A perturbation theory in the adiabatic representation

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Abstract. A perturbative treatment in the adiabatic representation, which considers the Coriolis transition, and connects to the impact parameter Born theory at large impact parameters, is formulated and applied to the rotational excitation of the HDO molecule by ion collisions. By this method, the collision dynamics at large impact parameters are described much better than by the impact parameter Born theory. At very low energies, however, the collision dynamics are better described by neglecting the Coriolis transition.

1. Introduction

In the theory of the electronically inelastic collision between heavy particles at low velocities, the adiabatic (molecular) basis supplies a good description of the collision processes. When the inelastic transition is localised near the crossing or avoided crossing point, the processes are nicely described in terms of the Landau–Zener or Fano–Lichten model. In the absence of the crossing or avoided crossing, the inelastic transition cannot easily occur: the transition probability is usually small at low velocities. Even in the vibrational and rotational transition processes, although the range of applicability is narrower than in the electronic transition processes, the adiabatic basis is a good representation to describe the slow collision (Levine et al 1970, Thiele and Katz 1971, Takayanagi 1978). In the vibrational and rotational transition processes, however, the crossing or avoided crossing does not seem to play a critical role as in the electronic transition processes (Baer et al 1980). In particular, for the rotational transition in slow collisions between an ion and a polar molecule, since the energy difference of the levels is small and the interaction is of a very long range, no localisation of the transition occurs. Integration over the whole duration of collisions is necessary to obtain the accurate transition probability both in the perturbed and unperturbed bases (Takayanagi 1978, Sakimoto 1981a).

When the transition probability is very small, the first-order perturbation theory is expected to be applicable. In the first-order (semiclassical) perturbation theory, we have the probability amplitude for the transition $\alpha \rightarrow \beta$ as

$$a_{\alpha \beta} = -\int_{-\infty}^{\infty} dt (\beta |d/dt|\alpha) \exp \left( i \int_{t'}^{t} (\epsilon_{\beta} - \epsilon_{\alpha}) \, dt' \right)$$

(1)

where $\epsilon_{\alpha}$ is the adiabatic potential, and $(\beta |d/dt|\alpha)$ is the non-adiabatic coupling. (Throughout this paper, atomic units will be used unless otherwise stated.) The adiabatic basis function is represented in the rotating frame because the intermolecular axis (which rotates during collisions) is chosen as the quantisation axis. This basis
function is, however, not always the optimum one to describe the collision picture. To demonstrate this, it is convenient to consider various Hund's cases for atom-atom collisions (see the appendix in the review of Delos 1981). When the state of the collision system belongs to Hund's case a or b, the projection of the orbital angular momentum of the electron on the intermolecular axis is well conserved. In the various calculations, this situation is implicitly assumed (Delos 1981), and under this situation the expression (1) is applicable when the transition probability is very small (Rudd and Macek 1972, Briggs 1975, 1976)—the state designation \( \alpha \) contains the magnetic quantum number of the angular momentum projected on the intermolecular axis. On the other hand, for Hund's case d or e, the projection of the angular momentum on the space-fixed axis is rather a good quantum number. This case is seen for the transition concerning the highly excited atom and the fine structure (Mies 1973, Delos 1981). If the projection of the angular momentum on the space-fixed axis is conserved, then in the representation in the rotating frame there exists the strong mixing among the magnetic quantum numbers (projected on the intermolecular axis). This fictitious mixing is the well known Coriolis transition (Thorson 1969), and this strong mixing cannot be described in terms of the perturbative treatment. Thus, equation (1) represented in the rotating frame is not a good approximation for Hund's case d or e even if the inelastic transition probability is very small.

Recently, Takayanagi (1978) utilised the adiabatic representation (which is represented in the rotating frame) to calculate the rotational excitation (the angular momentum \( J = 0 \rightarrow 1 \)) in ion–molecule collisions. In the same work he applied a perturbative treatment, but in a dissimilar manner to expression (1) in this paper. In this method, the inelastic transition (\( \Delta J = 1 \)) probability amplitude is calculated by the perturbation theory, but at the same time the mixing among the magnetic quantum numbers within \( J = 1 \) (projected on the intermolecular axis) is taken into account by the close-coupling theory. Takayanagi in fact obtained fairly good agreement using a more sophisticated method, especially at large impact parameters. As will be seen later, the mixing among the magnetic quantum numbers is mainly due to the Coriolis transition. Takayanagi, further, noted that the expression (1), which does not take the Coriolis transition into account, does not tend to the impact parameter (IP) Born theory in the large impact parameter limit.

In this paper, we formulate the new simple perturbation theory in which the Coriolis transition is taken into account and the IP Born theory is obtained in the large impact parameter limit. The comparison of the new perturbation theory, the expression (1) and the IP Born theory with the close-coupling theory is performed, as an example, for the rotational transition in a collision between an ion and a polar molecule.

2. Theory

2.1. A new perturbation theory

A set of coupled equations in the semiclassical theory is (for a recent review see Delos 1981)

\[
\frac{d}{dt} a_{\alpha J \Lambda} = - \sum_{\alpha J'\Lambda'} (a J \Lambda | d/dt | \alpha' J' \Lambda') \exp (i \eta_{\alpha J \Lambda, \alpha' J' \Lambda'}) a_{\alpha' J' \Lambda'}
\]  

(2)
where

\[ \eta_{aJ\Lambda,a'J'\Lambda'} = \int (\varepsilon_{aJ\Lambda} - \varepsilon_{a'J'\Lambda'}) \, dt' \]  

(3)

and \((J, \Lambda)\) are the angular momentum quantum number of atoms or molecules at infinite separation and its projection on the intermolecular axis, respectively, and \(\alpha\) is a suffix specifying the other degrees of freedom of the adiabatic state. If the trajectory of the relative motion is determined by a spherical potential, the time derivative in the non-adiabatic coupling is

\[ \frac{d}{dt} \frac{d\theta}{\delta \theta} + \frac{dR}{\delta R} \frac{\partial}{\partial R} \]

(4)

where \(\theta\) is the angle between the initial direction of the incident particle and the intermolecular axis, and \(R\) is the relative distance. The asymptotic form of the rotational coupling which causes the Coriolis transition was shown by (Delos 1981, Sakimoto 1981a) to be

\[ \frac{1}{2} \left[ (J \pm \Lambda + 1)(J \mp \Lambda) \right]^{1/2} \delta_{\Lambda \pm 1, \Lambda}. \]

(5)

The matrix element (5) does not vanish at infinite separation, and thus, the Coriolis coupling has a significant effect even at large separations. Retaining the asymptotic form (5) and neglecting the energy difference between the states concerned in the Coriolis transition, we obtain a modified first-order approximation of (2) for the \((aJ_0\Lambda_0) \rightarrow (aJ\Lambda)\) transition as

\[ \frac{d}{dt} a_{aJ_0\Lambda_0} = -\frac{1}{2} \frac{d\theta}{dt} \left[ (J_0 + \Lambda_0 + 1)(J_0 - \Lambda_0) \right]^{1/2} a_{aJ_0\Lambda_0+1} \]

\[ + \frac{1}{2} \frac{d\theta}{dt} \left[ (J_0 - \Lambda_0 + 1)(J_0 + \Lambda_0) \right]^{1/2} a_{aJ_0\Lambda_0-1} \]

(6)

\[ \frac{d}{dt} a_{aJ\Lambda} = -\frac{1}{2} \frac{d\theta}{dt} \left[ (J + \Lambda + 1)(J - \Lambda) \right]^{1/2} a_{aJ\Lambda+1} + \frac{1}{2} \frac{d\theta}{dt} \left[ (J - \Lambda + 1)(J + \Lambda) \right]^{1/2} a_{aJ\Lambda-1} \]

\[ - \sum_{\Lambda_0} (\alpha J\Lambda | d/\delta J_0 | \alpha J_0\Lambda_0') \exp(i \eta_{aJ\Lambda,\alpha J_0\Lambda_0}) a_{aJ_0\Lambda_0}. \]

(7)

If the projection of the angular momentum of atoms or molecules on the initial direction of the incident particle is denoted by \(M_0\), we obtain the initial condition for \(a_{aJ\Lambda}\),

\[ a_{aJ\Lambda}(t = -\infty) = \delta_{a\alpha_0} \delta_{J_0} \sum_M \delta_{MM_0} d_{M_0}^{J_0} (-\pi) \]

\[ = \delta_{a\alpha_0} \delta_{J_0} \delta_{-M_0\Lambda} (-1)^{J_0-\Lambda} \]

(8)

where \(d_{M_0}^{J_0}\) is the reduced matrix element of the rotation operator (Rose 1957). From (6) and (8), we can easily see that the solution of (6) is

\[ a_{aJ_0\Lambda_0}(t) = d_{M_0}^{J_0}[\theta(t)]. \]

(9)

If we put

\[ a_{aJ\Lambda}(t) = \sum_M b_{aJ_M}(t) d_{M_0}^{J_0}(\theta) \]
and substitute (9) into the equation (7), the latter becomes by the unitarity condition of \( d_{\Lambda \Lambda} \)

\[
\frac{d}{dt} b_{\alpha J M} = - \sum_{\Lambda \Lambda_0} (\alpha J \Lambda | d/dt | \alpha_0 J_0 \Lambda_0 ) \exp (i \eta_{\alpha J \Lambda, \alpha_0 J_0 \Lambda_0} ) d_{\Lambda \Lambda_0} (\theta) d_{M_0 \Lambda_0} (\theta).
\]

Thus, we obtain the solution of (7) as

\[
a_{\alpha J \Lambda}(+ \infty) = - \sum_{\Lambda' \Lambda_0} \int_{-\infty}^{+\infty} dt \ d_{\Lambda' \Lambda} (\theta - \theta) \ d_{M_0 \Lambda_0} (\theta) (\alpha J \Lambda') | d/dt | \alpha_0 J_0 \Lambda_0 ) \exp (i \eta_{\alpha J \Lambda', \alpha_0 J_0 \Lambda_0} ).
\]

(10)

where \( \theta = \theta (t = \infty) \) is the scattering angle. In deriving (10) we have used the following relations

\[
d_{\Lambda' \Lambda} (\theta) = d_{\Lambda' \Lambda} (- \theta)
\]

\[
\sum_{\Lambda} d_{\Lambda' \Lambda} (- \theta) d_{M \Lambda} (\theta) = d_{\Lambda' \Lambda} (\theta - \theta).
\]

The expression (10) has a clear meaning: for the Coriolis transition we consider only a fictitious transition (which appears as a result of the rotating transformation of the reference frame) and neglect its dynamical effect. This means that the Coriolis transition of the initial and final states is simply expressed by the matrix element of the rotation operator.

2.2. Connection to the first Born theory

We now choose the quantisation axis along the initial direction of the incident particle. Then, (10) becomes

\[
a_{\alpha J M}(+ \infty) = \sum_{\Lambda} d_{\Lambda \Lambda} (\theta) a_{\alpha J \Lambda}(+ \infty)
\]

\[
= - \sum_{\Lambda \Lambda_0} \int_{-\infty}^{+\infty} dt \ d_{\Lambda \Lambda_0} (\theta) d_{M_0 \Lambda_0} (\theta) (\alpha J \Lambda) | d/dt | \alpha_0 J_0 \Lambda_0 ) \exp (i \eta_{\alpha J \Lambda, \alpha_0 J_0 \Lambda_0} ).
\]

(11)

In order to see the large impact parameter limit of (11), we set for the exponential factor

\[
\eta_{\alpha J \Lambda, \alpha_0 J_0 \Lambda_0} \sim \omega_{\alpha J_0 J_0} t
\]

where \( \omega_{\alpha J_0 J_0} \) is the energy difference at infinite separation. For the wavefunction of the adiabatic state we set

\[
\chi_{\alpha J \Lambda} \sim \psi_{\alpha J \Lambda} + \sum_{\alpha J' \Lambda} (\psi_{\alpha J' \Lambda} | V | \psi_{\alpha J \Lambda} ) \psi_{\alpha J' \Lambda}
\]

where \( \psi_{\alpha J \Lambda} \) is the wavefunction at infinite separation, and \( V \) is the interaction. Then, the non-adiabatic coupling becomes

\[
(\alpha J \Lambda | d/dt | \alpha_0 J_0 \Lambda_0 )
\]

\[
\sim (\psi_{\alpha J \Lambda} | d/dt | \psi_{\alpha_0 J_0 \Lambda_0} ) + \left[ \psi_{\alpha J \Lambda} \frac{d}{dt} \left( \sum_{\alpha J_0} (\psi_{\alpha J_0 \Lambda_0} | V | \psi_{\alpha_0 J_0 \Lambda_0} ) \psi_{\alpha_0 J_0 \Lambda_0} \right) \right]
\]

\[
+ \left( \sum_{\alpha J'} (\psi_{\alpha J' \Lambda} | V | \psi_{\alpha J \Lambda} ) \psi_{\alpha J' \Lambda} \right) \frac{d}{dt} \psi_{\alpha J_0 \Lambda_0}.
\]

(12)
Referring to (4), we can easily see that the first term of the right-hand side of (12) vanishes. The wavefunction $\psi_{a_J\Lambda}$ is connected with the wavefunction $\psi_{aJM}^{SF}$ represented in the space-fixed frame by

$$\psi_{a_J\Lambda} = \sum_M d_{M\Lambda}^J (\theta) \psi_{aJM}^{SF}.$$ 

Thus, the second term of (12) is

$$\sum_M d_{M\Lambda}^J \frac{d}{dt} \left( \frac{\langle \psi_{aJ\Lambda_\alpha} | V | \psi_{aJ_0J_0\Lambda_\alpha} \rangle}{\omega_{aJ_0, aJ}} d_{M\Lambda_\alpha}^J \right)$$

and the third term of (12) is

$$\sum_M d_{M\Lambda_\alpha}^J \frac{\langle \psi_{aJ\Lambda_\alpha} | V | \psi_{aJ_0J_0\Lambda_\alpha} \rangle}{\omega_{aJ, aJ_0}} d_{M\Lambda_\alpha}^J.$$ 

Here, we have used the orthonormality of $\psi_{aJM}^{SF}$. Substituting these expressions into (11), and defining the matrix element in the space-fixed frame by

$$\langle \psi_{aJM}^{SF} | V | \psi_{aJ_0J_0M_0}^{SF} \rangle = \sum_{\Lambda} d_{M\Lambda}^J d_{M_0\Lambda}^{J_0} \langle \psi_{aJ\Lambda} | V | \psi_{aJ_0J_0\Lambda} \rangle$$

we obtain for (11)

$$a_{aJM}(+\infty) = \int_{-\infty}^{\infty} dt \frac{d}{dt} \left( \frac{\langle \psi_{aJM}^{SF} | V | \psi_{aJ_0J_0M_0}^{SF} \rangle}{\omega_{aJ, aJ_0}} \right) \exp(i\omega_{aJ, aJ_0} t). \quad (13)$$

Integrating (13) by parts gives

$$a_{aJM}(+\infty) = -i \int_{-\infty}^{\infty} dt \langle \psi_{aJM}^{SF} | V | \psi_{aJ_0J_0M_0}^{SF} \rangle \exp(i\omega_{aJ, aJ_0} t). \quad (14)$$

This is just the result from the IP Born theory.

Rudd and Macek (1972) and Briggs (1975) have derived the connection of the expression (1) and the IP Born theory. In their works, however, the Coriolis coupling and the transformation between the rotating frame and the space-fixed frame are neglected, so their derivation does not have an accurate meaning.

3. Numerical examples and discussion

For numerical examples, we consider the rotational excitation of the HDO molecule by ion collisions. For simplicity, we assume only the point-dipole interaction. Molecular quantities are: the rotational constants, $A = 1.07 \times 10^{-4}$ au, $B = 4.15 \times 10^{-5}$ au, $C = 2.92 \times 10^{-5}$ au; the dipole moment components, $\mu_a = 0.260$ au, $\mu_b = 0.681$ au. For further details, see Sakimoto (1981b). The adiabatic state for the molecular rotation, which is introduced by Takayanagi (1978), is called the perturbed rotational state (PRS). For slow collisions between an ion and a polar molecule, very large impact parameters contribute to the rotationally inelastic cross section. As a result, the adiabatic condition is satisfied at thermal energies (Takayanagi 1978, Sakimoto 1981a). The Coriolis transition is, however, important for collisions with large impact parameters (Thorson 1969). Thus, the collision between an ion and a
polar molecule is one of the most interesting cases for application of the new perturbation theory (10).

The degeneracy-averaged transition probability is obtained by

$$ P(\alpha_0 J_0 \rightarrow \alpha J) = \frac{1}{2J_0 + 1} \sum_{\Lambda_0 \Lambda} |a_{\alpha J, \alpha_0 J_0}(\infty)|^2 $$

where we explicitly denote the initial state $(\alpha_0 J_0 \Lambda_0)$ by the upper index. The result obtained for $P(\alpha_0 J_0 \rightarrow \alpha J)$ at various collision energies per atomic mass unit (amu) are shown in figures 1 and 2. In all the calculations, the trajectory is assumed to be a straight line. For the HDO molecule, $\alpha J = J, (-J \leq \tau \leq J)$, which is a familiar state designation for the rotation of an asymmetric-top rigid rotor. At large impact parameters, the present theory (equation (10)) agrees with the close-coupling theory, with full coupling among $J, = 0_0, 1_0, 1_1$ and 1_1 adiabatic states (Sakimoto 1981b), much better than with the IP Born theory except for 10.0 eV amu\(^{-1}\) in figure 1. Since the present perturbation theory (10) is based on the adiabatic basis, (10) should not

![Figure 1](image_url)

**Figure 1.** The impact parameter dependence of the $J, = 0_0 \rightarrow 1_1$ transition probability in ion-HDO collisions. $J, = 0_0$ and 1_1 denote, respectively, the ground and first excited rotational states of HDO. cc is the calculation by the close-coupling theory coupled with four adiabatic states (see text); C is the calculation by (10); A is the calculation by (1); B is the calculation by the IP Born theory.
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Figure 2. The same as in figure 1 except for the \( J_r = 0_0 \rightarrow 1_0 \) transition. \( J_r = 1_0 \) denotes the second excited rotational state of HDO.

be applied in high-energy collisions. At very low energies, the collision is almost adiabatic, and thus it is expected that even the Coriolis transition is diminished. In such a case, which is seen at 0.02 eV amu\(^{-1}\) in figure 1, the expression (1) is better than (10). In an energy region where expression (1) is better than (10), however, the inelastic cross section itself is very small for the present system (see figure 3). The 00-10 couplings are very strong at small separation; the 00-11 couplings are not so strong, even at small separation (Sakimoto 1981b). For this reason, the 00 \( \rightarrow \) 1-1 transition probability calculated by (1) and (10) is always less than unity. On the other hand, for the 00 \( \rightarrow \) 10 transition, the probability calculated by both (1) and (10) becomes larger than unity at small impact parameters. Thus, if we intend to obtain the cross section by use of (1) or (10), some modification is necessary for the 00 \( \rightarrow \) 10 transition. Such modification is always necessary for the present application of the IP Born theory (the modified Born theory): usually the probability is set to be 0.5 whenever the calculated probability is greater than 0.5.

The inelastic cross section is obtained by

\[
\sigma(\alpha_0J_0 \rightarrow \alpha J) = 2\pi \int_0^\infty P(\alpha_0J_0 \rightarrow \alpha J)b \, db
\]

where \( b \) is the impact parameter. The inelastic cross section for the 00 \( \rightarrow \) 1-1 transition is shown in figure 3. We consider only the lowest four adiabatic states in the framework of the present close-coupling theory, so that the results would not be fully converged in the energy region higher than the maximum peak. Nevertheless, the new perturbation theory (10) reproduces the overall picture of the close-coupling result better than do other perturbation theories. At higher energies, we see that the close-coupling result does not differ so much from the modified Born theory which should be a good approximation at very high energies. This indicates that the present close-coupling theory, and thus the new perturbation theory (10), may be of reasonable accuracy.
4. Summary

We formulated and numerically tested the new perturbation theory in which the Coriolis transition is taken into account. At large impact parameters, the new perturbation theory (10) is satisfactory. If the energy is very low the Coriolis transition can be neglected. Even if the energy is not so small, Sakimoto (1981c) has shown that the Coriolis transition is negligible at small impact parameters. Thus at very small impact parameters, expression (1) would be better than (10), but this situation is not seen clearly in the present examples since the transition probability is not so small. As the angular momentum $J$ increases, the Coriolis transition is more important (Sakimoto 1981c). The new perturbation theory (10) would be a very useful method for transitions associated with a large angular momentum.

We consider the Coriolis transition only in its asymptotic form. This approximation may be poor at finite separations. In particular, the energy difference between the states concerned in the Coriolis transition does not vanish at finite separations. This energy difference diminishes the Coriolis transition (Grosser 1981, Sakimoto 1981c). For the fine-structure transition, for instance, a more detailed treatment for the Coriolis transition is necessary (Mies 1973). If we diagonalise the Hamiltonian which consists of the internal Hamiltonian, the interaction operator and the kinetic operator concerned with the relative angular motion, we need not worry about the Coriolis transition (Mullaney and Truhlar 1979, Mies 1980). This new adiabatic basis is a very good description for the fine-structure transition (Mies 1980).

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