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MOLECULAR COLLISIONS XXI.

SEMICLASSICAL APPROXIMATION TO ATOM-SYMMETRIC

TOP ROTATIONAL EXCITATION

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SEMICLASSICAL APPROXIMATION TO ATOM-SYMMETRIC TOP ROTATIONAL EXCITATION *

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ABSTRACT

In Paper XIX of this series a distorted wave approximation to the T matrix for atom-symmetric top scattering was developed which is correct to first order in the part of the interaction potential responsible for transitions in the component of rotational angular momentum along the symmetry axis of the top. A semiclassical expression for this T matrix is derived by assuming large values of orbital and rotational angular momentum quantum numbers.

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In Paper XIX of this series[1] a distorted wave (DW) approximation to the T matrix for the scattering of an atom by a symmetric top (ST) was derived. The perturbing potential was taken to be that part of the interaction potential responsible for transitions in the component of angular momentum along the symmetry axis of the top. The T matrix was expressed in terms of the generalized phase shift (GPS) solution to the scattering of an atom by a symmetric top with a cylindrically symmetric potential. In this paper a semiclassical approximation is developed by assuming large orbital and rotational angular momentum quantum numbers except for the angular momentum component along the symmetry axis. At the total energy of interest this component remains small since it is assumed that the moment of inertia about the symmetry axis is small.

I. DISTORTED WAVE T MATRIX

The interaction potential $V(r,S)$ can be expressed as

$$V(r,S) = \sum_{\ell m} (8\pi^2)^{-1/2}(2\ell + 1)^{1/2} V_{\ell m}(r) D^{\ell}(S)_{m0} \tag{1}$$

where r is the distance between the atom and the ST center of mass; S represents the three Euler angles which specify the orientation of the principle axes of the ST with respect to a coordinate system whose z axis is fixed along the direction between the atom and ST center of mass; $V_{\ell m}(r)$ is an expansion coefficient dependent on r; $D^{\ell}(S)_{m0}$ is the usual representation coefficient of the three-dimensional rotation group.

This interaction potential can be partitioned into an isotropic part $V(r)$ given by

$$V(r) = (8\pi^2)^{-1/2} V_{00}(r) \tag{2}$$

or a cylindrically symmetric part[2] $V_0(r,S)$ which is adiabatic with respect to the component of angular momentum along the symmetry axis and is given by

$$V_0(r,S) = \sum_{\ell} (8\pi^2)^{-1/2} (2\ell + 1)^{1/2} V_{\ell 0}(r) D^{\ell}(S)_{00} \ . \tag{3}$$

For later use we also define the potentials $\bar{V}_0(r,S)$ and $V_m(r,S)$:

$$\bar{V}_0(r,S) = V_0(r,S) - V(r) \ ; \tag{4}$$

$$V_m(r,S) = \sum_{\ell} (8\pi^2)^{-1/2} (2\ell + 1)^{1/2} V_{\ell m}(r) D^{\ell}(S)_{m0} \ . \tag{5}$$

The ST eigenvalues $\mathcal{E}(\ell\nu)$ are given by

$$\mathcal{E}(\ell\nu) = \frac{\hbar^2 \ell(\ell + 1)}{2I_1} + \frac{\hbar^2 \nu^2}{2}\left(\frac{1}{I_3} - \frac{1}{I_1}\right) \tag{6}$$

where ℓ is the rotational angular momentum quantum number and ν the quantum number of the component of angular momentum along the ST symmetry axis; I_3 is the moment of inertia about the symmetry axis and I_1 the remaining moment. From Eq. (6) it can be seen that when $I_3 << I_1$ energy

conservation requires that the index ν remains small. The channel wave number $k(\ell\nu)$ is defined in the usual way:

$$k^2(\ell\nu) = \frac{2\mu}{\hbar^2}[E - \mathcal{E}(\ell\nu)] \tag{7}$$

where E is the total energy and μ is the reduced mass of the atom-ST system.

Solutions of the wave equation corresponding to different parts of the interaction potential can be defined. First we have the isotropic solutions $\psi^{(\pm)}(\lambda\ell\nu|\mathcal{r})$ which are solutions of the radial equation

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} - \frac{2\mu}{\hbar^2}V(r) + k^2(\ell\nu)\right]\psi^{(\pm)}(\lambda\ell\nu|\mathcal{r}) = 0 \tag{8}$$

with asymptotic form

$$\lim_{\mathcal{r}\to\infty} \psi^{(\pm)}(\lambda\ell\nu|\mathcal{r}) = \exp[\pm ik(\ell\nu)\mathcal{r}] \ . \tag{9}$$

The isotropic phase shift $\eta(\lambda\ell\nu)$ is defined by the solution of Eq. (8), $\psi(\lambda\ell\nu|\mathcal{r})$, which is finite for $\mathcal{r} = 0$:

$$\psi(\lambda\ell\nu|\mathcal{r}) = \frac{1}{2k(\ell\nu)}\left[i^{\lambda+1}\psi^{(-)}(\lambda\ell\nu|\mathcal{r}) + (-i)^{\lambda+1}\psi^{(\pm)}(\lambda\ell\nu|r)\right.$$
$$\left.\exp[2i\eta(\lambda\ell\nu)]\right] \ . \tag{10}$$

For later use it is convenient to define the quantities $f^{(\pm)}(\lambda\ell\nu|\mathcal{r})$:

$$f^{(+)}(\lambda\ell\nu|r) = k(\ell\nu)^{-1/2}\,\psi^{(-)}(\lambda\ell\nu|r) \tag{11}$$

$$f^{(-)}(\lambda\ell\nu|r) = (-1)^{\lambda}\,k(\ell\nu)^{-1/2}\,\psi^{(+)}(\lambda\ell\nu|r)\exp(2i\eta(\lambda\ell\nu)) \;. \tag{12}$$

We next define the GPS solutions $P^{(\pm)}(\lambda\ell\nu|r,S)$ and $Q^{(\pm)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r,S)$ of the scattering problem with interaction potential $V_0(r,S)$. Letting the single index γ represent the three indices λ, ℓ, ν the GPS quantities are solutions of the following equations:

$$\frac{d}{dr}\exp(iQ^{(\pm)}(\bar{\gamma}|r,S)) = -i\mu/\hbar^2\iint dS'dS''\bar{V}_0(r,S')F^{(\pm)}(\bar{\gamma}|r,S',S)$$

$$[F^{(+)}(\bar{\gamma}|r,S',S'')^*\exp[iQ^{(+)}(\bar{\gamma}|r,S'')] - F^{(-)}(\bar{\gamma}|r,S',S'')^*$$

$$\exp[iQ^{(-)}(\bar{\gamma}|r,S'')]] \tag{13}$$

$$\frac{d}{dr}\exp(iP^{(\pm)}(\gamma|r,S)) = i\mu/\hbar^2\iint dS'dS''\bar{V}_0(r,S')F^{(\mp)}(\gamma|r,S,S')^*$$

$$[F^{(+)}(\gamma|r,S'',S')\exp(iP^{(-)}(\gamma|r,S'')) - F^{(-)}(\gamma|r,S'',S')\exp(iP^{(+)}(\gamma|r,S''))] \tag{14}$$

The quantities $F^{(\pm)}(\bar{\gamma}|r,S,S'')$ appearing in Eqs. (13) and (14) are defined as

$$F^{(\pm)}(\bar{\gamma}|r,S,S'') = \sum_{\Lambda}\chi(\bar{\gamma}|\Lambda|S)f^{(\pm)}(\lambda\ell\bar{\nu}|r)\chi(\bar{\gamma}|\Lambda|S'')^* \tag{15}$$

where Λ represents the three indices of λ, ℓ, L and

$$\chi(\bar{\gamma}|\Lambda|S) = (8\pi^2)^{-1/2}\,(-1)^L[(2\lambda+1)(2\ell+1)(2L+1)]^{1/2}\sum_{\alpha\beta}(-i)^{\alpha+\beta}$$

$$\begin{pmatrix}\ell & \ell & L\\ -\bar{\nu} & \alpha & \bar{\nu}-\alpha\end{pmatrix}\begin{pmatrix}\lambda & \bar{\lambda} & L\\ 0 & -\beta & \beta\end{pmatrix}D^L(S)_{\alpha-\bar{\nu},\beta}\,. \tag{16}$$

The boundary conditions satisfied by the GPS solutions are

$$\lim_{r\to\infty} Q^{(-)}(\bar{\gamma}|r,S) = 2\eta(\bar{\gamma}) \tag{17}$$

$$\lim_{r\to 0} Q^{(+)}(\bar{\gamma}|r,S) = \lim_{r\to 0} Q^{(-)}(\bar{\gamma}|\quad,S) \tag{18}$$

$$\lim_{r\to\infty} P^{(+)}(\gamma|r,S) = -2\eta(\gamma) \tag{19}$$

$$\lim_{r\to 0} P^{(-)}(\gamma|r,S) = \lim_{r\to 0} P^{(+)}(\gamma|\quad,S) \tag{20}$$

The quantities $P^{(\pm)}(\gamma|r,S)$ and $Q^{(\pm)}(\gamma|r,S)$ are related as follows:

$$P^{(\pm)}(\lambda\ell\nu|r,S) = -Q^{(\mp)}(\lambda\ell-\nu|r,\{\pi 00\}S\{\pi 00\})^* \tag{21}$$

where the notation $\{\pi 00\}S\{\pi 00\}$ refers to a product of rotations.

From Eq. (XIX-84) the DW T matrix for transitions from initial states $(\bar{\lambda}\bar{\ell}\bar{\nu})$ to final states $(\lambda\ell\nu)$ when $\nu \neq \bar{\nu}$ is given by[3]

$$T_{DW}^{\bar{L}}(\gamma|\bar{\gamma}) = (-1)^{\bar{L}+\bar{\ell}+1} (i)^{\nu-\bar{\nu}} (\mu/4\pi h^2)\int d\mathcal{r}\int dS dS' dS'' V_{\nu-\bar{\nu}}(\mathcal{r},S)$$

$$[G^{(+)}(\gamma|\bar{\Lambda}|\mathcal{r},S'S)^* \exp(-iP^{(-)}(\gamma|\mathcal{r},S')^*) - G^{(-)}(\gamma|\bar{\Lambda}|\mathcal{r},S',S)^*$$

$$\exp[-iP^{(+)}(\gamma|\mathcal{r},S')^*][F^{(+)}(\bar{\gamma}|\mathcal{r},S,S'')^* \exp[iQ^{(+)}(\bar{\gamma}|\mathcal{r},S'')]$$

$$-F^{(-)}(\bar{\gamma}|\mathcal{r},S,S'')^* \exp[iQ^{(-)}(\bar{\gamma}|\mathcal{r},S'')] \tag{22}$$

where $V_{\nu-\bar{\nu}}(\mathcal{r},S)$ is given by Eq. (5) and

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\mathcal{r},S',S) = \sum_{L\Lambda'} (-1)^{\lambda'+\ell'} [(2\lambda+1)(2\ell+1)(2\bar{L}+1)(2L+1)(2L'+1)]^{1/2}$$

$$\begin{Bmatrix} L & L' & \bar{L} \\ \ell & \bar{\ell} & \ell' \end{Bmatrix} \begin{Bmatrix} L & L' & \bar{L} \\ \lambda & \bar{\lambda} & \lambda' \end{Bmatrix} \chi(\gamma|\Lambda'|S') f_{\lambda'}^{(\pm)}(\ell'\nu|\mathcal{r}) \chi(\bar{\lambda}\bar{\ell}\nu|\lambda'\ell'L|S)^* . \tag{23}$$

In terms of this T matrix the total degeneracy averaged cross-section $I(\ell\nu|\bar{\ell}\bar{\nu})$ is

$$I(\ell\nu|\bar{\ell}\bar{\nu}) = \frac{4\pi^3}{k(\bar{\ell}\bar{\nu})^2} \sum_{\bar{L}\bar{\lambda}\bar{\lambda}} \frac{(2\bar{\lambda}+1)}{(2\bar{L}+1)} (-1)^{\bar{L}+\bar{\ell}+\bar{\ell}} |T_{DW}^{\bar{L}}(\lambda\ell\nu|\bar{\lambda}\bar{\ell}\bar{\nu})|^2 . \tag{24}$$

II. SEMICLASSICAL APPROXIMATION

The semiclassical approximation to $T_{DW}^{\bar{L}}(\gamma|\bar{\gamma})$ is obtained by considering Eq. (22) for the case

$$\bar{\lambda},\bar{\ell} \gg \bar{L},\bar{\nu},\nu \tag{25}$$

For large values of λ and ℓ Eq. (8) is solved by WKB techniques. Under the conditions of Eq. (25) it can be shown that[4]

$$f^{(\pm)}(\lambda\ell\bar{\nu}|r) = f^{(\pm)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r)\exp[i\theta^{(\pm)}(\bar{\gamma}|r)(\bar{\lambda} - \lambda) + i\chi^{(\pm)}(\bar{\gamma}|r)(\ell - \bar{\ell})] \ . \tag{26}$$

The quantities $\theta^{(\pm)}(\bar{\gamma}|r)$ and $\chi^{(\pm)}(\bar{\gamma}|r)$ are defined as follows. With

$$C(\bar{\gamma}|r) = 1 - \frac{2\mu V(r)}{\hbar^2 k(\bar{\ell}\bar{\nu})^2} - \frac{(\bar{\lambda} + \frac{1}{2})^2}{k(\bar{\ell}\bar{\nu})^2 r^2} \tag{27}$$

and r_0 defined such that

$$C(\bar{\gamma}|r_0) = 0$$

we have

$$\theta^{(\pm)}(\bar{\gamma}|r) = \frac{(\bar{\lambda} + \frac{1}{2})}{k(\bar{\ell}\bar{\nu})} \int_r^\infty \frac{dr'}{r'^2 C(\bar{\gamma}|r')^2} \tag{28}$$

$$\theta^{(-)}(\bar{\gamma}|r) = 2\theta^{(+)}(\bar{\gamma}|r_0) - \theta^{(+)}(\bar{\gamma}|r) \ . \tag{29}$$

With

$$s(\bar{\gamma}|r) = r - \int_r^\infty [C(\bar{\gamma}|r')^{-1/2} - 1]dr' \tag{30}$$

we have

$$\chi^{(+)}(\bar{\gamma}|r) = \frac{\mu\bar{\ell}\mathcal{S}(\bar{\gamma}|r)}{I_1 k(\bar{\ell}\bar{\nu})} \tag{31}$$

$$\chi^{(-)}(\bar{\gamma}|r) = 2\chi^{(+)}(\bar{\gamma}|r_0) - \chi^{(+)}(\bar{\gamma}|r) \tag{32}$$

From Eq. (15A) of Appendix A we have the semiclassical expression for the 3-j symbol:

$$(2\ell + 1)^{1/2}\begin{pmatrix} \ell & \bar{\ell} & L \\ -\bar{\nu} & \alpha & \bar{\nu}-\alpha \end{pmatrix} = (-1)^{L+\ell+\alpha}\, D^L(\{0\ \tfrac{\pi}{2}\ 0\})_{\ell-\bar{\ell},\alpha-\bar{\nu}}\ . \tag{33}$$

Substituting Eq. (33) into Eq. (16) yields

$$\chi(\bar{\gamma}|\Lambda|S) = (8\pi^2)^{-1/2}\ (2L + 1)^{1/2}\ (-1)^{L+\lambda+\ell}\ (i)^{\bar{\nu}}\ D^L(USW)_{\ell-\bar{\ell},\bar{\lambda}-\lambda} \tag{34}$$

where

$$U = \{\tfrac{\pi}{2}\ \tfrac{\pi}{2}\ 0\} \tag{35}$$

$$W = \{0\ \tfrac{\pi}{2}\ \tfrac{\pi}{2}\} \tag{36}$$

When Eqs. (26) and (34) are substituted into Eq. (15) the semiclassical expression for $F^{(\pm)}(\bar{\gamma}|r,S,S'')$ is obtained:[4]

$$F^{(\pm)}(\bar{\gamma}|r,S,S'') = f^{(\pm)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r)\,\delta(S''|\bar{R}^{(\pm)}S\bar{T}^{(\pm)}) \tag{37}$$

with

$$\bar{R}^{(\pm)} = \{0\ \chi^{(\pm)}(\bar{\gamma}|\Lambda)\ 0\} \tag{38}$$

$$\bar{T}^{(\pm)} = \{0\ \theta^{(\pm)}(\bar{\gamma}|\Lambda)\ 0\} \quad . \tag{39}$$

The semiclassical expression for the 6-j coefficient appearing in Eq. (23) is[5]

$$(2\lambda + 1)^{1/2} \begin{Bmatrix} L & L' & \bar{L} \\ \lambda & \bar{\lambda} & \lambda' \end{Bmatrix} = \begin{pmatrix} L' & \bar{L} & L \\ \lambda-\lambda' & \bar{\lambda}-\lambda & \lambda'-\bar{\lambda} \end{pmatrix} . \tag{40}$$

With the aid of Eqs. (26), (36) and (40) the semiclassical expression for $G^{(\pm)}(\gamma|\bar{\Lambda}|\Lambda,S',S)$ is derived in Appendix B:

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\Lambda,S',S) = (-1)^{\bar{L}+\bar{\lambda}+\bar{\ell}}\ (2\bar{L} + 1)^{1/2}\ f^{(\pm)}(\lambda\ell\nu|\Lambda)$$
$$D^{\bar{L}}(USW)^{*}_{\ell-\bar{\ell},\bar{\lambda}-\lambda}\ \delta(S|R^{(\pm)}S'T^{(\pm)}) \tag{41}$$

where $R^{(\pm)}$ and $T^{(\pm)}$ are given by Eqs. (38) and (39) with γ replacing $\bar{\gamma}$.

Equations (37) and (41) are substituted into Eq. (22) to obtain

$$T^{\bar{L}}_{DW}(\gamma|\bar{\gamma}) = (-1)^{\bar{\lambda}+1} (i)^{\nu-\bar{\nu}} (2\bar{L}+1)^{1/2} (\mu/4\pi h^2)\int d\Lambda \int dS\, V_{\nu-\bar{\nu}}(\Lambda,S)$$

$$D^{\bar{L}}(USW)_{\ell-\bar{\ell},\bar{\lambda}-\lambda} [f^{(+)}(\gamma|\Lambda)^* \exp(-iP^{(-)}(\gamma|\Lambda,R^{(+)^{-1}}ST^{(+)^{-1}})^*)$$

$$- f^{(-)}(\gamma|\Lambda)^* \exp(-iP^{(+)}(\gamma|\Lambda,R^{(-)^{-1}}ST^{(-)^{-1}})^*)][f^{(+)}(\bar{\gamma}|\Lambda)^*$$

$$\exp(iQ^{(+)}(\bar{\gamma}|\Lambda,\bar{R}^{(+)}S\bar{T}^{(+)})) - f^{(-)}(\bar{\gamma}|\Lambda)^* \exp(iQ^{(-)}(\bar{\gamma}|\Lambda,\bar{R}^{(-)}S\bar{T}^{(-)}))] \quad (42)$$

Semiclassical expressions for the GPS solutions $P^{(\pm)}$ and $Q^{(\pm)}$ appearing in Eq. (42) are obtained by substituting Eq. (37) into Eqs. (13) and (14) to give

$$\frac{d}{d\Lambda} \exp(iQ^{(\pm)}(\bar{\gamma}|\Lambda,S)) = (\mp)(i\mu/\hbar^2)\bar{V}_0(\Lambda,\bar{R}^{(\pm)^{-1}}S\bar{T}^{(\pm)^{-1}})f^{(\pm)}(\bar{\gamma}|\Lambda)$$

$$[f^{(\pm)}(\bar{\gamma}|\Lambda)^* \exp(iQ^{(\pm)}(\bar{\gamma}|\Lambda,S)) - f^{(\mp)}(\bar{\gamma}|\Lambda)^*$$

$$\exp(iQ^{(\mp)}(\bar{\gamma}|\Lambda,\bar{R}^{(\mp)}\bar{R}^{(\pm)^{-1}}S\bar{T}^{(\pm)^{-1}}\bar{T}^{(\mp)}))] \quad (43)$$

$$\frac{d}{d\Lambda} \exp(iP^{(\pm)}(\gamma|\Lambda,S)) = (\mp)(i\mu/\hbar^2)\bar{V}_0(\Lambda,R^{(\mp)}ST^{(\mp)})f^{(\mp)}(\gamma|\Lambda)^*$$

$$[f^{(\mp)}(\gamma|\Lambda)\exp(iP^{(\pm)}(\gamma|\Lambda,S)) - f^{(\pm)}(\gamma|\Lambda)$$

$$\exp(iP^{(\mp)}(\gamma|\Lambda,R^{(\pm)^{-1}}R^{(\mp)}ST^{(\mp)}T^{(\pm)^{-1}}))] \quad (44)$$

It is assumed that the product $f^{(\mp)}(\gamma|\Lambda)^* f^{(\pm)}(\gamma|\Lambda)$ is highly oscillatory and terms containing it can be neglected in Eqs. (43) and (44) which then become

$$\frac{d}{dr}\exp(iQ^{(\pm)}(\bar{\gamma}|r,S)) = (\mp)(i\mu/\hbar^2)\bar{V}_0(r,\bar{R}^{(\pm)^{-1}}S\bar{T}^{(\pm)^{-1}})|f^{(\pm)}(\gamma|r)|^2 \exp(iQ^{(\pm)}(\bar{\gamma}|r,S)) \tag{45}$$

$$\frac{d}{dr}\exp(iP^{(\pm)}(\gamma|r,S)) = (\mp)(i\mu/\hbar^2)\bar{V}_0(r,R^{(\mp)}ST^{(\mp)})|f^{(\mp)}(\gamma|r)|^2 \exp(iP^{(\pm)}(\gamma|r,S)) \ . \tag{46}$$

It is now an easy matter to integrate Eqs. (45) and (46) with boundary conditions specified by Eqs. (17)-(20) to obtain the semiclassical expressions for $P^{(\pm)}$ and $Q^{(\pm)}$:

$$Q^{(-)}(\bar{\gamma}|r,S) = 2\eta(\bar{\gamma}) - (\mu/\hbar^2)\int_r^\infty |f^{(-)}(\bar{\gamma}|r')|^2\bar{V}_0(r',\bar{R}^{(-)^{-1}}S\bar{T}^{(-)^{-1}})dr' \tag{47}$$

$$Q^{(+)}(\bar{\gamma}|r,S) = 2\eta(\bar{\gamma}) - (\mu/\hbar^2)\int_0^\infty |f^{(-)}(\bar{\gamma}|r')|^2\bar{V}_0(r',\bar{R}^{(-)^{-1}}S\bar{T}^{(-)^{-1}})dr' - (\mu/\hbar^2)\int_0^r |f^{(+)}(\bar{\gamma}|r')|^2\bar{V}_0(r',\bar{R}^{(+)^{-1}}S\bar{T}^{(+)^{-1}})dr' \tag{48}$$

$$P^{(+)}(\gamma|r,S) = -2\eta(\gamma) + (\mu/\hbar^2)\int_r^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',R^{(-)}ST^{(-)})dr' \tag{49}$$

$$P^{(-)}(\gamma|r,S) = -2\eta(\gamma) + (\mu/\hbar^2)\int_0^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',R^{(-)}ST^{(-)})dr' + (\mu/\hbar^2)\int_0^r |f^{(+)}(\gamma|r')|^2\bar{V}_0(r',R^{(+)}ST^{(+)})dr' \ . \tag{50}$$

With these expression for $P^{(\pm)}$ and $Q^{(\pm)}$ the GPS quantities appearing in Eq. (42) can be given explicitly as

$$P^{(+)}(\gamma|r,R^{(-)^{-1}}ST^{(-)^{-1}}) = -2\eta(\gamma) + (\mu/\hbar^2)\int_r^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',S)dr' \tag{51}$$

$$P^{(-)}(\gamma|r,R^{(+)^{-1}}ST^{(+)^{-1}}) = -2\eta(\gamma) + (\mu/\hbar^2)\int_0^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',XSY)dr'$$
$$+ (\mu/\hbar^2)\int_0^r |f^{(+)}(\gamma|r')|^2\bar{V}_0(r',S)dr' \tag{52}$$

$$Q^{(+)}(\bar{\gamma}|r,\bar{R}^{(+)}S\bar{T}^{(+)}) = 2\eta(\bar{\gamma}) - (\mu/\hbar^2)\int_0^\infty |f^{(-)}(\bar{\gamma}|r')|^2\bar{V}_0(r',\bar{X}S\bar{Y})dr'$$
$$- (\mu/\hbar^2)\int_0^r |f^{(+)}(\bar{\gamma}|r')|^2\bar{V}_0(r',S)dr' \tag{53}$$

$$Q^{(-)}(\bar{\gamma}|r,\bar{R}^{(-)}S\bar{T}^{(-)}) = 2\eta(\bar{\gamma}) - (\mu/\hbar^2)\int_r^\infty |f^{(-)}(\bar{\gamma}|r')|^2\bar{V}_0(r',S)dr' \tag{54}$$

where

$$X = \{0\ 2(\chi^{(+)}(\gamma|r_0) - \chi^{(+)}(\gamma|r))\ 0\} \tag{55}$$

$$Y = \{0\ 2(\theta^{(+)}(\gamma|r_0) - \theta^{(+)}(\gamma|r))\ 0\} \tag{56}$$

Substituting Eqs. (51)-(54) into Eq. (42) the semiclassical T matrix can be written as

$$T_{DW}^{\bar{L}}(\gamma|\bar{\gamma}) = \int dr \int dS\Psi(\gamma|r,S)\mathcal{V}^{\bar{L}}(\gamma|\bar{\gamma}|r,S)\Psi(\bar{\gamma}|r,S) \tag{57}$$

with

$$\Psi(\gamma|r,S) = k(\ell\nu)^{-1/2}\,[\psi^{(+)}(\gamma|r)\exp(2i\eta(\gamma)$$

$$- (i\mu/\hbar^2)\int_0^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',XSY)\,dr'$$

$$- (i\mu/\hbar^2)\int_0^r |f^{(+)}(\gamma|r')|^2\bar{V}_0(r',S)\,dr')$$

$$+ (-1)^{\lambda+1}\,\psi^{(-)}(\gamma|r)\exp(-(i\mu/\hbar^2)\int_r^\infty |f^{(-)}(\gamma|r')|^2\bar{V}_0(r',S)\,dr')] \quad (58)$$

and

$$\mathcal{V}^{\bar{L}}(\gamma|\bar{\gamma}|r,S) = (-1)^{\bar{\lambda}+1}\,(i)^{\nu-\bar{\nu}}\,(2\bar{L}+1)^{1/2}\,(\mu/4\pi h^2)$$

$$D^{\bar{L}}(USW)_{\ell-\bar{\ell},\bar{\lambda}-\lambda}\,V_{\nu-\bar{\nu}}(r,S)\ . \quad (59)$$

If the terms in the product $\Psi(\gamma|r,S)\Psi(\bar{\gamma}|r,S)$ containing the highly oscillatory quantity $\psi^{(\pm)}(\gamma|r)\psi^{(\pm)}(\bar{\gamma}|r)$ are neglected we then have after using Eq. (26)

$$\Psi(\gamma|r,S)\Psi(\bar{\gamma}|r,S) = (-1)^{\lambda+\bar{\lambda}}\,[\Phi(\bar{\lambda}\bar{\ell}\nu\bar{\nu}|r,S)\exp(i\theta^{(-)}(\bar{\lambda}\bar{\ell}\nu|r)(\bar{\lambda}-\lambda)$$

$$+ i\chi^{(-)}(\bar{\lambda}\bar{\ell}\nu|r)(\ell-\bar{\ell})) - \Phi(\bar{\lambda}\bar{\ell}\bar{\nu}\nu|r,S)\exp(i\theta^{(+)}(\bar{\lambda}\bar{\ell}\nu|r)(\bar{\lambda}-\lambda)$$

$$+ i\chi^{(+)}(\bar{\lambda}\bar{\ell}\nu|r)(\ell-\bar{\ell})) \quad (60)$$

where

$$\Phi(\bar{\lambda}\bar{\ell}\bar{\nu}\nu|r,S) = f^{(-)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r)f^{(+)}(\bar{\lambda}\bar{\ell}\nu|r)\exp(-(i\mu/\hbar^2)$$

$$(\int_0^r |f^{(+)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r')|^2\bar{V}_0(r',S)dr' + \int_r^\infty |f^{(-)}(\bar{\lambda}\bar{\ell}\nu|r')|^2\bar{V}_0(r',S)dr'$$

$$+ \int_0^\infty |f^{(-)}(\bar{\lambda}\bar{\ell}\bar{\nu}|r')|^2\bar{V}_0(r',\bar{X}S\bar{Y})dr')) \quad . \tag{61}$$

Equations (57)-(61) give an approximate T matrix for atom-ST scattering which is first order in that part of the interaction potential responsible for transitions in the component of angular momentum along the symmetry axis and which is semiclassical in the orbital and rotational angular momentum.

APPENDIX A

With the definitions

$$n = \ell - \bar{\ell} \tag{1A}$$

$$m = \mu + \nu \tag{2A}$$

an explicit expression for the 3-j symbol is[4]

$$\begin{pmatrix} \ell & \bar{\ell} & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} = (-1)^{L+\bar{\ell}+\mu} \left[\frac{(L+n)!(L-n)!(\ell+\bar{\ell}-L)!}{(L+\ell+\bar{\ell}+1)!}\right]^{1/2}$$

$$\left[\frac{(L+m)!(L-m)!}{(\ell-\mu)!(\ell+\mu)!(\bar{\ell}-\nu)!(\bar{\ell}+\nu)!}\right]^{1/2} \sum_{\chi} (-1)^{\chi} \frac{(L+\bar{\ell}+\mu-\chi)!(\ell-\mu+\chi)!}{(L-n-\chi)!(L+m-\chi)!(\chi+n-m)!\chi!} \tag{3A}$$

The factors in Eq. (3A) are rearranged to give

$$\begin{pmatrix} \ell & \bar{\ell} & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} = (-1)^{L+\bar{\ell}+\mu} \sum_{\chi} (-1)^{\chi} \frac{[(L+n)!(L-n)!(L+m)!(L-m)!]^{1/2}}{(L-n-\chi)!(L+m-\chi)!(\chi+n-m)!\chi!}$$

$$\left[\frac{(\ell+\bar{\ell}-L)!}{(\ell+\bar{\ell}+L+1)!}\right]^{1/2} \left[\frac{(\bar{\ell}+L+\mu-\chi)!(\bar{\ell}+L+\mu-\chi)!}{(\bar{\ell}-\nu)!(\bar{\ell}+\nu)!}\right]^{1/2}$$

$$\left[\frac{(\ell-\mu+\chi)!(\ell-\mu+\chi)}{(\ell-\mu)!(\ell+\mu)!}\right]^{1/2} \tag{4A}$$

Under the conditions

$$\ell \gg L,\mu \tag{5A}$$

$$\bar{\ell} \gg L,\nu \tag{6A}$$

an approximation to the 3-j symbol may be derived by using the fact that

$$\frac{(N + k)!}{(N + \ell)!} \simeq N^{k-\ell} \tag{7A}$$

for N much larger than k and ℓ.

Using Eq. (7A) we obtain

$$\left[\frac{(\ell + \bar{\ell} - L)!}{(\ell + \bar{\ell} + L + 1)!}\right]^{1/2} = \frac{1}{(\ell + \bar{\ell})^{L+1/2}} \tag{8A}$$

$$\left[\frac{(\bar{\ell} + L + \mu - \chi)!(\bar{\ell} + L + \mu - \chi)!}{(\bar{\ell} - \nu)!(\bar{\ell} + \nu)!}\right]^{1/2} = (\bar{\ell})^{L+\mu-\chi} \tag{9A}$$

$$\left[\frac{(\ell - \mu + \chi)!(\ell - \mu + \chi)!}{(\ell - \mu)!(\ell + \mu)!}\right]^{1/2} = (\ell)^{\chi-\mu} \tag{10A}$$

Substituting Eqs. (8A)-(10A) into Eq. (4A) yields

$$(2\ell + 1)^{1/2} \begin{pmatrix} \ell & \bar{\ell} & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} = (-1)^{L+\bar{\ell}+\mu} \left(\frac{2\ell + 1}{2\ell - n}\right)^{1/2} \left(\frac{\bar{\ell}}{2\bar{\ell} + n}\right)^{L} \left(\frac{\ell - n}{\ell}\right)^{\mu}$$

$$\sum_{\chi} (-1)^{\chi} \frac{[(L + n)!(L - n)!(L + m)!(L - m)!]^{1/2}}{(L - n - \chi)!(L + m - \chi)!(\chi + n - m)!\chi!} \left(\frac{\bar{\ell} + n}{\bar{\ell}}\right)^{\chi} \tag{11A}$$

Since

$$\ell,\bar{\ell} \gg n \tag{12A}$$

$$(2\ell + 1)^{1/2} \begin{pmatrix} \ell & \bar{\ell} & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} = (-1)^{L+\bar{\ell}+\mu} \left(\frac{1}{2}\right)^L$$

$$\sum_{\chi} (-1)^{\chi} \frac{[(L+n)!(L-n)!(L+m)!(L-m)!]^{1/2}}{(L-n-\chi)!(L+m-\chi)!(\chi+n-m)!\chi!} \tag{13A}$$

From Eqs. (12.B-13) and (12.B-19) of Ref. 6

$$D^L(\{0\ \beta\ 0\})_{nm} = (-1)^{n+m} \sum_{\chi} (-1)^{\chi} \frac{[(L+n)!(L-n)!(L+m)!(L-m)!]^{1/2}}{(L-n-\chi)!(L+m-\chi)!(\chi+n-m)!\chi!}$$

$$(\cos^2 \frac{\beta}{2})^L (\tan \frac{\beta}{2})^{n-m+2\chi} . \tag{14A}$$

Setting $\beta = \frac{\pi}{2}$ in Eq. (14A) and then comparing with Eq. (13A) we obtain

$$(2\ell + 1)^{1/2} \begin{pmatrix} \ell & \ell & L \\ \mu & \nu & -\mu-\nu \end{pmatrix} = (-1)^{L+\ell+\nu} D^L(\{0\ \frac{\pi}{2}\ 0\})_{\ell-\bar{\ell},\mu+\nu} \tag{15A}$$

APPENDIX B

From Eq. (34),

$$\chi(\lambda\ell\nu|\lambda'\ell'L'|S')\chi(\bar{\lambda}\bar{\ell}\nu|\lambda'\ell'L|S)^* = (-1)^{L'+L}(8\pi^2)^{-1}(2L'+1)^{1/2}(2L+1)^{1/2}$$

$$D^{L'}(US'W)_{\ell'-\ell,\lambda-\lambda'}\, D^{L}(USW)^*_{\ell'-\bar{\ell},\bar{\lambda}-\lambda'} \tag{1B}$$

with U and W given by Eqs. (35) and (36). From Eq. (40),

$$(2\lambda+1)^{1/2}(2\ell+1)^{1/2}\begin{Bmatrix} L & L' & \bar{L} \\ \ell & \bar{\ell} & \ell' \end{Bmatrix}\begin{Bmatrix} L & L' & \bar{L} \\ \lambda & \bar{\lambda} & \lambda' \end{Bmatrix} = \begin{pmatrix} L' & \bar{L} & L \\ \ell-\ell' & \bar{\ell}-\ell & \ell'-\bar{\ell} \end{pmatrix}\begin{pmatrix} L' & \bar{L} & L \\ \lambda-\lambda' & \bar{\lambda}-\lambda & \lambda'-\bar{\lambda} \end{pmatrix} \tag{2B}$$

From Eq. (26),

$$f^{(\pm)}(\lambda'\ell'\nu|\Lambda) = f^{(\pm)}(\lambda\ell\nu|\Lambda)\exp(i\theta^{(\pm)}(\lambda-\lambda') + i\chi^{(\pm)}(\ell'-\ell)) . \tag{3B}$$

Substituting Eqs. (1B)-(3B) into Eq. (23) yields

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\Lambda,S',S) = (-1)^{\bar{L}+\bar{\lambda}+\bar{\ell}}(2\bar{L}+1)^{1/2}(8\pi^2)^{-1} f^{(\pm)}(\gamma|\Lambda)$$

$$\sum_{LL'\lambda'\ell'} (-1)^{\ell'-\bar{\ell}+\lambda'-\bar{\lambda}}(2L+1)(2L'+1)\begin{pmatrix} L' & \bar{L} & L \\ \ell'-\ell & \ell-\bar{\ell} & \bar{\ell}-\ell' \end{pmatrix}\begin{pmatrix} L' & \bar{L} & L \\ \lambda-\lambda' & \bar{\lambda}-\lambda & \lambda'-\bar{\lambda} \end{pmatrix}$$

$$D^{L'}(\{\chi^{(\pm)}00\}US'W\{\theta^{(\pm)}00\})_{\ell'-\ell,\lambda-\lambda'}\, D^{L}(USW)^*_{\ell'-\bar{\ell},\bar{\lambda}-\lambda'} . \tag{4B}$$

In obtaining Eq. (4B) we have used the property

$$e^{im\alpha}D^{\ell}(S)_{mn}e^{in\beta} = D^{\ell}(\{\alpha 00\}S\{\beta 00\})_{mn} . \tag{5B}$$

Since

$$(-1)^{\ell'-\bar{\ell}+\lambda'-\bar{\lambda}} \sum_{L} (2L+1) \begin{pmatrix} L' & \bar{L} & L \\ \ell'-\ell & \ell-\bar{\ell} & \bar{\ell}-\ell' \end{pmatrix} \begin{pmatrix} L' & \bar{L} & L \\ \lambda-\lambda' & \bar{\lambda}-\lambda & \lambda'-\bar{\lambda} \end{pmatrix}$$

$$D^{L}(USW)^{*}_{\ell'-\bar{\ell},\bar{\lambda}-\lambda'} = D^{L'}(USW)^{*}_{\ell'-\ell,\lambda-\lambda'} D^{\bar{L}}(USW)^{*}_{\ell-\bar{\ell},\bar{\lambda}-\lambda} \tag{6B}$$

we can write Eq. (4B) as

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\mathcal{r},S',S) = (-1)^{\bar{L}+\bar{\lambda}+\bar{\ell}} (2\bar{L}+1)^{\frac{1}{2}} f^{(\pm)}(\gamma|\mathcal{r})D^{\bar{L}}(USW)^{*}_{\ell-\bar{\ell},\bar{\lambda}-\lambda}$$

$$(8\pi^2)^{-1} \sum_{L'\lambda'\ell'} (2L'+1)D^{L'}(\{\chi^{(\pm)}00\}US'W\{\theta^{(\pm)}00\})_{\ell'-\ell,\lambda-\lambda'}$$

$$D^{L'}(USW)^{*}_{\ell'-\ell,\lambda-\lambda'} \tag{7B}$$

Since the representation coefficients are complete Eq. (7B) reduces to

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\mathcal{r},S',S) = (-1)^{\bar{L}+\bar{\lambda}+\bar{\ell}} (2\bar{L}+1)^{\frac{1}{2}} f^{(\pm)}(\gamma|\mathcal{r})D^{\bar{L}}(USW)^{*}_{\ell-\bar{\ell},\bar{\lambda}-\lambda}$$

$$\delta(\{\chi^{(\pm)}00\}US'W\{\theta^{(\pm)}00\}|USW) . \tag{8B}$$

The δ function in Eq. (8B) can be rewritten as

$$\delta(\{\chi^{(\pm)}00\}US'W\{\theta^{(\pm)}00\}|USW) = \delta(U^{-1}\{\chi^{(\pm)}00\}US'W\{\theta^{(\pm)}00\}W^{-1}|S) \ . \quad (10B)$$

The rotations U and W are such that

$$U^{-1}\{\alpha\ 0\ 0\}U = \{0\ \alpha\ 0\} \quad (11B)$$

$$W\{\alpha\ 0\ 0\}W^{-1} = \{0\ \alpha\ 0\} \ . \quad (12B)$$

In view of Eqs. (10B)-(12B) we rewrite Eq. (8B) as

$$G^{(\pm)}(\gamma|\bar{\Lambda}|\Lambda,S',S) = (-1)^{\bar{L}+\bar{\lambda}+\bar{\ell}}\ (2\bar{L}+1)^{1/2}\ f^{(\pm)}(\gamma|\Lambda)D^{\bar{L}}(USW)^{*}_{\ell-\bar{\ell},\bar{\lambda}-\lambda}$$
$$\delta(\{0\ \chi^{(\pm)}\ 0\}S'\{0\ \theta^{(\pm)}\ 0\}|S) \ . \quad (13B)$$

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1. D. Russell and C. F. Curtiss, J. Chem. Phys. 59, (1973). Equation numbers preceded by XIX refer to an equation in this paper.
2. $V_0(\Omega,S)$ is identical to the interaction potential for an atom-rigid rotor system.
3. Eq. (XIX-84) is expressed in terms of $Q^{(\pm)}$ solutions only. In making the semiclassical approximation it is convenient to use both $P^{(\pm)}$ and $Q^{(\pm)}$ in the T matrix expression.
4. C. F. Curtiss, J. Chem. Phys. 52, 4832 (1970). See Eqs. (50) and (55) of this reference which give the semiclassical expression for $\psi^{(\pm)}(\gamma|\Omega)$.
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