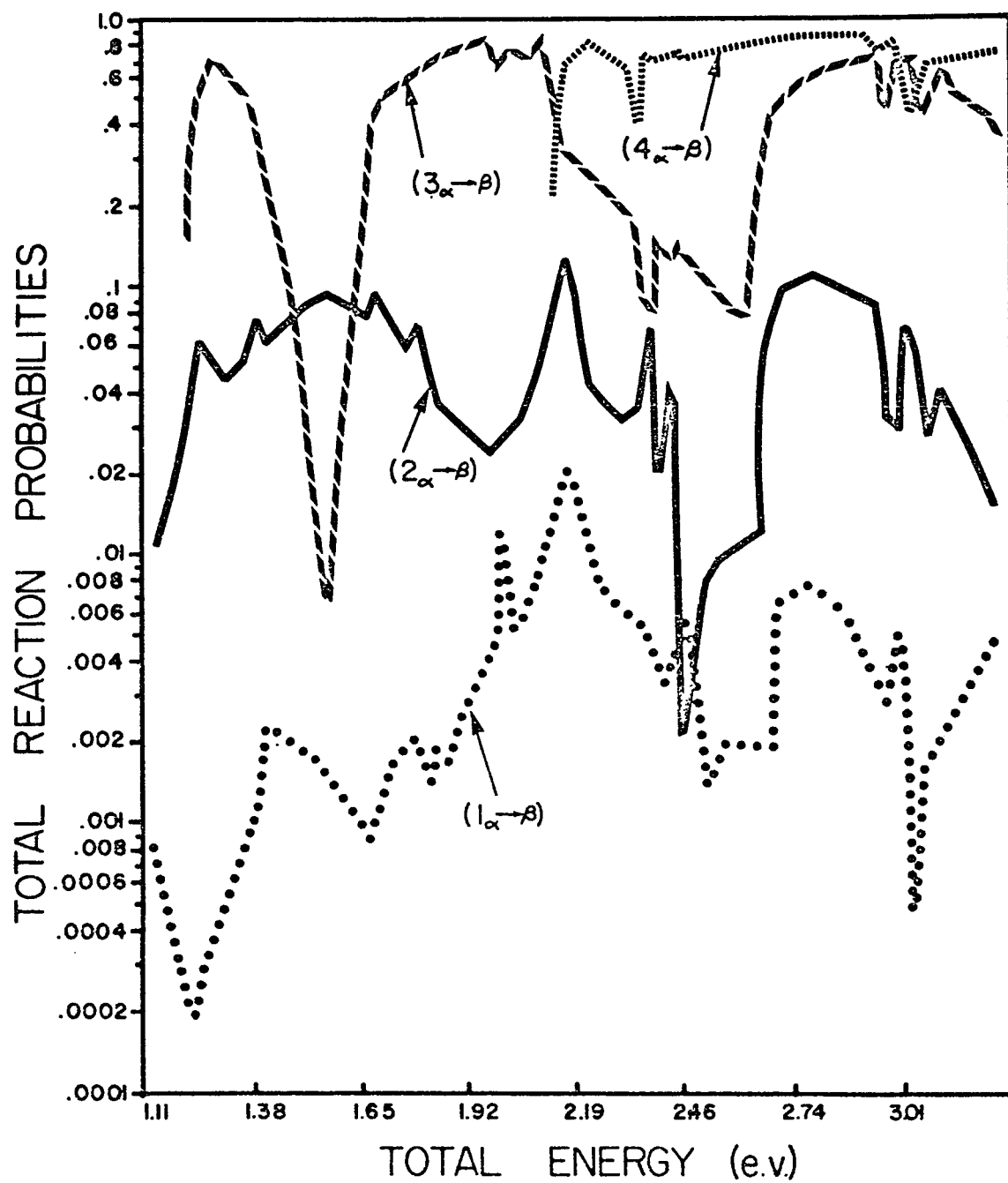


FIGURE 13

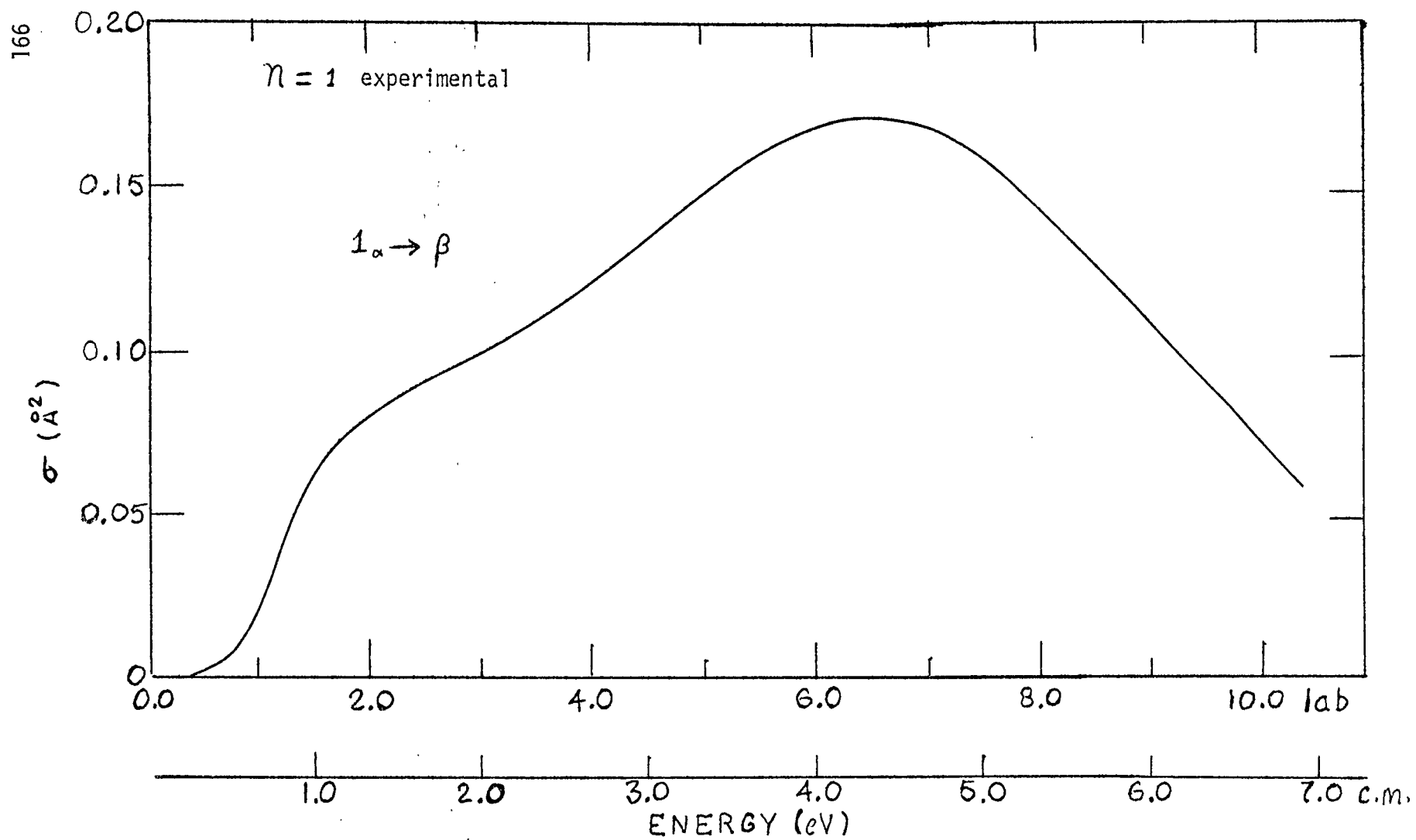


FIGURE 14

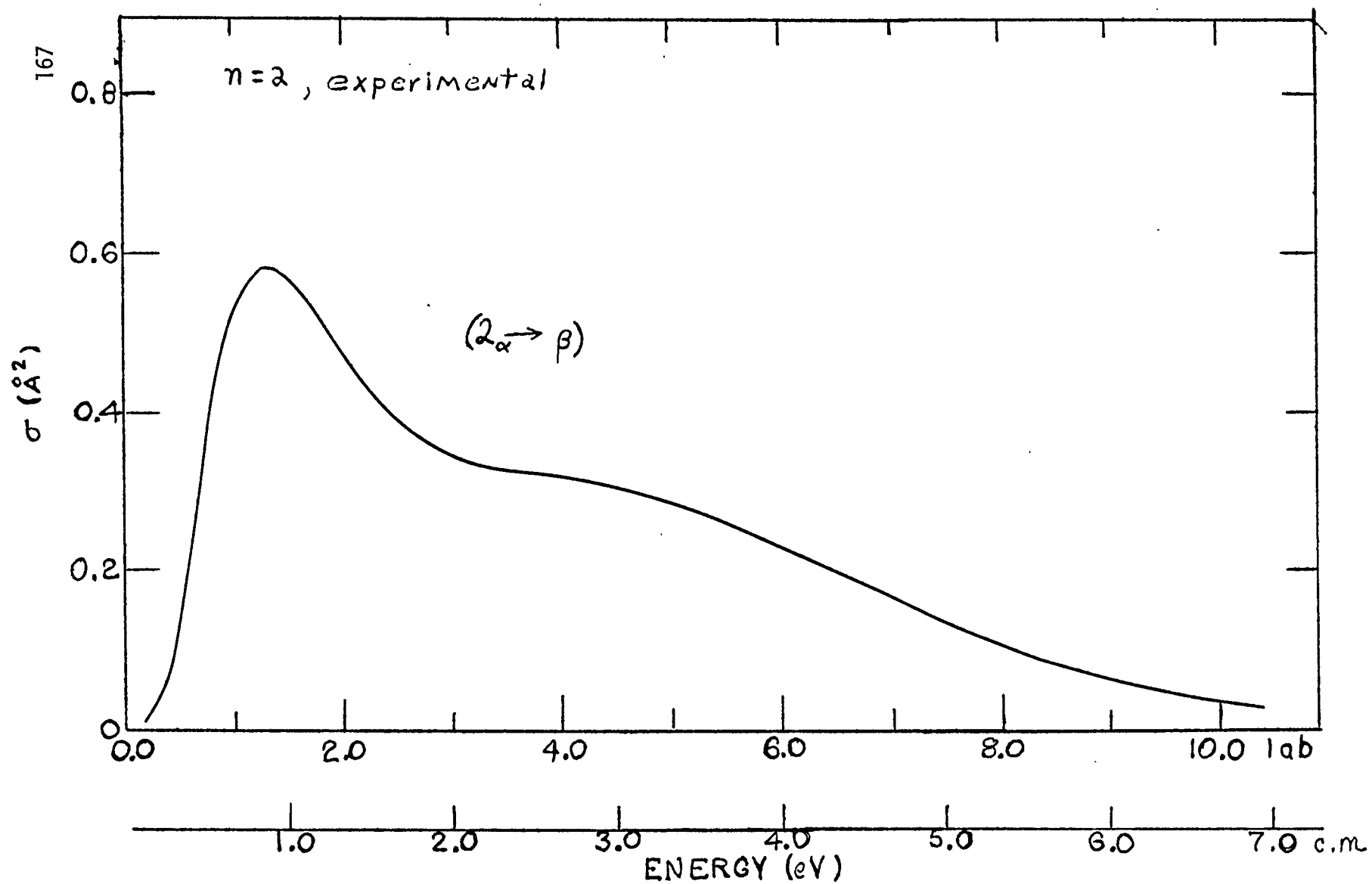


FIGURE 15

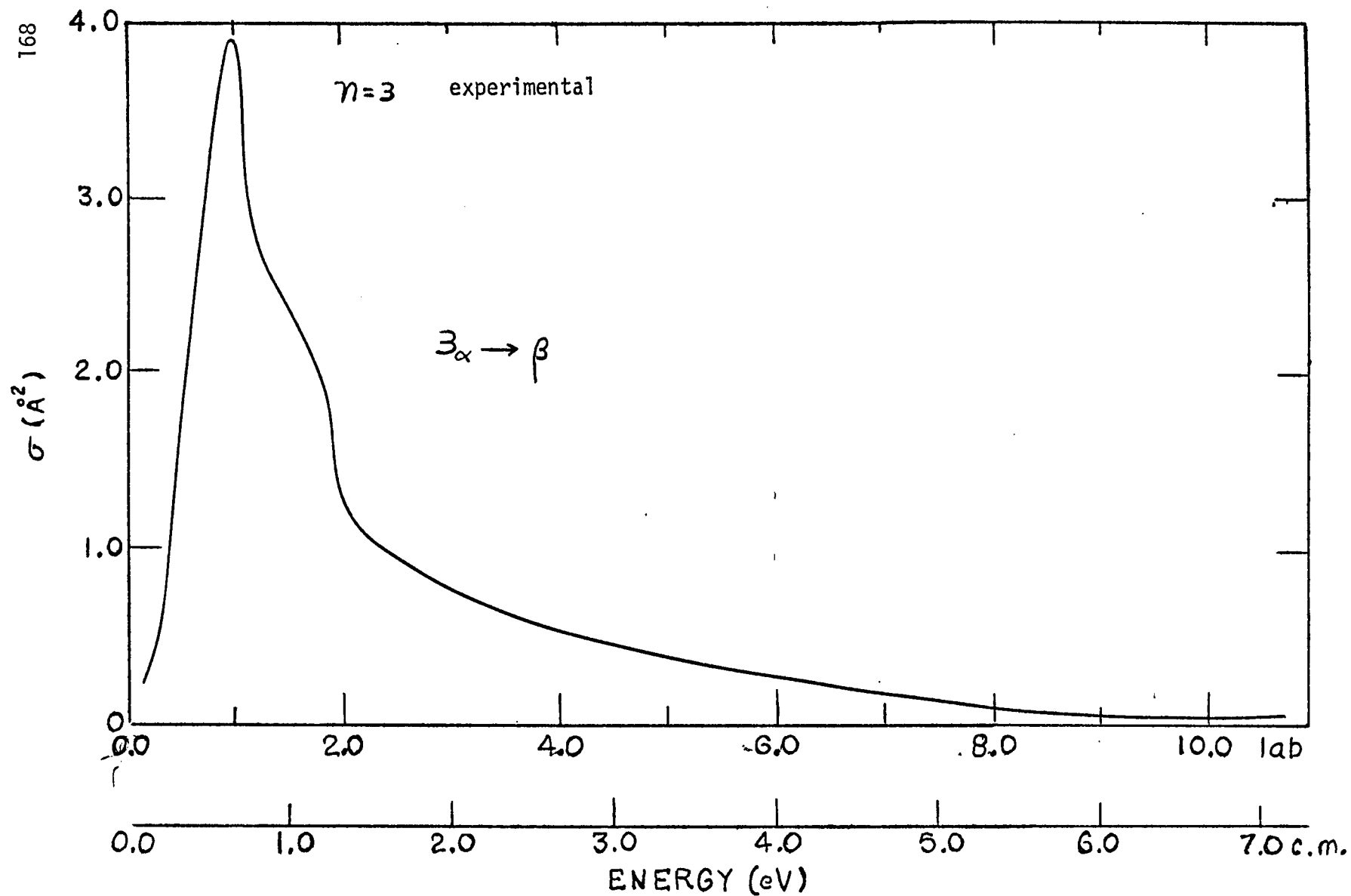


FIGURE 16

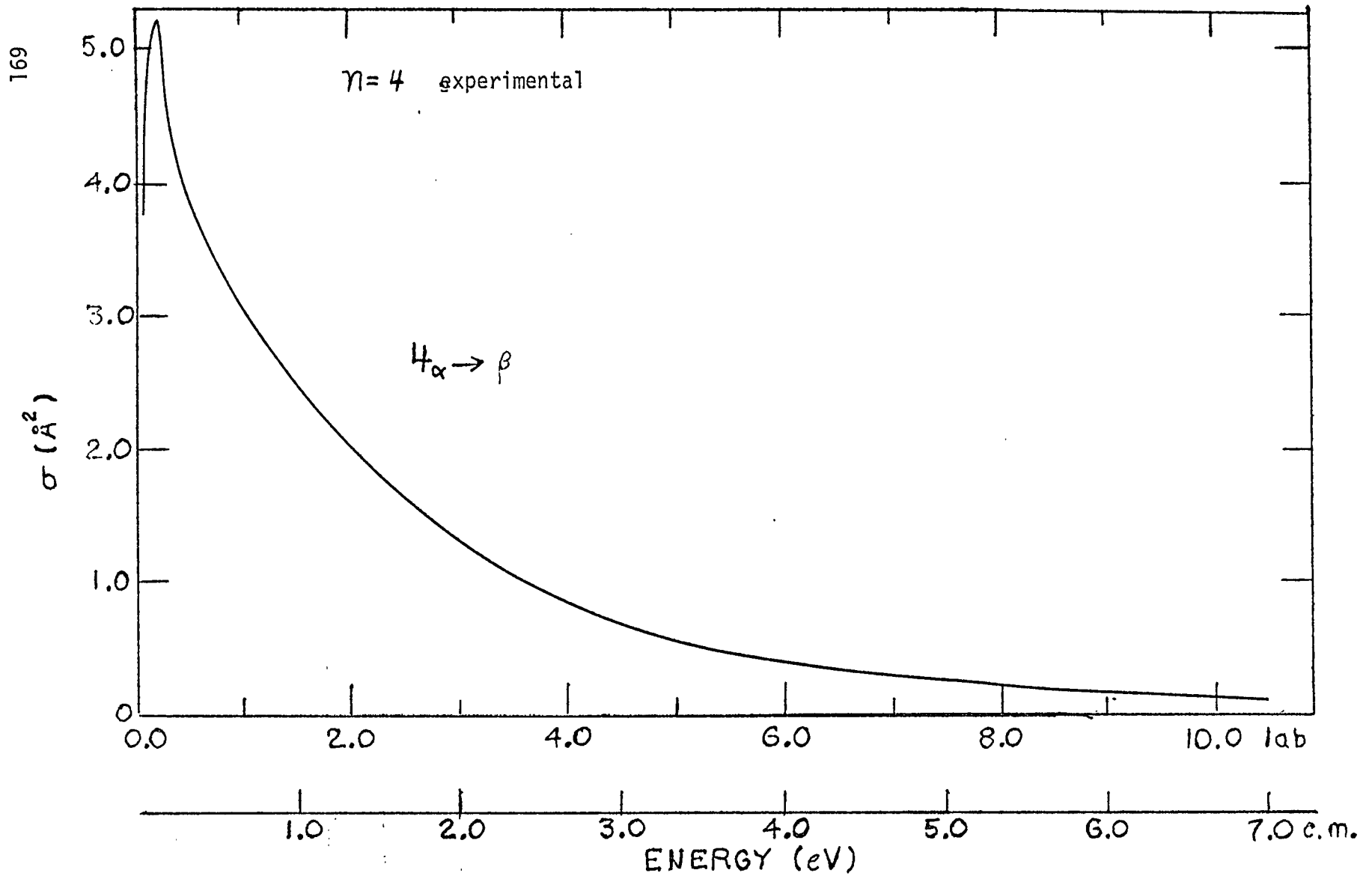


Figure 17

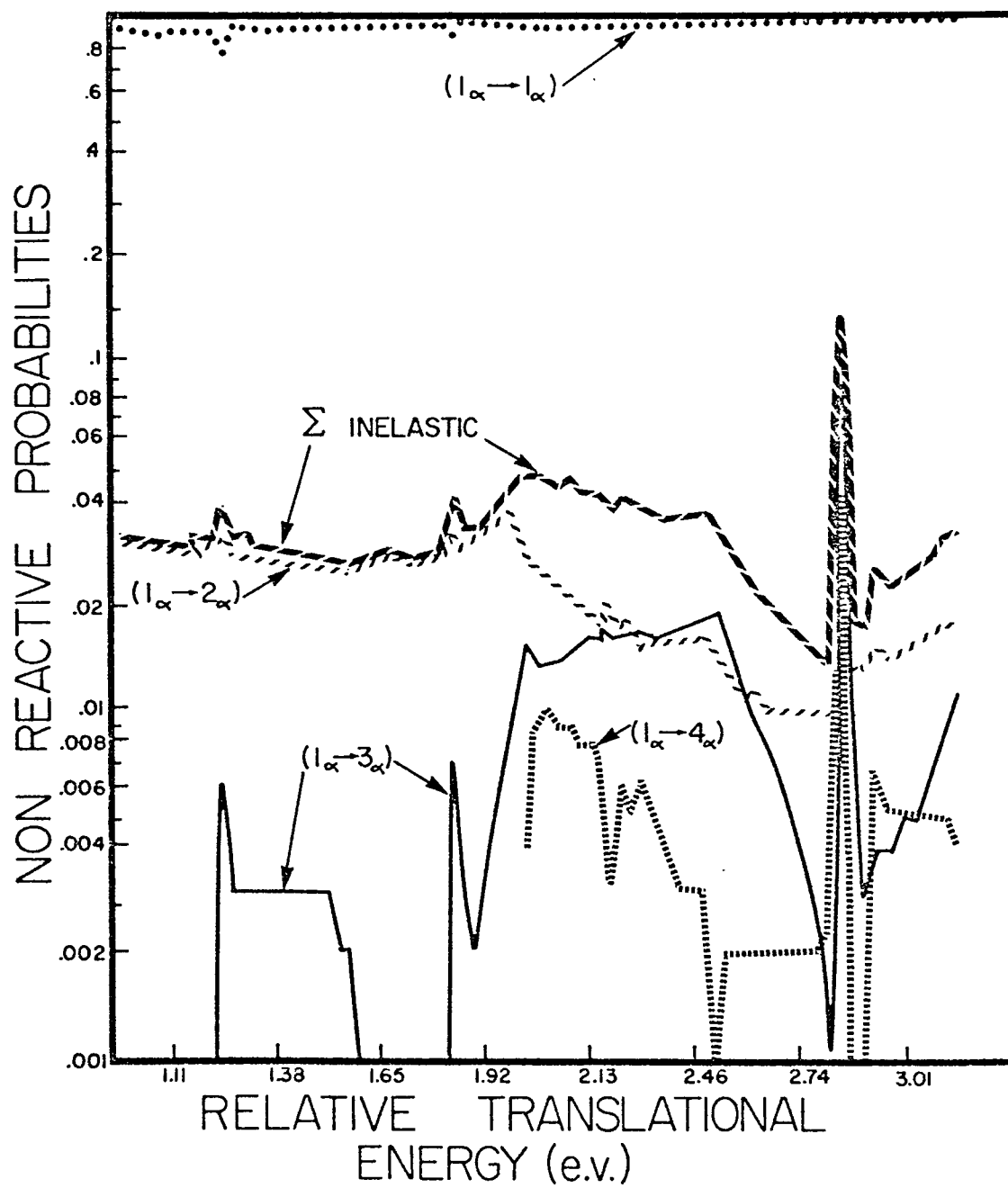


Figure 18

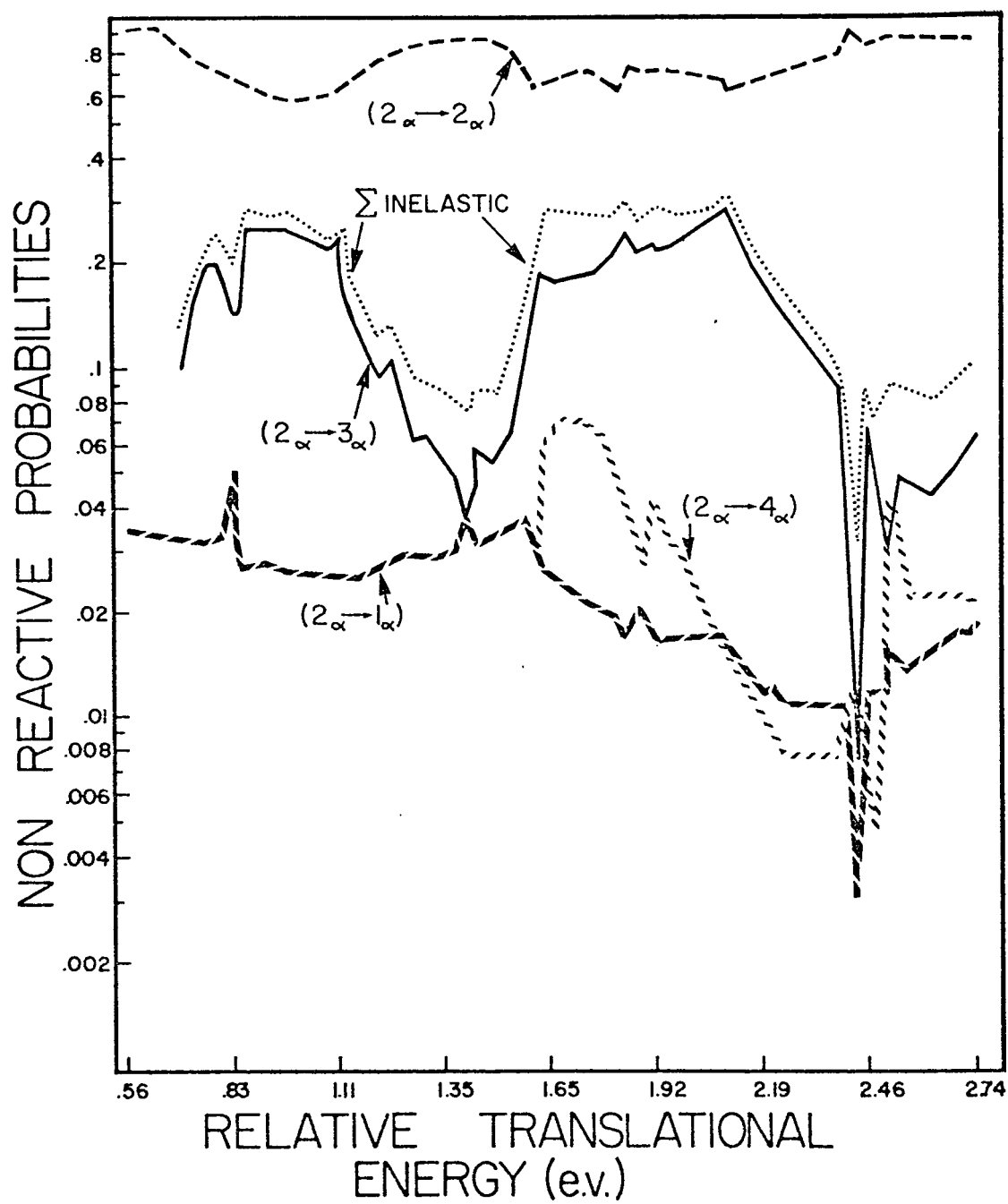


Figure 19

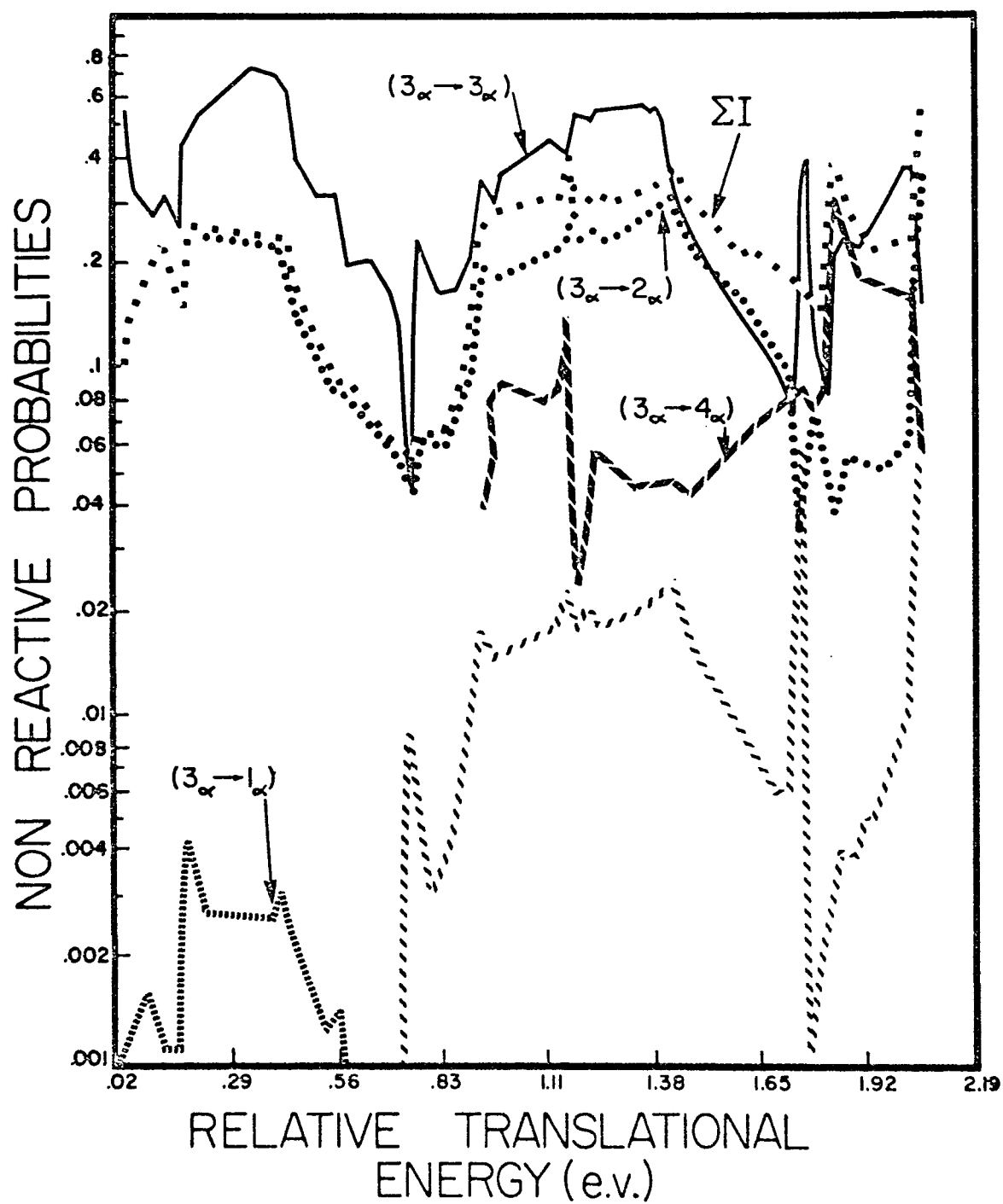
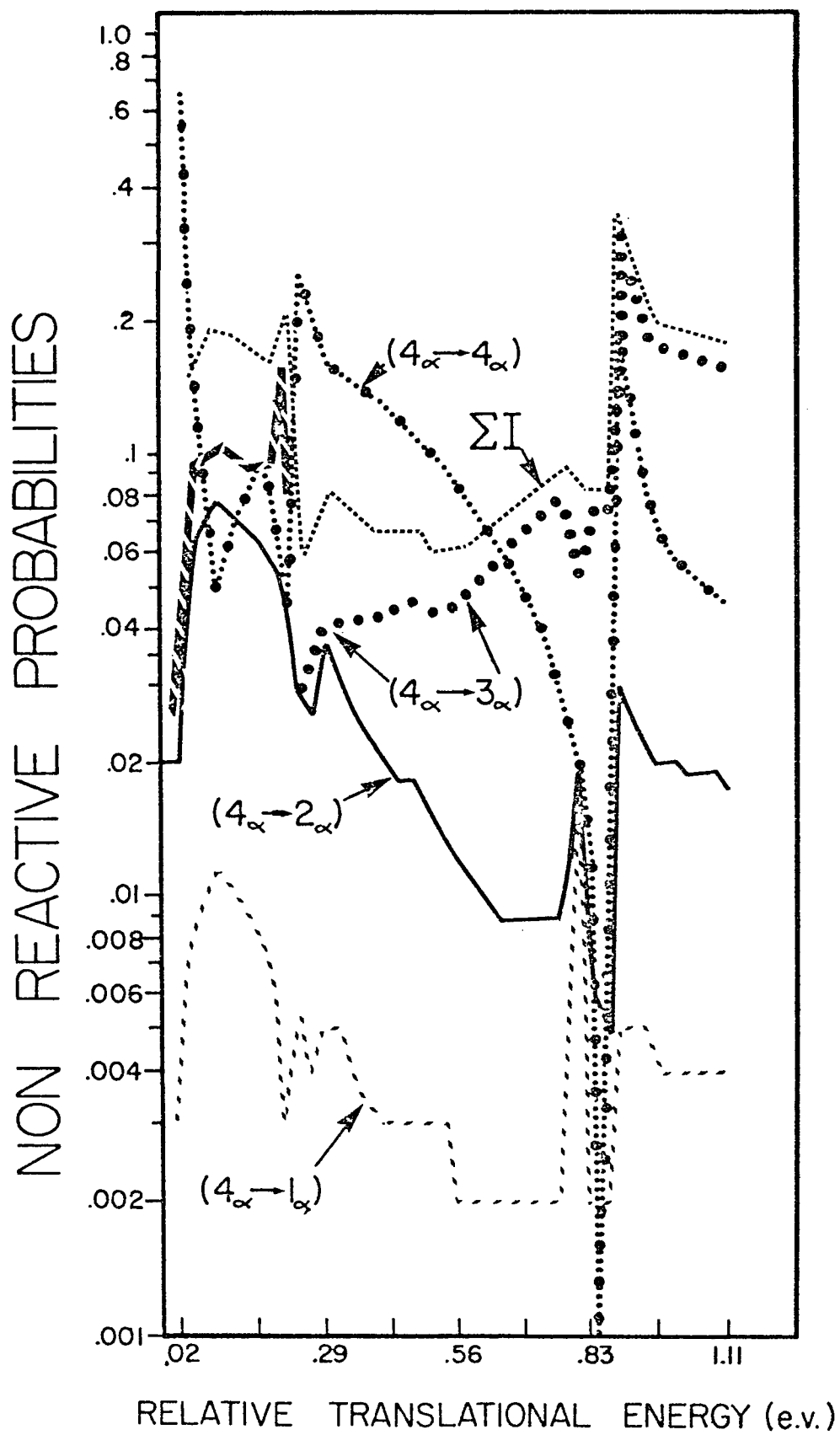


Figure 20



PROPOSAL

A Mathematical Model for Transformation in Bacillus subtilis

The proposed research consist of developing and testing a mathematical model to describe genetic transformation of Bacillus subtilis. This project is suggested by the conclusions of, for example, Erickson and Braun (10), Bodmer (3), Cooper (5) and Cooper and Evans (6) that recipient chromosomes of a competent culture possess target loci with which particular donor segments must interact in order to effect the particular transformations. It is further suggested that unbroken portions of single stranded donor DNA becomes integrated into recipient chromosomes (7) and that either of the two donor strands can produce a transformation (4). It is also well known that the target loci are not susceptible to transforming DNA unless the recipient culture is in the physiological state of competence (1).

By using this information and the fact that a replication map exists for B. subtilis chromosomes (9), a possible model for the transformation system may be assumed. For example, in a usual transformation experiment (1), the rate at which B. subtilis transformants accumulate would be assumed to depend on (a) the concentration and physical properties of donor DNA (11), (b) the time (11) of DNA incubation, (c) growth of the transformed cells during the incubation period, and (d) the concentration of receptive loci, i.e., those which can be

transformed.

By using these variables, a general mathematical model can be constructed to obtain an accurate description of the observable transforming events in cultures throughout the growth curve spectrum. It is anticipated that this model will involve several parameters and rate constants to be determined empirically. In turn, explicit forms of the mathematical model could render information concerning the possible mechanisms for describing DNA recombination. Thus, such mechanisms and their attendant mathematical models should suggest new experiments and/or ways of using data currently available.

Although Hotchkiss(13) and Fox and Hotchkiss (11) have considered some of the kinetic processes involved in transformation experiments, a more general example model for DNA induced transformation in a competent B. subtilis culture can now be considered where terms are defined in the following manner:

t = time

y = number of observed transformants

x = the number of loci receptive to transformation

x_0 = the number of receptive loci when $t = 0$

z = the number of loci not receptive to transformation

K_T = transformation constant; dependent on the physical properties and concentration of donor DNA and on the recipient locus to be transformed

K_R = replication constant for transformed loci

N = $x + z$

$K_{RI} \Rightarrow$ replication constant for receptive loci

$\delta_Z =$ competence constant governing the cell reaction $Z \xrightarrow{\delta_Z} X$
which changes the cell classification from Z to X .

$\delta_X =$ competence constant governing the cell reaction $X \xrightarrow{\delta_X} Z$
which changes the cell classification from X to Z .

With this example model, the number of transformed recipient loci, y , would change according to the equation.

$$\frac{dy}{dt} = K_T X + K_{RI} y \quad (1)$$

and the rate of change of X would be written as

$$\begin{aligned} \frac{dx}{dt} &= -K_T X + K_{RI} X + \delta_Z Z - \delta_X X \\ &= (K_{RI} - K_T - \delta_X) X + \delta_Z (N - X) = \mathcal{U} X + \delta_Z N \end{aligned} \quad (2)$$

where

$$\mathcal{U} = (K_{RI} - K_T - \delta_X - \delta_Z). \quad (3)$$

The equation for N is given by

$$N = N_0 e^{\mathcal{U}t} \quad (4)$$

where $\mathcal{U}$ is the usual growth constant and N_0 is the value of N at $t = 0$.

Equation (4) is substituted into Eq. (2) to give

$$\frac{dx}{dt} = \mathcal{U} X + \delta_Z N_0 e^{\mathcal{U}t} \quad (5)$$

which can be integrated to give an equation for X as

$$X(t) = \frac{1}{\lambda\ell - \omega} \left\{ \delta_z N_o e^{\lambda\ell t} + \left[X_o(\lambda\ell - \omega) - \delta_z N_o \right] e^{\omega t} \right\} \quad (6)$$

This expression for X is substituted into Eq. (1) to give

$$\frac{dy}{dt} - K_R y = K_T \left\{ \frac{1}{\lambda\ell - \omega} \left[\delta_z N_o e^{\lambda\ell t} + \left\{ X_o(\lambda\ell - \omega) - \delta_z N_o \right\} e^{\omega t} \right] \right\} \quad (7)$$

which is integrated to yield an equation for y as

$$y(t) = \frac{K_T}{\lambda\ell - \omega} \left\{ \frac{\delta_z N_o}{\lambda\ell - K_R} e^{\lambda\ell t} + \left(\frac{X_o(\lambda\ell - \omega) - \delta_z N_o}{\omega - K_R} \right) e^{\omega t} - \left(\frac{\delta_z N_o}{\lambda\ell - K_R} + \frac{X_o(\lambda\ell - \omega) - \delta_z N_o}{\omega - K_R} \right) e^{K_R t} \right\} \quad (8)$$

Due to the nature of genetic transfer in transformation, this process appears to be a logical first choice to consider in constructing a mechanistic model to describe genetic recombination in bacteria. For example, transformation is particularly amenable for investigating relationships between the physical structure of DNA and its biological functions; i.e., it is the only method currently available by which the effects of physical and/or chemical alterations in the structure of DNA may be correlated with its biological activity. The B. subtilis transformation system is particularly attractive because of extensive

genetic studies of this organism; these include transformation, transduction, and replication mapping. However, since transformation has recently been discovered in E. coli (2), a more meaningful comparison of transformation, transduction, and conjugation with respect to the modes of transfer and the recombination event itself is possible. Thus mathematical models of recombination for a transforming system could serve as a basis which could be expanded (or adapted) to describe bacteria recombination in general and/or the specific categories of recombination. Further, it is not improbable that "spontaneous" mutations are closely connected to the mechanisms involved with genetic recombination (14), whereas the latter appears to be associated with replication (8). Thus, models which correctly describe genetic recombination in bacteria could be applicable to more complex biological systems.

By experimentally measuring the various constants appearing in Eq. (8), one should hope to obtain a better understanding of the transformation process and perhaps modify the present model.

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