Semiclassical Decoupling Schemes in Molecular Collisions

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Several decoupling schemes are discussed for the semiclassical impact parameter treatment of collisions between atoms and linear rigid rotors. First, a decoupling method analogous to the quantum mechanical one originated from the conservation of parity is found also in the semiclassical treatment. Next, presently derived semiclassical versions of l-dominance and decoupled l-dominance approximations provide us with an intuitive understanding of the physical meaning of these approximations. Numerical applications are performed for the H^+-CO collision system.

§1. Introduction

When we investigate the molecular collisions quantum mechanically, the wavefunction of the collision system is expanded in terms of appropriate basis functions. This results in a set of close coupling (CC) equations where a sufficient number of the channel states should be included to assure desirable accuracy of the calculated physical quantities such as the S matrix and cross sections. In the CC calculation, the most cumbersome problem is the treatment of molecular rotation—a very large number of the rotational states must be included because the rotational energy spacings are usually much smaller than the collision energy and the 2j+1-fold degeneracy exists in each rotational state j.

Under these circumstances, many authors have introduced various kinds of approximate methods to decouple the rotational degrees of freedom (see, e.g., a recent review by Dickinson1). Of these methods, the coupled state (CS) approximation2) has been widely applied. The CS method is expected to work well for the collision system dominated by short-range forces or small impact parameter encounters.3,6) Its applications to vibrational excitation and chemical reaction are very interesting.1,5) For the collision process dominated by long-range forces or large impact parameter encounters, DePristo and Alexander6) have introduced the l-dominance (LD) approximation, which is based on their observation in their accurate CC calculations that at large total angular momentum J excitation process is dominated by the transition between smaller initial and final orbital angular momenta I_0 and I. (Such a propensity of l-dominance is seen in Table I for the H^+-CO collision7) for excitation the absolute value of the S matrix with I \leq J is an order of magnitude larger than that with I > J.) In the LD method all the channels with I_0, I > J are eliminated from the CC equations. DePristo and Alexander6) have explained this propensity of l-dominance in terms of the classical turning point—at larger values of l the turning point is located at larger relative distances where the interaction decreases, and thus the transition probability becomes small. This explanation is somewhat unsatisfactory. Note that |J-j| \leq I \leq J+j. The turning point for these l channels do not differ so much from each other when J \gg 1 and j \approx 1. Therefore, we cannot expect that the different locations of the turning points for the various l channels explain the differences in an order of magnitude of the transition probability. Furthermore, the l-dominance feature is found to hold very well for the final orbital angular momentum, but not very well for the initial orbital angular momentum; and is perhaps characterized as the propensity of the preferential transitions with I_0 > I rather than with I_0, l < J (see Table I). These facts cannot be simply explained in
Table I. $|S^j(jl; j_0l_0)|^2$ calculated by the CC method for the transition $j_0l_0\rightarrow jl$ by the $H^+\cdot CO$ collision at $J=50$. The total energy is 0.01 eV. The CC calculation is based on the perturbed rotational state theory.\(^7\) $-n$ denotes the power of ten by which the preceding figure is multiplied.

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terms of the turning points.

Recently, Alexander and Dagdijian\(^8\) and Alexander\(^9\) have found that the molecular orientation dependence of the rotationally inelastic collisions dominated by long-range forces is closely related to the propensity of $l$-dominance. In their findings, the largest flux corresponds to zero initial and final magnetic quantum numbers when the quantization axis is along either the initial or final wavevector. This suggests that the preferential orientation of $j$ in the inelastic collision is perpendicular to the collision plane. In fact, choosing the quantization axis perpendicular to the collision plane, Alexander\(^9\) have found that the largest absolute value of the magnetic quantum number ($\approx j$) corresponds to the largest population in the final channel distribution. The existence of the preferential orientation can be predicted by the propensity of $l$-dominance, because the smallest value of $l$, i.e., $l=J-j$ (extreme $l$-dominant limit), corresponds to $j$ parallel to $l$ in the classical sense. In this work, we show that the semiclassical (impact parameter) theory derived from the exact quantum mechanical theory contains a clear physical meaning of the relation between the preferential orientation and the propensity of $l$-dominance.

The semiclassical theory is a familiar approximation in the heavy particle collisions. In the distant collision, the semiclassical theory is applicable even at very-low energies;\(^7\) furthermore, the presently introduced semiclassical versions of the LD and decoupled $l$-dominance (DLD) approximations\(^10\) give very useful methods to investigate the rotationally inelastic processes. In the quantum mechanical theory, the CC equations are decomposed into two independent sets, each of which has a definite parity $(-1)^{J+j+l}$ under an inversion of the whole system. Also in the semiclassical theory, as we will see in this work, the similar decoupling schemes hold.

§2. General Theory

2.1 Quantum mechanical theory

In the standard quantum mechanical treatment of the collisions between atoms and linear rigid rotors,\(^11\) the total wavefunction is expanded in terms of eigenfunctions of the total angular momentum $J$ which is the vector sum of the molecular angular momentum $j$ and the orbital angular momentum $l$. Since $J$ is a good quantum number in an isolated collision system, a set of CC equations for the radial wavefunctions is block diagonal with respect to $J$, i.e., (in atomic units)

$$\left(\frac{d^2}{dR^2} + k_j^2 - \frac{l(l+1)}{R^2}\right)u_{j,l,l_0}(R) = 2\mu \sum_{j'l'} V_{j,l,l_0}(R) u_{j',j',l_0}(R),$$

where $R$ is the relative position vector, $k_j$ is the wavenumber for the $j$ channel, $\mu$ is the reduced mass of the collision system, and $(j_0, l_0)$ denotes the initial channel. Expanding the intermolecular
interaction in terms of the Legendre polynomials or the spherical harmonics,

\[ V(R, \mathbf{\hat{r}}) = \sum_n V_n(R) P_n(\mathbf{\hat{r}}) = \sum_{n,l} \frac{4\pi}{2n+1} V_n(R) Y_{n\ell}(\mathbf{\hat{r}}) Y_{n\ell}^*(\mathbf{\hat{r}}), \]

where \( \mathbf{\hat{r}} \) denotes the molecular orientation, we can express the potential coupling matrix element as

\[ V_{Jl}^{Jl'}(R) = \sum_n V_n(R) f^{nJ}_{JlJl'}, \]

where \( f^{nJ}_{JlJl'} \) is the usual Percival-Seaton coefficient.

\[ f^{nJ}_{JlJl'} = [(2j+1)(2j'+1)(2I+1)(2I'+1)]^{1/2} (-1)^{J+j+l} \begin{pmatrix} J & J' & l' \\ j & j' & n \\ l & l & j' \end{pmatrix} \begin{pmatrix} J & J' & l' \\ j & j' & n \\ l & l & j' \end{pmatrix} \begin{pmatrix} J & J' & l' \\ l & l & j' \end{pmatrix} \begin{pmatrix} J & J' & l' \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

where \( \{ : : \} \) and \( ( : : ) \) denote 6j and 3j symbols, respectively. From the properties of the 3j symbol, the Percival-Seaton coefficient vanishes unless \((-1)^{J+j+l} = (-1)^{J'+j'+l'}\), which represents the conservation of parity \((-1)^{J+j+l} \).

### 2.2 Semiclassical theory

The derivation of the \( S \) matrix and the CC equations in the semiclassical theory from the quantum mechanical counterparts have been fully discussed by Broglia et al.\(^1\)\(^2\) Hence, we give here only an outline of their work necessary for the present purpose.

In the semiclassical approximation the \( S \) matrix is given by\(^1\)

\[ S^J(Jl; j_0l_0) = \exp \left[ i(\eta_{Jl} + \eta_{j_0l_0}) \right] C^{Jj_0l_0}(t = \infty)(-1)^{l-l_0}. \]

The phase shift \( \eta_{Jl} \) is due to the diagonal element of the potential coupling matrix which primarily determines the relative motion. The function \( C^{Jj_0l_0}(t) \) satisfies the following set of time-dependent equations, and characterizes the time-evolution of the probability amplitude for the \((j_0, l_0) \rightarrow (J, l)\) transition:

\[ \frac{d}{dt} C^{Jj_0l_0}(t) = -i \sum_{Jl} V_{Jl}^{Jl'}(R(t))(-1)^{l-l'} \exp \left\{ i[(E_J - E_{J'})t + (l-l')\Psi(t)] \right\} C^{Jl'}(t) \]

with the initial condition

\[ C^{Jj_0l_0}(t = -\infty) = \delta_{Jj_0} \delta_{l_0}, \]

where \( E_J \) is the rotational energy of a molecule, and \( \Psi \) is the azimuth angle of \( R \) in the collision plane. We obtain eq. (6) from the quantum mechanical CC eq. (1) by introducing the following assumptions:

I. The radial wavefunction \( u_{Jj_0l_0}(R) \) is divided into the sum of two parts which represent the incoming \((t<0)\) and outgoing \((t>0)\) waves.

II. The relative motion characterized by the phase shift \( \eta_{Jl} \) is described by the WKB approximation.

III. The time \( t \) and the azimuth angle \( \Psi \) (intrinsically depending on the channels) are common variables. (This means that the angular momentum transfer is assumed not to affect the relative motion. Thus, the common trajectory lies in a plane, i.e., collision plane.)

When the angular momenta \( J \) and \( l \) are very large as compared with \( j \), we can use the asymptotic form for the \( 3j \) symbol\(^3\)

\[ \begin{pmatrix} j & l & J \\ m & m' & -M \end{pmatrix} = (-1)^{j+M}(2J+1)^{-1/2} D^{j}_{j-M} (0, \alpha, 0), \]

where

\[ \cos \alpha = \frac{m'}{[l(l+1)]^{1/2}}, \]

and \( D^{j}_{j-M} \) is the usual representation of rotation group. Noticing that the 6j symbol can be written
in terms of the $3j$ symbols, and also noticing the unitarity of the $D_{nm}$ functions, we can rewrite eq. (6) as

$$\frac{d}{dt} C_{j_m, j_{m_0}}(t) = -i \sum_{j'_{m_0}, l_{\lambda}} (-1)^m [4\pi(2j+1)(2j'+1)/(2n+1)]^{1/2} \left( j \ j' \ n \atop 0 \ 0 \ 0 \right) \left( j \ j' \ n \atop m \ -m' \ \lambda \right) \times V_n(R) Y_{n\lambda}(\pi/2, \Psi) \exp \left[ i(E_j - E_{j'} t) \right] C_{j'_{m'}, j_{m_0}}(t).$$  (9)

In eq. (9), we have introduced new quantities

$$J - l_0 = m_0, \quad J - l = m, \quad J - l' = m', \quad l - l' = \lambda.$$  (10)

Since the dependence of (9) on $J$ and $l$ is only through these quantities, we have given new suffixes to $C(t)$.

If we choose the reference frame I where the $z$-axis is perpendicular to the collision plane and the $x$-axis is oriented towards the point of closest approach of the relative motion, the usual CC equations derived from the semiclassical time-dependent Schrödinger equation coincide with eq. (9). (Notice the argument in the spherical harmonics.) The usage of the frame I in eq. (9) is quite natural when we notice that $J, l > j$. In this limit, $J - l$ is nearly equal to the projection of $j$ on $l$. Furthermore, since the $3j$ symbol $(j_{m - m_\lambda}^{j' n})$ appears in eq. (9), we can interpret $m = J - l$ as the magnetic quantum number of $j$ in the frame I.

§3. Decoupling Schemes

3.1 Conservation of parity

Since the semiclassical eq. (6) contains the potential coupling matrix and the Percival- Seaton coefficient, the parity $(-1)^{j+j'+l}$ is exactly conserved in eq. (6). A similar selection rule holds also in the usual semiclassical eq. (9). Notice that $Y_{n\lambda}(\pi/2, \Psi)$ and $(j_{m - m_\lambda}^{j' n})$ vanish unless $n - \lambda = \text{even}$ and $j + j' + n = \text{even}$, respectively, and $(j_{m - m_\lambda}^{j' n})$ requires $m - m' + \lambda = 0$.

Thus, we obtain a selection rule that the channels are coupled to each other only when $(-1)^{j+m} = (-1)^{j'+m'}$. This decoupling scheme is just the same as the quantum mechanical one originated from the conservation of parity, since $m = J - l$.

While the invariance under the inversion of the whole system results in the conservation of parity in the quantum mechanical theory, the conservation of parity $(-1)^{j+m} = (-1)^{j'+m'}$ in the semiclassical theory is based on the invariance under the inversion with respect to the collision plane. Under this inversion, the spherical harmonics $Y_{n\lambda}(\hat{r})$ in the intermolecular interaction (2) changes its sign as $(-1)^{n - \lambda}$. However, $Y_{n\lambda}(\pi/2, \Psi)$ restricts $n - \lambda$ only to even values, so that the intermolecular interaction is invariant under the inversion with respect to the collision plane. In the usual frame (frame II) where $z$-axis is along the initial wavevector and the $x$-$z$ plane coincides with the collision plane, we can set $\hat{R} = (0, \theta, 0)$ where $\theta$ is the polar angle. Then, it is easily seen that the intermolecular interaction is invariant under the inversion with respect to the collision plane; and we obtain the conservation of parity $(-1)^{j+m} = (-1)^{j'+m'}$ where $m(\geq 0)$ is the magnetic quantum number in the frame II and $\nu(=0, 1)$ is defined by a wavefunction of the molecular rotation

$$Y_{j_{m'}}^{\nu}(\hat{r}) = [2(1 + \delta_{m0})]^{-1/2} \times [Y_{j_{m'}}^{\nu}(\hat{r}) + (-1)^{\nu} Y_{j_{-m'}}^{\nu}(\hat{r})].$$  (11)

As a matter of course, the number of equations decoupled by $(-1)^{j+m} = (-1)^{j'+m'}$ in the frame II is just the same as that decoupled by $(-1)^{j+m} = (-1)^{j'+m'}$ in the frame I.

3.2 Propensity of $l$-dominance

The semiclassical version of $l$-dominance approximation $(l_0, l \leq J)$ is expressed in terms of the preferential transitions with $m_0, m \geq 0$ in frame I. We performed the semiclassical CC (SCC) calculations for the $H^+ - CO$ collision in frame I. We assumed the asymptotic form of the intermolecular interaction throughout the calculations—i.e., the charge-dipole, -quadrupole and the anisotropic part of the polarization interactions (for the molecular constants used, see ref. 7). In all the SCC and other (§3.3) calculations, the $j = 0, 1, 2, 3$ and
4 channels were coupled, and the straight-line trajectory was assumed for the relative motion.

Figures 1 and 2 show the excitation probabilities for the \((j_0, m_0) \rightarrow (j, m)\) transitions as a function of the classical orbital angular momentum \(L = k_j b\) (in atomic unit) where \(b\) is the impact parameter. In Fig. 1, we also plot the quantum mechanical CC results\(^7\) on the squared absolute values of the S matrix for the \((j_0, l_0) = (0, J) \rightarrow (j, l) = (1, J \pm 1)\) transitions as a function of \(J\). The comparison of the SCC and quantum mechanical results show that the semiclassical interpretation \(m = J - l\) is allowed except at small values of \(L\), and also that the semiclassical theory is applicable to the present case.

For the final \(m\) distribution, \(m > 0\) are favorable except at small values of \(L\), and the largest allowed value of \(m\) (§3.1) gives the largest transition probability. This confirms the finding of Alexander.\(^9\) In the LD method, the channels not only with \(l > J\) but also with \(l_0 > J\) are eliminated. Figure 2 shows, however, the transition probabilities with \(m_0 < 0\) are negligible only at \(L \gg 50\). Thus, it should be noted that the \(l\)-dominance feature may be interpreted as the propensity that the magnetic quantum number increases (or the orbital angular momentum decreases) in the excitation transitions. This polarized \(m\) distribution results from the phase difference in \(\exp[i(E_f - E_i)\tau]\) multiplied by a factor \(\exp[i(m' - m)\eta]\) of the spherical harmonics (see eq. (9)). In fact, crude estimates by the first-order perturbation theory show (see appendix) that the ratio of \(m_0 \rightarrow m\) and \(m_0 \rightarrow m'\) transition probabilities is \(\sim e^{2(m' - m)^2}\). This supports the conclusion that the magnetic quantum number increases in the transition, and the largest possible change \(\Delta m\) is most favorable. Furthermore, inspection of the asymptotic \((J, l \rightarrow \infty)\) expression of the Percival-Seaton coefficient (4) indicates that for small values of \(\eta = l - J + j = j - m\), the coupling with \(\Delta\eta = 0\) is preferred to the one with \(\Delta\eta \neq 0\).\(^{10}\)

The value of \(\eta\) measures the degree of deviation of the orientation of \(j\) from the \(z\)-axis (frame I). Thus, we can conclude that the torque driving the molecular rotation is predominantly oriented parallel to \(l\), and leads to the propensity of \(l\)-dominance.

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**Fig. 1.** Variation of \(|C_{jm, j_0m_0}(\infty)|^2\) (lines) with \(L\) for the \((j_0, m_0) = (0, 0) \rightarrow (j, m) = (1, m)\) and \((2, m)\) transitions by SCC method and of \(|S^2(jl; j_0l_0)|^2\) (circles) with \(J\) for the \((j_0, l_0) = (0, J) \rightarrow (j, l) = (1, J \pm 1)\) transitions by the CC method. The collision energy is 0.01 eV.

**Fig. 2.** Variation of the transition probabilities with \(L\) for the \(j_0 = 1 \rightarrow j = 2\) transitions calculated by the SCC method. The collision energy is 0.01 eV.

### 3.3 LD and DLD approximations

First, we consider the transition from the initial channel \(j_0 = 0\). The minimum value of \(l\) \((= J - j)\) corresponds to the maximum value of \(m\) \((= j)\) in the semiclassical sense. If we retain only the channels with \(m = j\) in eq. (9),
we obtain the semiclassical DLD (SDLD) approximation (DePristo and Alexander\textsuperscript{10}) assumed that $\Delta \eta = 0$; i.e., in the semiclassical version, $j - m = j_0 - m_0$). If we retain only the channels with $m \geq 0$ in eq. (9), this is the semiclassical LD (SLD) approximation. In Fig. 3, we plot so called opacities, which are defined as the transition probability times a factor of $2L + 1$, calculated by the SLD and SDLD methods. The agreement with the SCC method is very good. This agreement is encouraging for the calculations of the inelastic cross sections for $j_0 = 0$.

In Fig. 4, we plot the opacities for the initial channel $j_0 = 1$, where we sum over the final magnetic quantum numbers, but do not average over the initial magnetic quantum numbers. The SLD method retains only the channels with $m \geq 0$, and the SDLD method retains further smaller number of channels with $j - m = j_0 - m_0$. At large values of $L$, the SLD and SDLD methods are satisfactory when $m_0 = 0$ and 1. In order to have a reliable estimate of the degeneracy-averaged quantities by the SLD and SDLD methods, the contribution of the transitions with the initial channels $m_0 < 0$ must be negligible. This condition is, however, satisfied only at $L > 60$.

![Fig. 3. Variation of the degeneracy-averaged opacities with $L$ for the $j_0 = 0 \rightarrow j = 1$ and $2$ transitions calculated by the SCC, SLD and SDLD methods. The collision energy is $0.01$ eV.](image3.png)

![Fig. 4. Variation of the opacities with $L$ for the $j_0 = 1 \rightarrow j = 2$ transitions calculated by the SCC, SLD and SDLD methods. Opacities are summed over the final magnetic quantum numbers, but are not averaged over the initial magnetic quantum numbers. The collision energy is $0.01$ eV.](image4.png)

Nevertheless, if the first-order perturbation theory is applicable, we can give the following justification to neglect the contribution of the transition with the initial channels $m_0 < 0$. For simplicity, we assume that the exchange of the angular momentum is restricted only along $l$ (or $\Delta \eta = 0$). In the excitation from the initial channels $m_0 < 0$, the change $\Delta m$ must be larger than $2|m|$ since $j$ increases only along the $z$-axis (frame I) due to the propensity of increasing $m$ and $j > j_0$. When this change $\Delta m$ is larger than $n$ (see eq. (9)), this transition is forbidden in the first-order processes. Thus, the excitation probability from the initial channels $m_0 < 0$ would be very small. Then, the $l$-dominance assumption is justified also for the initial channels. Such an example is
seen in higher-energy collisions (see Fig. 5), where the SLD and SDLD methods would be useful for the calculations of the degeneracy-averaged quantities.

§4. Discussions

The propensity of $l$-dominance is found to hold well for the distant collision, i.e., the adiabatic collision. We now consider the sudden collision. In the sudden limit ($E_j = E_f$), we obtain for $C_{jm,j_0m_0}^{(s)}$:

$$C_{jm,j_0m_0}^{(s)} = \int Y_{jm}^*(\hat{r}) \exp \left(-i \int_{-\infty}^{\infty} V(R(t), \hat{r}) dt \right) \times Y_{j_0m_0}(\hat{r}) d\hat{r}. \quad (12)$$

Since the exponential factor in eq. (12) is invariant under time reversal, the time reversal operation\(^{13}\) on eq. (12) provides the following relation

$$|C_{jm,j_0m_0}^{(s)}| = |C_{j,-m,j_0,-m_0}^{(s)}|. \quad (13)$$

Notice that the relation (13) is valid within the sudden approximation and is different from the usual reciprocity relation $|C_{jm,j_0m_0}| = |C_{j_0,-m,j_0,-m}|.\(^{15}\)$ In obtaining eqs. (12) and (13), we can choose the direction of $z$-axis arbitrarily. From (13),

$$\sum_{m_0} |C_{jm,j_0m_0}^{(s)}|^2 = \sum_{m_0} |C_{j,-m,j_0,-m_0}^{(s)}|^2. \quad (14)$$

Thus, in the sudden approximation the final $m$ distribution is symmetric for $m = \pm |m|$ even in frame I. Jamieson\(^{16}\) showed this fact by the direct evaluation of the $j = 0 \rightarrow 1$ transition probabilities for the case of the charge-dipole interaction. We expect that the sudden approximation is applicable to the collision with very small impact parameters or with extremely high energies; and then, the propensity of $l$-dominance will be lost. This fact restricts the range of validity of the LD and DLD approximations within large impact parameter collisions and within low- or intermediate-energy collisions.

Our arguments can be extended to the collision processes between highly-excited atoms and charged particles where the major role is played by long-range forces. If we consider the $j$-changing processes (here $j$ denotes the orbital angular momentum of a Rydberg electron), then, the theoretical treatment becomes similar to that for the rotational excitation in ion-molecule collisions.\(^{17}\) Thus, it is very interesting to investigate whether the $l$-dominance feature is present in the collision between highly-excited atoms and charged particles. For hydrogenic atoms, Demkov et al.\(^{18}\) derived the closed form for the $j$-changing transition probability within the dipole approximation. Since this formula satisfies the same relation as (13), the propensity of $l$-dominance is absent. Perhaps, this fact is due to the degeneracy with respect to the quantum number $j$. If we consider nonhydrogenic atoms that have significant quantum defects, we will find the propensity of $l$-dominance. Then, especially for the transition from the $s$ ($j=0$) state the DLD method will be very useful.

§5. Conclusion

We can introduce the decoupling scheme in the semiclassical theory which is similar to the quantum mechanical one originated from the conservation of parity.

In distant collisions: 1) The propensity of $l$-dominance can be interpreted in terms of the increase of the magnetic quantum number $m = j - l$ due to the torque predominantly
oriented along \( I, 2 \) the \( l \)-dominance assumption is well satisfied for the final \( m \) distribution; but the inelastic transition from the initial channels \( m_0 < 0 \) \((l_0 > J)\) cannot be neglected at low energies.

The LD and DLD methods are very useful for the collision system dominated by long-range forces especially when \( j_0 = 0 \). When \( j_0 \neq 0 \), these methods should be applied at high energies.

When the energy differences between the \( j \) channels vanish or become very small, the propensity of \( l \)-dominance is not present. In order for the LD and DLD approximations to be applicable to the collisions between highly-excited atoms and charged particles, the atoms should be strongly nonhydrogenic.

**Acknowledgment**

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**Appendix:** Estimation by First-Order Perturbation Theory

Within the first-order perturbation theory, eq. (9) becomes

\[
C_{jm,jm_0}^{(n,l)}(\infty) = -i(-1)^{m_0}[4\pi(2j+1)(2j_0+1)/(2n+1)]^{1/2}(j \ j_0 \ n \ 0 \ 0 \ 0 \ m \ -m_0 \ \lambda) \\
\times \int_{-\infty}^{\infty} dt \ V_n(R) Y_{nl}(\frac{\pi}{2}, \Psi) \exp[i(E_j - E_{j_0})t]. \quad (A \cdot 1)
\]

The \( 3j \) symbols \((m \ j_0 \ \ell)\) are not essential for the propensity of \( l \)-dominance (and \( 3j \) symbols \((n = 1 \text{ or } 2)\) differ only in a factor for the variation of \( m \) when \( j_0 \approx 1 \)). When we assume \( V_n(R) \propto R^{-\rho} \), the dominant and interesting part of \((A \cdot 1)\) which determines the \( m_0 \to m \) transition is given by

\[
C_{jm,jm_0}^{(n,l)}(\infty) \propto \int_{-\infty}^{\infty} dt R^{-\rho} \exp[(\Delta E t - \Delta m \Psi)], \quad (A \cdot 2)
\]

where we have set \( \Delta m = m - m_0 \) and \( \Delta E = E_j - E_{j_0} \). For the straight-line trajectory,

\[
R^2 = v^2 t^2 + b^2, \quad \tan \Psi = \frac{vt}{b}, \quad (A \cdot 3)
\]

where \( v \) is the relative velocity. Since we consider large values of \( b \) and since the region near the turning point is important, we approximate the azimuth angle \( \Psi \) as

\[
\Psi = \frac{vt}{b}.
\]

Then, \((A \cdot 2)\) gives for excitation \((\Delta E > 0)\)

\[
C_{mm_0}^{(n,l)}(\infty) \propto K_{\nu-1/2} \left( \frac{\Delta E b}{v} - \Delta m \right), \quad (A \cdot 4)
\]

where \( K_\nu(x) \) is the modified Bessel function. When \( \Delta E b/v \gg 1 \), we have the following relation:

\[
C_{mm_0}^{(n,l)}(\infty)/C_{mm_0}^{(n,l)}(\infty) \approx e^{m - m_0}. \quad (A \cdot 5)
\]

Numerical estimates show that this relation approximately holds in the velocity range near \( \Delta E b/v \sim 1 \).

**References**