Validity of the Adiabatic Approximation

1989.10.18

Ref.
1) J.C. Tully, "Dynamics of Molecular Collisions, Part B", ed. W.H. Miller (Plenum, 1976).
2) P. Pechukas, Phys. Rev. <u>181</u>, 174 (1969).

§. System

$$H = T_R + h(r,R) \tag{1}$$

$$\begin{cases} T_R = -\sum_{I=1}^{N} \frac{\hbar^2}{2M} \nabla_{R_I}^2 & (2) \\ h(r,R) = -\sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_{r_i}^2 + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum_{I \neq J} \frac{(Ze)^2}{|R_I - R_J|} - \sum_{i,J} \frac{Ze^2}{|r_i - R_J|} & (3) \end{cases}$$

{ r and R : the election and the nucleus coordinates
{ Z : the change of a nucleus

§. Adiabatic Representation

$$\Psi(r,R,t) = \sum_k \psi_k(r,R)\, \chi_k(R,t) \; : \text{wave function} \tag{4}$$

where

$$h(r,R)\, \psi_k(r,R) = E_k(R)\, \psi_k(r,R) \tag{5}$$

(Schrödinger Equation)

$$i\hbar \frac{\partial}{\partial t} \Psi(r,R,t) = H\, \Psi(r,R,t) \tag{6}$$

$$(lhS) = \sum_k \psi_k(r,R) \left[i\hbar \frac{\partial}{\partial t} \chi_k(R,t) \right] \quad \text{—}(*)$$

$$(\mathrm{rhs}) = \sum_k \left[T_R + h(r,R) \right] \psi_k(r,R)\, \chi_k(R,t)$$

$$\left(\begin{aligned} & T_R\, \psi_k(r,R)\, \chi_k(R,t) \\ &= \left(-\frac{\hbar^2}{2M}\right) \sum_I \nabla_I \cdot \underbrace{\nabla_I (\psi \chi)}_{(\nabla_I \psi)\chi + \psi(\nabla_I \chi)} \\ &= \left(-\frac{\hbar^2}{2M}\right) \sum_I \left[\psi \nabla_I^2 \chi + 2\, \nabla_I \psi \cdot \nabla_I \chi + (\nabla_I^2 \psi)\, \chi \right] \end{aligned}\right)$$

$$= \sum_k \left\{ -\frac{\hbar^2}{2M} \sum_I \left[\psi \nabla_I^2 \chi + 2 \nabla_I \psi \cdot \nabla_I \chi + (\nabla_I^2 \psi)\chi \right] + h(r,R)\, \psi \chi \right\} \quad -(b)$$

$\int dr\, \psi_k^*(r,R) \times$ Eq. (4), using (#) and (b),

$$i\hbar \frac{\partial}{\partial t} \chi_k(R,t) = \sum_{k'} \left\{ -\frac{\hbar^2}{2M} \sum_I \left[\delta_{kk'} \nabla_I^2 \chi_{k'} + 2 \langle k | \nabla_I | k' \rangle \cdot \nabla_I \chi_{k'} + \langle k | \nabla_I^2 | k' \rangle\, \chi_{k'} \right] + \underbrace{\int dr\, \psi_k^*(r,R)\, h(r,R)\, \psi_{k'}(r,R)}_{\delta_{kk'} E_k(R)} \right\}$$

$$\left[i\hbar \frac{\partial}{\partial t} + \sum_I \frac{\hbar^2}{2M} \nabla_I^2 - E_k(R) \right] \chi_k(R,t)$$

$$= \sum_{k'} \sum_I \left(-\frac{\hbar^2}{M} \langle k | \nabla_I | k' \rangle \cdot \nabla_I \chi_{k'} - \frac{\hbar^2}{2M} \langle k | \nabla_I^2 | k' \rangle\, \chi_{k'} \right)$$

$$= \sum_{k'} \left[\sum_I \langle k | \tfrac{\hbar}{i} \nabla_I | k' \rangle \cdot \frac{\hbar}{iM} \nabla_I \chi_{k'} + \langle k | T_R | k' \rangle\, \chi_{k'} \right]$$

$$\boxed{\begin{aligned}&\left[i\hbar\frac{\partial}{\partial t} - T_R - E_k(R) - T_{kk}(R)\right] \chi_k(R,t) \\ &\quad = \sum_{k'\neq k} T_{kk'}(R)\ \chi_{k'}(R,t) \qquad (7)\end{aligned}}$$

where

$$T_{kk'}(R) = \sum_I \langle k|\frac{\hbar}{i}\nabla_I|k'\rangle_R \cdot \frac{\hbar}{iM}\nabla_I - \sum_I \langle k|\frac{\hbar^2}{2M}\nabla_I^2|k'\rangle \qquad (8)$$

§. Criteria for Dropping Nonadiabatic Couplings

$$\chi_k(R,t) = e^{-iE_k(R)t/\hbar}\,\zeta_k(R,t) \tag{9}$$

Substituting Eq. (9) in Eq. (7),

$$e^{-iE_k(R)t/\hbar}\left[i\hbar\frac{\partial}{\partial t} + \cancel{E_k(R)} - T_R - \frac{it}{\hbar}T_R E_k(R) - \cancel{E_k(R)} - T_{kk}(R)\right]\zeta_k(R,t)$$

$$= \sum_{k'\neq k} T_{kk'}(R)\,\zeta_{k'}(R,t)\,e^{-iE_{k'}(R)t/\hbar}$$

$$\left[i\hbar\frac{\partial}{\partial t} + T_R - \frac{it}{\hbar}T_R E_k(R) - T_{kk}(R)\right]\zeta_k(R,t)$$

$$= \sum_{k'\neq k} T_{kk'}(R)\,\zeta_{k'}(R,t)\,e^{i\underbrace{[E_k(R)-E_{k'}(R)]/\hbar}_{\omega_{kk'}(R)}\cdot t} \tag{10}$$

Assume $\zeta_k(R,t=0) = \delta_{k,0}$, then for $k \neq 0$,

$$\left[i\hbar\frac{\partial}{\partial t} - \cancel{T_R} - \cancel{\frac{i\hbar}{\hbar}T_R E_k(R)} - \cancel{T_{kk}(R)}\right]\zeta_k(R,t)$$

$$= T_{k0}(R)\,e^{i\omega_{0k}(R)t} \tag{11}$$

$$\therefore\ \zeta_k(R,t) = \frac{1}{i\hbar}\underbrace{\int_0^t dt'\,T_{k0}(R)\,e^{i\omega_{0k}(R)t}}_{T_{k0}(R)\,\frac{e^{i\omega_{0k}(R)t}-1}{i\omega_{0k}(R)}}$$

$$= -\frac{T_{k0}(R)}{E_{0k}(R)}\left[\underbrace{e^{i\omega_{0k}(R)t} - 1}_{e^{i\omega t/2}\left(\underbrace{e^{i\omega t/2} - e^{-i\omega t/2}}_{2i\sin(\omega t/2)}\right)}\right]$$

$$\therefore \ \zeta_k(R,t) = -2i e^{i\omega t/2} \sin(\omega t/2) \frac{T_{k0}(R)}{E_{0k}(R)}$$

$$\boxed{|\zeta_k(R,t)|^2 = 4 \left| \frac{T_{k0}(R)}{E_0(R) - E_k(R)} \right|^2 \sin^2\left(\frac{\omega_{0k}(R)\, t}{\hbar} \right) \qquad (12)}$$

For

$$\overline{T_{k0}(R)} \sim k_B T \ll E_k(R) - E_0(R),$$

no nonadiabatic transition occurs.