Research Report

Transition Probabilities for a Diatomic Molecule Interacting with a Third Particle

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1. Introduction

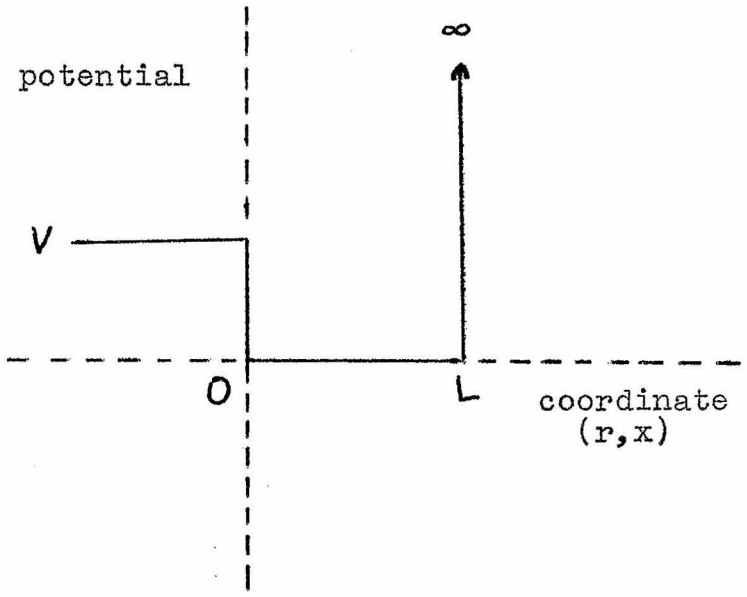
The study of molecular dynamics, the basis for the chemical reaction, is of fundamental importance in many fields. Theoretical calculations in this area consequently have a particularly wide applicability. Several references describing some recent developments in this field follow.

Energy transfer in collisions of gas molecules near room temperature was investigated by C. Zeuer in 1931.[1] He found that rotational transitions were considerably more probable than vibrational. Vibrational energy transfer probabilities were calculated by K. F. Herzfeld[2] for low energy interactions with the use of the selection rule $|\Delta v|=1$, which is not easily extended to higher energies.[3] Different models are necessary for higher energies.

One such model for translational and vibrational energy transfer is that of a hard, impulse collision on a harmonic oscillator. For this model, approximate solutions have been obtained.[4,5,6] In recent work, Shuler and Zwanzig have determined an accurate numerical solution to this problem.[7] However, a harmonic potential is an infinitely deep well and does not allow the possibility of dissociation. Still another method tried uses an assumed interaction potential to solve the time-dependent Schrödinger equation for a semi-classical collision process.[8] Predicted is a lack of validity of perturbation methods for high temperatures and changes in the vibrational quantum number v of magnitude considerably greater than unity.

2. Previous Work

Merle Riley[9] has been working on extending the model of Shuler and Zwanzig mentioned above to include the possibility of molecular dissociation. To elaborate, the problem consists of an incoming particle striking a diatomic molecule(assumed head-on at this stage). The diatomic molecule is represented by one particle bound in a truncated square well, and the other particle is free and interacts with the first one according to a hard sphere potential. A truncated square well as shown below was chosen due to its approximate similarity to a diatomic molecule potential, and its allowing of both bound and continuum ststes.



The striking particle does not feel the potential well; interaction with/ the molecule is only brought in as an impulsive hard sphere boundary condition. Explicitly, this sets the wavefunction of the total

system equal to zero when the coordinate of the incoming particle becomes identical with that of the bound particle. The wavefunctions for the striking particle are known(plane waves), and those of the bound particle are found from the Schrödinger equation. Normalizations and continuity requirements determine the wavefunctions to within a phase factor(the normalization for unbound states follows that of Kemble[10]).

When not colliding, the two particle system has a separable Hamiltonian due to the assumption of no interaction between the potential and the striking particle. Hence the total wavefunction can be expressed in terms of the products of the individual particle wavefunctions as follows:

$$\overset{U}{I}(x,r) = \sum_n c_n \phi_n(r)\theta(k_n',x) + \int_0^\infty c(k^-)\phi(k^-,r)\theta(k',x)dk^-, \qquad (1)$$

where the c_n are unknown constants, the $c(k^-)$ are unknown functions, the $\phi_n(r)$ and the $\phi(k^-,r)$ are, respectively, wavefunctions for the discrete and continuum ststes of the bound particle, and the $\theta(k',x)$ are the wavefunctions for the other particle, $\exp(\pm ik'x)$. The k are wave numbers related to the energies of the particles and will be defined precisely in a related case to be considered. Variables r and x are the independent coordinates measured from the origin indicated on page two, r for the particle initially bound, and x for the particle initially incident. The boundary condition is, after Shuler and Zwanzig, $\overset{U}{I}(r,r) = 0$, or

$$0 = \sum_n c_n \phi_n(r)\theta(k',r) + \int_0^\infty c(k^-)\phi(k^-,r)\theta(k',r)dk^- \ . \qquad (2)$$

We now need to solve this equation for the c_n and the $c(k^-)$ to find the behavior of the bound particle after collision, since $[c_n]^2$ is proportional to the probability of finding the particle in that particular bound state, and $\int_a^b [c(k^-)]^2 dk^-$ is proportional to the probability of finding the particle dissociated, having a value of k^- between a and b. From equation (2) we can easily obtain the following two equations:

$$(\overset{U}{I}(r,r),\ \phi_n(r)) = 0 \tag{3}$$

$$\lim_{\S k^- \to 0} \frac{1}{2\S k^-} (\overset{U}{I}(r,r),\ \S\phi(k^-,r)) = 0\ , \tag{4}$$

where $\S\phi$ is defined by

$$\S\phi(k^-,r) = \int_{k^- - \S k^-}^{k^- + \S k^-} \phi(k,r)\,dk.$$

More explicitly, these equations are

$$0 = \sum_n c_n \int_{-\infty}^{L} \phi_m^+(r)\phi_n(r)\theta(k',r)dr + \int_{-\infty}^{L} \phi_m^+(r)dr \int_0^{\infty} c(k^-)\phi(k^-,r)\theta(k',r)dk^- \tag{5}$$

$$0 = \lim_{\S k^- \to 0} \frac{1}{2\S k^-} \left\{ \sum_n c_n \int_{-\infty}^{L} \S\phi^+(k^\circ,r)\phi_n(r)\theta(k',r)dr + \int_{-\infty}^{L} \S\phi^+(k^\circ,r)dr \int_0^{\infty} c(k^-)\phi(k^-,r)\theta(k',r)dk^- \right\}, \tag{6}$$

where + signifies complex conjugate used as a superscript.

Riley[9] has attempted solutions to these equations by subdividing (k° an arbitrary value of k^-) the interval of integration over the unknown function $c(k^-)$ to determine numerically an average value of the function for each subinterval. Alternatively, the integral $\int_0^{k\ \mathrm{max.}} c(k^-)F(k^-)dk^-$ was broken up, and on each subinterval the function $c(k^-)F(k^-)$ approximated by a parabolic section, which then can be easily integrated. Neither of these methods gave a reasonable solution for $c(k^-)$, but rather one of oscillatory nature, where the oscillations

increased without limit as the approximation was improved(interval size reduced). Consequently, it is either possible that no satisfactory solution exists for the imposed boundary condition, or that some parts of the mathematical techniques involved in the two processes were not suited for the numerical calculations.

3. Three-Dimensional Model of Two-Particle Formulation

We carried out work in adapting Riley's case above into a three-dimensional model, which obviates the restriction of a head-on collision. This formulation uses a potential well with a cross-section very similar to that of the one-dimensional model. It is obtained precisely from the sketch on page two by shifting the well a distance L to the left along the coordinate axis, so that the infinite potential wall rises from the origin. Rotation about the potential axis, keeping the infinite potential barrier fixed, then generates the three-dimensional potential surface. $\overline{r}_1$ is the incoming particle position vector, and $\overline{r}_2$ is that of the particle initially bound, The incoming particle wavefunction, $\theta_I(\overline{r}_1)$, is assumed to be a plane wave, $\exp(-ik_I z)$, traveling along the z-axis toward the origin, while the outgoing wavefunctions are assumed to be expanding spherical waves. Spherical symmetry is supposed for for the bound states of the second particle for simplification, while general angular dependence is allowed for the continuum states.[13] The assumption of spherical symmetry does omit important states, so that this is a serious restriction. Equation (7) (next page) is the Schrödinger equation governing the system, with m the mass of

the incoming particle and M the reduced mass of the molecule.

$$-\frac{\hbar^2}{2M}\nabla^2_{r_2}\,\Psi^U_I(\bar{r}_1,\bar{r}_2) - \frac{\hbar^2}{2m}\nabla^2_{r_1}\,\Psi^U_I(\bar{r}_1,\bar{r}_2) = (E-V(r_2))\Psi^U_I(\bar{r}_1,\bar{r}_2) \qquad (7)$$

This equation can be simplified by factoring the total wavefunction Ψ^U_I into the product of the wavefunctions of the two individual particles. The two resulting equations are similar in form,

$$-\frac{\hbar^2}{2m}\nabla^2_{r_1}\,\theta(\bar{r}_1) = E_1\theta(\bar{r}_1), \qquad (8)$$

and

$$-\frac{\hbar^2}{2M}\nabla^2_{r_2}\,\phi(\bar{r}_2) + V(\bar{r}_2)\phi(\bar{r}_2) = E_2\phi(\bar{r}_2)\ , \qquad (9)$$

where $E_1 + E_2 = E$, the total energy of the system. Substituting for $\theta(\bar{r}_1)$ the product $R(r_1)Y(\theta_1,\phi_1)$, where the Y's are spherical harmonics, the radial equation is easily found, with solution[11]

$$R_l(r_1) = \frac{A^-}{\sqrt{r_1}}\,J_{l+1/2}(k_1r_1) + \frac{B^-}{\sqrt{r_1}}\,J_{-(l+1/2)}(k_1r_1)\ . \qquad (10)$$

A^- and B^- are constants, while the J's are Bessel functions. The condition of finiteness at the origin demands $B^- = 0$, allowing the constant A^- to be determined by normalization. Normalization of the angular part of the solution is routine, which gives

$$\theta_{l,m}(\bar{r}_1) = \frac{A}{\sqrt{r_1}}\,J_{l+1/2}(k_1r_1)Y_{l,m}(\theta_1,\phi_1), \qquad (11)$$

where A is the composite normalization factor, and k_1 is defined by $k_1^2 = \frac{2mE}{\hbar^2}$. Indices l and m indicate values of the total and the z-component of the total orbital angular momentum, respectively. Now $V(r_2)$, excluding the origin, is a step function, and over the duration of each step is constant. Consequently, this merely divides equation (9) into the two ranges of $\bar{r}_2$ evident from the diagram on page two, in each case with a form identical to that of equation (8). The distinction is that the $\phi(\bar{r}_2)$ are continuum states for $E_2 > V$, and

bound states for $E_2<V$; both are easily found from equation (9) in the manner just described. For the case $E_2>V$, we obtain

$$\phi_{l^-,m^-}(\bar{r}_2) = \begin{cases} \frac{B}{\sqrt{r_2}} J_{l^-+1/2}(k_2 r_2) Y_{l^-,m^-}(\theta_2,\phi_2) & 0<r_2<L \\ \frac{1}{\sqrt{r_2}} (C J_{l^-+1/2}(k_3 r_2) Y_{l^-,m^-}(\theta_2,\phi_2) & \\ \quad + D J_{-(l^-+1/2)}(k_3 r_2) Y_{l^-,m^-}(\theta_2,\phi_2)) & r_2>L \end{cases} \tag{12}$$

while for $E_2<V$, with the assumption of no angular dependence,

$$\phi_n = \begin{cases} \frac{F}{\sqrt{k_{2n}}} \frac{\sin k_{2n} r_2}{r_2} & 0<r_2<L \\ \frac{G}{\sqrt{k_{2n}}} \frac{e^{-[k_{3n}]r_2}}{r_2} \quad . & r_2>L \end{cases} \tag{13}$$

B, C, D, F, and G are constants still undetermined, while the remaining k's are given by

$$k_2^2 = \frac{2ME_2}{\hbar^2} \qquad k_3^2 = \frac{2M(E_2-V)}{\hbar^2} \quad . \tag{14}$$

The k_n and the ratio F/G are determined by matching ϕ_n and its first derivative across the boundary $r_2 = L$. Due/apparently to the presumed spherical symmetry of the bound states, the equation for the quantization of bound states is the same as for the one-dimensional case, viz.,

$$-\cot(k_{2n}L) = \sqrt{\frac{2MV}{\hbar^2 k_{2n}^2} - 1} \quad . \tag{15}$$

The coefficient ratio is given by

$$\frac{F}{G} = \sqrt{\frac{k_2}{k_3}} \frac{e^{-k_3 L}}{\sin(k_2 L)} \quad . \tag{16}$$

The results for the boundary matching of the continuum ϕ's are

$$C/B = \frac{(s_{l^-})k_3 + t_{l^-}}{(s_{l^-})k_2 + t_{l^-}} , \tag{17}$$

and $$D/B = \frac{J_{l^-+1/2}(k_2L) - \frac{(s_{l^-})k_3 + t_{l^-}}{(s_{l^-})k_2 + t_{l^-}} J_{l^-+1/2}(k_3L)}{J_{-(l^-+1/2)}(k_3L)} , \tag{18}$$

where $$s_{l^-} = \left\{ \frac{(l^-+1/2)}{L} J_{l^-+1/2}(k_2L) - J_{l^-+3/2}(k_2L) \right\} ,$$

and $$t_{l^-} = \left\{ \frac{(l^-+1/2)}{L} + \frac{J_{-(l^--1/2)}(k_3L)}{J_{-(l^-+1/2)}(k_3L)} \right\} J_{l^-+1/2}(k_3L).$$

Normalization determines the coefficients to within a phase factor, but this has not been completely worked out.

In analogy with the one-dimensional case, the wavefunction for the system can be written as follows:

$$\overset{U}{I}(\bar{r}_1,\bar{r}_2) = \theta_I(\bar{r}_1)\phi_I(\bar{r}_2) + \sum_n \sum_l \sum_m c_{nlm}\phi_n(\bar{r}_2)\theta_{nlm}(\bar{r}_1)$$

$$+ \sum_m \sum_l \sum_{m^-l^-} \int c_{mlm^-l^-}(k_2)\theta_{lm}(\bar{r}_1,k_1)\phi_{l^-m^-}(\bar{r}_2,k_2)dk_2. \tag{19}$$

ϕ can be represented as a function of k_2 only, since k_2 and k_3 are related by the equation $\frac{\hbar^2}{2M}(k_2^2-k_3^2) = V$. (20)

Also, k_2 is a function of k_1 from the requirement of conservation of energy, $\frac{\hbar^2}{2}(k_1^2/m + k_2^2/M) = E$. (21)

The I subscript found in equation (19) refers to the initial state of the problem before collision. Setting $\bar{r}_1 = \bar{r}_2$ and $\overset{U}{I}$ equal to

zero for the hard interaction requirement gives

$$0 = \theta_I(\bar{r})\phi(\bar{r}) + \sum_n \sum_l \sum_m c_{nlm}\phi_n(r)\theta_{nlm}(\bar{r}) + \sum_m \sum_l \sum_{m^-l^-} \int c_{mlm^-l^-}(k_2)\theta_{lm}(\bar{r},k_1)\phi_{l^-m^-}(\bar{r},k_2)dk_2. \quad (22)$$

Now we impose conservation of angular momentum: we require the sum $m + m^-$ to be constant. Initially, the m-value is assumed to be zero for the molecule(particle two), and by writing the incoming wave $\exp(-ik_I z_1)$ in expanded form,

$$\theta_I = e^{-ik_I z_1} = \sum_{l=0}^{\infty} \left\{\frac{2(2l+1)}{k_I r_1}\right\}^{1/2} (-i)^l J_{l+1/2}(k_I r_1) Y_{l,0}(\theta_1), \quad (23)$$

it is clear that the incoming particle also possesses $m = 0$. Consequently, we have $m = -m^-$, which eliminates one summation from each of the last two last terms on the right hand side of equation (22). This gives an equation with the following form, where the functions F, G, and H have been substituted temporarily for simplification:

$$0 = \sum_l F_l(r)Y_{l,0}(\theta) + \sum_n \sum_l G_{nl}(r)Y_{l,0}(\theta) + \sum_l \sum_m \sum_{l^-} \int H_{lml^-}(k_2,r)Y_{l,m}(\theta,\phi)Y_{l^-,-m}(\theta,\phi)dk_2 \quad (24)$$

We note that the ϕ dependence in the last term cancels, allowing us to write $Y_{l,m}(\theta,\phi)Y_{l^-,-m}(\theta,\phi) = \sum_{s=1}^{l+l^-} a_s Y_{s,0}(\theta)$, where the a_s are still to be determined. Since the $Y_{s,0}$ form an orthogonal set, we can match term by term their coefficients; for the coefficient of $Y_{L,0}$ we obtain the equation:

$$0 = F_L(r) + \sum_n G_{nL}(r) + \sum_l \sum_m \sum_{l^-}^{L \le l+l^-} \int H_{l,m,l^-}(k_2,r)a_L dk_2 . \quad (25)$$

Suppose we now require that this incoming state with total angular momentum L gives an equal angular momentum $L = l + l^-$ to the particles after the collision. This allows a further simplification, shown below, with the temporarily introduced functions replaced by their equivalent analytic expressions:

$$0 = \phi_I \pi \left\{\frac{2(2L+1)}{k_I r}\right\}^{1/2} (-i)^L J_{L+1/2}(k_I r) + \sum_n^N c_{nL} \phi_n \frac{A}{\sqrt{r}} J_{L+1/2}(k_{1n} r) \qquad (26)$$

$$+ \sum_{l=0}^{L} \sum_m Aa_{Llm} / c_{lm}(k_1) J_{l+1/2}(k_1 r) \left[\begin{matrix} B J_{L-l+1/2}(k_2 r) \\ C J_{L-l+1/2}(k_3 r) + D J_{l-L-1/2}(k_3 r) \end{matrix} \right] dk_2 .$$

Matching term by term above corresponds physically to conservation of total angular momentum for each partial wave forming the incoming particle. Mathematically it seems justified from the orthogonality of the $Y_{l,0}$. We obtain a series of equations, one for each value of L; hopefully those terms of higher l value would be of less significance, so that the c_{nL} and $c_{lm}(k_1)$ past a certain point in the series can be approximated by zero. This is to be expected from physical considerations, but as this model is only an approximate representation of reality, it is far from guaranteed. With N the number of bound states, equation (26) contains N of the unknown constants c_{nL}, and (L+1)(2L+1) of the unknown functions $c_{lm}(k_1)$.

The conservation of energy and angular momentum cited above are strictly valid for a three-particle system, while the conservation assumed for this constructed two particle representation

is correct only if the particle setting up the potential well is in reality fixed. We get an approximation to this if it is assumed that the mass of the particle setting up the potential (m_2) is significantly greater than that of the bound particle(m_1). Riley has been able to remove the restriction by some guesswork simplification of the general three-particle Schrödinger equation. It involves the use of a new k_1, obtained from the old by multiplication by the factor $m_2/(m_1+m_2)$, which clearly reduces to unity for $m_2>>m_1$. The new k_1, obtained for the one-dimensional case, appears to be a property of the imposed boundary conditions and physical orientations, and hence might be expected to hold also in the three-dimensional case.

Equation (26) can be seen to have a form rather similar to that of equation (3) for the one-dimensional case; similar difficulties were anticipated in its solution by usual numerical methods, and hence attention was turned to the development of other methods of solution of the one-dimensional equation.

4. Other Methods For Studying The One-Dimensional Model

Equations (5) and (6) can be rewritten as follows:

$$0 = N_{mI} + \sum_{n}^{N} c_n N_{mn} + \int_0^\infty c(k) R_m(k)\,dk \qquad (27)$$

$$0 = S_I(k^\circ) + \sum_{n}^{N} c_n S_n(k^\circ) + \int_0^\infty c(k) f(k^\circ,k)\,dk + Xc(f_1(k^\circ)) + Yc(f_2(k^\circ)) + Zc(f_3(k^\circ)). \qquad (28)$$

The subscripted N are constants, while N(without subscripts) signifies the number of bound states. The minus superscript has been removed from the k^- for simplicity, and k° is, as before, a partic-

ular value of k. X, Y, and Z are constants, and f_1, f_2, f_3 are functions arising from singularities in the integration dr of the second term of the right hand side of equation (6). The last three terms of equation (28) will be represented as $Ac(g(k^\circ))$ for simplification, as it does not change the nature of this attempt at solution.

Equation (27) is really N equations, one for each value of m selected; we can solve this series of equations for the c_n and obtain

$$c_n = a_n + \int_0^\infty c(k)\left(\sum_{l=1}^{N} b_{ln} R_l(k)\right)dk \ . \qquad (29)$$

(a_n, b_{ln} constants compatible with (27))

Substituting this result in equation (28), we obtain

$$0 = S_I(k^\circ) + \sum_{n}^{N}\left[a_n + \int_0^\infty c(k)\left(\sum_{l=1}^{N} b_{ln} R_l(k)\right)dk\right]S_n(k^\circ) + \int_0^\infty c(k) f(k^\circ,k)dk + Ac(g(k^\circ)), \qquad (30)$$

which, with the substitutions

$$Q(k^\circ,k) = f(k^\circ,k) + \sum_{n}^{N}\sum_{l}^{N} b_{ln} R_l(k) S_n(k^\circ) \qquad (31)$$

and

$$F(k^\circ) = S_I(k^\circ) + Ac(g(k^\circ)) + \sum_{n}^{N} a_n S_n(k^\circ), \qquad (32)$$

takes on the form of a more conventional integral equation,

$$0 = F(k^\circ) + \int_0^\infty c(k) Q(k^\circ,k)dk. \qquad (33)$$

It is to be noted that the complexity of the the functions Q and F, along with the difficulties in actually solving for the constants a_n and b_{ln} above, makes the equation still very difficult. To attempt one conventional method of solution,[12] the substitution

$$F(k^\circ) = H(k^\circ) - c(k^\circ) \qquad (34)$$

was made, resulting in the equation

$$c(k^\circ) = H(k^\circ) + \int_0^\infty c(k^\circ)Q(k^\circ,k)dk \ , \qquad (35)$$

which can be thought of as an equation in k° even though k° is given as a point in the range of k, since the point is arbitrary. The equation has been somewhat artificially converted into an integral equation of the second kind from one of the first kind. This is not completely satisfactory, because the $H(k^\circ)$ contains unknown functional dependence as a result of the definition in equation (34); some of the dependence is inherent from equation (32), with the definition of $F(k^\circ)$, however. Equation (35) is a singular integral equation, since it possesses a singular kernel $Q(k^\circ,k)$.[¶] There is no practical general method of solution to such an equation, however, and this particular one does not have any convenient properties to allow it to be solved more simply.[12] Hence this attempt at solution by modifying the form of the equation was not successful.

Several other methods utilizing standard techniques were conceived but not elaborated. The function of r on the right side of equation (2) could be least-squares fit directly to zero over some range of r, most conveniently $0<r<L$. Alternatively, the function could be zeroed at a certain number of points, or both the function and its derivative zeroed at half that number. These are all closely related methods of solution and did not seem vastly different from the numerical processes employed previously. Some

[¶]Singularities in Q occur in $\frac{1}{k^\circ-k+b}$ factors in $f(k;k)$, b a constant.

different, more nearly analytical methods were attempted.

In equation (2), if the incoming particle has sufficient energy to insure dissociation classically, we can neglect all the c_n except that of the incident state, resulting in the equation

$$0 = F(r) = \phi_I(r)\theta_I(r) + \int_0^\infty c(k^-)\phi(k^-,r)\theta(k',r)dk^-, \qquad (36)$$

where c_I has been set equal to unity for convenience. In explicit form, with q a constant, and A_I and $A(k^-)$ normalization constants, we obtain for the range $0<r<L$

$$0 = F(r) = A_I(e^{ik_I^+r} - qe^{-ik_I^+r})e^{ik_I'r} + \int_0^\infty c(k^-)A(k^-)(e^{ik^+r} - qe^{-ik^+r})e^{ik'r}\,dk^- . \qquad (37)$$

The A's are complex expressions, hence not included, as they are not essential to the method developed; k^- and k^+ obey a relation identical to that between k_2 and k_3 resp. (equation (20)). If we differentiate F(r) and set the result also equal to zero, we get

$$0 = \frac{dF}{dr} = A_I e^{ik_I'r}[k_I'(e^{ik_I^+r} - qe^{-ik_I^+r}) + k_I^+(e^{ik_I^+r} + qe^{-ik_I^+r})] + \int_0^\infty c(k^-)A(k^-)e^{ik'r}[k'(e^{ik^+r} - qe^{-ik^+r}) + k^+(e^{ik^+r} + qe^{-ik^+r})]dk^- . \qquad (38)$$

Calling the integral in equation (37) m(r), and the integral in equation (38) p(r), the two equations can be combined to eliminate k_I' from the exponents, with result

$$0 = p(r)(qe^{-ik_I^+r} - e^{ik_I^+r}) + m(r)[qe^{-ik_I^+r}(k_I^+ - k_I') + e^{ik_I^+r}(k_I^+ + k_I')] . \qquad (39)$$

If $k'_I >> k^+_I$, we have simply $p(r) = k'_I m(r)$, or

$$0 = \int_0^\infty c(k^-)A(k^-)e^{ik'r}[(k' - k'_I)(e^{ik^+r} - qe^{-ik^+r}) + k^+(e^{ik^+r} + qe^{-ik^+r})]dk^- . \quad (40)$$

This is an alternate equation for solution, perhaps more amenable to the numerical processes which can be used. Equation (36) could also be used to determine the $c(k^-)$, since the restriction employed eliminates the c_n from consideration. An easy verification of the steps above comes from noting that $ip(r) = \frac{dm(r)}{dr}$, which implies that $im(r)k'_I = \frac{dm(r)}{dr}$, or $m(r) = Ce^{ik'_I r}$, which is in agreement with equation (37), since $k'_I >> k^+_I$.

In another attempt, the function $[\overset{U}{I}(r)]^2$ was minimized by a variational technique, setting the partial derivatives with respect to each of the c_n equal to zero; this should make $\overset{U}{I}(r)$ as close to zero as possible. After the c_n were found in this manner, treating the integral as just an unknown function of r, the $c(k^-)$ could be broken up as before and perhaps the same method used on the resulting set of constants. ($\overset{U}{I}(r)$ is the right hand side of equation (2)). Unfortunately, the equations resulting from this treatment proved upon simplification to reduce to the original equation (2), and hence proved no help; this perhaps could have been predicted. This concludes the summarization of attempts at solution of the one-dimensional equation.

Consequently positive results for the past summer's work could best be described as minimal. The three-dimensional for-

mulation, fraught with assumptions, only simplifies to a much more difficult equation than for the one-dimensional case. And while the author learned quite a bit about the solution of integral equations, the attempts at solution of equation (2) were unsuccessful. It would seem advisable that future work center more on an alternate formulation of the problem, in accordance with the possibility that the model of Shuler and Zwanzig is not suited for adaptation to include dissociation.

References

1. Phys. Rev. 37, 556(1931)
2. K. F. Herzfeld and T.A. Litovitz, Dispersion and Absorption of Ultrasonic Waves, Acad. Press Inc. New York 1959
3. R. Herman and K. E. Shuler, J. Chem. Physics 21, 373(1953)
4. Jackson and Mott, Proc. Roy. Soc.(London) A137, 703(1932)
5. Castellan and Hulburt, J. Chem. Phys. 18, 312(1950)
6. Widom, J. Chem. Phys. 30, 238(1959)
7. K. Shuler and Zwanzig, J. Chem. Phys. 33, 1778(1960)
8. D. Rapp and T. E. Sharp, J. Chem. Phys. 38, 2641(1963)
9. Merle Riley, California Institute of Technology, private communication.
10. Kemble, Quantum Mechanics, pp. 162-165
11. H. Wayland, Differential Equations, p. 197
12. Mikhlin, Integral Equations (1964) Chapter III
13. F. H. Mies and K. Shuler, J. Chem. Phys. 37,177(1962)