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Molecular Collisions, XII: Generalized Phase Shifts

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ABSTRACT

The previous development of the theory of rotational excitation in collisions of diatomic molecules is transformed to obtain equations for a set of generalized phase shifts. The resulting equations are in a form which may be interpreted in terms of trajectories and interference effects. Approximate equations valid in the semiclassical limit are obtained. A further approximation leads to the previously developed sudden approximation.

The theory of rotational excitation in collisions of diatomic molecules has been discussed in a series of papers,<sup>1</sup> referred to as Papers I - XI. This development is based on the time independent or partial wave approach to scattering theory. In the present paper, the resulting formulation is transformed to a form similar to approximations based on the time dependent approach. In particular it is shown that certain well defined approximations lead to the full sudden approximation. Corrections to the sudden approximation are discussed.

In Paper VIII of the series, the moments of the degeneracy averaged cross section are written in terms of the elements,  $S(\bar{\lambda}\Lambda)$ , of an S-matrix in the form<sup>2</sup> (Eq. VIII-8),

$$I(\bar{l}_a \bar{l}_b; l_a l_b; L) = (2L+1)(4k^2)^{-1} \sum (-1)^L (2\bar{\lambda}+1)(2\bar{\lambda}'+1) \\ [(2\lambda+1)(2\lambda'+1)]^{1/2} \begin{pmatrix} \lambda & \lambda' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \bar{\lambda} & \bar{\lambda}' & L \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} \lambda & \lambda' & L \\ \bar{\lambda}' & \bar{\lambda} & L \end{matrix} \right\} \\ [S(\bar{\lambda}|\Lambda) - S(\bar{l}\Lambda)] [S(\bar{l}_a \bar{l}_b \bar{\lambda}' 0 0 0 | l_a l_b \lambda' L_a L_b L) \\ - S(\bar{l}_a \bar{l}_b \bar{\lambda}'; l_a l_b \lambda' L_a L_b L)] \quad (1)$$

where the sum is over  $\lambda, \lambda', \bar{\lambda}, \bar{\lambda}', L_a, L_b,$  and  $L$ . Here and elsewhere the symbol  $\Lambda$  is used to indicate, collectively, the set of six indices  $l_a, l_b, \lambda, L_a, L_b, L$ ;  $l$  to indicate the set of three indices  $l_a, l_b, \lambda$ ;  $\bar{\Lambda}$  to indicate the set  $\bar{l}_a, \bar{l}_b, \bar{\lambda}, 0, 0, 0$ ; and  $\bar{l}$  to indicate the set  $\bar{l}_a, \bar{l}_b, \bar{\lambda}$ . Thus  $\delta(\bar{\Lambda}|\Lambda)$  indicates the product of six Kronecker deltas. The elements  $S(\bar{\lambda}\Lambda)$ , of the S-matrix may be defined in terms of the asymptotic form of the functions  $X(\bar{\lambda}\Lambda)$  by (Eq. VIII-6),

$$X(\bar{\rho}\Lambda) \rightarrow \frac{1}{2} (k\bar{k})^{-1/2} \left[ \delta(\bar{\lambda}|\Lambda) (i)^{\bar{\lambda}+1} \exp(-ikr) + (-i)^{\bar{\lambda}+1} \delta(\bar{\rho}\Lambda) \exp(ikr) \right] \quad (2)$$

A Green's function expression for the functions  $X(\bar{\rho}\Lambda)$  is given by Eq. IX-4,

$$X(\bar{\rho}\Lambda) = \delta(\bar{\lambda}|\Lambda) r \Psi_{\lambda}(k) + r G_{\lambda}(k) r^{-1} \sum_{\Lambda'} W'''(\bar{\rho}\Lambda\Lambda') X(\bar{\rho}\Lambda') \quad (3)$$

in terms of the Green's operator for the motion of the pair of molecules interacting through the orientation averaged potential,  $V^{(0)}$ . This operator is defined by Eq. V-26, in terms of the functions  $\psi_{\lambda}(k)$  and  $\tilde{\psi}_{\lambda}(k)$  which in turn are defined by Eqs. V-21 and 23.

#### Generalized Phase Shifts

Let us define the functions  $\psi^{(+)}(\ell)$  and  $\psi^{(-)}(\ell)$  as the solutions of the radial wave equation

$$\left[ -\frac{d^2}{dr^2} + \frac{\lambda(\lambda+1)}{r^2} + \frac{2M}{\hbar^2} V^{(0)} \right] \psi^{(\pm)}(\ell) = k^2 \psi^{(\pm)}(\ell) \quad (4)$$

which are asymptotically of the form

$$\psi^{(\pm)}(\ell) \rightarrow \exp(\pm ikr) \quad (5)$$

In terms of these functions, the functions  $\psi_{\lambda}(k)$  and  $\tilde{\psi}_{\lambda}(k)$ , defined by Eqs. V-21 and 23, are

$$\Psi_{\lambda}(k) = (2kR)^{-1} \left[ (-i)^{\lambda+1} e^{2i\gamma(\ell)} \Psi^{(+)}(\ell) + (i)^{\lambda+1} \Psi^{(-)}(\ell) \right] \quad (6)$$

$$\tilde{\Psi}_{\lambda}(k) = (kR)^{-1} A_{\lambda}(k) (-i)^{\lambda+1} \Psi^{(+)}(\ell) \quad (7)$$

where  $\eta(\ell)$  is the usual phase shift.

With Eqs. 6 and 7, it follows directly from Eqs. 3 and V-26 that

$$\begin{aligned} X(\bar{\ell}\lambda) = \frac{1}{2} (-i)^{\bar{\lambda}+1} (k\bar{k})^{-1/2} \left[ \Psi^{(+)}(\ell) Y^{(+)}(\bar{\ell}\lambda) \right. \\ \left. - (-1)^{\lambda} e^{-2i\gamma(\ell)} \Psi^{(-)}(\ell) Y^{(-)}(\bar{\ell}\lambda) \right] \quad (8) \end{aligned}$$

where

$$\begin{aligned} Y^{(-)}(\bar{\ell}\lambda) = e^{2i\gamma(\ell)} \left[ S(\bar{\lambda}|\lambda) - (i)^{\bar{\lambda}} (-1)^{\lambda} \left( \frac{\bar{k}}{k} \right)^{1/2} \frac{2M}{\hbar^2} \right. \\ \left. \sum_{\lambda'} \int_{\ell}^{\infty} \Psi^{(+)}(\ell) W'''(\bar{\ell}\lambda\lambda') X(\bar{\ell}\lambda') d\ell' \right] \quad (9) \end{aligned}$$

$$\begin{aligned} Y^{(+)}(\bar{\ell}\lambda) = e^{2i\gamma(\ell)} \left[ S(\bar{\lambda}|\lambda) + (i)^{\bar{\lambda}} \left( \frac{\bar{k}}{k} \right)^{1/2} \frac{2M}{\hbar^2} e^{-2i\gamma(\ell)} \right. \\ \left. \sum_{\lambda'} \int_0^{\ell} \Psi^{(-)}(\ell) W'''(\bar{\ell}\lambda\lambda') X(\bar{\ell}\lambda') d\ell' \right. \\ \left. - (i)^{\bar{\lambda}} (-1)^{\lambda} \left( \frac{\bar{k}}{k} \right)^{1/2} \frac{2M}{\hbar^2} \sum_{\lambda'} \int_0^{\infty} \Psi^{(+)}(\ell) W'''(\bar{\ell}\lambda\lambda') X(\bar{\ell}\lambda') d\ell' \right] \quad (10) \end{aligned}$$

It follows from Eq. 2 that

$$S(\bar{\ell}\lambda) = \lim_{\ell \rightarrow \infty} Y^{(+)}(\bar{\ell}\lambda) \quad (11)$$

Upon differentiation of Eqs. 9 and 10 and use of Eq. 8 one finds that

$$\frac{d}{dr} Y^{(\pm)}(\bar{\ell}\lambda) = -\frac{iM}{\hbar^2} f^{(\pm)}(\ell) \sum_{\lambda'} W^{(\pm)}(\bar{\ell}\lambda\lambda')$$

$$\left[ f^{(+)}(\ell')^* Y^{(+)}(\bar{\ell}\lambda') - f^{(-)}(\ell')^* Y^{(-)}(\bar{\ell}\lambda') \right]$$
(12)

where

$$f^{(+)}(\ell) = \hbar^{-1/2} \Psi^{(-)}(\ell)$$
(13)

$$f^{(-)}(\ell) = (-1)^\lambda e^{2i\gamma(\ell)} \hbar^{-1/2} \Psi^{(+)}(\ell)$$
(14)

and that as  $r \rightarrow \infty$

$$Y^{(-)}(\bar{\ell}\lambda) \rightarrow \delta(\bar{\lambda}|\lambda) e^{2i\gamma(\ell)}$$
(15)

and as  $r \rightarrow 0$

$$Y^{(+)}(\bar{\ell}\lambda) \rightarrow Y^{(-)}(\bar{\ell}\lambda)$$
(16)

This set of differential equations along with the boundary conditions may be used to determine the functions  $Y^{(\pm)}(\bar{\ell}\lambda)$ . Furthermore, in an approximation the two sets of equations uncouple; the product  $f^{(+)}(\ell) f^{(+)}(\ell')^*$  (and  $f^{(-)}(\ell) f^{(-)}(\ell')^*$ ) is slowly varying in  $r$ ,

but the product  $f^{(+)}(\ell) f^{(-)}(\ell')^*$  (and  $f^{(-)}(\ell) f^{(+)}(\ell')^*$ ) is highly oscillatory. The functions  $Y^{(-)}(\bar{\ell}\Lambda)$  describe the amplitudes of the incoming waves and the functions  $Y^{(+)}(\bar{\ell}\Lambda)$  describe the amplitudes of the outgoing waves. The coupling between the two sets of equations is associated with interference effects between the incoming and outgoing waves. As indicated by Eqs. 1 and 11 the cross sections are determined by the amplitudes of the outgoing waves.

The functions  $\chi(\bar{\ell}\Lambda S_a S_b)$  are introduced in Paper VIII and given explicitly by Eq. VIII-26. It is convenient to make use of the completeness of these functions to expand the functions  $Y^{(+)}(\bar{\ell}\Lambda)$  and  $Y^{(-)}(\bar{\ell}\Lambda)$  in the form

$$Y^{(\pm)}(\bar{\ell}\Lambda) = (-1)^{\bar{\ell}_a + \bar{\ell}_b + \bar{\ell}} (8\pi^2)^{-1} \iint \chi(\bar{\ell}\Lambda S_a S_b) \left[ \exp i Q^{(\pm)}(\bar{\ell} S_a S_b) \right] dS_a dS_b \quad (17)$$

With this definition it follows from Eq. VIII-54, the orthonormality of  $\chi(\bar{\ell}\Lambda S_a S_b)$ , Eq. VIII-28, and the boundary conditions, Eqs. 15 and 16, that as  $r \rightarrow \infty$

$$Q^{(-)}(\bar{\ell} S_a S_b) \rightarrow 2\gamma(\bar{\ell}) \quad (18)$$

and as  $r \rightarrow 0$

$$Q^{(+)}(\bar{\ell} S_a S_b) \rightarrow Q^{(-)}(\bar{\ell} S_a S_b) \quad (19)$$

Equations for the generalized phase shifts  $Q^{(+)}(\bar{\ell} S_a S_b)$  and  $Q^{(-)}(\bar{\ell} S_a S_b)$  may be obtained from Eq. 12 and the orthonormality of the  $\chi(\bar{\ell}\Lambda S_a S_b)$ , Eq. VIII-27,

$$\begin{aligned} \frac{d}{dn} Q^{(\pm)}(\bar{l} s_a s_b) &= - \frac{M}{\hbar^2} \left[ \exp - i Q^{(\pm)}(\bar{l} s_a s_b) \right] \\ &\sum_{\Lambda \Lambda'} f^{(\pm)}(l) W^{(1)}(\bar{l} \Lambda \Lambda') \iint \chi(\bar{l} \Lambda s_a s_b)^* \chi(\bar{l} \Lambda' s'_a s'_b) \\ &\left\{ f^{(+)}(l')^* \left[ \exp i Q^{(+)}(\bar{l} s'_a s'_b) \right] \right. \\ &\quad \left. - f^{(-)}(l')^* \left[ \exp i Q^{(-)}(\bar{l} s'_a s'_b) \right] \right\} ds'_a ds'_b \end{aligned} \quad (20)$$

As indicated by Eq. VIII-23, the  $\chi(\bar{l} \Lambda s_a s_b)$  are eigenvectors of the matrix  $W^{(1)}(\bar{l} \Lambda \Lambda')$  with eigenvalues  $V^{(1)}(s_a s_b)$ , the anisotropic part of the intermolecular potential. It thus follows from Eq. VIII-23 that

$$W^{(1)}(\bar{l} \Lambda \Lambda') = \iint \chi(\bar{l} \Lambda' s_a s_b)^* V^{(1)}(s_a s_b) \chi(\bar{l} \Lambda s_a s_b) ds_a ds_b \quad (21)$$

With this relation the last equation may be rewritten in the form

$$\begin{aligned} \frac{d}{dn} Q^{(\pm)}(\bar{l} s_a s_b) &= - \frac{M}{\hbar^2} \left[ \exp - i Q^{(\pm)}(\bar{l} s_a s_b) \right] \iiint V^{(1)}(s'_a s'_b) \\ &F^{(\pm)}(\bar{l} s_a s_b s'_a s'_b) \left\{ F^{(+)}(\bar{l} s''_a s''_b s'_a s'_b)^* \left[ \exp i Q^{(+)}(\bar{l} s''_a s''_b) \right] \right. \\ &\quad \left. - F^{(-)}(\bar{l} s''_a s''_b s'_a s'_b)^* \left[ \exp i Q^{(-)}(\bar{l} s''_a s''_b) \right] \right\} ds'_a ds'_b ds''_a ds''_b \end{aligned} \quad (22)$$

where

$$F^{(\pm)}(\bar{l} S_a S_b S'_a S'_b) = \sum_{\Lambda} \chi(\bar{l} \Lambda S_a S_b)^* f^{(\pm)}(l) \chi(\bar{l} \Lambda S'_a S'_b) \quad (23)$$

This is an exact set of coupled equations for the generalized phase shifts,  $Q^{(\pm)}(\bar{l} S_a S_b)$ . In the next section, the scattering cross sections and transition probabilities are written in terms of these quantities. In the following section, a semiclassical approximation to these equations is discussed.

### Scattering Cross Sections

Let us define

$$S(\bar{l} S_a S_b) = \lim_{l \rightarrow \infty} \exp i Q^{(+)}(\bar{l} S_a S_b) \quad (24)$$

It then follows from Eqs. 11 and 17 that

$$S(\bar{l} \Lambda) = (-1)^{\bar{l}_a + \bar{l}_b + \bar{\lambda}} (8\pi^2)^{-1} \iint S(\bar{l} S_a S_b) \chi(\bar{l} \Lambda S_a S_b) dS_a dS_b \quad (25)$$

and using the explicit expression for the functions  $\chi(\bar{l} \Lambda S_a S_b)$ , Eq.

VIII-26, that

$$S(\bar{\lambda} \Lambda) - S(\bar{l} \Lambda) = (-1)^{\bar{l}_a + \bar{l}_b + \bar{\lambda}} \alpha(\Lambda) \sum_{\alpha \beta \gamma \nu} (-i)^{\alpha + \beta + \gamma} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & \alpha & -\alpha \end{pmatrix}$$

$$\begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & \beta & -\beta \end{pmatrix} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & \gamma & -\gamma \end{pmatrix} \begin{pmatrix} L_a & L_b & L \\ -\nu & \nu - \gamma & \gamma \end{pmatrix}$$

$$T(\bar{l} L_a \alpha -\nu L_b \beta, \nu - \gamma) \quad (26)$$

where

$$T(\bar{l} L_a \alpha \nu L_b \beta \tau) = \frac{1}{(8\pi^2)^2} \iint D^{L_a}(S_a)_{\alpha \nu} D^{L_b}(S_b)_{\beta \tau} [1 - \mathcal{S}(\bar{l} S_a S_b)] dS_a dS_b \quad (27)$$

It may be shown that

$$\sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) \begin{pmatrix} \lambda & \lambda' & \mathcal{L} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & \gamma & -\gamma \end{pmatrix} \begin{pmatrix} \lambda' & \bar{\lambda}' & L \\ 0 & \gamma' & -\gamma' \end{pmatrix} \begin{pmatrix} \lambda & \lambda' & \mathcal{L} \\ \bar{\lambda} & \bar{\lambda}' & L \end{pmatrix} = \delta(\gamma|\gamma') (-1)^{\lambda+L+\gamma} \begin{pmatrix} \bar{\lambda} & \bar{\lambda}' & \mathcal{L} \\ -\gamma & \gamma & 0 \end{pmatrix} \quad (28)$$

With this relation and Eq. 26, the expression for the moments of the degeneracy averaged cross section given by Eq. 1 may be written in the form

$$I(\bar{l}_a \bar{l}_b; l_a l_b; \mathcal{L}) = (2l_a+1)(2l_b+1)(2\mathcal{L}+1)(4\bar{l}_a^2)^{-1} \sum (i)^{\alpha'+\beta'-\alpha-\beta} (-1)^{\nu+\mu} (2L_a+1)(2L_b+1)(2\bar{\lambda}+1)(2\bar{\lambda}'+1) \begin{pmatrix} \bar{\lambda} & \bar{\lambda}' & \mathcal{L} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \bar{\lambda} & \bar{\lambda}' & \mathcal{L} \\ \nu+\mu & -\nu-\mu & 0 \end{pmatrix} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & \alpha & -\alpha \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & \beta & -\beta \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & \beta' & -\beta' \end{pmatrix} T(\bar{l}_a \bar{l}_b \bar{\lambda} L_a \alpha \nu L_b \beta \mu) T(\bar{l}_a \bar{l}_b \bar{\lambda}' L_a \alpha' \nu L_b \beta' \mu)^* \quad (29)$$

where the sum is over  $\bar{\lambda} \bar{\lambda}' L_a L_b \nu \mu \alpha \beta \alpha' \beta'$ .

In Paper II, (see Eq. II-5.7), the degeneracy averaged cross section for scattering in the direction  $\chi$  is written in the form

$$I(\bar{l}_a \bar{l}_b; l_a l_b; \chi) = 2\pi \sum_{\mathcal{L}} I(\bar{l}_a \bar{l}_b; l_a l_b; \mathcal{L}) P_{\mathcal{L}}(\cos \chi) \quad (30)$$

in terms of the moments of the cross section. Using the last two relations it follows that

$$I(\bar{l}_a \bar{l}_b; l_a l_b; \chi) = 2\pi \sum (2L_a + 1)(2L_b + 1) \left| \tilde{f}(\bar{l}_a \bar{l}_b l_a l_b L_a \nu L_b \mu; \chi) \right|^2 \quad (31)$$

where the sum is over  $L_a L_b \nu \mu$  and

$$\begin{aligned} \tilde{f}(\bar{l}_a \bar{l}_b l_a l_b L_a \nu L_b \mu; \chi) &= \frac{1}{2k_0} \left[ (2l_a + 1)(2l_b + 1) \right]^{1/2} \\ &\sum_{\bar{\lambda} \alpha \beta} (-i)^{\alpha + \beta} (2\bar{\lambda} + 1) \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & \alpha & -\alpha \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & \beta & -\beta \end{pmatrix} \\ &T(\bar{l} L_a \alpha \nu L_b \beta \mu) D^{\bar{\lambda}}(0 \chi 0)_{0, \nu + \mu} \end{aligned} \quad (32)$$

The latter quantity may conveniently be written in terms of a generalized scattering amplitude

$$f(\bar{l}_a \bar{l}_b \chi; S_a S_b \chi) = \frac{1}{2k_0} \sum_{\bar{\lambda}} (2\bar{\lambda} + 1) \left[ 1 - S(\bar{l} S_a S_b) \right] D^{\bar{\lambda}}(0 \chi 0)_{0 \chi} \quad (33)$$

In terms of this quantity

$$\begin{aligned} \tilde{f}(\bar{l}_a \bar{l}_b; l_a l_b; L_a \nu; L_b \mu; \chi) &= [(2l_a+1)(2l_b+1)]^{1/2} (8\pi^2)^{-2} \\ &\sum_{\alpha\beta} (-i)^{\alpha+\beta} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & \alpha & -\alpha \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & \beta & -\beta \end{pmatrix} \\ &\iint D^{L_a}(S_a)_{\alpha\nu} D^{L_b}(S_b)_{\beta\mu} f(\bar{l}_a \bar{l}_b, \nu+\mu; S_a S_b \chi) dS_a dS_b \end{aligned} \quad (34)$$

It is readily shown from the properties of the representation coefficients that

$$\begin{aligned} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & \alpha & -\alpha \end{pmatrix} D^{L_a}(S_a)_{\alpha\nu} &= \sum_{\rho} (-1)^{\rho+\nu} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ \rho & -\rho & -\nu \end{pmatrix} \\ &D^{\bar{l}_a}(S_a)_{-\rho, \nu}^* D^{l_a}(S_a)_{\rho, \nu+\nu} \end{aligned} \quad (35)$$

Using this relation in Eqs. 31 and 34 yields another expression for the differential cross section in terms of the generalized scattering amplitude

$$I(\bar{l}_a \bar{l}_b; l_a l_b; \chi) = 2\pi (2l_a+1)(2l_b+1) \quad (36)$$

$$\begin{aligned} \sum_{\nu\mu\sigma\tau} \left| \sum_{\alpha\beta} (i)^{\alpha+\beta} (8\pi^2)^{-2} \iint D^{\bar{l}_a}(S_a)_{\alpha\nu}^* D^{\bar{l}_b}(S_b)_{\beta\tau}^* \right. \\ \left. f(\bar{l}_a \bar{l}_b, \nu+\mu-\sigma-\tau; S_a S_b \chi) D^{l_a}(S_a)_{\sigma\nu} D^{l_b}(S_b)_{\sigma\mu} dS_a dS_b \right|^2 \end{aligned}$$

On integrating the last expression over the angle of deflection  $\chi$ , one finds that the total cross section may be written in the form

$$I(\bar{l}_a \bar{l}_b; l_a l_b) = (\pi/k^2) \sum_{\bar{\lambda}} (2\bar{\lambda}+1) P(\bar{l}_a \bar{l}_b; l_a l_b; \bar{\lambda}) \quad (37)$$

where

$$P(\bar{l}_a \bar{l}_b; l_a l_b; \bar{\lambda}) = (2l_a+1)(2l_b+1) \sum_{\nu\mu\sigma\tau} \left| \sum_{\alpha\beta} (i)^{\alpha+\beta} (8\pi^2)^{-2} \iint D^{\bar{l}_a}(s_a)_{\alpha\sigma}^* D^{\bar{l}_b}(s_b)_{\beta\tau}^* [1 - \mathcal{S}(\bar{\lambda} s_a s_b)] D^{l_a}(s_a)_{\sigma\nu} D^{l_b}(s_b)_{\tau\mu} ds_a ds_b \right|^2 \quad (38)$$

may be interpreted as a transition probability as a function of the initial relative angular momentum associated with the index  $\bar{\lambda}$ .

The expressions given by Eqs. 36 and 38 are exact expressions for the cross sections and transition probabilities in terms of the  $\mathcal{S}(\bar{\lambda} s_a s_b)$ , which in turn are defined in terms of the generalized phase shifts by Eq. 24. The generalized phase shifts may be obtained through the solution of the exact set of coupled equations, Eqs. 22. In the following section we discuss an approximate solution of these coupled equations.

### Semiclassical Approximation

The WKB approximation to the radial wave function is<sup>3</sup>

$$\psi^{(\pm)}(r) = F(r)^{-1/4} \exp[\pm i S(r)] \quad (39)$$

where

$$F^{(0)}(\ell) = \left[ 1 - \frac{2M V^{(0)}}{\hbar^2 \ell^2} - \frac{\lambda(\lambda+1)}{\ell^2 r^2} \right] \quad (40)$$

$$S(\ell) = \hbar \ell - \hbar \int_r^\infty \left[ F^{(0)}(\ell)^{1/2} - 1 \right] dr \quad (41)$$

Thus in the semiclassical limit

$$\Psi^{(\pm)}(\ell) = \Psi^{(\pm)}(\bar{\ell}) \exp \pm i [S(\ell) - S(\bar{\ell})] \quad (42)$$

where

$$S(\ell) - S(\bar{\ell}) = \left[ (\lambda - \bar{\lambda}) \frac{\partial}{\partial \bar{\lambda}} + (\hbar - \bar{\hbar}) \frac{\partial}{\partial \bar{\hbar}} \right] S(\bar{\ell}). \quad (43)$$

It may easily be shown that

$$\frac{\partial}{\partial \bar{\lambda}} S(\bar{\ell}) = \theta(\bar{\ell}) = \frac{2\bar{\lambda} + 1}{2\bar{\hbar}} \int_r^\infty \frac{dr}{r^2 F^{(0)}(\bar{\ell})^{1/2}} \quad (44)$$

$$\frac{\partial}{\partial \bar{\hbar}} S(\bar{\ell}) = \rho(\bar{\ell}) = r - \int_r^\infty \left[ F^{(0)}(\bar{\ell})^{-1/2} - 1 \right] dr \quad (45)$$

and

$$(\hbar - \bar{\hbar}) = -(\ell_a - \bar{\ell}_a) \frac{M \bar{\ell}_a}{\bar{\hbar} I_a} - (\ell_b - \bar{\ell}_b) \frac{M \bar{\ell}_b}{\bar{\hbar} I_b} \quad (46)$$

Thus

$$S(\rho) - S(\bar{\rho}) = (\lambda - \bar{\lambda})\theta - (l_a - \bar{l}_a)\psi_a - (l_b - \bar{l}_b)\psi_b \quad (47)$$

where

$$\psi_a = M \bar{l}_a S(\bar{\rho}) / \hbar I_a \quad (48)$$

The angle  $\theta$  is simply related to the classical angle of deflection  $\chi = \pi - 2\theta^{(o)}$ , where  $\theta^{(o)}$  is the value of  $\theta$  at the classical turning point. The angles  $\psi_a$  and  $\psi_b$  may be interpreted in a similar classical manner. First, the quantity  $M s / \hbar k$  is a measure of time along a classical trajectory and second  $\hbar \bar{l}_a / I_a$  may be interpreted as a classical angular velocity of rotation of the molecule. Thus  $\psi_a$  and  $\psi_b$  are classical angles of rotation of the molecules.

With the expression for the radial wave function given by Eqs. 42 and 47 and the relation developed in the Appendix, Eq. 98, one may show that in the classical limit the quantity defined by Eq. 23 is<sup>4</sup>

$$\begin{aligned} F^{(+)}(\bar{\rho} s_a s_b s'_a s'_b) &= (8\pi^2)^{-2} f^{(+)}(\bar{\rho}) \sum (2L_a+1)(2L_b+1)(2L+1) \\ &\begin{pmatrix} L_a & L_b & L \\ -\nu & \nu-\gamma & \gamma \end{pmatrix} \begin{pmatrix} L_a & L_b & L \\ -\nu' & \nu'-\gamma' & \gamma' \end{pmatrix} D^{L_a}(s_a)_{\alpha, -\nu}^* D^{L_a}(s'_a)_{\alpha', -\nu'} \\ &D^{L_a}(\pi, \psi_a, \pi)_{\alpha', \alpha}^* D^{L_b}(s_b)_{\beta, \nu-\gamma}^* D^{L_b}(s'_b)_{\beta', \nu'-\gamma'} \\ &D^{L_b}(\pi, \psi_b, \pi)_{\beta', \beta}^* D^L(\pi, \theta, \pi)_{\gamma \gamma'} \end{aligned} \quad (49)$$

where the sum is over  $L_a L_b L \alpha \beta \gamma \nu \alpha' \beta' \gamma' \nu'$ . Then using the properties of the 3-j symbols this becomes

$$F^{(+)}(\bar{\ell} s_a s_b s'_a s'_b) = (8\pi^2)^{-2} f^{(+)}(\bar{\ell}) \sum (2L_a+1)(2L_b+1) \\ D^{L_a}(T_a^{(+)})_{\alpha\nu}^* D^{L_a}(S'_a)_{\alpha\nu} D^{L_b}(T_b^{(+)})_{\beta\gamma}^* D^{L_b}(S'_b)_{\beta\gamma} \quad (50)$$

where the sum is over  $L_a L_b \alpha \beta \gamma \nu$ , and  $T_a^{(+)}, T_b^{(+)}$  are each products of three rotations, e.g.

$$T_a^{(+)} = (\pi, \psi_a, \pi)(s_a)(\pi, \theta, \pi) \quad (51)$$

It thus follows from the orthogonality of the representation coefficients that

$$F^{(+)}(\bar{\ell} s_a s_b s'_a s'_b) = f^{(+)}(\bar{\ell}) \delta(T_a^{(+)} | s'_a) \delta(T_b^{(+)} | s'_b) \quad (52)$$

In a similar manner it is found that in the classical limit

$$F^{(-)}(\bar{\ell} s_a s_b s'_a s'_b) = f^{(-)}(\bar{\ell}) \delta(T_a^{(-)} | s'_a) \delta(T_b^{(-)} | s'_b) \quad (53)$$

where

$$T_a^{(-)} = (\pi, 2\psi_a^{(c)} - \psi_a, \pi)(s_a)(\pi, 2\theta^{(c)} - \theta, \pi) \quad (54)$$

Since the inverse of the rotation  $(0, \theta, 0)$  is  $(\pi, \theta, \pi)$ ,

$$\delta(T_a^{(+)} | S'_a) = \delta(S_a | U_a^{(+)}) \quad (55)$$

where

$$U_a^{(+)} = (0, \psi_a, 0) (S'_a) (0, \theta, 0) \quad (56)$$

and

$$\delta(T_a^{(-)} | S'_a) = \delta(S_a, U_a^{(-)}) \quad (57)$$

where

$$U_a^{(-)} = (0, 2\psi_a^{(0)} - \psi_a, 0) (S'_a) (0, 2\theta^{(0)} - \theta, 0) \quad (58)$$

It follows from these relations and Eqs. 22 that in the classical limit

$$\begin{aligned} \frac{d}{d\lambda} Q^{(\pm)}(\bar{x} S_a S_b) &= \mp \frac{M}{\hbar^2} V''(T_a^{(\pm)} T_b^{(\pm)}) f^{(\pm)}(\bar{x}) \\ &\left\{ f^{(\pm)}(\bar{x})^* - f^{(\mp)}(\bar{x})^* \exp \left[ i Q^{(\mp)}(\bar{x} R_a^{(\pm)} R_b^{(\pm)}) - i Q^{(\pm)}(\bar{x} S_a S_b) \right] \right\} \end{aligned} \quad (59)$$

where

$$\begin{aligned} R_a^{(+)} &= (0, 2\psi_a^{(0)} - \psi_a, 0) (\pi, \psi_a, \pi) (S_a) (\pi, \theta, \pi) (0, 2\theta^{(0)} - \theta, 0) \\ &= (0, 2\psi_a^{(0)} - 2\psi_a, 0) (S_a) (0, 2\theta^{(0)} - 2\theta, 0) \end{aligned} \quad (60)$$

and

$$\begin{aligned}
 R_a^{(-)} &= (0, \Psi_a, 0)(\pi, 2\Psi_a^{(0)} - \Psi_a, \pi)(S_a)(\pi, 2\theta^{(0)} - \theta, \pi)(0, \theta, 0) \\
 &= (\pi, 2\Psi_a^{(0)} - 2\Psi_a, \pi)(S_a)(\pi, 2\theta^{(0)} - 2\theta, \pi)
 \end{aligned} \tag{61}$$

The second term on the right of Eq. 59 represents interference effects between the incoming and outgoing waves. In the approximation that this term is zero, the equation may be solved by straightforward integration. It then follows from the boundary conditions, Eqs. 18 and 19 that

$$Q^{(-)}(\bar{x} S_a S_b) = 2\gamma(\bar{x}) - \frac{M}{\hbar^2} \int_{\bar{x}}^{\infty} |f^{(-)}(\bar{x})|^2 V'''(T_a^{(-)}, T_b^{(-)}) d\bar{x}' \tag{62}$$

$$\begin{aligned}
 Q^{(+)}(\bar{x} S_a S_b) &= 2\gamma(\bar{x}) - \frac{M}{\hbar^2} \int_{\bar{x}_0}^{\infty} |f^{(-)}(\bar{x})|^2 V'''(T_a^{(-)}, T_b^{(-)}) d\bar{x}' \\
 &\quad - \frac{M}{\hbar^2} \int_{\bar{x}_0}^{\bar{x}} |f^{(+)}(\bar{x})|^2 V'''(T_a^{(+)}, T_b^{(+)}) d\bar{x}'
 \end{aligned} \tag{63}$$

and from Eq. 24 that

$$\begin{aligned}
 S(\bar{x} S_a S_b) &= \exp \left\{ 2i\gamma(\bar{x}) - i \frac{M}{\hbar^2} \int_{\bar{x}_0}^{\infty} |f^{(+)}(\bar{x})|^2 \right. \\
 &\quad \left. [V'''(T_a^{(+)}, T_b^{(+)}) + V'''(T_a^{(-)}, T_b^{(-)})] d\bar{x}' \right\}
 \end{aligned} \tag{64}$$

The exponential of this expression is correct (in the semi-classical limit) to first order in the anisotropic part of the interaction potential.

The last equation along with Eq. 38 leads to an approximation to the transition probability. In the last expression, the rotations,  $T_a^{(+)}$  and  $T_b^{(+)}$  are defined by Eqs. 51 and 54 in terms of the rotations,  $S_a$  and  $S_b$  and the angles  $\theta$ ,  $\psi_a$ , and  $\psi_b$ , given by Eqs. 44 and 48. The interpretation of this expression is that the integrations over  $r$  represent integrations over the incoming and outgoing branches of the trajectory determined by the spherical part of the potential. (It is only the spherical part of the potential because of the linearization referred to above). The effect of the angle  $\theta$  is the effect of the motion along the trajectory on the relative orientations of the molecules; the effect of the angles  $\psi_a$  and  $\psi_b$  is the effect of the rotations of the molecules themselves.

In a further approximation, the angles  $\psi_a$  and  $\psi_b$  in the defining equations of  $T_a^{(+)}$  and  $T_b^{(+)}$ , Eqs. 51 and 54 may be taken to be zero. In this approximation,  $\mathcal{J}(\bar{S}_a S_b)$  is independent of the third Eulerian angles of  $S_a$  and  $S_b$ . In this case then the sums on  $\alpha$  and  $\beta$  of the expression for the transition probability, Eq. 38, reduce to a single term,  $\alpha = \beta = 0$ . The resulting expression is precisely the full sudden approximation.<sup>5</sup>

The anisotropic part of the interaction potential may be expanded as indicated by Eq. V-5 in the form

$$V^{(n)}(S_a S_b) = \sum_{L_a L_b \nu} v^{(n)}(L_a L_b \nu) D^{L_a}(S_a)_{0, -\nu} D^{L_b}(S_b)_{0, \nu} \quad (65)$$

It then follows from the definitions of Eqs. 51 and 54 that

$$\begin{aligned}
 V'''(T_a^{(+)} T_b^{(+)}) + V'''(T_a^{(-)} T_b^{(-)}) &= \sum_{L_a L_b \nu} \nu'''(L_a L_b \nu) \\
 &D^{L_a}(s_a)_{\alpha\alpha'} D^{L_b}(s_b)_{\beta\beta'} \left[ D^{L_a}(\pi, \Psi_a, \pi)_{\alpha\alpha'} D^{L_b}(\pi, \theta, \pi)_{\beta\beta', -\nu} \right. \\
 &D^{L_b}(\pi, \Psi_b, \pi)_{\beta\beta'} D^{L_b}(\pi, \theta, \pi)_{\beta\beta', \nu} + D^{L_a}(\pi, 2\Psi_a^{(0)} - \Psi_a, \pi)_{\alpha\alpha'} \\
 &\left. D^{L_a}(\pi, 2\theta^{(0)} - \theta, \pi)_{\alpha\alpha', -\nu} D^{L_b}(\pi, 2\Psi_b^{(0)} - \Psi_b, \pi)_{\beta\beta'} D^{L_b}(\pi, 2\theta^{(0)} - \theta, \pi)_{\beta\beta', \nu} \right]
 \end{aligned}
 \tag{66}$$

where the sum is over  $L_a L_b \nu \alpha \alpha' \beta \beta'$ .

If the interaction potential is small, the second exponential of Eq. 64 may be expanded to give as a linear approximation

$$\begin{aligned}
 \delta(\bar{x} s_a s_b) &= e^{2i\gamma(\bar{x})} \left\{ 1 - i \frac{M}{\hbar^2} \int_{r_0}^{\infty} |f^{(+)}(\bar{x})|^2 \right. \\
 &\left. \left[ V'''(T_a^{(+)} T_b^{(+)}) + V'''(T_a^{(-)} T_b^{(-)}) \right] dr \right\}
 \end{aligned}
 \tag{67}$$

If this linear expression, and the expression above, are used in the expression for the transition probability, Eq. 38, one finds that

$$\begin{aligned}
P(\bar{l}_a \bar{l}_b; l_a l_b; \bar{\lambda}) &= (2l_a + 1)(2l_b + 1) \\
&\sum_{\nu \mu s t} \left| \frac{\delta(\bar{l}_a s \bar{l}_b t | l_a \nu l_b \mu)}{(2l_a + 1)(2l_b + 1)} (1 - e^{2i\gamma(\bar{\lambda})}) \right. \\
&-i \frac{M}{\hbar^2} e^{2i\gamma(\bar{\lambda})} \sum_{L_a L_b \nu' \alpha \beta} (-i)^{\alpha+\beta} (-1)^{s+t} \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & -\alpha & \alpha \end{pmatrix} \\
&\begin{pmatrix} l_a & \bar{l}_a & L_a \\ \nu & -s & s-\nu \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & -\beta & \beta \end{pmatrix} \begin{pmatrix} l_b & \bar{l}_b & L_b \\ \mu & -t & t-\mu \end{pmatrix} \\
&\int_{r_0}^{\infty} |f^{(+)}(\bar{r})|^2 v^{(1)}(L_a L_b \nu') \left[ D^{L_a}(\pi, \psi_a, \pi)_{0\alpha} D^{L_a}(\pi, \theta, \pi)_{s-\nu, -\nu'} \right. \\
&D^{L_b}(\pi, \psi_b, \pi)_{0\beta} D^{L_b}(\pi, \theta, \pi)_{t-\mu, \nu'} + D^{L_a}(\pi, 2\psi_a^{(0)} - \psi_a, \pi)_{0\alpha} \\
&D^{L_a}(\pi, 2\theta^{(0)} - \theta, \pi)_{s-\nu, -\nu'} D^{L_b}(\pi, 2\psi_b^{(0)} - \psi_b, \pi)_{0\beta} \\
&\left. D^{L_b}(\pi, 2\theta^{(0)} - \theta, \pi)_{t-\mu, \nu'} \right] dr \Big|^2 \tag{68}
\end{aligned}$$

Next let us specialize to the case of atom diatomic molecule collisions and furthermore assume that only one term appears in the expansion of the potential, Eq. 65. That is, we assume that the only nonzero value of  $v^{(1)}(L_a L_b \nu)$  is

$$v^{(1)}(L \ 0 \ 0) = v^{(1)}(L) \tag{69}$$

In this case, the value of  $P(\bar{l}_a; l_a; \bar{\lambda})$  for a transition  $(\bar{l}_a \neq l_a)$  is

$$\begin{aligned}
P(\bar{\lambda}_a; \lambda_a; \bar{\lambda}) &= \frac{M^2(2\lambda_a + 1)}{\hbar^4(2L + 1)} \\
&\sum_{\rho} \left| \sum_{\alpha} (-i)^{\alpha} (-1)^{\rho} \begin{pmatrix} \lambda_a & \bar{\lambda}_a & L \\ 0 & \alpha & -\alpha \end{pmatrix} \int_{\rho_0}^{\infty} v'''(L) |f^{(\pm)}(\bar{\lambda})|^2 \right. \\
&\left[ D^L(\pi, \psi_a, \pi)_{\rho\alpha} D^L(\pi, \theta, \pi)_{\rho\alpha} + D^L(\pi, 2\psi_a^{(0)} - \psi_a, \pi)_{\rho\alpha} \right. \\
&\left. D^L(\pi, 2\theta^{(0)} - \theta, \pi)_{\rho\alpha} \right] d\rho \left. \right|^2 \tag{70}
\end{aligned}$$

In the approximation that  $\psi_a = 0$ , this expression reduces directly to that based on the linearized sudden approximation and given explicitly by Eqs. X-39, 41, and 44.

### Classical Limit

In this section we consider the classical limit of the generalized phase shifts. To obtain this limit, the set of differential equations for the functions  $Y^{(\pm)}(\bar{\lambda})$ , Eqs. 12 are differentiated once again with respect to  $r$ . In the resulting equations the first derivatives are eliminated by use of the original set of equations, Eqs. 12. The resulting set of equations is

$$\begin{aligned}
\frac{d^2}{d\rho^2} Y^{(\pm)}(\bar{\lambda}) &= -\frac{iM}{\hbar^2} \sum_{\lambda'} \left\{ Y^{(+)}(\bar{\lambda}\lambda') \frac{d}{d\rho} \left[ f^{(\pm)}(\rho) \mathcal{W}(\bar{\lambda}\lambda') f^{(+)}(\rho')^* \right] \right. \\
&\left. - Y^{(-)}(\bar{\lambda}\lambda') \frac{d}{d\rho} \left[ f^{(\pm)}(\rho) \mathcal{W}'''(\bar{\lambda}\lambda') f^{(-)}(\rho')^* \right] \right\} \tag{71}
\end{aligned}$$

The differential equations, Eqs. 12, may also be "solved" to obtain the set

$$\begin{aligned} & f^{(+)}(\rho)^* \gamma^{(+)}(\bar{\rho}\Lambda) - f^{(-)}(\rho)^* \gamma^{(-)}(\bar{\rho}\Lambda) \\ &= \frac{i\hbar^2}{M} \sum_{\Lambda'} f^{(\pm)}(\rho')^{-1} \mathcal{W}'''(\bar{\rho}\Lambda\Lambda') \frac{d}{d\rho} \gamma^{(\pm)}(\bar{\rho}\Lambda') \end{aligned} \quad (72)$$

where  $W^{(1)}(\bar{\rho}\Lambda\Lambda')^{-1}$  is the matrix inverse to  $W^{(1)}(\bar{\rho}\Lambda\Lambda')$ . This result may be used in Eqs. 71 to decouple the two sets of equations and obtain the sets,

$$\begin{aligned} \frac{d^2}{d\rho^2} \gamma^{(\pm)}(\bar{\rho}\Lambda) &= -\frac{iM}{\hbar^2} \sum_{\Lambda'} [f^{(\mp)}(\rho')^*]^{-1} \gamma^{(\pm)}(\bar{\rho}\Lambda') \\ &\quad \left\{ f^{(-)}(\rho')^* \frac{d}{d\rho} [f^{(+)}(\rho) \mathcal{W}'''(\bar{\rho}\Lambda\Lambda') f^{(+)}(\rho')^*] \right. \\ &\quad \left. - f^{(+)}(\rho')^* \frac{d}{d\rho} [f^{(+)}(\rho) \mathcal{W}'''(\bar{\rho}\Lambda\Lambda') f^{(-)}(\rho')^*] \right\} \\ &+ \sum_{\Lambda'\Lambda''} [f^{(\mp)}(\rho')^* f^{(\pm)}(\rho'')]^{-1} \mathcal{W}'''(\bar{\rho}\Lambda'\Lambda'')^{-1} \\ &\quad \left[ \frac{d}{d\rho} \gamma^{(\pm)}(\bar{\rho}\Lambda'') \right] \frac{d}{d\rho} [f^{(\pm)}(\rho) \mathcal{W}'''(\bar{\rho}\Lambda\Lambda') f^{(\mp)}(\rho')^*] \end{aligned} \quad (73)$$

The functions  $\gamma^{(\pm)}(\bar{\rho}\Lambda)$  may be expanded in the form indicated by Eq. 17. When this form is used in the last equation one obtains the set

$$\begin{aligned}
& i \frac{d^2}{dR^2} Q^{(\pm)}(\bar{\rho} s_a s_b) - \left[ \frac{d}{dR} Q^{(\pm)}(\bar{\rho} s_a s_b) \right]^2 \\
&= \frac{iM}{\hbar^2} \sum_{\Lambda \Lambda'} \left[ f^{(\mp)}(\rho')^* \right]^{-1} \left\{ f^{(-)}(\rho')^* \frac{d}{dR} \left[ f^{(\pm)}(\rho) \mathcal{W}'''(\bar{\rho} \Lambda \Lambda') f^{(+)}(\rho')^* \right] \right. \\
&\quad \left. - f^{(+)}(\rho') \frac{d}{dR} \left[ f^{(\pm)}(\rho) \mathcal{W}'''(\bar{\rho} \Lambda \Lambda') f^{(-)}(\rho')^* \right] \right\} \iint \chi(\bar{\rho} \Lambda s_a s_b)^* \\
&\quad \chi(\bar{\rho} \Lambda' s'_a s'_b) \exp \left[ i Q^{(\pm)}(\bar{\rho} s'_a s'_b) - i Q^{(\pm)}(\bar{\rho} s_a s_b) \right] ds'_a ds'_b \\
&\quad + i \sum_{\Lambda \Lambda' \Lambda''} \left[ f^{(\mp)}(\rho')^* f^{(\pm)}(\rho'') \right]^{-1} \mathcal{W}'''(\bar{\rho} \Lambda' \Lambda'')^{-1} \\
&\quad \frac{d}{dR} \left[ f^{(\pm)}(\rho) \mathcal{W}'''(\bar{\rho} \Lambda \Lambda') f^{(\mp)}(\rho')^* \right] \iint \chi(\bar{\rho} \Lambda s_a s_b)^* \\
&\quad \chi(\bar{\rho} \Lambda'' s'_a s'_b) \left[ \frac{d}{dR} Q^{(\pm)}(\bar{\rho} s'_a s'_b) \right] \\
&\quad \exp \left[ i Q^{(\pm)}(\bar{\rho} s'_a s'_b) - i Q^{(\pm)}(\bar{\rho} s_a s_b) \right] ds'_a ds'_b
\end{aligned} \tag{74}$$

It follows from the properties of the radial wave equation, Eq. 4, and the definitions, Eqs. 5, that the Wronskian of the two solutions is

$$\Psi^{(-)}(\rho) \frac{d}{dR} \Psi^{(+)}(\rho) - \Psi^{(+)}(\rho) \frac{d}{dR} \Psi^{(-)}(\rho) = 2i k \tag{75}$$

It then follows from the definitions, Eqs. 13 and 14, that

$$f^{(+)}(\rho) \frac{d}{d\rho} f^{(+)}(\rho) - f^{(+)}(\rho) \frac{d}{d\rho} f^{(+)}(\rho) = -2i(-1)^\lambda e^{2i\gamma(\rho)} \quad (76)$$

With this relation, the expression for  $W^{(1)}(\bar{\rho}\Lambda\Lambda')$  given by Eq. 21, and the analogous relation for the inverse matrix,  $W^{(1)}(\bar{\rho}\Lambda\Lambda')^{-1}$ ,

Eq. 74 may be rewritten in the form

$$\begin{aligned} & i \frac{d^2}{d\rho^2} Q^{(\pm)}(\bar{\rho} s_a s_b) - \left[ \frac{d}{d\rho} Q^{(\pm)}(\bar{\rho} s_a s_b) \right]^2 \\ &= \frac{2M}{\hbar^2} \iiint F^{(\pm)}(\bar{\rho} s_a s_b s'_a s'_b) V'''(s'_a s'_b) F^{(\pm)}(\bar{\rho} s'_a s'_b s''_a s''_b)^{-1} \\ & \quad \exp \left[ i Q^{(\pm)}(\bar{\rho} s''_a s''_b) - i Q^{(\pm)}(\bar{\rho} s_a s_b) \right] ds'_a ds'_b ds''_a ds''_b \\ &+ i \int \dots \left\{ \left[ G^{(\pm)}(\bar{\rho} s'_a s'_b s''_a s''_b) + \delta(s'_a s'_b | s''_a s''_b) \frac{\partial}{\partial \rho} \right] \right. \\ & \quad \left. F^{(\pm)}(\bar{\rho} s_a s_b s'_a s'_b) V'''(s'_a s'_b) \right\} \left[ V'''(s''_a s''_b) \right]^{-1} \\ & \quad F^{(\pm)}(\bar{\rho} s''_a s''_b s'''_a s'''_b)^{-1} \left[ \frac{d}{d\rho} Q^{(\pm)}(\bar{\rho} s''_a s''_b) \right] \\ & \quad \exp \left[ i Q^{(\pm)}(\bar{\rho} s'''_a s'''_b) - i Q^{(\pm)}(\bar{\rho} s_a s_b) \right] ds'_a ds'_b ds''_a ds''_b ds'''_a ds'''_b \end{aligned} \quad (77)$$

where

$$G^{(\pm)}(\bar{\rho} s_a s_b s'_a s'_b) = \sum_{\Lambda} \chi(\bar{\rho} \Lambda s_a s_b)^* \chi(\bar{\rho} \Lambda s'_a s'_b) \left[ f^{(\pm)}(\rho) \right]^{-1} \frac{d}{d\rho} f^{(\pm)}(\rho) \quad (78)$$

$F^{(\pm)}(\bar{\rho} s_a s_b s'_a s'_b)$  is the matrix defined by Eq. 23,

and  $F^{(\pm)}(\bar{\ell} S_a S_b S_a' S_b')^{-1}$  is the matrix inverse.

This set of equations for the  $Q^{(\pm)}(\bar{\ell} S_a S_b)$  is equivalent to the set, Eqs. 22. The present set, however, is more convenient for the discussion of the classical limit.

A semiclassical approximation to the wave functions and the quantities  $F^{(\pm)}(\bar{\ell} S_a S_b S_a' S_b')$  is discussed in the previous section. It follows from the definitions, Eqs. 13, 14, and 78, and the WKB approximations to the wave functions that the semiclassical approximation to  $G^{(\pm)}(\bar{\ell} S_a S_b S_a' S_b')$  is

$$G^{(\pm)}(\bar{\ell} S_a S_b S_a' S_b') = \mp i \bar{\hbar} F^{(0)}(\bar{\ell})^{1/2} \delta(S_a S_b | S_a' S_b') \quad (79)$$

where  $F^{(0)}(\bar{\ell})$  is the quantity defined by Eq. 40. With this relation and the limiting forms of  $F^{(\pm)}(\bar{\ell} S_a S_b S_a' S_b')$  given by Eqs. 52 and 53, it follows that in the semiclassical approximation, Eq. 77 reduces to

$$\begin{aligned} i \frac{d^2}{dn^2} Q^{(\pm)}(\bar{\ell} S_a S_b) - \left[ \frac{d}{dn} Q^{(\pm)}(\bar{\ell} S_a S_b) \right]^2 \\ = \frac{2M}{\hbar^2} V'''(T_a^{(\pm)} T_b^{(\pm)}) \pm 2 \bar{\hbar} F^{(0)}(\bar{\ell})^{1/2} \frac{d}{dn} Q^{(\pm)}(\bar{\ell} S_a S_b) \\ + i \left[ V'''(T_a^{(\pm)} T_b^{(\pm)}) \right]^{-1} V''''(T_a^{(\pm)} T_b^{(\pm)})' \frac{d}{dn} Q^{(\pm)}(\bar{\ell} S_a S_b) \end{aligned} \quad (80)$$

where  $V'''(T_a^{(\pm)} T_b^{(\pm)})'$  is the derivative of the anisotropic part of the potential evaluated at the indicated orientations. This set of uncoupled equations is equivalent to the set of coupled equations, Eqs. 59.

In order to consider the classical limit one may consider a formal expansion of  $Q^{(\pm)}(\bar{l} S_a S_b)$  in powers of  $\hbar$ . If such an expansion is used in the last equation it is easily shown that the lowest order term is of order  $\hbar^{-1}$  and that the equation for the lowest order term or classical limit is

$$\left[ \frac{d}{d\bar{l}} Q^{(\pm)}(\bar{l} S_a S_b) \right]^2 \pm 2 \bar{k} F^{(0)}(\bar{l})^{1/2} \left[ \frac{d}{d\bar{l}} Q^{(\pm)}(\bar{l} S_a S_b) \right] + \frac{2M}{\hbar^2} V^{(1)}(T_a^{(\pm)} T_b^{(\pm)}) = 0 \quad (81)$$

This equation may readily be solved to give

$$\frac{d}{d\bar{l}} Q^{(\pm)}(\bar{l} S_a S_b) = \mp \bar{k} F^{(0)}(\bar{l})^{1/2} \pm \bar{k} F^{(\pm)}(\bar{l})^{1/2} \quad (82)$$

where

$$F^{(\pm)}(\bar{l}) = 1 - \frac{2M V^{(0)}}{\hbar^2 \bar{k}^2} - \frac{\lambda(\lambda+1)}{\bar{k}^2 \bar{l}^2} - \frac{2M}{\hbar^2 \bar{k}^2} V^{(1)}(T_a^{(\pm)} T_b^{(\pm)}) \\ = 1 - \frac{2M}{\hbar^2 \bar{k}^2} V(T_a^{(\pm)} T_b^{(\pm)}) - \frac{\lambda(\lambda+1)}{\hbar^2 \bar{l}^2} \quad (83)$$

Of the two roots of the quadratic equation, the root given above is the only correct one. It follows directly from Eq. 22 that the derivative is identically zero if the anisotropic part of the potential is zero. The alternate root is an extraneous root introduced by the differentiation which leads to Eq. 71.

Equation 82 may be readily integrated and hence it follows directly from this equation and the boundary conditions on the  $Q^{(\pm)}(\bar{\lambda}, S_a, S_b)$ , Eqs. 18 and 19, that

$$Q^{(-)}(\bar{\lambda}, S_a, S_b) = 2\gamma(\bar{\lambda}) - \bar{k} \int_{r_0}^{\infty} [F^{(0)}(\bar{\lambda})^{1/2} - F^{(-)}(\bar{\lambda})] d\lambda \quad (84)$$

$$\begin{aligned} Q^{(+)}(\bar{\lambda}, S_a, S_b) &= 2\gamma(\bar{\lambda}) \\ &- \bar{k} \lim_{R \rightarrow \infty} \left[ \int_{r_0}^R F^{(0)}(\bar{\lambda})^{1/2} d\lambda - \int_{r_-}^R F^{(-)}(\bar{\lambda})^{1/2} d\lambda \right] \\ &- \bar{k} \int_{r_0}^{r_+} F^{(0)}(\bar{\lambda})^{1/2} d\lambda + \bar{k} \int_{r_+}^{r_-} F^{(+)}(\bar{\lambda})^{1/2} d\lambda \end{aligned} \quad (85)$$

where  $r_-$  and  $r_+$  are the zeros of  $F^{(\pm)}(\bar{\lambda})$ . Thus from the definition, Eq. 24,

$$S(\bar{\lambda}, S_a, S_b) = \exp 2i H(\bar{\lambda}, S_a, S_b) \quad (86)$$

where

$$\begin{aligned} H(\bar{\lambda}, S_a, S_b) &= \gamma(\bar{\lambda}) + \frac{1}{2} \bar{k} \lim_{R \rightarrow \infty} \left[ \int_{r_+}^R F^{(+)}(\bar{\lambda})^{1/2} d\lambda \right. \\ &\left. + \int_{r_-}^R F^{(-)}(\bar{\lambda})^{1/2} d\lambda - 2 \int_{r_0}^R F^{(0)}(\bar{\lambda})^{1/2} d\lambda \right] \end{aligned} \quad (87)$$

The WKB approximation to the usual phase shift is

$$\gamma(\bar{\lambda}) = \frac{\pi}{2} [\bar{\lambda}(\bar{\lambda}+1)]^{1/2} - \bar{k} r_0 + \bar{k} \int_{r_0}^{\infty} [F^{(0)}(\bar{\lambda})^{1/2} - 1] d\lambda \quad (88)$$

Using this expression, the last expression for the generalized phase shift may be rewritten in a very similar form

$$\begin{aligned}
 H(\bar{\ell} s_a s_b) &= \frac{\pi}{2} [\bar{\lambda}(\bar{\lambda}+1)]^{1/2} - \frac{1}{2} \bar{k} (r_- + r_+) \\
 &+ \frac{1}{2} \bar{k} \int_{r_+}^{\infty} [F^{(+)}(\bar{\ell})^{1/2} - 1] dr \\
 &+ \frac{1}{2} \bar{k} \int_{r_-}^{\infty} [F^{(-)}(\bar{\ell})^{1/2} - 1] dr
 \end{aligned} \tag{89}$$

This expression for the generalized phase shift is valid in the classical limit. The expression for this quantity given in the exponent of Eq. 64 is an approximation which is valid to first order in the anisotropic part of the potential.

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Appendix

An explicit expression for the coupling coefficients was obtained by Wigner.<sup>6</sup> Written in terms of the 3-j symbols the explicit expression is

$$\begin{aligned} \begin{pmatrix} l & \bar{l} & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} &= (-1)^{L+\bar{l}+\mu} \left[ \frac{(L+l-\bar{l})!(L-l+\bar{l})!(l+\bar{l}-L)!}{(L+l+\bar{l}+1)!} \right]^{1/2} \\ &\left[ \frac{(L+\mu+\nu)!(L-\mu-\nu)!}{(l-\mu)!(l+\mu)!(\bar{l}-\nu)!(\bar{l}+\nu)!} \right]^{1/2} \\ &\sum_x \frac{(-1)^x (L+\bar{l}+\mu-x)!(l-\mu+x)!}{(L-l+\bar{l}-x)!(L+\mu+\nu-x)! x! (x+l-\bar{l}-\mu-\nu)!} \end{aligned} \quad (90)$$

Let us now consider the special case in which  $\mu = 0$  and consider the limit in which  $l$  and  $\bar{l}$  are large and

$$n = \bar{l} - l \quad (91)$$

and  $L$  are small. In this limit

$$\begin{aligned} (2l+1)^{1/2} \begin{pmatrix} l & \bar{l} & L \\ 0 & \nu & -\nu \end{pmatrix} &= \\ \frac{(-1)^{L+\bar{l}}}{2^L} \sum_x \frac{(-1)^x [(L-n)!(L+n)!(L-\nu)!(L+\nu)!]^{1/2}}{(L+n-x)!(L+\nu-x)! x! (x-n-\nu)!} \end{aligned} \quad (92)$$

Explicit expressions for the representation coefficients have also been obtained and are given, for example, by Eqs. 12.B-13 and 19 of Ref. 3. It follows directly from Eqs. 92 and 12.B-19 (of Ref. 3) that

$$(2\ell+1)^{1/2} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \nu & -\nu \end{pmatrix} = (-1)^{L+\ell+\nu} d^L\left(\frac{\pi}{2}\right)_{-n\nu} \quad (93)$$

and therefore from Eq. 12.B-13 (of Ref. 3)

$$(2\ell+1)^{1/2} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \nu & -\nu \end{pmatrix} = (-1)^{L+\ell} D^L\left(\pi, \frac{\pi}{2}, 0\right)_{-n\nu} \quad (94)$$

From the last relation it follows that

$$\begin{aligned} & \sum_{\ell} (2\ell+1) \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \alpha & -\alpha \end{pmatrix} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \nu & -\nu \end{pmatrix} e^{i\ell\theta} \\ &= e^{i\bar{\ell}\theta} \sum_n D^L\left(\pi, \frac{\pi}{2}, 0\right)_{-n\alpha} e^{-in\theta} D^L\left(\pi, \frac{\pi}{2}, 0\right)_{-n\nu} \\ &= e^{i\bar{\ell}\theta} \sum_{nm} D^L\left(\pi, \frac{\pi}{2}, 0\right)_{\alpha, -n} D^L(\theta, 0, 0)_{-n, -m} D^L\left(\pi, \frac{\pi}{2}, 0\right)_{-m\nu} \\ &= e^{i\bar{\ell}\theta} D^L(T)_{\alpha\nu} \end{aligned} \quad (95)$$

where  $T$  is the product of three rotations

$$T = \left(\pi, \frac{\pi}{2}, 0\right) (\theta, 0, 0) \left(\pi, \frac{\pi}{2}, 0\right) \quad (96)$$

It may be shown in a straightforward manner that

$$T = \left(\frac{\pi}{2}, \theta, \frac{3\pi}{2}\right) \quad (97)$$

Thus, in the limit that  $\ell$  and  $\bar{\ell}$  are large and  $L$  and  $\bar{\ell} - \ell$  are not large

$$\sum_{\ell} (2\ell+1) \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \alpha & -\alpha \end{pmatrix} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \nu & -\nu \end{pmatrix} e^{i\ell\theta} \\ = e^{i\bar{\ell}\theta} D^L\left(\frac{\pi}{2}, \theta, \frac{3\pi}{2}\right)_{\alpha\nu} \quad (98)$$

In the special case that  $\theta = 0$ , this result reduces to the orthonormality property of the 3-j symbols.

Footnotes

1. G. Gioumouisis and C. F. Curtiss, J. Chem. Phys. 29, 996 (1958); J. Math. Phys. 2, 96 (1961). G. Gioumouisis, *ibid.* 2, 723 (1961). G. Gioumouisis and C. F. Curtiss, *ibid.* 3, 1059 (1962). C. F. Curtiss and A. Hardisson, J. Chem. Phys. 46, 2618 (1967). C. F. Curtiss, *ibid.* 48, 1725 (1968). L. Biolsi and C. F. Curtiss, *ibid.* 48, 4508 (1968). C. F. Curtiss, *ibid.* 49, 1952 (1968). C. F. Curtiss and R. B. Bernstein, *ibid.* 50, 1168 (1969). R. W. Fenstermaker, C. F. Curtiss, and R. B. Bernstein, *ibid.* 51, 2439 (1969), C. F. Curtiss, *ibid.* (in press).
2. Equation numbers preceded by a Roman numeral refer to equations of Papers I to XI (Ref. 1).
3. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954), p. 65.
4. In this expression and elsewhere a rotation is specified either symbolically, e.g., ( $S_a$ ), or explicitly by the appropriate Eulerian angles ( $\alpha, \beta, \gamma$ ), e.g. ( $\Pi, \theta_a, \Pi$ ).
5. K. H. Kramer and R. B. Bernstein, J. Chem. Phys. 40, 200 (1964). R. B. Bernstein and K. H. Kramer, *ibid.*, 44, 4473 (1966).
6. E. Wigner, Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren (Friedr. Vieweg und Sohn Akt.-Ges., Braunschweig, 1931).