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Dynamical-state representation and nonadiabatic electronic transitions in atomic collisions

Hiroki Nakamura
Division of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Quantum-mechanical elucidation is applied to the semiclassical theory in the dynamical-state representation previously proposed to deal analytically with the nonadiabatic rotationally induced transitions. A general path-integral formulation of the scattering matrix is given in terms of a product of two kinds of matrices. This enables us to treat a multistate curve-crossing problem involving both radial and rotational couplings. Discussions are made on the qualitative difference in collision-energy dependences of the ordinary Landau-Zener-type radial transitions and rotationally induced transitions.

I. INTRODUCTION

In previous papers[1,2] the dynamical-state representation is employed to deal with the nonadiabatic atomic collision processes involving both radial and rotational couplings in a unified semiclassical way. This representation transforms the analytical structure of rotational-coupling problems into the one equal to that of the ordinary radial-coupling problems; thus enables us to apply the conventional analytical formulas such as the Landau-Zener-Stueckelberg or the Rosen-Zener formula. A big advantage of this representation lies in the fact that both radial and rotational nonadiabatic transitions are made to occur locally at the avoided crossing points of the dynamical-state potential energies. The localization of transitions is very important and useful, since the two-state collision theories can be extended so as to be applicable to a more complicated multistate collision problem and also to a chemical reaction process.

Rotational coupling is known to play an important role in atomic collisions not only in the high-energy[3] but also in the low-energy regions.[4,5] The transition induced by this coupling, however, is not localized in the adiabatic state representation; thus the path-integral formulation[6] is not applicable to the many-state collision systems which involve rotational couplings. The dynamical-state representation makes this application possible. Furthermore it is necessary to investigate a role of rotational coupling in chemical reaction systems. This coupling opens a new transition; for instance, a transition between the A' and A'' states of the C_s symmetry of triatomic systems. These states can not be connected to each other by the ordinary radial coupling because of the difference in the reflection symmetry with respect to molecular plane. As is well known, electronically nonadiabatic chemical reactions induced by radial coupling have been treated quite successfully by the surface-hopping classical-trajectory method[7] and the semiclassical scattering matrix theory.[6] One can not apply these methods in a straightforward way to the reaction processes involving rotational couplings. The dynamical-state representation would enable us to apply the methods, since the transitions are made localized at the region of avoided crossings of the dynamical potential-energy hypersurfaces.

The dynamical-state representation is essentially equal to the electronic-rotational state representation,[8–10] X representation,[11] and angular- (or rotationally) adiabatic representation[12] discussed by several authors. Crothers used the terminology "dynamical adiabatic."[13] Since the rotational coupling is a dynamic coupling, and actually the potential depends on velocity (or angular momentum), the expression "adiabatic" is considered not to be very pertinent as was already mentioned in the previous paper.[2] Besides any one of the terminologies does not seem yet to be commonly and widely accepted; so the "dynamical-state representation" is used in this paper by following the original terminology of Crothers.[13]

An application of this representation to a study of the rotationally induced nonadiabatic electronic transitions was discussed by Knudson and Thorson,[11] and by Crothers.[13] Knudson and Thorson discussed the transition between the $2p\sigma_u$ and $2p\pi_u$ states of $H_2{}^+$. They concluded from the viewpoint of numerical solutions of coupled equations that the representation was not useful. Our viewpoint is, however, different, and is akin to that of Crothers. Our interest is to obtain an analytical formula to be applicable to a many-state collision problem in the semiclassical path-integral formalism. For this purpose localization of the transitions is very important, as mentioned before frequently. The better localizability in the dynamical-state representation was proved not only by looking into the analytical properties of the representation, but also by the numerical calculations.[2] The similar representation is used also in heavy-ion nuclear collisions.[14]

Section II of this paper is devoted to a quantum-mechanical formulation of the dynamical-state representation to make clear the nature of the semiclassical approximation employed previously.[1,2] In Sec. III the scattering matrix in a general multistate curve-crossing problem involving both radial and rotational couplings is formulated in terms of a product of two kinds of matrices within a framework of the path-integral method. The first kind of matrix is a diagonal propagation matrix which represents a probability amplitude propagation from one avoided crossing point to the other. The second kind of matrix is a nondiagonal transition matrix which gives a probability distribution between two coupled states at an avoided crossing. Phase corrections due to the analytic continuation of a path into the complex R (internuclear distance) plane are incorporated in these matrices. Section IV is denoted to a discussion on the qualitative difference of the collision-energy dependence of cross sections for the rotationally induced transitions from that of the radially induced transitions. It is shown that the semiclassical theory gives the following collision-velocity (v) dependence of the cross sections (Q): (a) $Q \sim v^{2/3}$ for the case of united-atom degeneracy and (b) $Q \sim v^2$ for the case of constant adiabatic energy difference. These dependences agree with the exact ones obtained from a dimension analysis of the time-dependent coupled equations, indicating the effectiveness of the semiclassical theory based on the dynamical-state representation.

II. QUANTUM-MECHANICAL FORMULATION OF DYNAMICAL-STATE REPRESENTATION

In previous papers[1,2] discussions are made only in the framework of the semiclassical collision theory. It is necessary to give a quantum-mechanical foundation to the semiclassical approximation and to clarify its nature.

The starting Hamiltonian for the collision system should be the one expressed in the molecule-fixed coordinate system which is discussed by several authors.[8,9] Here the following explicit expression given by Thorson[8(a)] is employed:

$$H = H_{\rm el} - \frac{\hbar^2}{2\mu R^2}\left[\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\right] + H_{\rm rot} + H_{\rm cor}^{(1)} + H_{\rm cor}^{(2)} , \tag{2.1}$$

where

$$H_{\rm rot} = -\frac{\hbar^2}{2\mu R^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\left[\frac{\partial}{\partial\varphi} - iL_\zeta\cos\theta\right]^2 + L_\zeta^2\right] , \tag{2.2}$$

$$H_{\rm cor}^{(1)} = -\frac{\hbar^2}{2\mu R^2}(L_+U_+ + L_-U_-) , \tag{2.3}$$

$$H_{\rm cor}^{(2)} = -\frac{\hbar^2}{2\mu R^2}L^2 , \tag{2.4}$$

$$L_\pm = L_\xi \pm iL_\eta , \tag{2.5}$$

and

$$U_\pm = \mp\frac{\partial}{\partial\theta} + \frac{i}{\sin\theta}\frac{\partial}{\partial\varphi} + L_\zeta\cot\theta . \tag{2.6}$$

The following notations are used here. $H_{\rm el}$ is the electronic Hamiltonian, μ is the reduced mass of the collision system, θ and φ are the ordinary angle variables to define the molecular axis orientation with respect to the space-fixed frame, L is the electronic orbital angular momentum, and L_ξ, L_η, and L_ζ are components of L in the molecule-fixed coordinate system with the ζ axis along the molecular axis. Eigenfunctions of $H_{\rm rot}$ are given explicitly as

$$H_{\rm rot}\mathscr{Y}(KM_K\Lambda:\theta,\varphi) = [K(K+1) - 2\Lambda^2]\mathscr{Y}(KM_K\Lambda:\theta,\varphi) , \tag{2.7}$$

$$\mathscr{Y}(KM_K\Lambda:\theta,\varphi) = (-1)^\Lambda\left[\frac{2K+1}{4\pi}\right]^{1/2} d^K_{M_K\Lambda}(\theta)e^{iM_K\varphi} , \tag{2.8}$$

where K and M_K are the total angular momentum quantum number and its z component in the space-fixed coordinate system, i.e., $K = L + L_R$, L_R is the angular momentum of the relative motion of nuclei, Λ is the eigenvalue of L_ζ, and $d^K_{M_K\Lambda}(\theta)$ is the finite rotation matrix element.[15] The functions (2.8) can be shown to satisfy

$$U_\pm \mathscr{Y}(KM_K\Lambda:\theta,\varphi) = \lambda_\pm(K,\Lambda)\mathscr{Y}(KM_K,\Lambda\pm 1:\theta,\varphi)\ , \tag{2.9}$$

where

$$\lambda_\pm(K,\Lambda)=[(K\mp\Lambda)(K\pm\Lambda+1)]^{1/2}\ . \tag{2.10}$$

Let us define the adiabatic electronic eigenfunctions $\phi_e(\Lambda;r:R)$ of $H_{\rm el}$ by

$$H_{\rm el}\phi_e(\Lambda;r:R)=\epsilon(\Lambda:R)\phi_e(\Lambda;r:R)\ , \tag{2.11}$$

where r represents the totality of electron coordinates. The spin-orbit interaction is not explicitly taken into account here, but, if necessary, it can be included in $H_{\rm el}$. In the latter case the angular momentum L and the quantum number Λ should be replaced by $J=L+S$, the electronic total (orbital plus spin) angular momentum, and Ω, the molecular axis component of J. Let us next introduce the electronic-rotational basis functions defined as

$$\Phi^K_\pm(\Lambda)=\frac{1}{\sqrt{2}}[\phi_e(\Lambda^+)\mathscr{Y}(K\Lambda^+)\pm\phi_e(\Lambda^-)\mathscr{Y}(K\Lambda^-)]\ , \tag{2.12}$$

for $\Lambda\neq 0$ and

$$\Phi^K(\Sigma)=\phi_e(\Sigma)\mathscr{Y}(K\Sigma)\ , \tag{2.13}$$

where $\Lambda\equiv|\Lambda|$, $\Lambda^\pm\equiv\pm\Lambda$, and $\mathscr{Y}(K\Lambda)$ is given by Eq. (2.8). These functions satisfy the following relations:

$$\langle\Phi^K_\pm(\Lambda_1)|\Phi^K_\pm(\Lambda_2)\rangle=\delta(\Lambda_1,\Lambda_2)\ , \tag{2.14}$$

$$\begin{aligned}&\langle\Phi^K_\pm(\Lambda_1)|\Phi^K_\mp(\Lambda_2)\rangle=0\ ,\\ &\langle\Phi^K_\pm(\Lambda_1)|H^{(1)}_{\rm cor}|\Phi^K_\mp(\Lambda_2)\rangle=0\ ,\end{aligned} \tag{2.15}$$

$$\begin{aligned}\langle\Phi^K_\pm(\Lambda_1)|H^{(1)}_{\rm cor}|\Phi^K_\pm(\Lambda_2)\rangle=-\frac{\hbar^2}{2\mu R^2}[&\lambda_-(K,\Lambda_2)\langle\phi_e(\Lambda_1^+)|L_-|\phi_e(\Lambda_2^+)\rangle\delta(\Lambda_1,\Lambda_2-1)\\ &+\lambda_+(K,\Lambda_2)\langle\phi_e(\Lambda_1^+)|L_+|\phi_e(\Lambda_2^+)\rangle\delta(\Lambda_1,\Lambda_2+1)]\ ,\end{aligned} \tag{2.16}$$

$$\langle\Phi^K(\Sigma)|H^{(1)}_{\rm cor}|\Phi^K_\pm(\Lambda)\rangle=\begin{cases}\sqrt{2}\langle\phi_e(\Sigma)|L_-|\phi_e(\Pi^+)\rangle[K(K+1)]^{1/2}\delta(\Lambda,1)\ ,\\ 0\ ,\end{cases} \tag{2.17}$$

$$\langle\Phi^K_\pm(\Lambda_2)|H^{(2)}_{\rm cor}|\Phi^K_\mp(\Lambda_2)\rangle=0\ , \tag{2.18}$$

$$\begin{aligned}\langle\Phi^K_\pm(\Lambda_1)|H^{(2)}_{\rm cor}|\Phi^K_\pm(\Lambda_2)\rangle&=-\frac{\hbar^2}{2\mu R^2}\langle\phi_e(\Lambda_1)|L^2|\phi_e(\Lambda_2)\rangle\delta(\Lambda_1,\Lambda_2)\\ &\equiv-\frac{\hbar^2}{2\mu R^2}\langle L^2\rangle_{\Lambda_1}\delta(\Lambda_1,\Lambda_2)\ ,\end{aligned} \tag{2.19}$$

and

$$(H_{\rm el}+H_{\rm rot})\Phi^K_\pm(\Lambda)=\left[\epsilon(\Lambda:R)+\frac{\hbar^2}{2\mu R^2}[K(K+1)-2\Lambda^2]\right]\Phi^K_\pm(\Lambda)\ . \tag{2.20}$$

The interaction Hamiltonian matrix $(H^{(2)}_{\rm cor})$ is diagonal with respect to Λ, but nondiagonal in the manifold of states with the same Λ. In the limit $R\rightarrow 0$ the electronic functions $\phi_e(\Lambda)$ become eigenfunctions of L^2, and the matrix (2.19) becomes diagonal even in the manifold of states with the same Λ:

$$\langle\phi_e(i\Lambda_1)|L^2|\phi_e(j\Lambda_2)\rangle \underset{R\rightarrow 0}{\longrightarrow} L_i(L_i+1)\delta_{ij}\delta(\Lambda_1,\Lambda_2)\ . \tag{2.21}$$

The set of states $\{\Phi^K_\pm(\Lambda),\Phi^K(\Sigma)\}$ can thus be divided into two classes, namely, $\{\Phi^K_+(\Lambda),\Phi^K(\Sigma)\}$ and $\{\Phi^K_-(\Lambda)\}$, which have no connection to each other. The dynamical states are defined as the eigenfunctions of

$$H_{\rm dyn}\equiv H_{\rm el}+H_{\rm rot}+H^{(1)}_{\rm cor}+H^{(2)}_{\rm cor}\ , \tag{2.22}$$

to satisfy

$$H_{\rm dyn}\Psi_v^K(r,\hat{R}:R)=E_v^K(R)\Psi_v^K(r,\hat{R}:R)\ . \qquad (2.23)$$

The functions $\Psi_v^K(r,\hat{R}:R)$ can be obtained by an expansion in terms of the functions $\{\Phi_{\pm}^K(\Lambda)\}$,

$$\Psi_v^K(r,\hat{R}:R)=\sum_{\Lambda} C_v^{K\Lambda}(R)\Phi_{+}^K(\Lambda)\ , \qquad (2.24)$$

or

$$\Psi_v^K(r,\hat{R}:R)=\sum_{\Lambda\neq 0} D_v^{K\Lambda}(R)\Phi_{-}^K(\Lambda)\ , \qquad (2.25)$$

where $\Phi_{+}^K(\Lambda=0)$ implies $\Phi^K(\Sigma)$ defined by Eq. (2.13).

In order to see a more detailed structure of this representation let us take the simplest two-state approximation:

$$\Psi_v^K=C_v^{K\Lambda_1}\Phi_{+}^K(\Lambda_1)+C_v^{K\Lambda_2}\Phi_{+}^K(\Lambda_2)\ , \qquad (2.26)$$

where Λ_1 is assumed, for simplicity, to equal Λ_2+1. Following the conventional procedure of diagonalization of a 2×2 matrix, one has

$$E_{1,2}^K=\frac{1}{2}\left[\epsilon_K(\Lambda_1)+\epsilon_K(\Lambda_2)\right.$$
$$\left.\pm\left[(\Delta\epsilon)^2+\frac{\hbar^4}{\mu^2R^4}\lambda_{+}^2(K,\Lambda_2)V_0^2\right]^{1/2}\right]\ , \qquad (2.27)$$

$$C_{1,2}^{K\Lambda_1}=\frac{1}{\sqrt{2}}\left[1\pm\frac{\Delta\epsilon}{\Delta E_K}\right]^{1/2}\ , \qquad (2.28)$$

$$C_{1,2}^{K\Lambda_2}=\pm\frac{1}{\sqrt{2}}\left[1\mp\frac{\Delta\epsilon}{\Delta E_K}\right]^{1/2}\ , \qquad (2.29)$$

where

$$\Delta\epsilon=\epsilon_K(\Lambda_1)-\epsilon_K(\Lambda_2)\ , \qquad (2.30)$$

$$\epsilon_K(\Lambda)=\epsilon(\Lambda)+\frac{\hbar^2}{2\mu R^2}[K(K+1)-2\Lambda^2]$$
$$+\frac{\hbar^2}{2\mu R^2}\langle L^2\rangle_\Lambda\ , \qquad (2.31)$$

$$\Delta E_K=E_1^K-E_2^K=[(\Delta\epsilon)^2+4V_K^2]^{1/2}\ , \qquad (2.32)$$

$$V_K=\frac{\hbar^2}{2\mu R^2}\lambda_{+}(K,\Lambda_2)V_0\ , \qquad (2.33)$$

and

$$V_0=\langle\phi_e(\Lambda_1^{+})\,|\,L_{+}\,|\,\phi_e(\Lambda_2^{+})\rangle\ . \qquad (2.34)$$

The total wave function $\Psi_{\rm tot}^K$, which satisfies

$$H\Psi_{\rm tot}^K=\left[H_{\rm dyn}-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\right]\Psi_{\rm tot}^K$$
$$=E\Psi_{\rm tot}^K\ , \qquad (2.35)$$

is expanded in terms of the dynamical states as

$$\Psi_{\rm tot}^K=\frac{1}{R}F_1^K(R)\Psi_1^K+\frac{1}{R}F_2^K(R)\Psi_2^K\ . \qquad (2.36)$$

Insertion of this expansion into Eq. (2.35) leads to the following coupled equations:

$$\left[\frac{d^2}{dR^2}+\frac{2\mu}{\hbar^2}[E-E_1^K(R)]+\left\langle\Psi_1^K\,\middle|\,\frac{\partial^2\Psi_1^K}{\partial R^2}\right\rangle\right]F_1^K(R)=-\left[2\left\langle\Psi_1^K\,\middle|\,\frac{\partial\Psi_2^K}{\partial R}\right\rangle\frac{d}{dR}+\left\langle\Psi_1^K\,\middle|\,\frac{\partial^2\Psi_2^K}{\partial R^2}\right\rangle\right]F_2^K(R) \qquad (2.37)$$

and an equation with suffixes 1 and 2 interchanged, where

$$\left\langle\Psi_1^K\,\middle|\,\frac{\partial\Psi_2^K}{\partial R}\right\rangle=C_1^{K\Lambda_1}(C_2^{K\Lambda_1})'+C_1^{K\Lambda_2}(C_2^{K\Lambda_2})'=\frac{(\Delta\epsilon)'V_K-(\Delta\epsilon)V_K'}{(\Delta E_K)^2}\ , \qquad (2.38)$$

$$\left\langle\Psi_1^K\,\middle|\,\frac{\partial^2\Psi_2^K}{\partial R^2}\right\rangle=C_1^{K\Lambda_1}(C_2^{K\Lambda_1})''+C_1^{K\Lambda_2}(C_2^{K\Lambda_2})''+C_1^{K\Lambda_1}C_2^{K\Lambda_1}\langle\phi_e(\Lambda_1)\,|\,\phi_e''(\Lambda_1)\rangle+C_1^{K\Lambda_2}C_2^{K\Lambda_2}\langle\phi_e(\Lambda_2)\,|\,\phi_e''(\Lambda_2)\rangle\ . \qquad (2.39)$$

Here a prime means a differentiation with respect to R.

Let us next consider how the semiclassical theory employed in previous papers[1,2] is related to the quantum-mechanical formulation described above. Since in atomic collisions a contribution of collisions with large angular momenta of relative motion L_R (therefore with large total angular momenta K) is dominant, the quantum number Λ can be neglected compared to K which is replaced by $(\mu\rho v/\hbar)^{1/2}$, where ρ is the impact parameter, and v is the collision velocity. Since $\mathcal{Y}(K\Lambda^{+})=\mathcal{Y}(K\Lambda^{-})$ in this approximation, the electronic wave functions are separated out from Eqs. (2.12) and (2.26) to be

$$\phi_e^{\pm}(\Lambda)=\frac{1}{\sqrt{2}}[\phi_e(\Lambda^{+})\pm\phi_e(\Lambda^{-})]\ , \tag{2.40}$$

and

$$\psi_v^{\mathrm{el}}(r:R)=C_v^{\Lambda_1}\phi_e^{+}(\Lambda_1)+C_v^{\Lambda_2}\phi_e^{+}(\Lambda_2)\ . \tag{2.41}$$

The relative nuclear motion is solved separately. The coupling Hamiltonian $H_{\mathrm{cor}}^{(1)}$ can thus be approximated as

$$H_{\mathrm{cor}}^{(1)}\simeq-\frac{\hbar^2}{2\mu R^2}[K(K+1)]^{1/2}(L_{+}+L_{-})\ , \tag{2.42}$$

and one has

$$\begin{aligned}\langle\phi_e^{\pm}(\Lambda_1)\,|\,H_{\mathrm{cor}}^{(1)}\,|\,\phi_e^{\pm}(\Lambda_2)\rangle=-\frac{\hbar}{2R^2}\rho v[\,&\langle\phi_e(\Lambda_1^{+})\,|\,L_{-}\,|\,\phi_e(\Lambda_2^{+})\rangle\delta(\Lambda_1,\Lambda_2-1)\\&+\langle\phi_e(\Lambda_1^{+})\,|\,L_{-}\,|\,\phi_e(\Lambda_2^{+})\rangle\delta(\Lambda_1,\Lambda_2+1)]\ .\end{aligned} \tag{2.43}$$

The term $H_{\mathrm{cor}}^{(2)}$ does not appear in the semiclassical approximation. Expanding the total wave function in terms of ψ_v^{el},

$$\Psi=A_1(t)\psi_1^{\mathrm{el}}(r:R)+A_2(t)\psi_2^{\mathrm{el}}(r:R)\ ,$$

and inserting this into the time-dependent Schrödinger equation, one has the coupled equations (13) of Ref. 2,

$$\frac{dA_v}{dt}=-\frac{i}{\hbar}\tilde{E}_v(R)A_v-\left\langle\psi_v^{\mathrm{el}}\left|\frac{\partial\psi_{v'}^{\mathrm{el}}}{\partial t}\right.\right\rangle A_{v'},\quad v,v'=1,2\ (v\neq v') \tag{2.44}$$

where

$$\tilde{E}_{1,2}=\tfrac{1}{2}(\epsilon(\Lambda_1)+\epsilon(\Lambda_2)\pm\{[\epsilon(\Lambda_1)-\epsilon(\Lambda_2)]^2+4V^2\}^{1/2})\ , \tag{2.45}$$

$$V=\frac{\rho v}{2R^2}V_0\ , \tag{2.46}$$

$$V_0=\langle\phi_e(\Lambda_2^{+}+1)\,|\,L_{+}\,|\,\phi_e(\Lambda_2^{+})\rangle\quad(\text{when }\Lambda_1=\Lambda_2+1)\ , \tag{2.47}$$

$$\left\langle\psi_1^{\mathrm{el}}\left|\frac{\partial\psi_2^{\mathrm{el}}}{\partial t}\right.\right\rangle=C_1^{\Lambda_1}\dot{C}_2^{\Lambda_1}+C_1^{\Lambda_2}\dot{C}_2^{\Lambda_2}=\frac{[\dot{\epsilon}(\Lambda_1)-\dot{\epsilon}(\Lambda_2)]V-[\epsilon(\Lambda_1)-\epsilon(\Lambda_2)]\dot{V}}{(\Delta\tilde{E})^2}\ , \tag{2.48}$$

and

$$\Delta\tilde{E}=\tilde{E}_1-\tilde{E}_2=\{[\epsilon(\Lambda_1)-\epsilon(\Lambda_2)]^2+4V^2\}^{1/2}\ . \tag{2.49}$$

Equation (2.45) tells us that the effective potential with a centrifugal potential, i.e.,

$$\frac{\mu\rho^2v^2}{2R^2}+\tilde{E}_2\ ,$$

which corresponds to E_2^K of Eq. (2.27), is proportional to $-1/R^2$ in the limit $R\to 0$ when $\rho v\leq(2/\mu)V_0$. This should not be a reality, because the fall of a particle to the center may become possible in such a potential.[16] Since this could occur only at very low impact parameters or low velocities, this would not present a serious problem practically. It can be shown, however, that this does not occur in the quantum-mechanical formulation. Taking as an example a two-state (Σ and Π) case, one has from Eq. (2.27)

$$E_2^K\underset{R\to 0}{\longrightarrow}\frac{\hbar^2}{2\mu R^2}\left\{K(K+1)-1+\frac{\langle L^2\rangle_{\Sigma}+\langle L^2\rangle_{\Pi}}{2}-\left[\left[1+\frac{\langle L^2\rangle_{\Sigma}-\langle L^2\rangle_{\Pi}}{2}\right]^2+2K(K+1)V_0^2\right]^{1/2}\right\}\ . \tag{2.50}$$

When the two (Σ and Π) states are degenerate at the united-atom limit, one has

$$\langle L^2\rangle_{\Sigma,\Pi} \to L(L+1) \quad (R\to 0)$$

and

$$V_0 \to [L(L+1)]^{1/2} \quad (R\to 0)\ .$$

Therefore the expression in the curly brackets in Eq. (2.50) cannot be negative, since $K \geq L \geq 1$. When the two states correlate to different energy levels in the united-atom limit, V_0 is generally very small (zero in the one-electron approximation) in that limit and again E_2^K does not become proportional to $-1/R^2$.

III. PATH-INTEGRAL FORMULATION OF A MULTISTATE CURVE-CROSSING PROBLEM

The most important point of the dynamical-state representation consists in the analytical structures of the energy difference (2.32) or (2.49) and the coupling term (2.38) or (2.48) as a function of the complex variable R. Because of the radical sign in Eqs. (2.32) and (2.49) ΔE_K and $\Delta\widetilde{E}$ have zeros of order $\frac{1}{2}$. The coupling terms (2.38) and (2.48) have a pole of order unity at the position of the zeros, since these terms are inversely proportional to the square of the energy difference. These analytical structures are the same as those of the radial-coupling problems in the ordinary adiabatic representation. On the other hand, the dynamical-state representation does not alter the analytical structure of the radial-coupling problems. This means that one can apply the formulas developed in the radial-coupling problems to a more general multistate curve-crossing problem involving both radial and rotational couplings (if necessary, the spin-orbit interaction can be included in the beginning to define adiabatic states), since all the transitions are made to occur locally at avoided crossings of the dynamical-state potential-energy curves.

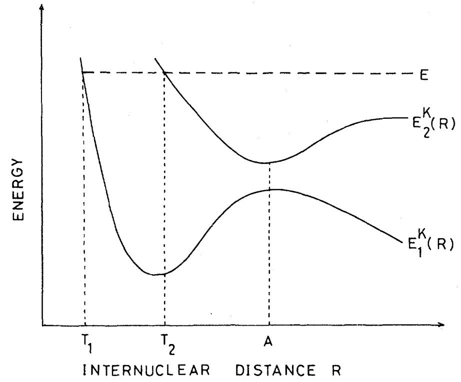

FIG. 1. Schematic potential-energy diagram of two dynamical states.

In the previous paper[2] the straight-line trajectory approximation is used for simplicity to study a three-state model problem. From the arguments mentioned above it is clear that a multistate curve-crossing problem can be formulated in the general path-integral approach based on the assumption of localized transitions.[6] The scattering matrix can be expressed as a product of matrices of two kinds in a similar way to Ref. 17. Proper phase corrections are included in the formulation here. The first kind of matrix is a diagonal propagation matrix which represents an evolution of the system from one avoided crossing point to the other without any transition. The second kind is a transition matrix which represents a distribution of probability amplitude between the two relevant states at the avoided crossing point. The most basic scattering matrix for the two-state problem shown in Fig. 1 can be obtained by using the comparison equation method[18-20] as follows:

$$S^K = P^+_{\infty A} O_A P_{ATA} I_A P^-_{A\infty}\ , \tag{3.1}$$

where P_{AB} and P_{ATA} are diagonal propagation matrices, and I_A (O_A) is the transition matrix corresponding to the incoming (outgoing) segment of the trajectory. These matrices are defined by

$$[P^+_{BA}]_{nm} = [P^-_{AB}]_{nm} = \exp\left[i \int_A^B k_n^K(R)dR \right]\delta_{nm}\ , \tag{3.2}$$

$$P_{ATA} = \begin{bmatrix} \exp\left[2i\int_{T_1}^A k_1^K(R)dR + i\tau\right], & 0 \\ 0, & \exp\left[2i\int_{T_2}^A k_2^K(R)dR - i\tau\right] \end{bmatrix}, \tag{3.3}$$

$$I_A = \begin{bmatrix} \sqrt{1-p}\, e^{-i\phi_0}, & \sqrt{p}\, e^{i\sigma_0} \\ -\sqrt{p}\, e^{-i\sigma_0}, & \sqrt{1-p}\, e^{i\phi_0} \end{bmatrix}, \tag{3.4}$$

$$[O_A]_{nm}=[I_A]_{mn} \ , \tag{3.5}$$

$$k_n^K(R)=\{(2\mu/\hbar^2)[E-E_n^K(R)]\}^{1/2} \ , \tag{3.6}$$

$$\tau=\tfrac{1}{2}\tan^{-1}\frac{1}{2\gamma}+\gamma\ln\frac{\gamma}{(\gamma^2+1/4)^{1/2}} \ , \tag{3.7}$$

$$\phi_0=\gamma-\frac{\gamma}{2}\ln(\gamma^2+\tfrac{1}{4})+\arg\Gamma(1+i\gamma)-\frac{\pi}{4}+\tfrac{1}{2}\tan^{-1}\frac{1}{2\gamma} \ , \tag{3.8}$$

$$\sigma_0+i\delta=\int_A^{R_*}[k_1^K(R)-k_2^K(R)]dR \ , \tag{3.9}$$

$$p=\exp(-2\delta) \ , \tag{3.10}$$

$$\delta=\pi\gamma \ , \tag{3.11}$$

$$A=R_e(R_*) \ , \tag{3.12}$$

$$E_1^K(R_*)=E_2^K(R_*) \ , \tag{3.13}$$

$\Gamma(x)$ is the gamma function, $E_n^K(R)$ is the dynamical-state energy, and T_n is the turning point in the nth potential. The S-matrix elements are explicitly given by (see also Ref. 13)

$$\begin{aligned} S_{1\to 1}^K=S_{11}^K= {} & \exp\left[2i\int_{T_1}^{\infty}k_1^K(R)dR-i\tau\right] \\ & \times\left\{(1-p)e^{2i\phi_s}+p\exp\left[-2i\left[\sigma+\int_{T_1}^{A}k_1^K(R)dR-\int_{T_2}^{A}k_2^K(R)dR\right]\right]\right\} \ , \end{aligned} \tag{3.14}$$

$$\begin{aligned} S_{1\to 2}^K=S_{21}^K= {} & 2i[p(1-p)]^{1/2}\exp\left[i\int_{T_1}^{\infty}k_1^K(R)dR+i\int_{T_2}^{\infty}k_2^K(R)dR\right] \\ & \times\sin\left[\int_{T_1}^{A}k_1^K(R)dR-\int_{T_2}^{A}k_2^K(R)dR+\sigma_0+\phi_s\right] \ , \end{aligned} \tag{3.15}$$

$$S_{2\to 1}^K=S_{12}^K=S_{21}^K \ , \tag{3.16}$$

$$\begin{aligned} S_{2\to 2}^K=S_{22}^K= {} & \exp\left[2i\int_{T_2}^{A}k_2^K(R)dR+i\tau\right] \\ & \times\left\{(1-p)e^{-2i\phi_s}+p\exp\left[2i\left[\sigma_0+\int_{T_1}^{A}k_1^K(R)dR-\int_{T_2}^{A}k_2^K(R)dR\right]\right]\right\} \ , \end{aligned} \tag{3.17}$$

where ϕ_s is the so-called Stokes phase and is given by

$$\phi_s=\tau-\phi_0=\gamma\ln\gamma-\gamma-\arg\Gamma(1+i\gamma)+\frac{\pi}{4} \ . \tag{3.18}$$

In the case of Rosen-Zener-type transitions the phase corrections τ and ϕ_0 are not necessary, and the transition probability p for one passage of the avoided crossing point is given by

$$p=p_{\mathrm{RZ}}=\frac{1}{1+e^{2\delta}} \ . \tag{3.19}$$

The matrix element I_{nm} (O_{nm}) represents a transition from state m to state n (state 2 is the higher of the two).

The matrix formulation given above can easily be generalized to a multistate problem. Taking as an example the three-state problem shown in Fig. 2, one has

$$S^K=P_{\infty B}^{+}O_BP_{BA}^{+}O_AP_{ATA}I_AP_{AB}^{-}I_BP_{B\infty}^{-} \ , \tag{3.20}$$

where

$$P_{ATA}=\begin{bmatrix}\exp\left[2i\int_{T_1}^{A}k_1^K(R)dR+i\tau_A+i\tau_B\right] & 0 & 0\\ 0 & \exp\left[2i\int_{T_2}^{A}k_2^K(R)dR-i\tau_A+i\tau_B\right] & 0\\ 0 & 0 & \exp\left[2i\int_{T_3}^{A}k_3^K(R)dR-i\tau_B\right]\end{bmatrix}, \tag{3.21}$$

$$I_A=\begin{bmatrix}\sqrt{1-p_A}e^{-i\phi_0^A}, & \sqrt{p_A}e^{i\sigma_0^A}, & 0\\ -\sqrt{p_A}e^{-i\sigma_0^A}, & \sqrt{1-p_A}e^{i\phi_0^A}, & 0\\ 0, & 0, & 1\end{bmatrix}, \tag{3.22}$$

and

$$I_B=\begin{bmatrix}1, & 0, & 0\\ 0, & \sqrt{1-p_B}e^{-i\phi_0^B}, & \sqrt{p_B}e^{i\sigma_0^B}\\ 0, & -\sqrt{p_B}e^{-i\sigma_0^B}, & \sqrt{1-p_B}e^{i\phi_0^B}\end{bmatrix}. \tag{3.23}$$

The suffixes A and B indicate the quantities corresponding to the avoided crossings A and B, respectively.

Figures 3(b) and 3(c) demonstrate the usefulness of the semiclassical theory based on the dynamical-state representation. A comparison is made with the quantum-mechanical calculations. The two-state collision system employed is a system of the second-lowest Σ state and the lowest Π state of the LiNa$^+$ molecule which correlate Li$^+$ + Na(3s) and Li(2p) + Na$^+$, respectively, at the separated-atom limit. Adiabatic potential energies are taken from Wijnaendts van Resandt *et al.*[21] who fitted analyti-

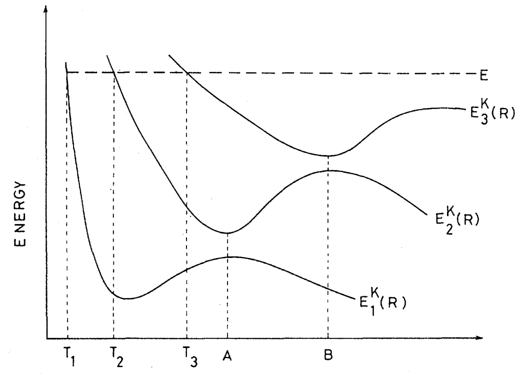

FIG. 2. Schematic potential-energy diagram of three dynamical states.

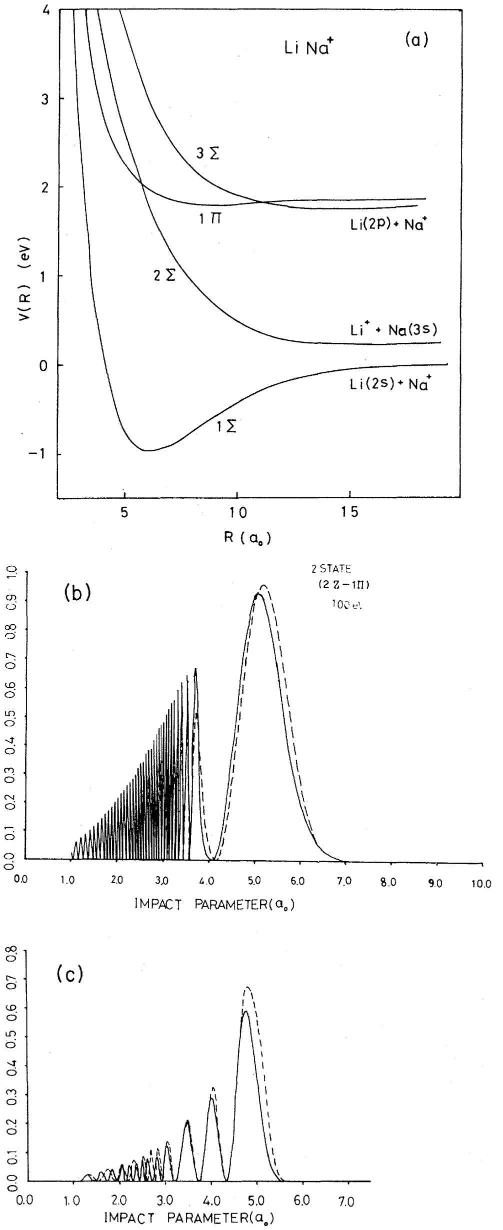

FIG. 3. (a) Adiabatic potential-energy curves of the lowest three states of (LiNa)$^+$. (b) Transition probabilities (from 2Σ to 1Π) vs impact parameter ρ ($\simeq\hbar K/\mu v$) at $E=100$ eV. ——, quantum-mechanical close coupling; ------, semiclassical theory [Eq. (3.15)]. (c) The same as (b) at $E=10$ eV.

cal expressions to the calculations of Habitz and Schwarz[22] [Fig. 3(a)]. The rotational-coupling matrix element is taken from Melius and Goddard.[23] The quantum-mechanical results are plotted as a function of ρ by using the replacement $K \simeq \mu\rho v/\hbar$. It is interesting to note that there is always a main peak in such a region of impact parameters that the turning point and the crossing point ($R \simeq 5.7a_0$) come close to each other. Although the narrow peaks in Fig. 3(b) are lower and a main peak in Fig. 3(c) is somewhat larger in the semiclassical approximation, the agreement between the two results is fairly good. This indicates the usefulness of the semiclassical theory. The $(\mathrm{LiNa})^+$ collision system is well investigated experimentally.[21,24] For instance, the differential cross sections are measured at several collision energies for various processes. In order to compare with these experiments at least three-state calculations are necessary by including the lowest Σ state. These calculations are now in progress using the path-integral approach outlined in this section.

IV. COLLISION-ENERGY DEPENDENCE OF ROTATIONALLY INDUCED TRANSITIONS

As was mentioned before, the dynamical-state representation transforms the analytical structure of rotational-coupling problems into the same one as that of radial-coupling problems, and enables us to employ the Landau-Zener-Stueckelberg (or Rosen-Zener) formula. The nature of the rotationally induced transitions is, however, quite different from that of the radial transitions, because a rotational coupling depends on the impact parameter ρ as well as the velocity v, or on the angular momentum K in the quantum-mechanical formulation. Total cross sections for the transitions induced by rotational coupling increase monotonically as a function of velocity. This is not the case for radial-coupling problems. In this section the velocity dependence of the rotationally induced transitions is investigated within the framework of the semiclassical approximation based on the dynamical-state representation. For simplicity, the straight-line trajectory approximation is used; thus the results obtained below are correct at relatively high energies.

In the semiclassical approximation the total cross section can be expressed as

$$Q = 8\pi \int_0^\infty d\rho\, \rho\, e^{-2\delta}(1-e^{-2\delta})\sin^2\sigma \tag{4.1}$$

for the Landau-Zener case, or

$$Q = 8\pi \int_0^\infty d\rho\, \rho\, \mathrm{sech}^2(\delta)\sin^2\sigma \tag{4.2}$$

for the Rosen-Zener case, where

$$\sigma + i\delta = \int_0^{t_*} \Delta E\, dt = \frac{\rho}{v}\int_0^{z_*} \Delta E\, dz\ , \tag{4.3}$$

$$\Delta E(t_*) = 0\ , \tag{4.4}$$

$$R^2 = \rho^2 + v^2 t^2 = \rho^2(1+z^2)\ , \tag{4.5}$$

$$z_* = \frac{v}{\rho} t_* = x_* + i y_*\ , \tag{4.6}$$

and ΔE is the adiabatic (in the case of ordinary radial-coupling problem) or the dynamical-state (in the case of rotational-coupling problem) energy difference. The phase corrections taken into account in the preceding section are neglected here for simplicity. If $\delta \propto \rho^b/v^a$ and $\sigma \propto v^{-c}\rho^{-d}$ at high ρ and v, then one has from Eqs. (4.1) and (4.2) $Q \propto v^{2(a/b-c-ad/b)}$ (when $d > 0$). In the case of radial Landau-Zener problem it can be shown that at large impact parameters

$$\sigma \propto 1/v\rho \quad \text{and} \quad \delta \propto \rho^3/v\ , \tag{4.7}$$

and that

$$Q \propto v^{-2} \tag{4.8}$$

for large v. In radial Rosen-Zener case δ is proportional to ρ/v at high ρ [σ behaves the same as Eq. (4.7)]; and Q is shown again to be proportional to v^{-2} at high energies. Let us next consider the following cases of rotational coupling.[2]

(a) Degeneracy at the united-atom limit. The adiabatic energy difference $\Delta\epsilon$ and the coupling term V are approximated as

$$\Delta\epsilon = \beta R^2$$

and

$$V = \frac{\rho v}{R^2} V_0$$

with β and V_0 constant. Then one has

$$E = \beta\rho^2\overline{\Delta E} = \beta\rho^2 \left[(1+z^2)^2 + \frac{4\alpha^4}{(1+z^2)^2} \right]^{1/2}\ , \tag{4.9}$$

$$\begin{bmatrix} x_* \\ y_* \end{bmatrix} = \frac{1}{\sqrt{2}}\{[(\alpha-1)^2+\alpha^2]^{1/2} \pm (\alpha-1)\}^{1/2}\ , \tag{4.10}$$

and

$$\sigma+i\delta=\beta\frac{\rho^3}{v}\int_0^{z_*}\overline{\Delta E}\,dz=\frac{V_0}{\alpha^2}\int_0^{z_*}\overline{\Delta E}\,dz\ , \tag{4.11}$$

where

$$\alpha=\left[\frac{vV_0}{\beta\rho^3}\right]^{1/2} . \tag{4.12}$$

Since the integral in Eq. (4.11) is a function only of α, one has

$$\sigma=V_0\sigma_1(\alpha)\ \text{ and }\ \delta=V_0\delta_1(\alpha)\ , \tag{4.13}$$

where $\sigma_1(X)$ and $\delta_1(X)$ are certain functions of X. Inserting Eq. (4.13) into Eq. (4.1) and transforming the integration variable from ρ to α, one has

$$Q=\frac{16}{3}\pi\left[\frac{V_0v}{\beta}\right]^{2/3}\times\int_0^\infty d\alpha\,\alpha^{-7/3}e^{-2V_0\delta_1(\alpha)}(1-e^{-2V_0\delta_1(\alpha)})\times\sin^2[V_0\sigma_1(\alpha)]\propto\left[\frac{v}{\beta}\right]^{2/3} . \tag{4.14}$$

(b) No curve crossing—constant $\Delta\epsilon$. Using the notations of Eqs. (4.3)—(4.6), one has

$$\Delta E=\Delta\epsilon\left[1+\frac{\alpha^2}{(1+z^2)^2}\right]^{1/2} , \tag{4.15}$$

$$\left[\begin{matrix}x_*\\ y_*\end{matrix}\right]=\frac{1}{\sqrt{2}}[(1+\alpha^2)^{1/2}\mp 1]^{1/2} , \tag{4.16}$$

and

$$\sigma+i\delta=2\frac{V_0}{\alpha}\int_0^{z_*}\left[1+\frac{\alpha^2}{(1+z^2)^2}\right]^{1/2}dz\ , \tag{4.17}$$

where

$$\alpha=2\frac{v}{\rho}\frac{V_0}{\Delta\epsilon} . \tag{4.18}$$

Thus one has, as before,

$$\sigma=2V_0\sigma_2(\alpha)\ \text{ and }\ \delta=2V_0\delta_2(\alpha)\ , \tag{4.19}$$

where $\sigma_2(X)$ and $\delta_2(X)$ are again certain functions of X. From Eq. (4.2) one has

$$Q=8\pi\left[2\frac{v}{\Delta\epsilon}V_0\right]^2\times\int_0^\infty d\alpha\,\alpha^{-3}\text{sech}^2[2V_0\delta_2(\alpha)]\times\sin^2[2V_0\sigma_2(\alpha)]\propto\left[\frac{v}{\Delta\epsilon}\right]^2 . \tag{4.20}$$

Unfortunately, we cannot derive a simple velocity dependence such as Eqs. (4.14) and (4.20) in the third important case of curve crossing at the finite internuclear distance.[2,25] The velocity dependences obtained in Eqs. (4.14) and (4.20) are the rigorous ones which can be derived from a dimension analysis of the time-dependent coupled equations. This fact indicates the appropriateness of the semiclassical theory. Although δ goes to zero as the velocity becomes infinity and the transition becomes "diabatic"[26] as in the Landau-Zener case, the velocity dependences of cross sections are qualitatively different from the radial-coupling case. The transitions at high v are generally less diabatic compared to those of radial Landau-Zener case, since the energy difference (2.44) increases with v. Besides the velocity and impact-parameter dependence of σ are different from Eq. (4.7).

V. SUMMARY AND DISCUSSION

The quantum-mechanical elucidation was applied to the semiclassical theory of the dynamical-state representation proposed previously. The semiclassical theory is valid at such collision velocities as

$$v_{\text{min}}\lesssim v\lesssim v_{\text{max}}\ ,$$

where

$$v_{\text{min}}=\max\left[2\frac{V_0(R=0)}{\mu\rho_{\text{int}}},\frac{\Lambda}{\mu\rho_{\text{int}}}\right] , \tag{5.1}$$

$$v_{\text{max}}=\frac{1}{R_{\text{int}}} \tag{5.2}$$

(in atomic units), R_{int} is the effective radius of interaction region, and ρ_{int} is the corresponding impact parameter. The first condition in Eq. (5.1) corresponds to the negative divergence of the semiclassical dynamical-state energy in the limit $R\to 0$ (see the discussion at the end of Sec. II). This condition can be easily removed by using the correct quantum-mechanical energies given by Eq. (2.27). The second condition in Eq. (5.1) is due to the approximation $K\gg\Lambda$. Because of the large mass of atomic nuclei the above-mentioned quantum-mechanical effects do not become serious as usual, unless collision energies are much lower than thermal energies. The condition (5.2) originates from the electron momentum-transfer effect or the ETF effect,[12,27,28] which is neglected throughout this paper and makes the cross sections decrease eventually in the high-energy limit. The ETF's introduce additional coupling terms (matrix A of Ref. 28) in the close-coupled equations. It would be worthwhile to try to take the ETF effects into basis states by diagonalizing again the Hamiltonian matrix composed not only of the diagonal adiabatic electronic energies and off-diagonal rotational-coupling terms, but also of the matrix A. The condition (5.2) could be removed in the semiclassical approximation based on that new representation with the ETF effects incorporated.

The general path-integral formulation was given in terms of the propagation and the transition matrices to deal with the general multistate atomic collision processes. The formulation enables us to treat them in a unified way.

It was shown that the velocity dependences of the cross sections for the rotationally induced transitions can be reproduced by the semiclassical theory.

An analytical problem still left to be solved in relation to rotational coupling is the problem of degeneracy of three or more molecular states at the same position, for instance, the problem of transitions among the σ, π, and δ states degenerate at the united-atom limit.[29,30] It is also highly desirable to investigate a role of rotational coupling in chemical reactions. The dynamical-state representation makes it easier, since it enables us to apply the surface-hopping classical-trajectory method.

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