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SEMICLASSICAL THEORY OF ROTATIONAL AND VIBRATIONAL EXCITATION IN COLLISIONS OF ATOMS WITH DIATOMIC MOLECULES*

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ABSTRACT

A theory of rotationally and vibrationally inelastic collisions in atom-diatomic molecule scattering is presented in which both rotations and vibrations are treated semiclassically. The formalism, however, allows for an unambiguous specification of the initial and final quantum states even though the S-matrix itself is calculated in the classical limit. This development is particularly suited to the description of inelastic collision processes among the highly excited rotational-vibrational states which lie near the continuum.

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In the generalized phase shift, GPS, treatment of rotationally inelastic atom-diatom collisions, the S-matrix is transformed (through a transformation involving vector coupling coefficients and representation coefficients) in such a manner that the indices describing the final quantum states of the rotor are replaced by a set of Euler angles which in the semiclassical regime become continuous. Here we present an analogous treatment of the coupled rotational-vibrational problem. The S-matrix which is labelled by discrete indices describing the initial and final vibrational and rotational states of the diatomic molecule is transformed (through a similar transformation which now involves, in addition, the vibrational wave functions of the isolated diatomic molecule) to one in which the indices associated with the final states are replaced by three Euler angles, as in the GPS development, and a continuous parameter associated with the vibrational motion. This parameter is the internuclear separation coordinate of the diatomic molecule. The resulting equations are especially suited to a semiclassical analysis paralleling that given earlier[1] for rotationally inelastic scattering. Since the present development parallels that in reference 1, equations of that paper are denoted by a prefix I, i.e. Eq. (I-).

This semiclassical development is believed to be well suited to the description of vibrational transitions among the highly excited states of the diatomic molecule. In particular it is applicable to such problems as the termolecular recombination of hydrogen[2] <u>via</u> the mechanism

$$H + H \leftrightarrow H_2^*$$

$$H_2^* + M \rightarrow H_2 + M \ .$$

The stabilization of the metastable H_2^* by collision with the third body M (M = Ar, He, etc.) involves both vibrational and rotational de-excitations within the levels close to the continuum.[3] The application of this semiclassical method to this problem is currently being investigated.

The problem considered is the nonreactive collision of an atom and a diatomic molecule interacting through a Born-Oppenheimer potential. A center of mass coordinate system is chosen in which $\underline{\xi}$ is the vector between the atoms comprising the molecule and $\underline{r}$ is the vector between the atom and the center of mass of the diatomic molecule. The internal state of the diatomic molecule is described by the wave function

$$Z(v\ell;\xi)\ Y_\ell^m(\hat{\xi})$$

and is labelled by the vibrational quantum number v and rotational quantum numbers ℓ and m. The $Y_\ell^m(\hat{\xi})$ are normalized spherical harmonics and the radial functions $Z(v\ell;\xi)$ are eigenfunctions of the differential equation

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{d\xi^2} + V_\xi + \frac{\hbar^2\ \ell(\ell+1)}{2M\xi^2} - E_b(v\ell)\right]Z(v\ell;\xi) = 0 \ . \qquad (1)$$

In this equation M and V_ξ, respectively, are the reduced mass and potential energy of the isolated diatomic molecule and E_b ($E_b < 0$; measured from the separated atom limit) is the binding energy of the molecule. These radial functions satisfy the completeness and orthogonality conditions that

$$\sum_v Z(v\ell;\xi)^* Z(v\ell;\xi') = \delta(\xi-\xi') \tag{2}$$

and

$$\int Z(v\ell;\xi)^* Z(v'\ell;\xi)d\xi = \delta_{vv'} . \tag{3}$$

An integration over continuum states is implicitly contained in the completeness relation Eq. (2).

All of the information about the scattering process is contained in a set of complex functions, $Q^{(\pm)}(\bar{v}\bar{\ell}\bar{\lambda};S\xi r)$, which satisfy the following pair of coupled equations;[4]

$$\begin{aligned}\frac{d}{dr}\exp[iQ^{(\pm)}(\bar{v}\bar{\ell}\bar{\lambda};S\xi r)] = \frac{-i\mu}{\hbar^2}\int dS'\, d\xi'\, dS''\, d\xi'' \\ F^{(\pm)}(\bar{\ell}\bar{\lambda};S\xi S'\xi';r)\, V^{(1)}(r\xi'\theta') \\ \{F^{(+)}(\bar{\ell}\bar{\lambda};S''\xi''S'\xi';r)^* \exp[iQ^{(+)}(\bar{v}\bar{\ell}\bar{\lambda};S''\xi''r)] \\ - F^{(-)}(\bar{\ell}\bar{\lambda};S''\xi''S'\xi';r)^* \exp[iQ^{(-)}(\bar{v}\bar{\ell}\bar{\lambda};S''\xi''r)]\} .\end{aligned} \tag{4}$$

This pair of equations is obtained by suitably transforming those obtained from an integral equation based upon a separation of the total atom-molecule interaction potential $V(r\xi\theta)$ into elastic, $V^{(0)}(r)$, and inelastic, $V^{(1)}(r\xi\theta)$, contributions. The angle θ is that between the

vectors $\underline{r}$ and $\underline{\xi}$. The matrix elements $F^{(\pm)}(\bar{\ell}\bar{\lambda};S\xi S'\xi';r)$ are defined by

$$F^{(\pm)}(\bar{\ell}\bar{\lambda};S\xi S'\xi';r) = \sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi)^* \, f^{(\pm)}(v\ell\lambda;r) \, \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S'\xi') \tag{5}$$

in terms of the basis functions

$$\chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi) = (-1)^L (8\pi^2)^{-1/2} [(2\ell+1)(2\lambda+1)(2L+1)]^{1/2} \sum_{\nu\mu} (-i)^{\nu+\mu} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \nu & -\nu \end{pmatrix} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & -\mu & \mu \end{pmatrix} D^L(S)_{\nu\mu} \, Z(v\ell;\xi)^* \, . \tag{6}$$

The $f^{(\pm)}(v\ell\lambda;r)$ are solutions of the radial wave equation involving only the elastic part of the interaction potential. They are defined in detail in reference 4.

The coupled equations, Eq. (4), may be written in a more compact form by defining an operator $F^{(\pm)}$ by its action on an arbitrary function $Y(\Omega)$ as

$$F^{(\pm)} \, Y(\Omega) \equiv \int F^{(\pm)}(\bar{\ell}\bar{\lambda};\Omega\Omega';r) \, Y(\Omega') \, d\Omega' \, , \tag{7}$$

where Ω stands for the combined indices $S\xi$ and $d\Omega \equiv d\xi \, dS$. It follows that

$$\frac{d}{dr} \exp[iQ^{(\pm)}] = \frac{-i\mu}{\hbar^2} F^{(\pm)} \, V^{(1)} \{F^{(+)\dagger} \exp[iQ^{(+)}] - F^{(-)} \exp[iQ^{(-)}]\} \, . \tag{8}$$

Another operator, G, is defined by

$$G^{(\pm)}\, Y(\Omega) = \int G^{(\pm)}(\bar{\ell}\bar{\lambda};\Omega\Omega';r)\, Y(\Omega')\, d\Omega' , \tag{9}$$

where

$$G^{(\pm)}(\bar{\ell}\bar{\lambda};\Omega\Omega';r) = \sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)^* \left[\frac{d}{dr} f^{(\pm)}(v\ell\lambda;r)\right] \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega') . \tag{10}$$

It follows immediately from these definitions that

$$G^{(\pm)} = F^{(\pm)-1}\, F^{(\pm)\prime} = F^{(\pm)\prime}\, F^{(\pm)-1} \tag{11}$$

and

$$F^{(\pm)}\, G^{(\pm)} = G^{(\pm)}\, F^{(\pm)}, \tag{12}$$

where a "prime" indicates differentiation with respect to r. The equations for $Q^{(+)}$ and $Q^{(-)}$ can be uncoupled to give the second order differential equations[5]

$$\begin{aligned} i\hbar^2 \frac{\partial^2}{\partial r^2} Q - \left(\hbar \frac{\partial}{\partial r} Q\right)^2 &= 2\mu\, e^{-iQ}\, F\, V^{(1)}\, F^{-1}\, e^{iQ} \\ &\quad + \hbar^2\, e^{-iQ}\left[G + F\left(\frac{\partial}{\partial r} \ln V^{(1)}\right) F^{-1}\right. \\ &\quad \left. + F\, V^{(1)}\, G\, V^{(1)-1}\, F^{-1}\right]\left(\frac{\partial}{\partial r}\, e^{iQ}\right) , \end{aligned} \tag{13}$$

where (to simplify the notation) the superscipts $(\pm)$ have been omitted. This expression may also be written as

$$\begin{aligned} i\hbar^2 \frac{\partial^2}{\partial r^2} Q - \left(\hbar \frac{\partial}{\partial r} Q\right)^2 &= 2\mu\, e^{-iQ}\, V\, e^{iQ} \\ &\quad + i\hbar^2\, e^{-iQ}\left[G + U\, V^{-1} + V\, G\, V^{-1}\right] e^{iQ}\, \frac{\partial}{\partial r} Q , \end{aligned} \tag{14}$$

where U and V are two additional operators defined by

$$V = F\, V^{(1)} F^{-1} \tag{15}$$

and

$$U = F\left(\frac{\partial}{\partial r} V^{(1)}\right) F^{-1} . \tag{16}$$

Useful properties of the operators F and G are obtained in a manner analogous to that discussed in reference 1. To this end, operators K and J are defined as

$$K = (2M\xi^2)^{-1} \left[L_1^2 + L_2^2 - L_3^2 - 2 \sum_n \frac{(-1)^n (\tfrac{1}{2})!}{(\tfrac{1}{2}-n)!\,n!} K^{(\frac{1}{2})-n} L_3^n L_2 L_3^n\right] + V_\xi - \bar{E} - \frac{\hbar^2}{2M} \frac{d^2}{d\xi^2} \tag{17}$$

and

$$J = M_1^2 + M_2^2 - M_3^2 + 2 \sum_n \frac{(-1)^n (\tfrac{1}{2})!}{(\tfrac{1}{2}-n)!\,n!} J^{(\frac{1}{2})-n} M_3^n M_2 M_3^n . \tag{18}$$

The angular momentum operators, L_j and M_j, are those used in I. The factors K and J are given in terms of the initial angular momentum quantum numbers as

$$K = \bar{\ell}(\bar{\ell}+1)\hbar^2 \tag{19}$$

and

$$J = \bar{\lambda}(\bar{\lambda}+1)\hbar^2 , \tag{20}$$

while $\bar{E}$ is defined in terms of the total initial binding energy of the diatomic molecule, E_b $(E_b < 0)$, by

$$\bar{E} = E_b(\bar{v}\bar{\ell}) - \frac{\hbar^2}{2M\xi^2}\,\bar{\ell}(\bar{\ell}+1) \ . \qquad (21)$$

These K and J operators have the very interesting and useful properties that χ is an eigenfunction of K^* and J^* with the eigenvalues being the energy inelasticity and the change in the relative angular momentum, viz.

$$K^*\ \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi) = -(E-\bar{E})\ \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi) \qquad (22)$$

and

$$J^*\ \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi) = \hbar^2[\lambda(\lambda+1) - \bar{\lambda}(\bar{\lambda}+1)]\ \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi) \ . \qquad (23)$$

The energies

$$\bar{E} = \frac{\hbar^2\bar{k}^2}{2\mu} = E_t - E_b(\bar{v}\bar{\ell}) \qquad (24)$$

and

$$E = E_t - E_b(v\ell) \qquad (25)$$

are the relative translational energies of the molecules before and after a collision; E_t is the total center of mass energy.

The functions $f^{(\pm)}(v\ell\lambda)$ central to the operators F and G can be written in the form (see Eq. (I-39))

$$f^{(\pm)}(v\ell\lambda) = (\frac{\hbar^2}{2\mu})\ \exp[\frac{i}{\hbar}\ S^{(\pm)}(v\ell\lambda)] \ . \qquad (26)$$

The functions $S^{(\pm)}(v\ell\lambda)$, or dropping the superscripts, $S(v\ell\lambda)$, depend on v, ℓ and λ only through the quantities E and $\lambda(\lambda+1)\hbar^2$.

Therefore, they may be expanded in a double Taylor series about their values at $E = \bar{E}$ and $\lambda(\lambda+1)\hbar^2 = J$;

$$S(v\ell\lambda) = \sum_{mn} \frac{1}{m!n!} S_{mn}(E - \bar{E})^m \, [\lambda(\lambda+1)\hbar^2 - J]^n \tag{27}$$

where

$$S_{mn} = \frac{\partial^m}{\partial \bar{E}^m} \frac{\partial^n}{\partial J^n} S(\bar{v}\bar{\ell}\bar{\lambda}) \ . \tag{28}$$

These properties enable the integral operators F and G to be written in differential forms. By the definition Eq. (8), F acting on an arbitrary function $Y(\Omega)$ is given by

$$\begin{aligned} F\,Y(\Omega) &= \sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)^* \, f(v\ell\lambda) \int \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega') \, Y(\Omega') \, d\Omega' \\ &= \left(\frac{\hbar^2}{2\mu}\right)^{1/4} \sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)^* \, e^{(i/\hbar)S(v\ell\lambda)} \int \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega') \, Y(\Omega') \, d\Omega' \ . \end{aligned} \tag{29}$$

From the eigenvalue relations Eqs. (22) and (23) and the expansion Eq. (27), it follows that

$$\begin{aligned} F\,Y(\Omega) = \left(\frac{\hbar^2}{2\mu}\right)^{1/4} \sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)^* \int Y(\Omega') \exp\left[\frac{i}{\hbar} \sum_{mn} \frac{(-1)^m}{m!n!} S_{mn}(K^*)^m (J^*)^n\right] \\ \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega') d\Omega' \ . \end{aligned} \tag{30}$$

Since the operators K and J are hermitian and the $\chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)$ obey the completeness relation that

$$\sum_{v\ell\lambda L} \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega)^* \, \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;\Omega') = \delta(\Omega-\Omega') = \delta(S-S') \, \delta(\xi-\xi') \ , \tag{31}$$

Eq. (30) is equivalent to the expression

$$F\, Y(\Omega) = \left(\frac{\hbar^2}{2\mu}\right) \exp\left[\frac{i}{\hbar} S\right] Y(\Omega) , \tag{32}$$

where

$$S = \sum_{mn} \frac{(-1)^m}{m!n!} S_{mn} K^m J^n . \tag{33}$$

Because $Y(\Omega)$ is an arbitrary function, F has the differential form

$$F = \left(\frac{\hbar^2}{2\mu}\right)^{1/4} \exp\left[\frac{i}{\hbar} S\right] . \tag{34}$$

Similarly, G can be expressed as

$$G = \frac{i}{\hbar} S' . \tag{35}$$

A semiclassical solution to the equation for Q can be obtained after suitable approximations are made concerning the operator F. First, the function $S^{(0)}$, defined by Eqs. (I-37) and (I-38), is written in the series form

$$S^{(0)}(\bar{v}\bar{\ell}\bar{\lambda}) = S_0^{(0)} + i\hbar\, S_1^{(0)} - \hbar^2\, S_2^{(0)} + \ldots , \tag{36}$$

where the $S_n^{(0)}$ are given by Eqs. (I-53) through (I-56). In a similar manner, the functions $S^{(\pm)}(v\ell\lambda)$ [or $S(v\ell\lambda)$] and the operators K and J have the series representations

$$S(\bar{v}\bar{\ell}\bar{\lambda}) = \sum_{n=0}^{\infty} (i\hbar)^n S_n , \tag{37}$$

$$K = \sum_{n=0}^{\infty} (i\hbar)^n K_n , \tag{38}$$

and

$$J = \sum_{n=1}^{\infty} (i\hbar)^n J_n , \tag{39}$$

where

$$K_0 = V(\xi) - \bar{E}(\xi) , \tag{40}$$

$$K_{2n+1} = \frac{i(\frac{1}{2})!}{(\frac{1}{2}-n)!n!\hbar^{2n+1}} \frac{K^{(\frac{1}{2})-n}}{M\xi^2} L_3^n L_2 L_3^n ; \qquad n = 0,1,2,\ldots , \tag{41}$$

$$K_2 = -\frac{1}{2M\xi^2\hbar^2}(L_1^2 + L_2^2 - L_3^2) + \frac{1}{2M}\frac{d^2}{d\xi^2} , \tag{42}$$

$$K_{2n} = 0 ; \qquad n = 2,3,4,\ldots , \tag{43}$$

$$J_{2n+1} = \frac{-2i(\frac{1}{2})!}{(\frac{1}{2}-n)!n!\hbar^{2n+1}} J^{(\frac{1}{2})-n} M_3^n M_2 M_3^n ; \qquad n = 0,1,2,\ldots , \tag{44}$$

$$J_2 = -\frac{1}{\hbar^2}(M_1^2 + M_2^2 - M_3^2) \tag{45}$$

$$J_{2n} = 0 ; \qquad n = 2,3,4,\ldots . \tag{46}$$

The operator S defined by Eq. (33) may now be expanded as

$$S = \sum_{n=0}^{\infty} (i\hbar) S_n , \tag{47}$$

each of the S_n, in turn, being written as a finite series

$$S_n = \sum_{k=0}^{n} S_{nk} \cdot \tag{48}$$

Each operator S_{nk} is at most of order k in derivatives with respect to angles and the internal separation distance of the diatomic molecule. Specifically, the first few terms are

$$S_{n0} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} K_0^m S_{n,m,0} \tag{49}$$

$$S_{n1} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} K_0^m [S_{n-1,m,1} J_1 - S_{n-1,m+1,0} K_1] \tag{50}$$

and

$$S_{n2} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} K_0^m [\tfrac{1}{2} S_{n-2,m+2,0} K_1^2 + \tfrac{1}{2} S_{n-2,m,2} J_1^2$$

$$- S_{n-2,m+1,1} J_1 K_1 + S_{n-2,m,1} J_2] \tag{51}$$

$$+ \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \sum_{\delta=0}^{m-1} K_0^{\delta} K_2 K_0^{m-\delta-1} S_{n-2,m,0}$$

where

$$S_{p,m,n} = \left(\frac{\partial}{\partial \bar{E}}\right)^m \left(\frac{\partial}{\partial J}\right)^n S_p \cdot \tag{52}$$

Except for the last term in S_{n2}, the infinite sums that appear in the S_{nk} have the effect of just replacing the initial translational energy $\bar{E}$, which parameterizes the $S_{p,mn}$, by the effective energy $E_t - \frac{K}{2M\xi^2} - V(\xi)$;

$$\sum_{m=0}^{\infty} \frac{(-1)^m}{m!} K_0^m S_{n,m+\delta,t} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} [V(\xi) - \bar{E}(\xi)]^m \frac{\partial^m}{\partial \bar{E}^m} S_{n,\delta,t}$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!} [E_t - \frac{K}{2M\xi^2} - V(\xi) - \bar{E}]^m (\frac{\partial}{\partial \bar{E}})^m S_{n,\delta,t} \qquad (53)$$

$$= S_{n,\delta,t} \Big|_{\bar{E}=E_t - \frac{K}{2M\xi^2} - V(\xi)} \equiv S(\xi)_{n,\delta,t} .$$

In terms of the $S(\xi)_{n,m\delta}$ just defined, the S_{nk} are given by

$$S_{n0} = S(\xi)_{n,00} = S(\xi)_n , \qquad (54)$$

$$S_{n1} = -S(\xi)_{n-1,1,0} K_1 + S(\xi)_{n-1,0,1} J_1 , \qquad (55)$$

$$S_{n2} = S(\xi)_{n-2,0,1} J_2 + \tfrac{1}{2} S(\xi)_{n-2,2,0} K_1^2 - S(\xi)_{n-2,1,1} K_1 J_1$$

$$+ \tfrac{1}{2} S(\xi)_{n-2,0,2} J_1^2 - S(\xi)_{n-2,1,0} K_2 - \tfrac{1}{2} S(\xi)_{n-2,2,0} [K_0, K_2] \qquad (56)$$

$$- \tfrac{1}{6} S(\xi)_{n-2,3,0} [K_0, [K_0, K_2]] ,$$

where the results of the Appendix have been used in the expression for S_{n2}. The expressions for S_{n0} and S_{n1} are identical in form to Eqs. (I-68) and (I-69) with $S_{n,\delta t}$ replaced by the corresponding ξ-parametrized quantities $S(\xi)_{n,\delta t}$. The expression for S_{n2} contains additional terms involving commutators of K_0 with K_2.

In this way, the central quantities that must be calculated for the description of the full vibration-rotation inelastic scattering problem are reduced to expressions similar to those arising in the rotation problem alone. The difference is that now the generalized action

integrals are parameterized by the internuclear separation distance of the diatomic molecule. This only affects the effective translational energy at which the generalized action integrals are evaluated.

Using the expansion, Eq. (47), one finds that

$$e^{(i/\hbar)S} = [\sum_n (i\hbar)^n R_n]\, e^{-S_{11}}\, e^{-S_1}\, e^{(i/\hbar)S_0} \tag{57}$$

and

$$e^{-(i/\hbar)S} = e^{-(i/\hbar)S_0}\, e^{S_1}\, e^{S_{11}} [\sum_n (i\hbar)^n P_n] \,. \tag{58}$$

The operators R_n and P_n are given by Eqs. (I-75) through (I-81), but once again the appropriate ξ-parameterized quantities must be used.

The problem is thus reduced to that of reference I and the further analysis is not repeated here. The essential difference is that the various quantities have an additional dependence on the variable ξ.

The result is that when Q is written in the semiclassical form

$$Q = \frac{1}{\hbar} \sum_n (i\hbar)^n Q_n \,, \tag{59}$$

the coefficients Q_0 and Q_1 satisfy the equations

$$(\frac{\partial}{\partial r} Q_0)^2 - \tilde{G}_{00}(\frac{\partial}{\partial r} Q_0) + 2\mu\, \tilde{V}_{00} = 0 \tag{60}$$

and

$$\begin{aligned} 2[\tilde{G}_{00} - (\frac{\partial}{\partial r} Q_0)](\frac{\partial}{\partial r} Q_1) &= -2\mu\, \tilde{V}_1 - \frac{\partial^2}{\partial r^2} Q_0 \\ &+ \{\tilde{U}_{00}\, \tilde{W}_{00} + \tilde{W}_{00}[\tilde{G}_{11}, \tilde{V}_{00}] + \tilde{W}_{00}[\tilde{V}_{11}, \tilde{G}_{00}] - 2\tilde{G}_1\}(\frac{\partial}{\partial r} Q_0) \,. \end{aligned} \tag{61}$$

The expressions for the quantities $\tilde{G}$, $\tilde{V}$ and $\tilde{W}$ are the same as those in I. It is remarked once again that all of these quantities depend on ξ through the $S(\xi)_{n,\delta t}$ which are central to their definitions. It should also be noted that $\bar{V}^{(1)}$ implicit in the expressions for $\tilde{G}$, $\tilde{V}$ and $\tilde{W}$ is still given by

$$\bar{V}^{(1)} = V^{(1)}(S',\xi), \tag{62}$$

but the angles ψ and θ used to specify the rotation S',

$$S' = (\pi,\psi,\pi)\, S(\pi,\theta,\pi)\,, \tag{63}$$

depend on ξ as well;

$$\psi = \psi(\xi) = -\frac{K^{1/2}}{M\xi}\, S(\xi)_{0,1,0}\,, \tag{64}$$

$$\theta = \theta(\xi) = -2J^{1/2}\, S(\xi)_{0,0,1}\,. \tag{65}$$

To first order in the inelasticity, the solutions[6] of Eq. (60) are given by

$$Q_0^{(-)}(\bar{v}\bar{\ell}\bar{\lambda}S\xi r) = \ln Z(\bar{v}\bar{\ell};\xi) + 2\eta(\bar{v}\bar{\ell}) - \frac{\mu}{\hbar^2}\int_r^\infty |f^{(-)}(\bar{v}\bar{\ell}\bar{\lambda})|^2\, V^{(1)}(T^{(-)},\xi)dr' \tag{66}$$

and

$$Q_0^{(+)}(\bar{v}\bar{\ell}\bar{\lambda}S\xi r) = \ln Z(\bar{v}\bar{\ell};\xi) + 2\eta(\bar{v}\bar{\ell}) - \frac{\mu}{\hbar^2}\int_{r_0(\xi)}^\infty |f^{(-)}(\bar{v}\bar{\ell}\bar{\lambda})|^2\, V^{(1)}(T^{(-)},\xi)dr' - \frac{\mu}{\hbar^2}\int_{r_0(\xi)}^r |f^{(+)}(\bar{v}\bar{\ell}\bar{\lambda})|^2\, V^{(1)}(T^{(+)},\xi)dr'\,. \tag{67}$$

The rotations $T^{(\pm)}$ are given by

$$T^{(+)} = (\pi,\psi(\xi),\pi)\ S(\pi,\theta(\xi),\pi)\ , \tag{68}$$

and

$$T^{(-)} = (\pi,2\psi^{(0)}(\xi)-\psi(\xi),\pi)\ S(\pi,2\theta^{(0)}(\xi)-\theta(\xi),\pi)\ , \tag{69}$$

where $\psi^{(0)}(\xi)$ and $\theta^{(0)}(\xi)$ are the values of $\psi(\xi)$ and $\theta(\xi)$ at the turning point $r_0(\xi)$. The results Eqs. (66) and (67) may then be used in Eq. (61) to generate the solutions $Q_1^{(+)}$ and $Q_1^{(-)}$.

Knowledge of the $Q^{(+)}(\bar{v}\bar{\ell}\bar{\lambda}S\xi)$ is sufficient to determine the S-matrix (in an unusual representation)

$$S(\bar{v}\bar{\ell}\bar{\lambda}S\xi) = \lim_{r\to\infty} e^{iQ^{(+)}(\bar{v}\bar{\ell}\bar{\lambda}S\xi)}\ , \tag{70}$$

in which the initial state of the system is specified but the final state indices are replaced by the angles S and the distance ξ. From this S-matrix, the transition amplitude, $T(\bar{v}\bar{\ell}\bar{\lambda};v\ell\lambda L)$, may readily be determined;

$$T(\bar{v}\bar{\ell}\bar{\lambda};v\ell\lambda L) = \delta(\bar{v}\bar{\ell}\bar{\lambda}0|v\ell\lambda L) - (-1)^{\bar{\ell}+\bar{\lambda}}\ (8\pi^2)^{-1/2} \int \chi(\bar{\ell}\bar{\lambda};v\ell\lambda L;S\xi)\ S(\bar{v}\bar{\ell}\bar{\lambda}S\xi)d\xi\ dS\ . \tag{71}$$

These expressions, Eqs. (70) and (71), for the S- and T-matrices are exact but when combined with the previous results for $Q(\bar{v}\bar{\ell}\bar{\lambda}S\xi)$ provide an approximation in which the rotational-vibrational scattering

is treated in a semiclassical manner. Despite the semiclassical nature of the development, the initial and final quantum states are unambiguously specified in the scattering amplitude.

APPENDIX

Since K_0 and K_2 do not commute, the sums in the expression

$$\sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \sum_{\delta=0}^{m-1} K_0^{\delta} K_2 K_0^{m-\delta-1} S_{n-2,m0}$$

(which is the last term in S_{n2}, Eq. (51)) cannot be evaluated as in Eq. (53). However, these sums may be evaluated in the following way;[7]

$$\sum_{m=1}^{\infty} \sum_{\delta=0}^{m-1} \frac{(-1)^m}{m!} K_0^{\delta} K_2 K_0^{m-\delta-1} S_{n-2,m0} = \sum_{t=0}^{\infty} \sum_{\delta=0}^{t} \frac{(-1)^{t+1}}{(t+1)!} K_0^{\delta} K_2 K_0^{t-\delta} S_{n-2,t+1,0}$$

$$= \sum_{\delta=0}^{\infty} \sum_{p=0}^{\infty} \frac{(-1)^{p+\delta+1}}{(p+\delta+1)!} p!\delta! \frac{K_0^{\delta}}{\delta!} K_2 \frac{K_0^{p}}{p!} S_{n-2,p+\delta+1,0}$$

$$= -\sum_{\delta p} \frac{p!\delta!}{(p+\delta+1)!} \frac{(-K_0 \frac{\partial}{\partial \bar{E}})^{\delta}}{\delta!} K_2 \frac{(-K_0 \frac{\partial}{\partial \bar{E}})^{p}}{p!} S_{n-2,10} \qquad \text{(A-1)}$$

$$= -\sum_{\delta p} \int_0^1 d\alpha (1-\alpha)^{\delta} \alpha^{p} \frac{(-K_0 \frac{\partial}{\partial \bar{E}})^{\delta}}{\delta!} K_2 \frac{(-K_0 \frac{\partial}{\partial \bar{E}})^{p}}{p!} S_{n-2,10}$$

$$= -\int_0^1 e^{(\alpha-1)K_0(\partial/\partial \bar{E})} K_2 e^{-\alpha K_0(\partial/\partial \bar{E})} S_{n-2,10} ,$$

where the substitution $p = t - \delta$, the integral representation for the beta function[8] $p!\delta!/(p+\delta+1)!$, and the definition of the $S_{p,mn}$, Eq. (52), have been used. The integral is evaluated by defining a commutator superoperator Δ as

$$\Delta A = [K_0 \frac{\partial}{\partial E}, A] \tag{A-2}$$

where A is any operator. It follows that

$$\int_0^1 d\alpha \exp[(\alpha-1) K_0 \frac{\partial}{\partial E}] K_2 \exp[-\alpha K_0 \frac{\partial}{\partial E}]$$

$$= \exp[-K_0 \frac{\partial}{\partial E}] \int_0^1 e^{\alpha\Delta} d\alpha K_2 \tag{A-3}$$

$$= \exp[-K_0 \frac{\partial}{\partial E}] \frac{[\exp(\Delta) - 1]}{\Delta} K_2 .$$

Since K_2 is a second-order differential operator, the effect of $[\exp(\Delta) - 1]/\Delta$ on K_2 may be evaluated explicitly with the result that

$$\frac{\exp(\Delta) - 1}{\Delta} K_2 = K_2 + \tfrac{1}{2}[K_0, K_2]\frac{\partial}{\partial E} + \tfrac{1}{6}[K_0,[K_0,K_2]](\frac{\partial}{\partial E})^2 . \tag{A-4}$$

These results together with Eq. (53) imply that

$$\sum_{m=1}^{\infty} \sum_{\delta=0}^{m} \frac{(-1)^m}{m!} K_0^{\delta} K_2 K_0^{m-\delta-1} S_{n-2,m0} = -S(\xi)_{n-2,10} K_2$$

$$-\tfrac{1}{2} S(\xi)_{n-2,20}[K_0,K_2] - \tfrac{1}{6} S(\xi)_{n-2,30}[K_0,[K_0,K_2]] . \tag{A-5}$$

REFERENCES

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1. C. F. Curtiss, J. Chem. Phys. 63, 2738 (1975).

2. The theory of hydrogen recombination has been discussed by many authors. Among them are the following: D. L. Bunker, J. Chem. Phys. 32, 1001 (1960); J. C. Keck, ibid. 32, 1035 (1960); R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, ibid. 50, 5163 (1969); V. H. Shui and J. P. Appleton, ibid. 55, 3126 (1971); R. T. Pack, R. L. Snow, and W. D. Smith, ibid. 56, 926 (1972); P. A. Whitlock, J. T. Muckerman, and R. E. Roberts, Chem. Phys. Lett. 16, 460 (1972) and J. Chem. Phys. 60, 3658 (1974); V. H. Shui, J. Chem. Phys. 58, 4868 (1973); A. Jones and J. L. J. Rosenfeld, Proc. Roy. Soc. A333, 419 (1973).

3. It was thought that rotational de-excitation was the primary mechanism for the stabilization of metastable H_2 [R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, J. Chem. Phys. 50, 5163 (1969)], but later investigations have revealed that vibrational and rotational de-excitation are of comparable importance [P. A. Whitlock, J. T. Muckerman and R. E. Roberts, J. Chem. Phys. 60, 3658 (1974); N. C. Blais and D. G. Truhlar, J. Chem. Phys. 65, 5335 (1976)].

4. C. F. Curtiss, J. Mol. Phys. 00, 0000 (1977). The radial functions used in the present discussion differ from those used by Curtiss by a factor of ξ ; Z(present) = ξ Z(former).

5. This equation is analogous to that given by C. F. Curtiss, J. Chem. Phys. 52, 4832 (1970); Eq. (30).

6. Solutions of Eq. (58) do not exist when ξ is a node of the radial function $Z(\bar{\nu}\bar{\ell};\xi)$. This, however, presents no difficulty in applications of the theory.

7. R. F. Snider, J. Math. Phys. 5, 1580 (1964).

8. A. Erdélyi, Higher Transcendental Functions (McGraw-Hill Book Co., Inc., New York, 1953), Vol. 1, Chapter 1.

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A theory of rotationally and vibrationally inelastic collisions in atom-diatomic molecule scattering is presented in which both rotations and vibrations are treated semiclassically. The formalism, however, allows for an unambiguous specification of the initial and final quantum states even though the S-matrix itself is calculated in the classical limit. This development is particularly suited to the description of inelastic collision processes among the highly excited rotational-vibrational states which lie near the continuum.