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QUANTUM MECHANICAL AND SEMICLASSICAL APPROACHES
TO MOLECULAR DYNAMICS

S. Shi
(Ph.D. Thesis)

September 1984

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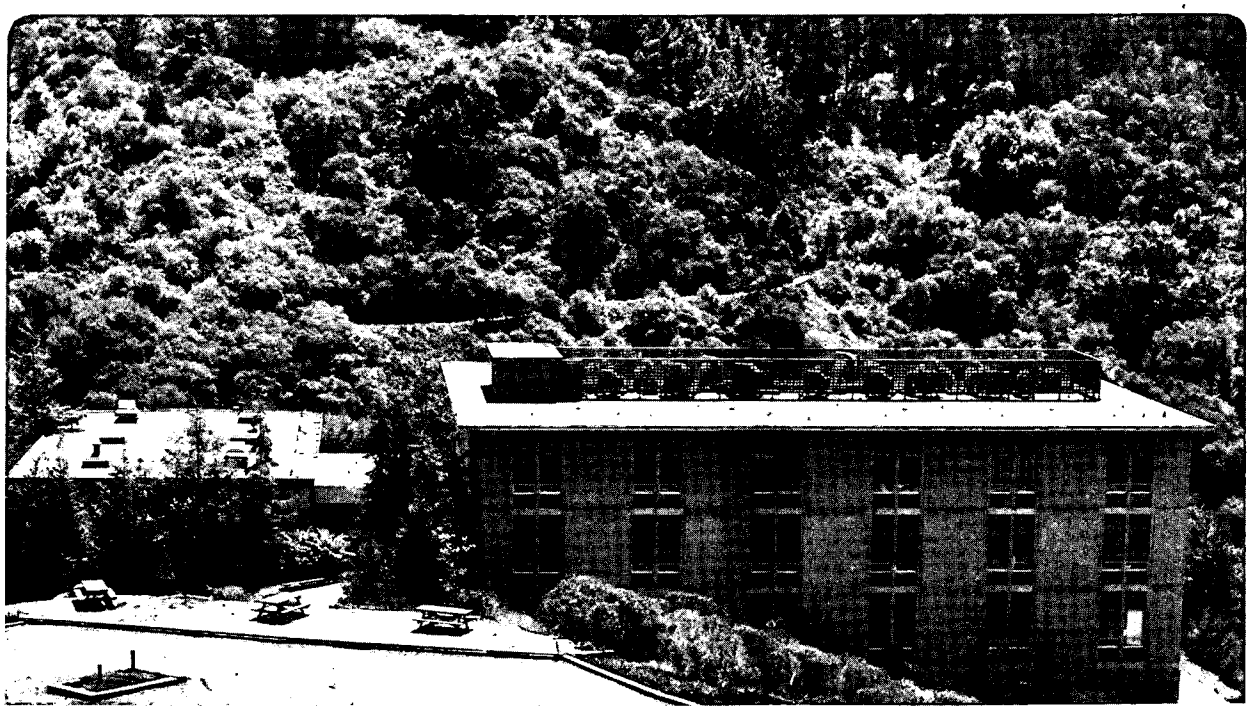

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Quantum Mechanical and Semiclassical Approaches To Molecular Dynamics

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(Ph.D. Thesis)

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Quantum Mechanical and Semiclassical Approaches To Molecular Dynamics

Shenghua Shi

ABSTACT

Several new quantum and semiclassical mechanical methods are proposed and tested by applying to a variety of problems in molecular dynamics.

A new multichannel exchange kernel formalism for reactive scattering is introduced. The central feature of the method is the expansion of the reactive scattering wavefunction in terms of the non-reactive coupled-channel scattering waves in all of the arrangements. The exact S matrix is found from the non-reactive wavefunction and the exchange kernel which are computed from the non-reactive coupled-channel scattering calculations in each arrangements. A approximate version of formula is obtained by virture of the distorted wave Born approximation (DWBA) where the non-reactive coupled-channel scattering wavefunction is utilized for distorted waves. Application to a standard test problem (collinear $H+H_2$) shows that multichannel DWBA is extremely accurate if the reaction probability is no larger than 0.1 and if ~ 3 to 4 vibrational states are included in the non-reactive coupled-channel expansion, and that the full exact calculation is stable, accurate and easy to implement.

Semiclassical perturbation theory combined with two approximate models for polyatomic Hamiltonian-- the reaction path model and the kinetic coupling model-- leads to extremely simple, analytical formulae for S-matrix and the spectra of overtone. The numerical tests indicate that these simple approximate methods are of useful accuracy.

A new semiclassical approach is proposed . In this approach the evolution of the states of a system, which are parameterized by label variables, is determined by calculating the time development of the label variables classically. The formalism for calculating the S-matrix within this framwork is developed. Sample calculations show that this method is very simple and describes quantum phenomena very well.

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I) Introduction

The development of modern experimental techniques which makes it possible to investigate processes at the level of molecular detail and the advent of powerful electronic digital computer have generated intense activity in the theoretical study of molecular dynamics beginning about twenty years ago. In progress towards the quantitative understanding the experimentally observed behavior of molecular systems and helping experimentalists in design of new experiments, many new theoretical approaches, models and computational procedures have been developed[1,2]. The active interaction of theory with experiment has been fruitfully leading to a better and deeper understanding of complicated physical and chemical processes in molecular systems. Some of the newly developed theoretical approaches in molecular dynamics are also finding useful application in certain areas of physics. However, the theoretical methodology developed up to now is still so inefficient that only for the simplest possible reactive system, i.e., the $H+H_2$ exchange reaction, and only for low energies, the fully converged, three dimensional exact quantum reactive scattering calculations have been finished[3-6]. Furthermore, it seems that there are few really new theoretical approaches which have been reported in recent years. In this thesis several new approaches towards improving the efficiency of theoretical treatments are explored.

In Chapter II a new exchange kernel approach to quantum reactive scattering is formulated in both exact and DWBA versions. The renormalized Numerov algorithm[7], which has been proposed to solve the

coupled-channel equations for non-reactive systems, is investigated for use in reactive scattering calculation within this formalism. Application to the test problem of the collinear $H+H_2$ exchange reaction is described. In Chapter III two practical approximate methods-- the combination of the semiclassical perturbation approximation (SCP) with two approximate models for the polyatomic Hamiltonian, the reaction path Hamiltonian model and the kinetic coupling model, -- are presented. Two numerical calculations have been carried out to test the models. The results are presented and discussed. In Chapter IV a new semiclassical approach, the label variable classical mechanics method, is developed. The sample calculations for testing its usefulness and accuracy are described and discussed. Chapter V concludes with remarks.

II) Quantum reactive scattering by the exchange kernel approach

I.a)Introduction

The development of practical methods for a quantum mechanically accurate description of molecular reactive scattering has been one of the most challenging subjects in theoretical dynamic study. The major complication in reactive scattering arises from the fact that coordinates descriptive of the asymptotic reactant arrangement differ from those appropriate to describe the asymptotic product arrangements. One had to solve the coupled-channel equations in each arrangement and match the solutions in the interaction region[8]. This is not an easy job to do. A great deal of effort has been concerned with devising elegant coordinate systems which facilitated the treatment of the rearrangment[9-12]. These methods, however, have to be tailored to match each problem.

A more general formalism originally given by Miller[13] has been applied to the collinear $H+H_2$ exchange reaction[14,15]. In this approach the total wavefunction is expanded in terms of the open channel internal states of all arrangments with the unknown radial functions, plus a set of the square-integrable "correlation functions" with the unknown coefficients to account for the effect of closed channels. The coefficients and the coupled-channel equations for the radial functions are obtained from the variational principle. The price paid is that the coupled equations contain a nonlocal exchage interaction, i.e., the coupled equations are coupled integro-differential equations. The ways which have been proposed to handle this exchange interaction[14,15] seem

difficult to implement in the 3 dimensional case.

In this work a easier and more general approach is explored. Here the total wavefunction is expanded in terms of the non-reactive scattering wavefunctions in all arrangements. It is discovered that the exchange interaction kernel obtained is energy independent, i.e., it has the character of a potential interaction. It is also of practical significance that within this framwork all the numerical methods for treating the inelastic scattering can be readily applied to calculation of reactive scattering.

II.b) Formulation

To illustrate the methodology let us consider an atom-diatomic exchange reaction A + BC $\longrightarrow$ AB + C, AC + B. The extension to more general reactive systems should be straightforward. We assume that using the Born-Oppenheimer approximation to seperate the electronic and nuclear motions is valid, and the resulting ground electronic state potential energy surface V is known. It is further assumed that there are no low -lying excited electronic states nearby in the energy range we are interested in, i.e., the electronic excitation is excluded. Let $\mathbf{R}_a$ be the position vector of A with respect to the center of mass of BC and $\mathbf{r}_a$ the position vector of C with respect to B. The vectors $\mathbf{r}_b$, $\mathbf{R}_b$ and $\mathbf{r}_c$, $\mathbf{R}_c$ are similarly defined, as indicated in Fig.(I.1) The α =a, b, c, is used as arrangement index with a$\equiv$ (A + BC) and b$\equiv$ (B +CA) and c$\equiv$ (C +AB). The reduced channel mass μ_a and the reduced internal masses m_α with α = a, b, c, are

$$m_a = m_C\, m_B \,/\, (m_C + m_B),$$

$$m_b = m_C\, m_A \,/\, (m_C + m_A),$$

$$m_c = m_A\, m_B \,/\, (m_A + m_B),$$

$$\mu_a = m_A\, (\, m_B + m_C\,) \,/\, M,$$

$$\mu_b = m_B\, (\, m_C + m_A\,) \,/\, M,$$

$$\mu_c = m_C\, (\, m_A + m_B\,) \,/\, M, \qquad \text{(II- 1a)}$$

with

$$M = m_A + m_B + m_C \quad , \qquad \text{(II- 1b)}$$

where m_A, m_B, amd m_C are the masses of the atom A, B, and C, respectively. Two other sets of coordinates which we could use are the three Euler angles $(\theta_\alpha, \phi_\alpha, \psi_\alpha)$ with $(\theta_\alpha, \phi_\alpha) = \hat{\mathbf{R}}_\alpha \equiv \mathbf{R}_\alpha \,/\, |\mathbf{R}_\alpha|$, and ψ_α =twist about $\mathbf{R}_\alpha$, which orient the triangle formed by the three atoms in three dimensional space and three additional coordinates either $(r_\alpha, R_\alpha, \gamma_\alpha)$ or $(R_\alpha, R_{\alpha'}, \gamma_{\alpha\alpha'})$ with $r_a = |\mathbf{r}_a|$, $R_\alpha = |\mathbf{R}_\alpha|$, $\cos\gamma_{\alpha\alpha'} = \hat{\mathbf{R}}_\alpha \bullet \hat{\mathbf{R}}_{\alpha'}$, and $\cos\gamma_\alpha = \hat{\mathbf{r}}_\alpha \bullet \hat{\mathbf{R}}_\alpha$, which specify the size and shape of the triangle. Then , it is easy to show that the volume integral reads

$$\int d\tau = \int R_\alpha^2\, dR_\alpha \int r_\alpha^2\, dr_\alpha \int \sin\theta_\alpha\, d\theta_\alpha \int \sin\gamma_\alpha\, d\gamma_\alpha \int d\psi_\alpha \int d\phi_\alpha$$

$$= c \int R_\alpha^2\, dR_\alpha \int R_{\alpha'}^2\, dR_{\alpha'} \int \sin\gamma_{\alpha\alpha'}\, d\gamma_{\alpha\alpha'} \int \sin\theta_\alpha\, d\theta_\alpha \int d\psi_\alpha \int d\phi_\alpha$$

$$\equiv \int R_\alpha^2\, dR_\alpha \int d\boldsymbol{\rho}_\alpha \quad , \qquad \text{(II- 2a)}$$

where $\quad c = \sin^{-3}\gamma_{\alpha\alpha'}, \qquad$ (II- 2b)

with

$$\cos\gamma_{\alpha\alpha'} = -\,[m_a\, m_b \,/\, (m_a + m_c\,)(m_b + m_c\,)]^{1/2}, \qquad \text{(II- 2c)}$$

and

$$\int d\boldsymbol{\rho}_\alpha \equiv \int r_\alpha^2\, dr_\alpha \int \sin\gamma_\alpha\, d\gamma_\alpha \int d\phi_\alpha \int \sin\theta_\alpha\, d\theta_\alpha$$

$$= c \int R_\alpha^2\, dR_\alpha \int \sin\gamma_{\alpha\alpha'}\, d\gamma_{\alpha\alpha'} \int d\phi_\alpha \int \sin\theta_\alpha\, d\theta_\alpha \int d\psi_\alpha \quad .$$

(II- 3)

The Hamiltonian for the three atom system can be written as

$$H = \frac{P_{R_\alpha}^2}{2\,\mu_\alpha} + \frac{L_\alpha^2}{2\,\mu_\alpha R_\alpha^2} + (V - v_\alpha) + h_\alpha \quad , \qquad \text{(II- 4)}$$

where P_{R_α} is the translational radial momentum operator, L_α is the orbital angular momentum operator, v_α is the potential for the diatomic molecule and h_α is the Hamiltonian for the diatomic molecule.

Now let $|\phi_{\alpha n}^{JM}>$ be a common eigenvector of the square of total angular momentum J^2, the component J_z of J on the space fixed z axis, the square of obital angular momentum L_α^2 and the Hamiltonian of the diatomic molecule h_α, i.e.,

$$L_\alpha^2 |\phi_{\alpha n}^{JM}> = \ell_\alpha(\ell_\alpha + 1)\, |\phi_{\alpha n}^{JM}> \qquad \text{(II- 5a)}$$

$$h_\alpha\, |\phi_{\alpha n}^{JM}> = \varepsilon_n^\alpha\, |\phi_{\alpha n}^{JM}> \qquad \text{(II- 5b)}$$

with **n** denoting a set of quantum numbers. If $|u_{\alpha n \leftarrow \alpha' n'}^{JM}>$ is a vector in the subspace R_α, then the total wavevector of the system can be expanded in terms of the direct product states $|\phi_{\alpha n}^{JM}>|u_{\alpha n \leftarrow \alpha' n'}^{JM}>$ in all arrangements

$$|\Psi> = \sum_{\alpha, n} |\phi_{\alpha n}^{JM}>|u_{\alpha n \leftarrow \alpha' n'}^{JM}> \qquad \text{(II- 6)}$$

with α = a,b,c. Then from the Schrödinger equation it is obtained that

$$0 = <\phi_{\alpha n}^{JM}|\, H - E_0\, |\Psi>$$

$$= \sum_{\alpha',\mathbf{n}'} \langle \phi^{JM}_{\alpha\mathbf{n}} \mid H - E_0 \mid \phi^{JM}_{\alpha'\mathbf{n}'} \rangle \mid u^{JM}_{\alpha'\mathbf{n}'+\alpha_1\mathbf{n}_1} \rangle$$

$$= (T_{R_\alpha} - E_0 + \epsilon^{\alpha}_{\mathbf{n}}) \mid u^{JM}_{\alpha\mathbf{n}+\alpha_1\mathbf{n}_1} \rangle$$

$$+ [\ell_\alpha(\ell_\alpha+1)/2\mu R_\alpha] \mid u^{JM}_{\alpha\mathbf{n}+\alpha_1\mathbf{n}_1} \rangle$$

$$+ \sum_{\mathbf{n}'} \langle \phi^{JM}_{\alpha\mathbf{n}} \mid V - v_\alpha \mid \phi^{JM}_{\alpha,\mathbf{n}'} \rangle \mid u^{JM}_{\alpha\mathbf{n}'+\alpha_1\mathbf{n}_1} \rangle$$

$$+ \sum_{\alpha'\neq\alpha,\mathbf{n}'} \langle \phi^{JM}_{\alpha\mathbf{n}} \mid H - E_0 \mid \phi^{JM}_{\alpha'\mathbf{n}'} \rangle \mid u^{JM}_{\alpha'\mathbf{n}'+\alpha_1\mathbf{n}_1} \rangle \qquad \text{(II- 7a)}$$

with $\quad T_{R_\alpha} = P^2_{R_\alpha}/(2\mu_\alpha) \quad , \qquad$ (II- 7b)

where E_0 is the total energy of the system. To write it in a more compact form with matrices we denote

$$(H - E_0)\, \mathbf{I} = \check{\mathbf{T}} + \check{\mathbf{V}} + \check{\mathbf{E}} \quad , \qquad \text{(II- 8a)}$$

with

$$\check{\mathbf{T}} \equiv \begin{pmatrix} \mathbf{I}\, T_{R_a} & \mathbf{0} & 0 \\ 0 & \mathbf{I}\, T_{R_b} & \mathbf{0} \\ 0 & 0 & \mathbf{I}\, T_{R_c} \end{pmatrix} \quad , \qquad \text{(II- 8b)}$$

$$\check{\mathbf{V}} \equiv \begin{pmatrix} \mathbf{I}\, [(V-v_a)+L^2{}_a/(2\mu_a R_a)] & 0 & 0 \\ 0 & \mathbf{I}\, [(V-v_b)+L^2{}_b/(2\mu_b R_b)] & 0 \\ 0 & 0 & \mathbf{I}\, [(V-v_c)+L^2{}_c/(2\mu_c R_c)] \end{pmatrix} ,$$

and $\qquad$ (II- 8c)

$$\tilde{\mathbf{E}} \equiv \begin{pmatrix} \mathbf{I}\,(E_o-h_a) & 0 & 0 \\ 0 & \mathbf{I}\,(E_o-h_b) & 0 \\ 0 & 0 & \mathbf{I}\,(E_o-h_c) \end{pmatrix} , \qquad \text{(II- 8d)}$$

where **I** is a unit matrix. Then the Eq.(II-7) can be written in a matrix form

$$(\tilde{\mathbf{H}}^o - \mathbf{E})\tilde{\mathbf{u}} = \tilde{\mathbf{V}}_{ex}\,\tilde{\mathbf{u}} \quad , \qquad \text{(II- 9a)}$$

with

$$\tilde{\mathbf{H}}^o \equiv \tilde{\mathbf{T}} + \tilde{\mathbf{V}}^o \quad , \qquad \text{(II- 9b)}$$

$$\tilde{\mathbf{V}}^o \equiv \mathbf{\Phi}^T\,\mathbf{Y}\,\tilde{\mathbf{V}}\,\mathbf{\Phi} \quad , \qquad \text{(II- 9c)}$$

$$\tilde{\mathbf{V}}_{ex} = -\,\mathbf{\Phi}^T\,[\,(\mathbf{H}-E_o)\,\mathbf{X}\,]\,\mathbf{\Phi} \,, \qquad \text{(II- 9d)}$$

and

$$\mathbf{E} \equiv \mathbf{I}\,E_o - \boldsymbol{\varepsilon} \quad , \qquad \text{(II- 9e)}$$

where the superscript T denotes the transpose and the matrix $\boldsymbol{\varepsilon}$ is diagonal, with elements

$$\varepsilon_{\alpha n,\,\alpha' n'} = \varepsilon^{\alpha}_{n}\,\delta_{\alpha,\alpha'}\,\delta_{n,n'} \quad ; \qquad \text{(II- 9f)}$$

the matrix **X** has no diagonal elements in arrangements

$$X_{\alpha n,\,\alpha n'} = (1 - \delta_{\alpha,\alpha'}) \quad ; \qquad \text{(II- 9g)}$$

while the matrix **Y** is diagonal in arrangement

$$Y_{\alpha n,\,\alpha' n'} = \delta_{\alpha,\alpha'} \quad ; \qquad \text{(II- 9h)}$$

and the matrices $\tilde{u}$ and Φ are defined by

$$\tilde{u}_{\alpha n,\alpha' n'} \equiv \left| u^{JM}_{\alpha n} \; {}_{+\alpha' n'} \right> , \quad \alpha = a,b,c \quad ; \tag{II- 9i}$$

and

$$\Phi_{\alpha n,\alpha' n'} = \delta_{\alpha,\alpha'}\delta_{n,n'} \left| \phi^{JM}_{\alpha n} \right> \quad . \tag{II- 9j}$$

If $\tilde{u}^o$ is the solution of the homogeneous equation

$$(\tilde{H}^o - E)\tilde{u}^o = 0 \tag{II-10a}$$

and a matrix operator is introduced

$$\tilde{G}^o \equiv [\tilde{H}^o - E]^{-1} \quad , \tag{II-10b}$$

then the slution of Eq.(II-9a) can be formally expressed as

$$\tilde{u} = \tilde{u}^o + \tilde{G}^o \; \tilde{V}_{ex} \; \tilde{u}$$

$$= \tilde{u}^o + \tilde{G}^o \; \tilde{V}_{ex}\tilde{u}^o + \tilde{G}^o \; \tilde{V}_{ex}\tilde{G}^o \; \tilde{V}_{ex}\tilde{u}$$

$$= \tilde{u}^o + \tilde{G}^o \; \tilde{T}_{ex}\tilde{u}^o \quad , \tag{II- 11}$$

where

$$\tilde{T}_{ex} \equiv \tilde{V}_{ex} + \tilde{V}_{ex} \; \tilde{G}^o \; \tilde{V}_{ex}$$

$$+ \; \tilde{V}_{ex}\tilde{G}^o \; \tilde{V}_{ex}\tilde{G}^o \; \tilde{V}_{ex} +$$

$$= \tilde{V}_{ex} [I + \tilde{G}^o (\tilde{V}_{ex} + \tilde{V}_{ex} \tilde{G}^o \tilde{V}_{ex} + \quad)]$$

$$= \tilde{V}_{ex} [I + \tilde{G}^o \tilde{T}_{ex}]$$

$$= (I - \tilde{V}_{ex} \tilde{G}^o)^{-1} \tilde{V}_{ex} \quad . \qquad \text{(II- 12)}$$

Substituting Eq.(II-12) into Eq.(II-11) gives

$$\tilde{u} = \tilde{u}^o + \tilde{G}^o (I - \tilde{V}_{ex} \tilde{G}^o)^{-1} \tilde{V}_{ex} \tilde{u}^o \quad . \qquad \text{(II- 13)}$$

According to the definition the exchange kernel $\tilde{V}_{ex}$ seems dependent on energy. Fortunately, in Eq.(II-13) instead of $\tilde{V}_{ex}$ we can use another matrix $\tilde{w}$ which is energy independent and has the character of a potential. The $\tilde{w}$ matrix is obtained from the definition of $\tilde{V}_{ex}$ by using Eqs.(II-8a),(II-9c),and (II-10a)

$$- \tilde{V}_{ex} \tilde{u}^o = \Phi^T [(H-E_o)X] \Phi \tilde{u}^o$$

$$= \Phi^T [X (\tilde{T} + \tilde{V} + \tilde{E})] \Phi \tilde{u}^o$$

$$= (\Phi^T X \Phi) (\tilde{T} + E) \tilde{u}^o + \Phi^T (X \tilde{V}) \Phi \tilde{u}^o$$

$$= \Phi^T X [\Phi (-\tilde{V}^o) + \tilde{V} \Phi] \tilde{u}^o$$

$$= \tilde{w} \tilde{u}^o \quad , \qquad \text{(II- 14)}$$

with

$$\tilde{w} \equiv \Phi^T X \tilde{V} \Phi - \Phi^T X \Phi \tilde{V}^o$$

$$= \Phi^T \mathbf{X} \, [(\tilde{V} - \Phi \, \Phi^T \mathbf{Y} \, \tilde{V} \,] \Phi$$

$$= \Phi^T \, \hat{\mathbf{w}} \, \Phi \quad , \tag{II-15a}$$

and

$$\hat{\mathbf{w}} \equiv [\ \mathbf{X} - \mathbf{X} \, \Phi \, \Phi^T \, \mathbf{Y}] \, \tilde{V} \quad . \tag{II-15b}$$

To see the physical meaning of the matrix $\tilde{\mathbf{w}}$, we write out the element of matrix $\tilde{\mathbf{w}}$

$$\tilde{w}_{\alpha n, \alpha' n'} = \begin{cases} 0 & \text{for } \alpha = \alpha' \\ \langle \phi^{JM}_{\alpha' n'} \mid V - v_{\alpha'} \mid \phi^{JM}_{\alpha n} \rangle & \\ - \sum_{n''} \langle \phi^{JM}_{\alpha n} \mid \phi^{JM}_{\alpha' n''} \rangle \langle \phi^{JM}_{\alpha' n''} \mid V - v_{\alpha'} \mid \phi^{JM}_{\alpha' n'} \rangle & \text{for } \alpha \neq \alpha' \end{cases} \tag{II-15c}$$

Eq.(II-15c) states that the exchange kernel consists of two parts: the first part $\langle \phi^{JM}_{\alpha n} \mid V - v_{\alpha'} \mid \phi^{JM}_{\alpha' n'} \rangle$ is the direct exchange interaction between the states in different arrangements; while the second term on the right side of Eq.(II-15c) is the indirect exchange interaction via the intermediate states in initial arrangement.

Similarly by using Eq.(II-10b) one obtains

$$- \tilde{V}_{ex} \, \tilde{G}^o = \Phi^T [\ \mathbf{X} \, (H - E_o)] \, \Phi \, \tilde{G}^o$$

$$= (\ \Phi^T \, \mathbf{X} \, \Phi \ ) \ (\ \tilde{T} + E) \ \tilde{G}^o + \Phi^T \ (\mathbf{X} \, \tilde{V}) \ \Phi \, \tilde{G}^o$$

$$= (\Phi^T \mathbf{X} \Phi) - (\Phi^T \mathbf{X} \Phi)\, \tilde{\mathbf{V}}_o\, \tilde{\mathbf{G}}^o + \Phi^T (\mathbf{X}\, \tilde{\mathbf{V}})\, \Phi\, \tilde{\mathbf{G}}^o$$

$$= \tilde{\mathbf{S}} + \tilde{\mathbf{w}}\, \tilde{\mathbf{G}}^o \quad , \qquad \text{(II-16)}$$

where

$\tilde{\mathbf{S}} \equiv (\Phi^T \mathbf{X} \Phi)$ is the overlap between the basis states in different arrangements since the elements of matrix $\tilde{\mathbf{S}}$ are

$$\tilde{\mathbf{S}}_{\alpha n, \alpha' n'} = \begin{cases} 0 & \text{for } \alpha \neq \alpha' , \\ \langle \phi^{JM}_{\alpha n} \,|\, \phi^{JM}_{\alpha' n'} \rangle & \text{for } \alpha \neq \alpha' \quad . \end{cases} \qquad \text{(II-17)}$$

Using Eq.(II-15) and Eq.(II-13) in Eq.(II-16) gives

$$\tilde{\mathbf{u}} = \tilde{\mathbf{u}}^o - \tilde{\mathbf{G}}^o\, (\, \mathbf{I} + \tilde{\mathbf{S}} + \tilde{\mathbf{w}}\, \tilde{\mathbf{G}}^o\,)^{-1}\, \tilde{\mathbf{w}}\, \tilde{\mathbf{u}}^o \quad . \qquad \text{(II- 18)}$$

In position representation (in R subspace) Eq.(II-9a),Eq.(II-10a) and Eq.(II-10b) reads as

$$(\mathbf{H}^o - \mathbf{E}\,)\, \mathbf{u}(R) = \int dR'\, \mathbf{V}_{ex}(R,R'\,)\, \mathbf{u}(R') \quad , \qquad \text{(II- 19)}$$

$$(\, \mathbf{H}^o - \mathbf{E}\,)\, \mathbf{u}^o(R) = 0, \qquad \text{(II- 20)}$$

and

$$(\, \mathbf{H}^o - \mathbf{E}\,)\, \mathbf{G}^o\, (R,R'\,) = \delta(R,R') \quad , \qquad \text{(II- 21)}$$

where

$$\mathbf{H}^o \equiv \mathbf{T}(R) + \mathbf{V}^o\, (R), \qquad \text{(II-22a)}$$

with

$$T_{\alpha n, \alpha' n'}\, (R) \equiv -(\hbar^2/2\mu_\alpha)\, (\, d^2/dR_\alpha^2\,)\, \delta_{\alpha,\alpha'} \delta_{n,n'} \quad , \qquad \text{(II-22b)}$$

$$V^{o}_{\alpha n,\alpha' n'}(R) \equiv [\langle \phi^{JM}_{\alpha n} | V(R_\alpha) - v_\alpha | \phi^{JM}_{\alpha n'} \rangle$$

$$+ \ell_\alpha(\ell_\alpha + 1)/(2\mu_\alpha R^2_\alpha)\ \delta_{n,n'}\ ]\ \delta_{\alpha,\alpha'} \quad ; \qquad \text{(II-22c)}$$

$\mathbf{V}_{ex}(R,R')$ has the elements

$$V_{ex\ \alpha n,\alpha' n'}(R,R') \equiv R_\alpha \langle R_\alpha | (\tilde{\mathbf{V}}_{ex})_{\alpha n,\alpha' n'} | R'_{\alpha'} \rangle R'_{\alpha'} \quad ; \qquad \text{(II-22d)}$$

$\mathbf{G}^{o}(R,R')$ denotes the Green's functions with

$$G^{o}_{\alpha n,\alpha' n'}(R,R') \equiv R_\alpha \langle R_\alpha | \tilde{\mathbf{G}}_{\alpha,n,\alpha' n'} | R'_{\alpha'} \rangle R'_{\alpha'} \quad ; \qquad \text{(II-22e)}$$

the wavefunctions $\mathbf{u}(R)$ are

$$u_{\alpha n,\alpha' n'}(R) \equiv R_\alpha \langle R_\alpha | u^{JM}_{\alpha n \leftarrow \alpha' n'} \rangle \quad ; \qquad \text{(II-22f)}$$

$\boldsymbol{\delta}(R,R')$ is a diagonal matrix with the elements

$$\delta_{\alpha n,\alpha' n'}(R,R') = \delta(R_\alpha,R_{\alpha'})\ \delta_{\alpha,\alpha'}\ \delta_{n,n'} \quad ; \qquad \text{(II-22g)}$$

the nonreactive wavefunctions $\mathbf{u}^{o}(R)$ are

$$u^{o}_{\alpha n,\alpha' n'}(R) \equiv R_\alpha \langle R_\alpha | u^{oJM}_{\alpha n \leftarrow \alpha' n'} \rangle \quad ; \qquad \text{(II-22h)}$$

and the elements of $\int dR'\ \mathbf{V}_{ex}(R,R')\ \mathbf{u}(R')$ are

$$\sum_{\alpha'',\mathbf{n}''} \int dR_{\alpha''} R_\alpha \langle R_\alpha | \tilde{\mathbf{V}}_{ex\ \alpha\mathbf{n},\alpha''\mathbf{n}''} | R_{\alpha''} \rangle R_{\alpha''}$$

$$\times R_{\alpha''} \langle R_{\alpha''} | u^{JM}_{\alpha''\mathbf{n}''+\alpha'\mathbf{n}'} \rangle \quad . \qquad \text{(II-22i)}$$

Here the unity identity has been used, i.e.,

$$\mathbf{I} \equiv \int dR\ R\ |R\rangle\langle R|\ R,$$

where

$$(\int dRR|R\rangle\langle R|R)_{\alpha\mathbf{n},\alpha'\mathbf{n}'} \equiv (\int R_\alpha^2\ dR_\alpha |R_\alpha\rangle\langle R_\alpha|)\delta_{\alpha,\alpha'}\delta_{\mathbf{n},\mathbf{n}'}.$$

(II- 23)

By using definitions, Eqs.(II-22e), (II-22f), (II-22h), and unity identity, Eq.(II-23), Eq.(II-18) in position representation becomes

$$\mathbf{u}(R) = \mathbf{u}^\circ(R) - \int dR'\ \mathbf{G}^\circ(R,R')\ \mathbf{Z}(R') \quad , \qquad \text{(II-24a)}$$

where

$$\mathbf{Z}(R') \equiv \int dR''\ dR'''\ R'\ \langle R'|(\ \mathbf{I} + \mathbf{S} + \tilde{\mathbf{w}}\ \tilde{\mathbf{G}}^\circ\ )^{-1}|R''\rangle\ R''$$

$$\times\ \mathbf{w}(R'',R''')\ \mathbf{u}^\circ(R''') \quad , \qquad \text{(II-24b)}$$

where $\mathbf{w}(R,R')$ has the elements

$$w_{\alpha\mathbf{n},\alpha'\mathbf{n}'}(R,R') \equiv R_\alpha \langle R_\alpha | \tilde{\mathbf{w}}_{\alpha\mathbf{n},\alpha'\mathbf{n}'} | R'_{\alpha'} \rangle R'_{\alpha'} \quad . \qquad \text{(II-24c)}$$

Now let $\mathbf{f}^\circ(R)$ and $\mathbf{g}^\circ(R)$ be the regular and irregular solution of Eq.(II-20) with real boundary conditions, i.e.,

$$\mathbf{f}^\circ(0)=0, \quad \lim_{R\to\infty} \mathbf{f}^\circ(R) = \lim_{R\to\infty} \mathbf{J}(R) + \mathbf{N}(R)\ \mathbf{K}^\circ + \mathbf{Si}(R) + \mathbf{C}(R)\mathbf{K}^\circ \quad , \qquad \text{(II-25a)}$$

and

$$\lim_{R\to\infty} \mathbf{g}^{o}(R) = \lim_{R\to\infty} \mathbf{N}(R) \to \mathbf{C}(R) \quad , \tag{II-25b}$$

where $\mathbf{K}^{o}$ is a constant matrix , $\mathbf{J}(R)$ and $\mathbf{N}(R)$ are given by

$$J_{\alpha\mathbf{n},\alpha'\mathbf{n}'}(R) \equiv \begin{cases} \hat{j}_{\ell_\alpha}(k_{\alpha\mathbf{n}}R_\alpha)/(v_{\alpha\mathbf{n}})^{1/2}\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for open channels ,} \\ I_{\ell_\alpha+1/2}(k_{\alpha\mathbf{n}}R_\alpha)\ (\pi\mu_\alpha R_\alpha)^{1/2}\delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for closed channels,} \end{cases} \tag{II-26a}$$

$$N_{\alpha\mathbf{n},\alpha'\mathbf{n}'}(R) \equiv \begin{cases} \hat{n}_{\ell}(k_{\alpha\mathbf{n}}R_\alpha)/(v_{\alpha\mathbf{n}})^{1/2}\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for open channels ,} \\ K_{\ell_\alpha+1/2}(k_{\alpha\mathbf{n}}R_\alpha)(\mu_\alpha R_\alpha/\pi)^{1/2}\delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for closed channels,} \end{cases} \tag{II-26b}$$

where $k_{\alpha\mathbf{n}} = [2\mu_\alpha(E_o - \varepsilon^{\alpha}_{\mathbf{n}})]^{1/2}$ is the channel wave number, $v_{\alpha\mathbf{n}} = \hbar k_{\alpha\mathbf{n}}/\mu_\alpha$ is the translational velocity, $I_{\ell+1/2}$ and $K_{\ell+1/2}$ are the modified spherical Bessel functions of the first and third kinds, $\hat{j}_\ell$ amd $\hat{n}_\ell$ are Riccati-Bessel functions, the elements of matrices $\mathbf{Si}(R)$ and $\mathbf{C}(R)$ are

$$Si_{\alpha\mathbf{n},\alpha'\mathbf{n}'} = \begin{cases} [1/(v_{\alpha\mathbf{n}})^{1/2}]\ \sin(k_{\alpha\mathbf{n}}R_\alpha-\ell_\alpha\pi/2)\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for open channels} \\ [1/(2v_{\alpha\mathbf{n}})^{1/2}]\ \exp(k_{\alpha\mathbf{n}}R_\alpha)\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'}\ , & \text{for closed channels} \end{cases} \tag{II-26c}$$

$$C_{\alpha\mathbf{n},\alpha'\mathbf{n}'} = \begin{cases} [-1/v_{\alpha\mathbf{n}}{}^{1/2}]\cos(k_{\alpha\mathbf{n}}R_\alpha-\ell_\alpha\pi/2)\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for open channels} \\ [1/(2v_{\alpha\mathbf{n}})^{1/2}]\exp(-k_{\alpha\mathbf{n}}R_\alpha)\ \delta_{\alpha,\alpha'}\ \delta_{\mathbf{n},\mathbf{n}'} & \text{for closed channels .} \end{cases} \tag{II-26d}$$

Then it can be shown (Appendix A) that the Green's functions are

$$\mathbf{G}^{o}(R,R') = \begin{cases} (2/\hbar^2)\mathbf{f}^{o}(R)\ \mathbf{w}_r^{-1}\ \mathbf{g}^{oT}(R') & \text{for } R' > R \quad , \quad \text{(II-27a)} \\ (2/\hbar^2)\mathbf{g}^{o}(R)\ (\mathbf{w}_r^{T})^{-1}\mathbf{f}^{oT}(R') & \text{for } R > R' \quad , \quad \text{(II-27b)} \end{cases}$$

where superscript T stands for transpose, and the matrix version of the Wronskian $\mathbf{w}_r$ of two solution $\mathbf{f}^{o}(R)$ and $\mathbf{g}^{o}(R)$ is defined by

$$\mathbf{w}_r \equiv \mathbf{f}^{o\prime T}(R)\ \mathbf{g}^{o}(R) - \mathbf{f}^{oT}(R)\ \mathbf{g}^{o\prime}(R) = \text{const. matrix} \quad , \qquad \text{(II- 28)}$$

where prime denotes the derivative with respect to R. It should be noticed that the Wronskian matrix is a constant matrix (for details, see Appendix A). Especially, for the choice of the boundary condition Eqs.(II-25) it is equal to the unit matrix. From Eqs.(II-24), (II-25) it is obvious that the regular solution of Eq.(II-19) for reactive scattering in the asymptotic region takes the form

$$\lim_{R\to\infty} \mathbf{f}(R) = \lim_{R\to\infty} \mathbf{f}^{o}(R) + \lim_{R\to\infty} \mathbf{g}^{o}(R)\ \mathbf{K}^{1}$$

$$= \mathbf{Si}(R) + \mathbf{C}(R)\ \mathbf{K}^{o} + \mathbf{C}(R)\ \mathbf{K}^{1}$$

$$= \mathbf{Si}(R) + \mathbf{C}(R)\ \mathbf{K} \quad , \qquad \text{(II-29a)}$$

with

$$\mathbf{K} \equiv \mathbf{K}^{o} + \mathbf{K}^{1} \quad , \qquad \text{(II-29b)}$$

where

$$\mathbf{K}^{1} = -(2/\hbar^2) \int dR \int dR' \int dR''\, \mathbf{f}^{oT}(R)$$
$$R\langle R \,|\, (\mathbf{I} + \tilde{\mathbf{S}} + \tilde{\mathbf{w}}\tilde{\mathbf{G}}^{o})^{-1} \,|\, R'\rangle R'\ \mathbf{w}(R',R'')\ \mathbf{f}^{o}(R'') \quad . \qquad \text{(II-29c)}$$

It is very crucial to find out a way to calculate $\mathbf{K}^1$. Our strategy is that first one expands the inverse matrix operator into a geometric series. Then all the integration is carried out by the trapezoidal rule, i.e., the approximation

$$\int dR_\alpha \, f(R_\alpha) \cong \Delta \sum_i f(R_{\alpha i}) \quad , \tag{II-30a}$$

$$I \equiv \int dR_\alpha \, R_\alpha |R_\alpha\rangle\langle R_\alpha| \, R_\alpha\rangle \simeq \Delta \sum_i R_{\alpha i} |R_{\alpha i}\rangle\langle R_{\alpha i}| \, R_{\alpha i} \quad , \tag{II-30b}$$

and

$$R_{\alpha i}\langle R_{\alpha i}|R_{\alpha i'}\rangle R_{\alpha i'} \simeq \frac{1}{\Delta} \delta_{i,i'} \tag{II-30c}$$

is used. Here Δ is the grid spacing. If Δ has a same value for all integrals in Eq.(II-29c), the $\mathbf{K}^1$ can be expressed as

$$\mathbf{K}^1 = -(2/\hbar^2)\, \mathbf{f}^{oT} (\Delta)^2 \, [\, \mathbf{I} + \sum_{k=1}^{\infty} (\Delta\, \mathbf{s} + (\Delta)^2\, \mathbf{w}\, \mathbf{G}^o)^k]\, \mathbf{w}\, \mathbf{f}^o$$

$$= -(2/\hbar^2)\, \mathbf{f}^o \, [\, \mathbf{I}/(\Delta)^2 + \mathbf{s}/\Delta + \mathbf{w}\, \mathbf{G}^o \,]^{-1} \, \mathbf{w}\, \mathbf{f}^o \quad , \tag{II- 31}$$

where $\mathbf{f}^o(R)$ is a matrix whose elements are

$$f^o_{i\alpha n, i'\alpha' n'} \equiv f^o_{\alpha n, \alpha' n'}(R_{\alpha i}, R_{\alpha i'})\, \delta_{\alpha,\alpha'} \quad , \tag{II-32a}$$

the elements of Green function matrix $\mathbf{G}^o$ are

$$G^o_{i\alpha n, i'\alpha' n'} \equiv G^o_{\alpha n, \alpha' n'}(R_{\alpha i}, R_{\alpha i'})\, \delta_{\alpha,\alpha'} \quad , \tag{II-32b}$$

the overlap matrix $\mathbf{s}$ is defined by

$$s_{i\alpha n,i'\alpha' n'} \equiv R_{\alpha i}\langle R_{\alpha i}|\tilde{\mathbf{S}}_{\alpha n,\alpha' n'}|R_{\alpha' i'}\rangle R_{\alpha' i'} \qquad \text{(II-32c)}$$

and the elements of $\mathbf{w}$ are given by

$$w_{i\alpha n,i'\alpha' n'} \equiv w_{\alpha n,\alpha' n'}(R_{\alpha i},R_{\alpha' i'}) \quad . \qquad \text{(II-32d)}$$

Thus, solving Eq.(II-20) with the boundary condition, Eqs.(II-25), for $\mathbf{f}^{o}(R)$, $\mathbf{g}^{o}(R)$ and $\mathbf{K}^{o}$, and using Eq.(II-31) to calculate $\mathbf{K}^{1}$, one can determine $\mathbf{K}$. Physically, we are only interested in the wavefunctions $\mathbf{f}_{oo}(R)$ corresponding to the open-open channels which in the asymptotic region are given by

$$\lim_{R\to\infty} \mathbf{f}_{oo}(R) \to \mathbf{Si}_{oo} + \mathbf{C}_{oo}\,\mathbf{K}_{oo} \quad , \qquad \text{(II- 33)}$$

where $\mathbf{Si}_{oo}$, $\mathbf{C}_{oo}$ and $\mathbf{K}_{oo}$ are open-open submatrices of matrices $\mathbf{Si}$, $\mathbf{C}$ and $\mathbf{K}$, respectively. Since $\mathbf{Si}_{oo}$ and $\mathbf{C}_{oo}$ are diagonal matrices, we have

$$(\mathbf{Si}_{oo})_{\alpha n,\alpha' n'} = (1/v_{\alpha n}^{1/2})\,\sin(k_{\alpha n}R_{\alpha}-\ell_{\alpha}\,\pi/2)\,\delta_{\alpha,\alpha'}\,\delta_{n,n'}$$

$$= [(\,1/\mathbf{v}^{1/2})\,\sin\,(\mathbf{kR} - \boldsymbol{\ell}\,\pi/2)]_{\alpha n,\alpha' n'} \quad , \qquad \text{(II-34a)}$$

$$(\mathbf{C}_{oo})_{\alpha n,\alpha' n'} = -\left(\frac{1}{v_{\alpha n}}\right)^{1/2}\cos(k_{\alpha n}R_{\alpha}-\ell_{\alpha}\pi/2)\,\delta_{\alpha,\alpha'}\,\delta_{n,n'}$$

$$= [(-\,1/\mathbf{v}^{1/2})\,\cos\,(\mathbf{kR} - \boldsymbol{\ell}\,\pi/2)]_{\alpha n,\alpha' n'} \quad , \qquad \text{(II-34b)}$$

or

$$\mathbf{Si}_{oo} = (\ 1/\mathbf{v}^{1/2})\ \sin\ (\mathbf{kR} - \boldsymbol{\ell}\ \pi/2) \quad , \tag{II-35a}$$

$$\mathbf{C}_{oo} = (-\ 1/\mathbf{v}^{1/2})\ \cos\ (\mathbf{kR} - \boldsymbol{\ell}\ \pi/2) \quad , \tag{II-35b}$$

where matrices $\mathbf{v}$, $\mathbf{kR}$ and $\boldsymbol{\ell}$ are all diagonal with elements

$$v_{\alpha\mathbf{n},\alpha'\mathbf{n}'} \equiv \delta_{\alpha,\alpha'}\delta_{\mathbf{n},\mathbf{n}'}\ v_{\alpha\mathbf{n}} \quad , \tag{II-36a}$$

$$(\mathbf{kR})_{\alpha\mathbf{n},\alpha'\mathbf{n}'} \equiv \delta_{\alpha,\alpha'}\delta_{\mathbf{n},\mathbf{n}'}\ k_{\alpha\mathbf{n}} \quad , \tag{II-36b}$$

$$\ell_{\alpha\mathbf{n},\alpha'\mathbf{n}'} \equiv \delta_{\alpha,\alpha'}\delta_{\mathbf{n},\mathbf{n}'}\ \ell_{\alpha} \quad . \tag{II-36c}$$

By using Eqs.(II-35), Eq.(II-33) becomes

$$\lim_{R\to\infty} \mathbf{f}_{oo}(R) \simeq (\ 1/\mathbf{v}^{1/2})\ \sin\ (\mathbf{kR} - \boldsymbol{\ell}\ \pi/2) - (1/\mathbf{v}^{1/2})\ \cos\ (\mathbf{kR} - \boldsymbol{\ell}\ \pi/2),$$

$$= (\ 1/\mathbf{v}^{1/2})\ \exp[-i(\mathbf{kR} + \boldsymbol{\ell}\ \pi/2)](\mathbf{K}_{oo} + i\mathbf{I})/2$$
$$- (\ 1/\mathbf{v}^{1/2})\ \exp[\ i(\mathbf{kR} + \boldsymbol{\ell}\ \pi/2)](\mathbf{K}_{oo} - i\mathbf{I})/2 \quad , \tag{II- 37}$$

or

$$\lim_{R\to\infty} \mathbf{f}_{oo}(R)\ 2i(\mathbf{I} - i\ \mathbf{k}_{oo})^{-1} \cong$$
$$(\ 1/\mathbf{v}^{1/2})\ \exp[-i(\mathbf{kR} + \boldsymbol{\ell}\ \pi/2)]$$
$$+ (\ 1/\mathbf{v}^{1/2})\ \exp[\ i(\mathbf{kR} + \boldsymbol{\ell}\ \pi/2)](\mathbf{I}+i\mathbf{K}_{oo})(\mathbf{I}-i\mathbf{K}_{oo})^{-1} \quad . \tag{II- 38}$$

On the other hand we know that the outgoing wavefunction satisfies the boundary condition :

$$\lim_{R\to\infty} \mathbf{f}^{+}(R) \sim (\ 1/\mathbf{v}^{1/2})\ \exp[-i(\mathbf{kR} + \boldsymbol{\ell}\ \pi/2)]$$

$$+ (1/v^{1/2}) \exp[i(kR + \ell \pi/2)] S \quad , \qquad \text{(II- 39)}$$

where S is the scattering matrix . Comparing Eq.(II-39) with Eq.(II-38) one obtains

$$f^{+}(R) = f_{oo}(R)\ 2i(I - iK_{oo})^{-1} \quad , \qquad \text{(II-40a)}$$

$$S = (I+iK_{oo})(I-iK_{oo})^{-1} \quad . \qquad \text{(II-40b)}$$

II.c) The distorted wave Born approximation (DWBA).

The distorted wave Born approximation basically is a first order quantum mechanical perturbation theory. In the threshold region of a chemical reaction with an activation barrier, the reactive cross section is small compared to the nonreactive cross section. In the formulation above the exchange kernel is the interaction "causing" the reaction. It is conceivable that the exchange kernel $\mathcal{V}_{ex}$ is small relative to the direct interaction $\mathcal{V}^{o}$ in the threshold region. Thus, one should be able to describe the tunneling behavior of the threshold region perturbatively in the framework developed above. Applying the DWBA to Eq.(II-11), i.e., using $\mathcal{V}_{ex}$ for $\mathcal{T}_{ex}$ gives

$$\tilde{u} \cong \tilde{u}^{o} + \tilde{G}^{o}\ \mathcal{V}_{ex}\ \tilde{u}^{o} \quad . \qquad \text{(II- 41)}$$

The corresponding approximate expression for the regular reactive radial wavefunction in the asymptotic region becomes

$$\lim_{R\to\infty} f(R) \sim Si(R) + C(R)\ K^{o} + C(R)\ K^{1}_{DWBA}$$

$$= \mathbf{S}i(R) + \mathbf{C}(R)\ \mathbf{K}^{DWBA} \quad , \tag{II-42a}$$

where

$$\mathbf{K}^{DWBA} \equiv \mathbf{K}^{\circ} + \mathbf{K}^{1}{}_{DWBA} \quad , \tag{II-42b}$$

with

$$\mathbf{K}^{1}_{DWBA} = \mathbf{f}^{\circ T}\ \mathbf{w}\ \mathbf{f}^{\circ} \quad . \tag{II-42c}$$

Then, the corresponding DWBA scattering matrix S^{DWBA} reads

$$\mathbf{S}^{DWBA} \simeq (\mathbf{I} + i\ \mathbf{K}^{DWBA}_{oo})(\mathbf{I} - i\ \mathbf{K}^{DWBA}_{oo})^{-1}$$

$$=[(\mathbf{I} + i\ \mathbf{K}^{\circ}_{oo} + i\ (\mathbf{K}^{1}{}_{DWBA})_{oo}]\ [\mathbf{I} - i\ \mathbf{K}^{\circ}_{oo} - i\ (\mathbf{K}^{1}{}_{DWBA})_{oo}]^{-1}$$

$$\simeq (\mathbf{I}+i\mathbf{K}^{\circ}_{oo})(\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1} + i\ (\mathbf{K}^{1}{}_{DWBA})_{oo}\ (\mathbf{I}-i\mathbf{K}^{\circ}_{oo})^{-1}$$

$$+ i\ (\mathbf{I}+i\mathbf{K}^{\circ}_{oo})(\mathbf{I}-i\mathbf{K}^{\circ}_{oo})^{-1}\ (\mathbf{K}^{1}{}_{DWBA})_{oo}\ (\mathbf{I} - i\ \mathbf{K}^{\circ}_{oo})^{-1}$$

$$= \mathbf{S}^{\circ} + \mathbf{S}^{DWBA}_{r} \quad , \tag{II-43a}$$

where the terms which are higher than quadratic in $\mathbf{K}^{DWBA}_{oo}$ have been neglected,

$$\mathbf{S}^{\circ} \equiv (\mathbf{I}+i\mathbf{K}^{\circ}_{oo})(\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1} \tag{II-43b}$$

is a non-reactive scattering matrix, and $\mathbf{S}^{DWBA}_{r}$ is a DWBA reactive scattering matrix

$$\mathbf{S}^{DWBA}_{r} \equiv 2i\ (\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1}\ (\mathbf{K}^{1}_{DWBA})_{oo}\ (\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1}$$

$$= 2i\ (\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1}\ (\mathbf{f}^{\circ T}\ \mathbf{w}\ \mathbf{f}^{\circ})_{oo}\ (\mathbf{I}-\mathbf{K}^{\circ}_{oo})^{-1} \qquad . \quad \text{(II-43c)}$$

II.d) Sample calculation ----- H + H_2 collinear reactive scattering.

To explore the use of this approach for reactive scattering we apply the formalism developed above to the standard test problem --- the collinear H + H_2 reaction on the Porter-Karplus potential energy surface (16).

In the collinear case there are only two arrangements. It is straightforward to obtain the formalism for collinear A + BC reaction. The unity identity reads as

$$\mathbf{I} \equiv \int dR\ |R\rangle\langle R| \ ,$$

with

$$(\int dR|R\rangle\langle R|)_{\alpha n,\alpha' n'} \equiv (\int dR_\alpha\ |R_\alpha\rangle\langle R_\alpha|)\delta_{\alpha,\alpha'}\delta_{n,n'}$$

$$\simeq (\ \Delta \sum_i |R_{\alpha i}\rangle\langle R_{\alpha i'}|)\delta_{\alpha,\alpha'}\delta_{n,n'} \qquad . \qquad \text{(II-44b)}$$

The wavefunctions $\mathbf{u}(R)$ are

$$u_{\alpha n,\alpha' n'}(R) \equiv \langle R_\alpha|u_{\alpha n,\alpha' n'}\rangle \qquad ; \qquad \text{(II-45a)}$$

and the non-reactive wavefunctions $\mathbf{u}^{o}$ are

$$u^{o}_{\alpha n,\alpha' n'}(R) \equiv \langle\ R_\alpha\ |u^{o}_{\alpha n,\alpha' n'}\rangle \qquad . \qquad \text{(II-45b)}$$

The Green's functions take the form

$$G^{o}_{\alpha n,\alpha' n'}(R,R') \equiv \langle R_\alpha|\ \tilde{\mathbf{G}}^{o}_{\alpha n,\alpha' n'}|R'_{\alpha'}\rangle \qquad ; \qquad \text{(II-45c)}$$

the direct interaction potential matrix $\mathbf{V}^{o}(R)$ has the elements

$$V^{o}_{\alpha n,\alpha' n'}(R) \equiv \langle\phi^{\alpha}_{n}|V(R_{\alpha}) - v_{\alpha}|\phi^{\alpha}_{n'}\rangle\ \delta_{\alpha,\alpha'} \quad , \tag{II-45d}$$

the elements of the exchange kernel $\mathbf{V}_{ex}(R,R')$ are

$$V_{ex\ \alpha n,\alpha' n'}(R,R') \equiv \langle R_{\alpha}|\langle\phi^{\alpha}_{n}|H - E_{o}|\phi^{\alpha'}_{n'}\rangle|R'_{\alpha'}\rangle\ [1 - \delta_{\alpha,\alpha'}] \ ; \tag{II-45e}$$

Corresponding to Eq.(II-32c) and Eq.(II-32d), the elements of the overlap matrix $\mathbf{s}$ are

$$s_{i\alpha n,i'\alpha' n'} \equiv \langle R_{\alpha i}\ |\langle\phi^{\alpha}_{n}|\ \phi^{\alpha'}_{n'}\rangle|R_{\alpha' i'}\rangle(1 - \delta_{\alpha,\alpha'})$$

$$= c\ \phi^{\alpha}_{n}(r_{\alpha i})\ \phi^{\alpha'}_{n'}(r_{\alpha' i'})\ (1 - \delta_{\alpha,\alpha'}) \tag{II-45f}$$

with

$$c \equiv \frac{dr_{\alpha}}{dR_{\alpha'}}\ ,\ r_{\alpha i} = r_{\alpha}(R_{\alpha i}\ ,\ R_{\alpha' i'}\ ),\quad r_{\alpha' i'} = r_{\alpha'}(R_{\alpha i},R_{\alpha' i'}\ ) \quad , \tag{II-45g}$$

and the elements of the $\mathbf{w}$ matrix are

$$w_{i\alpha n,i'\alpha' n'} = [\ \langle R_{\alpha i}|\langle\phi^{\alpha}_{n}|(V - v_{\alpha'})|\phi^{\alpha'}_{n'}\rangle|R_{\alpha' i'}\rangle$$

$$- \sum_{n''}\langle R_{\alpha i}|\langle\phi^{\alpha}_{n}|\phi^{\alpha''}_{n''}\rangle\ \langle\phi^{\alpha''}_{n''}|V - v_{\alpha'}]|\phi^{\alpha'}_{n'}\rangle|R'_{\alpha'}\ \rangle]\ (1 - \delta_{\alpha,\alpha'})$$

$$= c\ \phi^{\alpha}_{n}(r_{\alpha i})[(V - v_{\alpha'})\phi^{\alpha'}_{n'}(r_{\alpha' i'}) - \sum_{n''}\ \phi^{\alpha''}_{n''}(r_{\alpha' i'})\langle\phi^{\alpha''}_{n''}|V - v_{\alpha'}|\phi^{\alpha'}_{n'}\rangle]$$

$$\times\ (\ 1 - \delta_{\alpha,\alpha'}\ ) \quad , \tag{II-45h}$$

where $|\phi^{\alpha}_{n}\rangle$ is the vibrational eigenvectors of diatomic molecule. Eq.(II-20) and Eq.(II-21) are solved numerically for the nonreactive

wavefunction, $f^o(R)$, $g^o(R)$ and Green's functions, $G^o(R,R')$, with the boundary conditions

$$f^0(0) = 0, \lim_{R\to\infty} f^0(R) \to \mathbf{Si}(R) + \mathbf{C}(R)\,\mathbf{K}^0 , \lim_{R\to\infty} g^0(R) \to \mathbf{C}(R) \quad ,$$

and (II-46a)

$$\mathbf{G}^o(R,R') = 0, \lim_{R\to\infty} \mathbf{G}^o(R,R') = \text{real} \quad , \tag{II-46b}$$

where the elements of matrices $\mathbf{Si}(R)$ and $\mathbf{C}(R)$ are

$$Si_{\alpha n,\alpha' n'}(R) = \begin{cases} \{\sin k_{\alpha n} R_\alpha / v_{\alpha n}^{1/2}\}\, \delta_{\alpha,\alpha'}\, \delta_{n,n'} & \text{for open channel,} \\ \{\exp[k_{\alpha n} R_\alpha/(2v_{\alpha n})^{1/2}]\}\, \delta_{\alpha,\alpha'}\delta_{n,n'} & \text{for closed channel,} \end{cases} \tag{II-47a}$$

and

$$C_{\alpha n,\alpha' n'}(R) = \begin{cases} \{\cos k_{\alpha n} R_\alpha / v_{\alpha n}^{1/2}\}\, \delta_{\alpha,\alpha'}\, \delta_{n,n'} & \text{for open channel,} \\ \{\exp[-k_{\alpha n} R_\alpha/(2v_{\alpha n})^{1/2}]\}\, \delta_{\alpha,\alpha'}\delta_{n,n'} & \text{for closed channel,} \end{cases}$$

with (II-47b)

$$k_{\alpha n} = [2\mu_\alpha(E_o - \varepsilon_n^\alpha)]^{1/2}/\hbar, \qquad v_{\alpha n} = \hbar k_{\alpha n}/\mu_\alpha, \tag{II-47c}$$

where ε_n^α is the vibrational energy corresponding to the state $|\phi^\alpha{}_n\rangle$ in arrangement α. The transition matrix S, then, can be calculated by using Eq.(II-40b) and Eq.(II-31).

One might expect that the Green's function matrix $\mathbf{G}^o(R,R')$ could be readily calculated, since one could use the well developed methods for non-reactive scattering to calculate the non-reactive scattering wavefunction $\mathbf{f}(R)$ and $\mathbf{g}(R)$. In practice, however, no methods seem available for computing the $\mathbf{f}(R)$ and $\mathbf{g}(R)$ accurate enough that one could

calculate the Greens's matrix $\mathbf{G}^{o}(R,R')$ with reasonable accuracy. The basic difficulty comes from the exponential growing and decaying wavefunction for closed channels in $\mathbf{f}(R)$ and $\mathbf{g}(R)$. To avoid this difficulty one could put $\mathbf{G}^{o}(R,R')$ in another form which only involves the log-derivative matrices and the ratio matrices (for details, see appendix B), then many numerical methods for non-reactive scattering become applicable in calculating the Green's matrix $\mathbf{G}^{o}(R,R')$. Two numerical mathods--the renormalized Numerov method[7] and the method for integrating the coupled second order ordinary differential equations, i.e., the trajectory integrator program[17]-- have been used. It is found that the Numerov method is much more efficient than the normal integrator. For the same accuracy the former is about forty times faster than the latter. All results presented here are obtained by using the renormalized Numerov method described in Appendix B.

II.e) Results and discussion.

The calculations for the collinear $H+H_2$ reaction on the Porter-Karplus potential energy surface have been carried out by using both the exact and the DWBA formalism. Table II.1 and Table II.2 give the DWBA and exact results for various numbers of channels (i.e., vibrational states) used in the expansion for the non-reactive scattering wavefunctions. For comparison the results of other exact quantum calculations[18] are also included in Table II.1 and Table II.2.

The most important feature seen in Table II.1 and Table II.2 is that the results converge quickly with respect to the number of channels in term which the non-reactive wavefunction is expanded. In the low

energy region ($E^o <$ 0.4546ev), where the reactive transition probabilities are less than 0.1, the DWBA version gives excellent results in contrast to other DWBA reactive scattering calculations[19-26] which often seemed to give poor results for the reactive probabilities. The basic reason is that in their calculations the distorted wavefunction essentially described only elastic scattering in each arrangement, while our distorted wave function is the non-reactive scattering wavefunction which includes inelastic as well as elastic scattering wavefunctions. One might be confused by the apparently unreasonable result that the DWBA values are better than the exact values in the low energy region. There are two reasons for that. First, although the procedure for obtaining the non-reactive wavefunction are the same in both the exact and DWBA versions, in the exact version one has to invert a huge matrix, $\mathbf{M}^{-1} \equiv (\frac{1}{\Delta^2} + \frac{\mathbf{s}}{\Delta} + \mathbf{w}\,\mathbf{G}^o)^{-1}$,or more precicely, to calculate $\mathbf{M}^{-1}\mathbf{w}$. Fortunately, $\mathbf{w}$ and $\mathbf{s}$ both are short range matrices in R. That is, if one divides the grids along R into two parts: the short range part P and the long range part Q, then in terms of the grid points in R the matrices $\mathbf{s}$, $\mathbf{w}$ and $\mathbf{G}^o$ can be approximately written as

$$\mathbf{w} \simeq \begin{pmatrix} \mathbf{w}_{PP} & 0 \\ 0 & 0 \end{pmatrix} , \quad \mathbf{s} \simeq \begin{pmatrix} \mathbf{s}_{PP} & 0 \\ 0 & 0 \end{pmatrix} , \text{ and } \mathbf{G}^o = \begin{pmatrix} \mathbf{G}_{PP} & \mathbf{G}_{PQ} \\ \mathbf{G}_{QP} & \mathbf{G}_{QQ} \end{pmatrix} \qquad \text{(II- 49)}$$

Since $\mathbf{w}$ only has the block $\mathbf{w}_{PP}$, one only needs calculate $(\mathbf{M}^{-1})_{PP}$. By using Eq.(II-49) it is easy to show that

$$\mathbf{M}^{-1}\mathbf{w} \simeq (\mathbf{M}^{-1})_{PP}\mathbf{w}_{PP} \quad , \qquad \text{(II-50a)}$$

and

$$(\mathbf{M}^{-1})_{PP} = \left(\frac{1}{\Delta^2} + \frac{\mathbf{s}_{PP}}{\Delta} + \mathbf{w}_{PP}\,\mathbf{G}^o_{PP} \right)^{-1} \quad , \qquad \text{(II-50b)}$$

All the exact results presented here are calculated by using Eqs.(II-50) in which the short range P is about 40% of the whole range. However, it should be pointed out that Eq.(II-50a) is only an approximation. In the low energy region $\mathbf{w}_{PP}$ itself is small, thus, one has to extend the region P over the whole range to obtain accurate results. Due to the limitation of the computer capacity such a whole range computation has not been done yet. On the other hand, in the DWBA calculations the whole range matrix $\mathbf{w}$ is used. Second, in exact calculation the trapezoidal rule has been used in the integrations, while in the DWBA calculations the Simpson's rule was used.

In the middle energy region ($0.8ev > E_o > 0.4546$ ev) the exact version works very well, while the DWBA version begins to fail as one knows it must. This shows up in the present calculations by a lack of convergence in the reaction probability as the number of channels in the non-reactive distorted wavefunction is increased. For the exact calculation in the high energy region ($E_o > 0.8ev$), where more than two channels are open, the number of grid points and the number of channels in the non-reactive wavefunctions required for obtaining converged results increase. This is an undesirable flaw, since the computing time is approximately proportional to the cube of the product of the number of grid points and the number of channels. Nevertheless, this approach is very general, straightforward and easy to implement.

III. The semiclassical perturbation (SCP) theory in dynamic calculations of polyatomic system.

III.a) Introduction

As one has seen from the discussion above, the exact quantum calculations for inelastic and reactive molecular collision processes requires rather substantial amount of computational labor even for the simplest nontrivial case of A + BC collinear collision. For a large molecule, such as a small hydrocarbon, even approximately solving Schrödinger's equation is still an intractable problem. Semiclassical mechanics-- e.g., multidimensional WKB methods like the classical S-matrix theory [27]-- in principle, provides an appealing alternative approach, since it combines the computational simplicity of classical mechanics with an approximate description of quantum effects. In practice, however, for a polyatomic system the exact semiclassical mechanics approach also is too involed to implement. Besides the difficulty with the dynamical calculation the enormous ab initio quantum chemistry calculation required for a polyatomic system makes it impossible to determine the complete potential energy surface needed.

In light of the great difficulties encountered in exact calculation, in this chapter we explore the application of the semiclassical perturbation theory in the dynamics of polyatomic molecule. It is our hope that the approximate semiclassical theory combined with the approximate interaction models for a polyatomic system would lead to a simple and amenable formalism by which one would be able to obtain a reasonably good understanding of the dynamics of the system of our interest, i.e., the quantities which characterize the dynamic

processes are all quantitatively obtainable in a ab initio , but simple and straightforward way.

III.b) The semiclassical perturbation approximation for the classical S-matrix

The formalism of the first order perturbation approximation to the initial value representation[28] of the classical S-matrix theory for a very general class of potential interaction has been discussed by Miller and Smith[29]. Here we generalize the formalism to the more general cases where there is kinetic coupling as well as potential interaction.

Consider a system of F degrees of feedom. The classical Hamiltonian of the system reads

$$H(P_s,s,\mathbf{n},\mathbf{q}) = \frac{P_s^2}{2\mu} + V_o(s) + \varepsilon(\mathbf{n}, s) + H_1(P_s,s,\mathbf{n},\mathbf{q})$$

$$\equiv H_o(P_s,s,\mathbf{n}) + H_1(P_s,s,\mathbf{n},\mathbf{q}) \quad , \qquad \text{(III- 1a)}$$

with

$$H_o \equiv \frac{P_s^2}{2\mu} + V_o(s) + \varepsilon(\mathbf{n},s) \quad , \qquad \text{(III- 1b)}$$

where (P_s,s) are the coordinate and momentum for a special degree of freedom (e.g., the reaction coordinate), μ is the reduced mass related to the motion s, $\varepsilon(\mathbf{n},s)$ and $(\mathbf{n},\mathbf{q}) = \{(n_i,q_i)\}$, $i=2,\ldots,F$, are the Hamiltonian and the action- angle variables for the remaining F-1 degrees of freedom. The initial value representation for the classical S-matrix is given by[28]

$$S_{\mathbf{n}_1\ \mathbf{n}_2} = \int_0^{2\pi} \frac{d\mathbf{q}}{(2\pi)^{F-1}} \left[\frac{\partial \mathbf{q}_2(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1}\right]^{1/2} \exp i\{\Phi(\mathbf{q}_1,\ \mathbf{n}_1)$$

$$+ \mathbf{q}_2\ (\mathbf{q}_1,\mathbf{n}_1)[\ \mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1) - \mathbf{n}_2]\}, \qquad \text{(III- 2a)}$$

with

$$\mathbf{q} = \mathbf{q} - \mathbf{q}_o^o \quad , \qquad \text{(III- 2b)}$$

where $\mathbf{q}_o^o$ is the zeroth order values of the angle variables $\mathbf{q}$ defined below (Eq.III-5)), $\mathbf{q}_2(\mathbf{q}_1,\mathbf{n}_1)$ and $\mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1)$ are the final values of variables $\mathbf{q}$ and $\mathbf{n}$ determined by the classical trajectory with the initial values $\mathbf{q}_1$ and $\mathbf{n}_1$, and the action $\Phi(\mathbf{q}_1,\mathbf{n}_1)$ is more precisely designated by

$$\Phi(\mathbf{q}_1,\mathbf{n}_1) = \Phi[\mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1),\mathbf{n}_1]. \qquad \text{(III- 3)}$$

The zeroth order values P_s^o, s^o, q^o and $\mathbf{n}^o$ are determined by the zeroth order Hamiltoninan, i.e.,

$$\dot{\mathbf{n}}^o = 0 \ , \ \mathbf{n}^o(t) = \mathbf{n}_1 \quad , \qquad \text{(III- 4a)}$$

$$\dot{\mathbf{q}}^o = -\frac{\partial \varepsilon(\mathbf{m}^o, s^o)}{\partial\ \mathbf{n}^o} = \boldsymbol{\omega}(s^o), \quad \mathbf{q}^o = \int_{t_o}^{t} \omega[s^o(t')]\ dt' + c, \qquad \text{(III- 4b)}$$

$$\dot{S}^o = \frac{\partial H^o}{\partial P_s^o} = P_s^o \ , \ \dot{P}_s^o = -\frac{\partial H^o}{\partial s} \quad . \qquad \text{(III- 4c)}$$

If we choose c = 0, then one obtains

$$q_o^o = \int_{t_o}^{t} \omega[s\ (t')]\ dt' \ . \qquad \text{(III- 5)}$$

From Eq.(III-2b) and Eq.(III-4b) it is obvious that to zeroth order, $\mathbf{q}$

are the constants, i.e.,

$$\mathbf{q}^{o} = q^{o} - q_{o}^{o} = \text{const.} = \mathbf{q}_1{}^{o} \quad ,$$

and thus (III- 6a)

$$\mathbf{q}^{o} = \mathbf{q}_1 + q_{o}^{o} = \mathbf{q}_1 + \int_{t_o}^{t} dt' \; \omega[s(t')]. \tag{III- 6b}$$

If we treat H_1 as a small perturbation relative to H_o, then to first order $\mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1)$ is given by

$$\mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1) = \mathbf{n}_1 + \int_{t_1}^{t_2} dt \; \mathbf{n} = \mathbf{n}_1 + \int_{t_1}^{t_2} dt \; \left(-\frac{\partial H}{\partial \mathbf{q}_1}\right)$$

$$\simeq \mathbf{n}_1 - \int_{t_1}^{t_2} dt \; \frac{\partial H_1 \{s^{o}(t'),P_s^{o}(t'),\mathbf{q}_1 + \int_{t_1}^{t_2} dt' \; \omega[s^{o}(t')],\mathbf{n}_1\}}{\partial \mathbf{q}_1}$$

$$= \mathbf{n}_1 - \frac{\partial \Delta\Phi}{\partial \mathbf{q}_1} \quad , \tag{III- 7a}$$

with

$$\Delta\Phi(\mathbf{q}_1^{o},\mathbf{n}_1) = \int_{t_1}^{t_2} dt \; H_1 \{s^{o}(t'),P_s^{o}(t'),\; \mathbf{q}_1 + \int_{t_o}^{t} \omega[s^{o}(t')] \; dt',\mathbf{n}_1\}. \tag{III- 7b}$$

The derivative of the action integral $\Phi(\mathbf{q}_1,\mathbf{n}_1)$ with respect to $\mathbf{q}_1$ is given by

$$\frac{\partial \Phi(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1} = -\, \mathbf{q}_2(\, \mathbf{q}_1,\mathbf{n}_1) \; \frac{\partial \mathbf{n}_2(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1} = \mathbf{q}_1 \frac{\partial^2 \Delta\Phi(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1^2} \; , \tag{III- 8}$$

where $\mathbf{q}_2$ is determined only to zeroth order:

$$\mathbf{q}_2(\mathbf{q}_1,\mathbf{n}_1) \simeq \mathbf{q}_1. \tag{III- 9}$$

Integrating Eq.(III-8) gives

$$\Phi(\mathbf{q}_1,\mathbf{n}_1) = \Phi_o + \int d\mathbf{q}_1 \; \mathbf{q}_1 \frac{\partial^2 \Delta\Phi(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1^2}$$

$$= \Phi - \Delta\Phi(\mathbf{q}_1,\mathbf{n}_1) + \mathbf{q}_1 \frac{\partial^2 \Delta\Phi(\mathbf{q}_1,\mathbf{n}_1)}{\partial \mathbf{q}_1^2} , \qquad \text{(III- 10)}$$

where Φ_o is the value of $\Phi(\mathbf{q}_1,\mathbf{n}_1)$ if $H_1 = 0$, i.e., Φ_o is the zeroth order WKB phase shift

$$\Phi_o = -sP_s^o\Big|_{s_1}^{s_2} + \int P_s^o(s)\, ds \quad . \qquad \text{(III- 11)}$$

Substituting Eq.(III-9),Eq.(III-10) and Eq.(III-7a) into the initial value representation Eq.(III-2a) one obtains

$$S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1} = e^{i\Phi_o} \frac{1}{(2\pi)^{F-1}} \int_0^{2\pi} d\mathbf{q}_1 e^{-i(\mathbf{n}_2 - \mathbf{n}_1)\mathbf{q}_1} e^{-i\Delta\Phi(\mathbf{q}_1,\mathbf{n}_1)} \quad . \qquad \text{(III- 12)}$$

As it stands, the S-matrix in Eq.(III-12) is not symmetric (as the exact S-matrix is) and it can be symmetrized in following way:

$$n_1 \longrightarrow \frac{1}{2}(n_1 + n_2) = n \quad . \qquad \text{(III- 13)}$$

The symmetrized version of the perturbation approximation of the classical S-matrix thus reads

$$S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1} = e^{i\Phi_o} \int_0^{2\pi} \frac{d\mathbf{q}_1}{(2\pi)^{F-1}} e^{-i\Delta\mathbf{n}\mathbf{q}_1} e^{-i\Delta\Phi(\mathbf{q}_1,\mathbf{n})} \qquad \text{(III-14a)}$$

with

$$\Delta\mathbf{n} = \mathbf{n}_1 - \mathbf{n}_2 , \qquad \text{(III-14b)}$$

$$\Delta\Phi(\mathbf{q}_1, \mathbf{n}_1) = \int_{t_1}^{t_2} dt\ H_1\{s^o(t'), P_s^o(t'), \mathbf{q}_1 + \int_{t_o}^{t} dt\ \omega[s^o(t')], \mathbf{n}\} \quad , \tag{III-14c}$$

where $s^o(t)$ and $P_o^o(t)$ are determined by Eq.(III-4c).

III.c) The semiclassical perturbation (SCP) reaction path model

As already mentioned, to obtain a complete potential surface for a polyatomic system is an unfeasable task. However, the advance in <u>ab initio</u> quantum chemistry has provided us with the methods for the accurate and efficient calculation of the gradient of a potential energy surface[30]. This has made it feasable to determine the reaction path on a potential surface. This is the path of steepest descent (if mass-weighted coordinates are used) from a saddle point on the potential surface to various minima

The reaction path Hamiltonian model developed by Miller, Handy and Adams[31] is based on the reaction path and a harmonic approximation to the potential surface about it. The model states that a classical Hamiltonian for a general non-rotating molecular system can be constructed as

$$H(P\ ,s,n,q) =$$

$$\frac{\frac{1}{2}\left\{ P_s - \sum_{k,k'=2}^{F} B_{k,k'}(s)\ [(2n_k+1)(2n_{k'}+1)]^{1/2}\ \left(\frac{\omega_{k'}(s)}{\omega_k(s)} \sin q_k \cos q_{k'}\right)\right\}^2}{\left[\ 1 + \sum_{k=2}^{F} B_{k,1}\ (s)\ \left(\frac{2n_k+1}{\omega_k(s)}\right)^{1/2} \sin q_k\right]^2}$$

$$+ V_o(s) + \sum_{k=2}^{F} (n + 0.5)\ \omega_k(s) \quad , \tag{III-15a}$$

where $F = 3N-6$ with N being the number of atoms of the system; (s,P_s) are the reaction coordinate along the reaction path and the conjugate momentum; $(\mathbf{n},\mathbf{q})$, $k=2,\ldots, F$, are the action-angle variables for the normal modes of vibrations normal to the reaction path with the frequencies ω_k, which are functions of the reaction coordinate s; $V_o(s)$ is the potential energy along the reaction path; the coupling elements $B_{k,k'}(s)$ for $k \neq k'$ describe the coupling between the (F-1) vibrational modes induced by motion along the reaction coordinate, and $B_{k,1}(s)$ couples vibrational mode k to the reaction coordinate (which is designated mode k = 1). The coupling elements $B_{k,1}(s)$ are a measure of how the curvature of the reaction path couples to mode k. The total curvature of the reaction path κ is related to these elements by[29]

$$\kappa(s) = [\sum_{k=2}^{F} B_{k,1}(s)^2]^{1/2} \quad . \qquad \text{(III-15b)}$$

The coupling elements $B_{k,k}(s)$ are due to the change of the frequencies of normal modes along the reaction path:

$$B_{k,k}(s) \equiv -\frac{\omega_k'(s)}{2\omega_k(s)} \quad , \qquad \text{(III- 16)}$$

where the prime denotes the derivative with respect to s. The coupling functions as well as $v_o(s)$ and $\{\omega_k(s)\}$, $k=2,\ldots, F$, are obtainable from the <u>ab initio</u> quantum chemistry calculation of the reaction path and the force constant matrix along it[31]. The Hamiltonian for nonzero total angular momentum has also been derived[31] ,but it is more complicated.

If all the coupling elements are small, the reaction path Hamiltonian Eq.(III-21) can be approximated to first order as

$$H(P_s,s,\mathbf{n},q) \simeq H_o(P_s,s,\mathbf{m}) + H_1(P_s,s,\mathbf{n},q) \ , \qquad \text{(III-17a)}$$

with

$$H_o(P_s,s,\mathbf{n}) = \frac{1}{2} P_s^2 + \sum_{k=2}^{F} (n_k + \frac{1}{2}) \, \omega_k(s) + V_o(s) \ , \qquad \text{(III-17b)}$$

and

$$H_1(P_s,s,\mathbf{m},\mathbf{q}) = - P_s^2 \sum_{k=2}^{F} B_{k,1}(s) \left(\frac{2n_k + 1}{\omega_k(s)} \right)^{1/2} \sin q_k$$

$$- P_s \sum_{k,k'=2}^{F} B_{k,k'}(s) \left[(2n_k+1)(2n_{k'}+1) \frac{\omega_{k'}(s)}{\omega_k(s)} \right]^{1/2} \sin q_k \cos q_{k'} \ . \qquad \text{(III-17c)}$$

Now we apply the semiclassical perturbation formula Eq.(III-14) to the approximate reaction path Hamiltonian Eqs.(III-17). First, we rewrite Eq.(III-14c) as

$$\Delta\Phi(\mathbf{q}_1,\mathbf{m}) = \int_{t_1}^{t_2} dt \ H_1 = \int_{s_1}^{s_2} \frac{ds}{\dot{s}} H_1 \ . \qquad \text{(III- 18)}$$

It is necessary to determine $\dot{s}$ and P_s only to zeroth order by Eqs.(III-4):

$$\dot{s} = \frac{\partial H}{\partial P_s} = P_s \simeq \frac{\partial H_o}{\partial P_s} = \pm \{ 2[E - V_a(s)] \}^{1/2} \equiv \pm \left| P_s^o \right| \ , \qquad \text{(III-19a)}$$

and

$$q_{ok}^o = \int_{t_o}^{t} \omega_k[s(t')] \, dt' \simeq \int_{s_o}^{s} \frac{\omega_k(s)}{\pm |P_s^o|} ds \ , \qquad \text{(III-19b)}$$

with

$$V_a(s) = \sum_{k=2}^{F} (n_k + \frac{1}{2}) \, \omega_k(s) - V_o(s) \ , \qquad \text{(III-19c)}$$

where $V_a(s)$ is the vibrationally adiabatic potential. By using Eqs.(III-18)-(III-19) in Eq.(III-14) the semiclassical perturbation expression for the classical S-matrix reads

$$S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1}(E) = \frac{e^{i\Phi_o}}{(2\pi)^{F-1}} \int_0^{2\pi} d\mathbf{q} \exp\{ -i\, \Delta\mathbf{n}\, \mathbf{q}$$

$$+ i \int_{-\infty}^{\infty} ds\, |P_s^o(s)| \sum B_{k,l}(s) \left(\frac{2n_k+1}{\omega_k(s)} \right)^{1/2} \sin(q_k + q_{ok}^o)$$

$$+ \sum_{k,k'=2}^{F} B_{k,k'}(s) \left[(2n_k+1)(2n_{k'}+1) \frac{\omega_{k'}(s)}{\omega_k(s)} \right]^{1/2} \sin(q_k + q_{ok}^o) \cos(q_{k'} + q_{ok'}^o) \Big] , \tag{III-20a}$$

where

$$\Phi_o = - P_s^o(s)\, s \Big|_{s_1}^{s_2} + \int_{s_1}^{s_2} ds\, P_s^o(s) \quad \text{with } s_2 \longrightarrow \infty ,\ s_1 \longrightarrow -\infty . \tag{III-20b}$$

If one negelects the coriolis coupling $B_{k,k'}(s)$ (they are often less significant than the curvature couplings $B_{k,l}(s)$ and the frequency couplings $B_{k,k}(s)$), the S-matrix given by Eq.(III-31) takes an especially simple form:

$$S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1}(E) = e^{i\Phi_o} \prod_{k=2}^{F} \Big\{ \int_0^{2\pi} \frac{dq_k}{2\pi}\, e^{-i\Delta n_k q_k}\, e^{i|\gamma_k| \sin(q_k + \delta_k)}$$

$$\times\, e^{i|\beta_k| \sin(2q_k + \eta_k)} \Big\} , \tag{III-21a}$$

where

$$\gamma_k = \int_{-\infty}^{\infty} ds\, |P_s^o(s)|\, B_{k,l}(s) \left[\frac{2n_k+1}{\omega_k(s)} \right]^{1/2} e^{iq_{ok}^o} , \tag{III-21b}$$

$$\beta_k = \int_{-\infty}^{\infty} ds\, (n_k + 1/2)\, B_{k,k}(s)\, e^{i2q_{ok}^o} , \tag{III-21c}$$

and

$$\delta_k = \arg(\gamma_k), \qquad \eta_k = \arg(\beta_k) . \tag{III-21d}$$

Introducing the identities

$$1 = \sum_{m=-\infty}^{\infty} \int_0^{2\pi} dQ_k \; \delta(Q_k - 2q_k - 2m\pi) \qquad \text{for } 0 < q_k < 2\pi \,, \tag{III-22a}$$

$$\sum_{m=-\infty}^{\infty} \delta(Q_k - 2q_k - 2\pi m) = \sum_{m=-\infty}^{\infty} \frac{1}{2\pi} \sum_{\ell=-\infty}^{\infty} \exp[-i\ell_k(Q_k - 2q_k)] \,, \tag{III-22b}$$

and interchanging the order of summation and integration, one can integrate Eq.(III-21a):

$$S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1}(E) = e^{i\Phi_o} \prod_{k=2}^{F} \Big\{ \sum_{\ell_k=-\infty}^{\infty} \int_0^{2\pi} \frac{dq_k}{2\pi} e^{-i(\Delta n_k - 2\ell_k)q_k} e^{i|\gamma_k|\sin(q_k+\delta_k)}$$

$$\times \int_0^{2\pi} \frac{dQ_k}{2\pi} e^{-i\ell_k Q_k} e^{i|\beta_k|\sin(Q_k + \eta_k)} \Big\}$$

$$= e^{i\Phi_o} \prod_{k=2}^{F} e^{i\Delta n_k \delta_k} \Big\{ \sum_{\ell_k=-\infty}^{\infty} \exp[-i\ell_k(\delta_k - 2\eta_k)] \, J_{\Delta n_k - 2\ell_k}(|\gamma_k|) \, J_{\ell_k}(|\beta_k|) \Big\} \,, \tag{III- 23}$$

where $J_{\Delta n_k - 2\ell_k}$ and $J_{\ell k}$ are the regular Bessel functions. Then the transition probability is given by

$$P_{\mathbf{n}_2 \leftarrow \mathbf{n}_1}(E) = \prod_{k=2}^{F} \Big| \sum_{\ell_k=-\infty}^{\infty} \exp[-i\ell_k(\delta_k - 2\eta_k)] \, J_{\Delta n_k - 2\ell_k}(|\gamma_k|) \, J_{\ell_k}(|\beta_k|) \Big|^2 \,, \tag{III- 24}$$

where $J_{\Delta n_k}$ is the regular Bessel function.

If $\omega_k' = 0$, i.e., $B_{k,k} = 0$, then $\beta_k = 0$, so that only the term with $\ell_k = 0$ contributes to the sum, and one has

$$P_{\mathbf{n}_2 \leftarrow \mathbf{n}_1} = \prod_{k=2}^{F} |J_{\Delta n_k}(|\gamma_k|)|^2 \tag{III- 25}$$

On the other hand, if the reaction path is approximately straight, so that $\gamma_k = 0$, $k=2,\ldots, F$, the only terms which contributes to the sum is $\ell_k = \Delta n_k / 2$. Since ℓ_k are integers, Δn_k are required to be

even, and

$$P_{\mathbf{n}_1 \leftarrow \mathbf{n}_2} = \prod_{k=2}^{F} \left| J_{\Delta n_k/2}(|\beta_k|) \right|^2 \quad , \; k = 2, \ldots, F \; , \qquad \text{(III- 26)}$$

i.e., without reaction path curvature, there is a selection rule:

$$\Delta n_k = 0, \pm 2, \pm 4, \cdots \quad .$$

The semiclassical perturbation reaction path model can also be used to describe tunneling through a transition state (i.e., saddle point) region of a potential energy surface. For the total reaction probabilities

$$P_R(E) = \sum_{\Delta \mathbf{n}=0}^{\infty} \left| S_{\mathbf{n}_2 \leftarrow \mathbf{n}_1}(E) \right|^2 \quad , \qquad \text{(III- 27)}$$

the closure relation

$$\sum_{\Delta \mathbf{n}=0}^{\infty} e^{i \Delta \mathbf{n}(\mathbf{q}-\mathbf{q}')} = (2\pi)^{F-1} \, \delta(\mathbf{q}-\mathbf{q}') \; , \qquad \text{(III- 28)}$$

and Eqs.(II-20) give

$$P_R(E) = \int_0^{2\pi} \frac{d\mathbf{q}}{(2\pi)^{F-1}} \left| i\Phi_o + i\Delta\Phi(\mathbf{q}) \right|^2 \; . \qquad \text{(III- 29)}$$

The action integral Φ_o and $\Delta\Phi(\mathbf{q})$ are complex inside the barrier region, i.e., where $E < V_a(s)$, so that Eq.(III-29) becomes

$$P_R(E) = e^{-i\theta_o} \int_0^{2\pi} \frac{d\mathbf{q}}{(2\pi)^{F-1}} \, e^{-2\Delta\theta(\mathbf{q})} \; , \qquad \text{(III-30a)}$$

where θ_o is the vibrationally adiabatic barrier penetration integral

$$\theta_o = \int_{s_<}^{s_>} ds\ [2(V_a(s) - E]^{1/2}, \qquad \text{(III-30b)}$$

and $\Delta\theta$ is the first order correction due to the curvature of the reaction path and the frequency change along the reaction path

$$\Delta\theta(\mathbf{q}) = \theta_1 \sin\mathbf{q} + \theta_2 \cos 2\mathbf{q} \quad , \qquad \text{(III-31a)}$$

with

$$\theta_1 = \int_{s_<}^{s_>} ds \{2[V_a - E]\}^{1/2} \sum_{k=2}^{F} B_{k,1}(s)\ [\omega_k(s)]^{-1/2} \cosh q_{ok}^{o} \ , \qquad \text{(III-31b)}$$

$$\theta_2 = \int_{s_<}^{s_>} ds \sum_{k=2}^{F} \frac{\omega_k'(s)}{2\omega_k(s)} \sinh 2q_{ok}^{o} \ , \qquad \text{(III-31c)}$$

and

$$q_{ok}^{o} = \int_0^s ds \frac{\omega_k(s)}{\{2[V_a(s) - E]\}^{1/2}} \ , \qquad \text{(III-31d)}$$

where $s_<$ and $s_>$ are the left and right classical turning points at the barrier, and the quantum number $\mathbf{n}$ has been set to 0. With Eq.(III-31a) for $\Delta\theta(\mathbf{q})$ the integral in Eq.(III-30a) is easily performed to give

$$P_R(E) = e^{-2\theta_o} [\sum_{\ell=-\infty}^{\infty} I_{2\ell}(2\theta_1)\ I_\ell(2\theta_2)] \ , \qquad \text{(III- 32)}$$

where $I_{2\ell}$ and I_ℓ are modified Bessel functions of the first kind. One notes that $e^{-2\theta_o}$ gives the vibrationally adiabatic zero curvature tunneling probability and the remaining factors in Eq.(III-32) provide the corrections.

III.d) Sample calculation: collinear He + H_2 inelastic scattering.

To illustrate the accuracy of the SCP reaction path model, calculations have been carried out for one of the standard inelastic scattering benchmarks, namely the Secrest-Johnson[32] collinear model of He + H_2 vibrationally inelastic scattering. This is a nonreactive process, but it is nevertheless possible to treat it via the reaction path model.

In dimensionless units, the Secrest-Johnson[32] Hamiltonian is

$$H(P,R,p,r) = \frac{P^2}{2\mu} + \frac{p^2}{2} + \frac{r^2}{2} + \exp[\alpha(r - R)] \qquad \text{(III- 33)}$$

and $\mu = 2/3$, $\alpha = 0.3$ for the He + H_2 case, where (R,P) are the cartesian coordinate and momentum for the translational motion of He atom relative to the center of the mass of H_2, and (r,p) are the cartesian coordinate and momentum for the vibrational motion of the molecule H_2. Figure (III-1) shows a contour plot of the potential surface V:

$$V(r,R) = \frac{1}{2} r^2 + \exp[\alpha(r-R)] \qquad \text{(III- 34)}$$

in the mass-weighted cartesian coordivates

$$x = \sqrt{\mu}\, R, \quad y = r \qquad \text{(III- 35)}$$

and the paths which were determined by following the gradient of potential V down from different initial points high up on the repulsive wall. As it is shown, all the gradient paths converged to a "reaction path " which is essentially independent of the initial position over the

energy region of interest. According to the standard procedure[31], the curvature $\kappa(s)$ and the normal mode frequency $\omega(s)$ along the "reaction path " were determined. The reaction path Hamiltonian for this system reads

$$H(P_s,s,n,q) = \frac{\frac{1}{2}\,[P_s+(n+\frac{1}{2})\,(\frac{\omega'(s)}{\omega(s)})\,\sin q\,\cos q\,]^2}{[\,1+(\frac{2n+1}{\omega(s)})^{1/2}\,\kappa(s)\,\sin q\,]^2}$$

$$+\,(n+\tfrac{1}{2})\,\omega(s)+V_o(s) \simeq H^o + H_1 \quad , \qquad \text{(III-36a)}$$

with

$$H_o = \frac{P_s^2}{2} + V_a(s) \quad , \; V_a(s) = (n+\tfrac{1}{2})\,\omega(s) + V_o(s) \; , \qquad \text{(III-36b)}$$

and

$$H_1 = -\,P_s^2\,(\frac{2n+1}{\omega(s)})^{1/2}\,\kappa(s)\,\sin q - P_s\,(n+\tfrac{1}{2})\,(\frac{\omega'(s)}{\omega(s)})\,\sin q\,\cos q \; . \qquad \text{(III-36c)}$$

Since this is an inelastic scattering problem, the nonreactive trajectory in s determined by H_o is from $s = +\infty$ to 0 (defined as the classical turning point) back to $+\infty$, rather than from $s = -\infty$ to $s = +\infty$ as the reactive case. Accordingly, the Eqs.(III-21) becomes

$$\gamma = \int_0^\infty ds\,\sqrt{2(E-V_a(s)}\,\kappa(s)\,(\frac{2n+1}{\omega(s)})^{1/2}\exp[-iq_o^o(s)] \text{ (incoming part)}$$

$$+\int_0^\infty ds\sqrt{2(E-V_a(s)}\,\kappa(s)(\frac{2n+1}{\omega(s)})^{1/2}\exp[iq_o^o(s)] \text{ (outgoing part)}$$

or

$$\gamma = 2\int_0^\infty ds\,\sqrt{2(E-V_a(s)}\,\kappa(s)(\frac{2n+1}{\omega(s)})^{1/2}\cos q_o^o(s) \; , \qquad \text{(III-37a)}$$

and

$$\beta = \int_0^\infty ds\,\frac{\omega'(s)}{2\omega(s)}\,(n+\tfrac{1}{2})\,\exp[-2iq_o^o(s)] \text{ (incoming part)}$$

$$-\int_0^\infty ds\,\frac{\omega'(s)}{2\omega(s)}\,(n+\tfrac{1}{2})\,\exp[2iq_o^o(s)] \text{ [outgoing part)}$$

or

$$\beta = -2i \int_0^\infty ds \, \frac{\omega'(s)}{2\omega(s)} \, (n+1/2) \, \sin 2q_o^o \, , \qquad \text{(III-37b)}$$

and

$$q_o^o = \int_0^\infty ds \; \omega(s) \; / \; \{ \, 2[E - V_a(s)] \}^{1/2} . \qquad \text{(III-37c)}$$

The vibrational transition probability is thus given by

$$P_{n_2 \leftarrow n_1} = \left| \sum_{\ell=-\infty}^{\infty} i^{\ell} \; J_{\Delta n - 2\ell}(|\gamma|) \; J_{\ell}(|\beta|) \right|^2 . \qquad \text{(III- 38)}$$

In the present case $|\beta|$ is so small that only the term with $\ell = 0$ makes a significant contribution to the sum in Eq.(III-38). So that one in effect has

$$P_{n_1 \leftarrow n_2} \simeq J_{\Delta n}(|\gamma|)^2 \; J_o(|\beta|)^2 \quad , \qquad \text{(III- 39)}$$

i.e., it is the coupling due to the curvature of the reaction path that causes the vibrational transition. The coupling due to the variation of $\omega(s)$ has negligible effect.

The results of Eq.(III-39) are given in Table (III-1) along with the exact quantum mechanical results of Ref.32. Some of these results are also shown pictorialy in Fig.(III-2). The SCP reaction path model is seen to provide a reasonable, semiquantitative description of the vibrationally inelastic process over a wide range of energies and also for large Δn transitions

III.e) The SCP kinetic coupling model for the intramolecular vibrational relaxation and spectra of the local mode overtone in polyatomic

molecules.

Another important aspect of polyatomic dynamics is intramolecular energy transfer, especially the vibrational relaxation of the local mode overtone, which plays a central role in the study of multiphoton excitation and bond selective chemistry. In light of the considerable interest in this area a great deal of experimental[33-34] and theoretical[35-39] work has been devoted to the investigation of the highly excited CH overtone states of polyatomic molecules. Here we show how the SCP approximation can be used to describe this problem quantitatively.

An essential difference of the local mode overtone dynamics from the normal mode study is that one has to be concerned with the large amplitude of oscillation. In other words, the local mode has to be treated specially. We use the action-angle variables (n_s, q_s) to describe the local mode as a special degree of freedom s. The remaining F-1 molecular degrees of freecom are described as a set of harmonic oscillators with the frequencies $\{\omega_k\}$, k=2,..., F, with a set of action-angle variables $(\mathbf{n},\mathbf{q})$. Now suppose that the Hamiltonian of the system is approximated as

$$H(n_s, q_s, \mathbf{n}, \mathbf{q}) = H_o(n_s, \mathbf{n}) + H_1(n_s, q_s, \mathbf{n}, \mathbf{q}) \qquad \text{(III-40a)}$$

and

$$H_o(n_s, \mathbf{n}) = \varepsilon(n_s) + \sum_{k=2}^{F} (n_k + 1/2)\, \omega_k \,. \qquad \text{(III-40b)}$$

If $|n_s=0, \mathbf{n}\rangle$ is the initial state of the molecule — and the state $\mathbf{n}$ of the normal modes will usually also be taken to be the ground state $\mathbf{o}$ — then the absorption spectrum $I(\omega)$ is given by[40]

$$I(\omega) = \int_{-\infty}^{\infty} dt\, e^{i(E_o + \hbar\omega)t/\hbar} \langle 0,\mathbf{n}|\, \mu\, e^{-iHt/\hbar}\, \mu|0,\mathbf{n}\rangle \quad , \qquad \text{(III- 41)}$$

where $E_o = \varepsilon(n_s=0) + \hbar \sum_{k=2}^{F} \omega_k(n_k + 1/2)$, and μ is the dipole moment function of the molecule. As is usual, one assumes that μ is a function only of the local mode coordinate, so that insertion of complete sets of states before and after the propagator in Eq.(III-41) gives

$$\langle 0,\mathbf{n}|\, \mu\, e^{-iHt/\hbar}\, \mu|0,\mathbf{n}\rangle = \sum_{n_s,n'_s} \langle 0|\mu|n_s\rangle\langle n_s\mathbf{n}|\, e^{-iHt/\hbar}\, |n'_s\mathbf{n}\rangle\langle n'_s|\mu|0\rangle \ . \qquad \text{(III- 42)}$$

If the local mode mixing, i.e., the terms with $n_{s'} \neq n_s$ in Eq.(III-42), is neglected, then the absorption spectrum associated with the $0 \to n_s$ overtone of the local mode s takes the standard form

$$I_{n_s,o}(\omega) = |\langle n_s|\mu|0\rangle|^2 \int_{-\infty}^{\infty} dt\, e^{i\Delta\omega t}\, C(t) \quad \text{with } \Delta\omega = \omega - \omega_{n_s,o} \ , \qquad \text{(III- 43)}$$

where $\omega_{n_s,o}$ is the normal position of the $0 \to n_s$ overtone absorption line

$$\omega_{n_s,o} = \varepsilon(n_s) - \varepsilon(0) \qquad \text{(III- 44)}$$

and the correlation function C(t) is

$$C(t) = e^{iE_{n_s\mathbf{n}}t}\, \langle n_s\mathbf{n}|\, e^{-iHt/\hbar}\, |n_s\mathbf{n}\rangle \qquad \text{(III-45a)}$$

with

$$E_{n_s\mathbf{n}} = \varepsilon(n_s) + \hbar \sum_{k=2}^{F} \omega_k(n_k + 1/2) \ . \qquad \text{(III-45b)}$$

In the framework of semiclassical mechanics the initial value

representation for the propagator is given by

$$\langle n_{s_2}\mathbf{n}_2|\, e^{-iHt/\hbar}\, |n_{s_1}\mathbf{n}_1\rangle = \int_0^{2\pi}\frac{dq_s}{2\pi}\int_0^{2\pi}\frac{d\mathbf{q}}{(2\pi)^{F-1}}\left[\frac{\partial(q_{s_2},\mathbf{q}_2)}{\partial(q_{s_1},\mathbf{q}_1)}\right]^{1/2}$$

$$\times \exp\{\frac{i}{\hbar}(\Phi[\mathbf{n}_2(\mathbf{q}_1,q_{s_1},n_{s_1},\mathbf{n}_1),n_{s_2}(\mathbf{q}_1,q_{s_1},n_{s_1}\mathbf{n}_1),\mathbf{n}_1,n_{s_1}]$$

$$+\mathbf{q}_1[\mathbf{n}_2(\mathbf{q}_1,q_{s_1},\mathbf{n}_1,n_{s_1})-\mathbf{n}_2]+q_{s_1}[n_{s_2}(\mathbf{q}_1,q_{s_1},\mathbf{n}_1,n_{s_1})-n_{s_2}])\}\,. \tag{III- 46}$$

By the same procedure as we used in section (III.b) it can be shown that with the SCP approximation to the propagator in Eq.(III-46) the correlation function Eq.(III-45a) takes the form

$$C(t) = \int_0^{2\pi}\frac{dq_s}{2\pi}\int_0^{2\pi}\frac{d\mathbf{q}}{(2\pi)^{F-1}}\exp[-\frac{i}{\hbar}\,\Delta\Phi(t)] \tag{III-47a}$$

with

$$\Delta\Phi(t) = \int_0^t dt'\, H_1(n_s,q_s+\omega_s t',\mathbf{n},\mathbf{q}+\boldsymbol{\omega}t')\ ,\ \boldsymbol{\omega} = \{\omega_k\}, k = 2,\ldots, F\ , \tag{III-47b}$$

and $\omega_s \equiv \varepsilon'(n_s)$,where the prime denotes the derivative with respect to n_s. Thus once $H_1(\mathbf{n},\mathbf{q},n_s,q_s)$ is known, Eq.(III-43) and Eqs.(III-47) are ready to be used to calculate the overtone absorption spectra of the local mode s. In fact, using the SCP reaction path model with the local mode coordinate as the reaction coordinate, one has obtained very compact, analytical expression for the line width of local mode overtone[41]. In practice, however, for a polyatomic molecule, even though reaction path model has reduced the computational effort significantly, it is still very time consuming to determine the interaction H_1. In this practical perspective the kinetic coupling model

(42-44) proposed originally by Gribov[45] seems a more appealing approximate dynamic model. In this model the internal displacement coordinates, x_i, $i = 1,\ldots, F$, i.e., the changes in bond lengths and bond angles, are used. One of the most important advantages of using internal coordinates is that in low orders of approximation, the anharmonic potential coupling terms between the local modes and the remaining degrees of freedom of the molecule, which are extremely difficult to determine, can be neglected. In the internal coordinate representation the kinetic coupling terms, resulting from the coordinate dependence of the effective mass on the internal coordinate motion, provide the dominant coupling responsible for the overtone line widths[44,46]. The kinetic energy can be written in terms of internal coordinates in the form[47]

$$T = \frac{1}{2} \sum_{i,j}^{F} g_{ij}(\mathbf{x})\, P_i P_j \quad , \qquad \text{(III- 48)}$$

where P_i are the momenta conjugate to x_i and $g_{ij}(\mathbf{x})$ are the Wilson G matrix elements which, in general, depend on the displacement coordinate $\mathbf{x}$[47]. The $g_{ij}(\mathbf{x})$ can be expressed by a Taylor series expansion in the displacemint coordinates $\mathbf{x}$ about the equilibrium geometry $\mathbf{x} = 0$,

$$g_{ij} = g^{o}_{ij} + \sum_{k=1}^{F} (\partial g_{ij} \,/\, \partial x_k)_{\mathbf{x}=0}\, x_k + \cdots , \qquad \text{(III- 49)}$$

where $g^{o}_{ij} \equiv g_{ij}(0)$ are determined by the atomic masses and the equilibrium geometry of molecule. Eq.(III-49) gives the kinetic energy to first order as

$$T = T^{o} + 1/2 \sum_{i,j,k}^{F} (\partial g_{ij} / x_k)_{x=0} x_k P_i P_j = T^{o} + T_1 \qquad \text{(III-50a)}$$

with

$$T^{o} = 1/2 \sum_{i,j}^{F} g_{ij} P_i P_j \quad \text{and} \quad T_1 = 1/2 \sum_{i,j,k}^{F} (\partial g_{ij} / \partial x_k)_{x=0} x_k P_i P_j \ . \qquad \text{(III-50b)}$$

Let the internal coordinate x_s correspond to the local mode of interest, which to a good approximation can be described by a Morse oscillator with the Morse potential

$$V_s = D\,(1 - e^{-\alpha x_s})^2 \ . \qquad \text{(III- 51)}$$

Then the potential energy can be expressed as

$$V(x) = V_s + \sum_{i \neq s} \{ \sum_{j} c_{ij} x_i x_j + \sum_{j,k} c_{ijk} x_i x_j x_k + \cdots \} \ , \qquad \text{(III- 52)}$$

where the potential energy at equilibrum geometry has been chosen as zero. The classical Hamiltonian to the first order, thus, reads

$$H = H_o + H_1 \qquad \text{(III-53a)}$$

with

$$H_o = \frac{1}{2} g_{ij} P_s^2 + V_s + \sum_{i,j \neq s} [c_{ij} x_i x_j + \frac{1}{2} g_{ij}^{o} P_i P_j] = h_s + h \ , \qquad \text{(III-53b)}$$

$$h_s = \frac{1}{2} g_{ij}^{o} P_s^2 + V_s, \ h = \sum_{i,j \neq s} [c_{ij} x_i x_j + \frac{1}{2} g_{ij}^{o} P_i P_j] \ , \qquad \text{(III-53c)}$$

$$H_1 = \sum_{i \neq s} c_{is} x_i x_s + \sum_{i,j \neq s} c_{ijs} x_i x_j x_s + \frac{1}{2} \sum_{i \neq s} g_{is}^{o} P_i P_s$$

$$+ \frac{1}{2} \sum_{i,j,k} (\partial g_{ij} / \partial x_k)_{x=0} x_k P_i P_j \ . \qquad \text{(III-53d)}$$

In the internal coordinates the anharmonic potential couplings (the second term on the right side of Eq.(III-53d)) usually are much smaller than the kinetic couplings[46] (the fourth term on the right side of Eq.(III-53d)). In the kinetic coupling model the anharmonic potential couplings are totally neglected. So that the Eq.(III-53d) becomes

$$H_1 \simeq \sum_{i\neq s} c_{is} x_i x_s + \frac{1}{2} \sum_{i\neq s} g^{o}_{is} P_i P_s + \frac{1}{2} \sum_{i,j,k} \left(\frac{\partial g_{ij}}{\partial x_k}\right)_{x=0} x_k P_i P_j \qquad \text{(III- 54)}$$

The coefficients c_{ij} in Eqs.(III-53) and Eq.(III-54) can be determined from the molecular force constants. Therefore, the kinetic coupling model makes the classical Hamiltonian easy to calculate.

Now if we do normal mode analysis[47] for the Hamiltonian h and find the normal mode coordinates Q_k, the corresponding eigenvalues ω_k^2 and eigenvector $\mathbf{L}_k$ with the elements $L_{ik}, i=1,\ldots, F-1$, then, the internal coordinates can be expressed in terms of the normal mode coordinates

$$x_i = \sum_k L_{ik} Q_k \qquad \text{(III- 55)}$$

and the momenta P_i are given by

$$P_i = \sum_\ell (L^{-1})^{\dagger}_{i\ell} \dot{Q}_\ell , \qquad \text{(III- 56)}$$

where dot denotes the time derivative and the coefficients $(L^{-1})^{\dagger}_{i\ell}$ are related to elements $L_{i\ell}$:

$$(L^{-1})^{\dagger}_{i\ell} = (L^{-1})^{*}_{\ell i} \qquad \text{and} \qquad \sum_k L_{ik} (L\ \ )^{-1}_{kj} = \delta_{ij} , \qquad \text{(III- 57)}$$

where star * denotes the complex conjugate. Substituting Eq.(III-55) and Eq.(III-56) into Eqs.(III-53)-(III-54) gives

$$H = H_o + H_1 \tag{III-58a}$$

with

$$H_o = \frac{1}{2} g_{ss} P_s^2 + D(1 - e^{-\alpha x_s})^2 + \frac{1}{2} \sum_{\ell=1}^{F-1} (\dot{Q}_\ell^2 + \omega_k^2 Q_\ell^2) \tag{III-58b}$$

and

$$\begin{aligned} H_1 = & \sum_{i \neq s} \sum_{\ell=1}^{F-1} c_{is} \{ L_{i\ell} Q_\ell x_s + \frac{1}{2} g_{is}^o (L^{-1})_{i\ell}^\dagger \dot{Q}_\ell P_s \} \\ & + \frac{1}{2} \sum_{\ell,m=1}^{F-1} \sum_{i,j \neq s} \{ (\frac{\partial g_{ij}}{\partial x_s})_{x=0} (L^{-1})_{i\ell}^\dagger (\bar{L}^1)_{jm}^\dagger \dot{Q}_\ell \dot{Q}_m x_s \\ & + (\frac{\partial g_{is}}{\partial x_j})_{x=0} L_{j\ell} (L^{-1})_{im}^\dagger Q_\ell \dot{Q}_m P_s \} \\ & + \frac{1}{2} \sum_{\ell,m,n=1}^{F-1} \sum_{i,j,k \neq s} (\frac{\partial g_{ij}}{\partial x_s})_{x=0} L_{kn} (L^{-1})_{i\ell}^\dagger (L^{-1})_{jm}^\dagger \dot{Q}_\ell \dot{Q}_m Q_n . \end{aligned} \tag{III-58c}$$

The zeroth order Hamiltonian H_o consistes of a Morse oscillator for the local mode and a normal mode "bath" for the remaining degrees of freedom. The H_1 provides the couplings between them. According to perturbation theory it is known that the importance of the terms in H_1 depends on the frequency diffrence between the local mode and the bath normal modes. If the frequency of the local mode is close to the frequencies of the bath normal modes, then the first sumation in H_1 is much more important than the last two. However, if the local mode frequency is about twice as much as the frequencies of the bath normal modes, then the second sumation is most important. The last sumation provides the coupling between the normal modes.

To use the SCP formulae one carries out a canonical transformation from the local mode and normal mode coordinates to the action-angle

variable n_s, q_s and $\mathbf{n}, \mathbf{q}$ with

$$\mathbf{n} \equiv \{n_k\},\ k = 1, \ldots, F-1 \quad ,$$

and

$$\mathbf{q} \equiv \{q_k\},\ k = 1, \ldots, F-1 \quad .$$

In terms of action-angle variables the normal mode coordinates Q_k are given by

$$Q_k = \left(\frac{2n_k+1}{\omega_k}\right)^{1/2} \sin q_k \quad , \quad Q_k = [(2n_k + 1)\ \omega_k]^{1/2} \cos q_k \quad , \qquad \text{(III- 59)}$$

and the local mode coordinate and momentum x_s and P_s are given by[48]

$$x_s = \alpha^{-1} \log\{\lambda^{-2}\ [1 - (1-\lambda^2)^{1/2} \cos q_s\ ]\} \quad , \qquad \text{(III-60a)}$$

and

$$P_s = \frac{1}{g_{ss}} \frac{\omega_s}{\alpha} \frac{(1 - \lambda^2)^{1/2} \sin q_s}{[1 - (1 - \lambda^2)^{1/2} \cos q_s\ ]} \quad , \qquad \text{(III-60b)}$$

with

$$\lambda = 1 - (n_s + \tfrac{1}{2})\ \alpha\ /\ (2D/g_{ss})^{1/2} , \qquad \text{(III-60c)}$$

and

$$\omega_s = \frac{\partial h_s(n_s)}{\partial n_s} = \alpha \sqrt{2Dg_{ss}}\ \lambda \quad , \qquad h_s(n_s) = -D\lambda^2 \quad , \qquad \text{(III-60d)}$$

where the units has been used such that $\hbar$=1. If the local mode overtones of interest are not too high in energy, i.e., $\lambda \sim 1$, the Eq.(III-60a) and Eq.(III-60b) can be approximated as

$$x_s \simeq -\frac{1}{\alpha} (1 - \lambda^2)^{1/2} \cos q_s \text{ and } P_s \simeq \frac{\omega_s}{g_{ss}\alpha} (1 - \lambda^2)^{1/2} \sin q_s \quad . \qquad \text{(III- 61)}$$

Now if the kinetic coupling model, Eqs.(III-58), is used in the SCP expression for the absorption spectrum Eq.(III-43) and Eqs.(III-47),

then with the help of Eqs.(III-60) and Eqs.(III-61) the local mode overtone spectrum has the expression

$$I_{n_s,o}(\omega) = \left|\langle n_s|\mu|o\rangle\right|^2 \int_{-\infty}^{\infty} dt\, e^{i\omega t} C(t) \,, \tag{III-62a}$$

and

$$C(t) = \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{d\mathbf{q}}{(2\pi)^{F-1}} \exp[-i\Delta\Phi(t)] \tag{III-62b}$$

with

$$\Delta\Phi(t) = \int_0^t \frac{dt'}{\hbar} H_1[n_s, q_s+\omega_s t', \mathbf{n}, \mathbf{q}+\boldsymbol{\omega} t'] = \mathrm{I} + \mathrm{II} + \mathrm{III} \,, \tag{III-62c}$$

where

$$\mathrm{I} = \int_0^t dt' \sum_{\ell=1}^{F-1} \sum_{i\neq s} \{-c_{is} L_{i\ell} \frac{(1-\lambda^2)^{1/2}}{\alpha} \left(\frac{2n_s+1}{\omega_s}\right)^{1/2} \sin(q_\ell+\omega_\ell t') \cos(q_s+\omega_s t')$$

$$+ g^o_{is} (L^{-1})^\dagger_{i\ell} \frac{\omega_s}{g_{ss}\alpha} [(1-\lambda^2)(2n_\ell+1)\omega_\ell]^{1/2} \cos(q_\ell+\omega_\ell t') \sin(q_s+\omega_s t') \}$$

$$\simeq \sum_{\ell=1}^{F-1} W_\ell \sin(q_s - q_\ell + \delta_\ell) \quad , \tag{III-63a}$$

with

$$W_\ell = \sqrt{(2n_\ell+1)\omega_\ell}\, \frac{(1-\lambda^2)^{1/2}}{2\alpha} \frac{\sin\left(\frac{\omega_s-\omega_\ell}{2}\right)t}{\omega_s-\omega_\ell} \sum_{i\neq s} \left[-\frac{c_{is}L_{i\ell}}{\omega_\ell} + \frac{g^o_{is}}{g_{ss}} (L^{-1})^\dagger_{is}\omega_s \right] \tag{III-63b}$$

and

$$\delta_\ell = \pi - \frac{\omega_s - \omega_\ell}{2} t \;; \tag{III-63c}$$

$$\mathrm{II} \simeq \sum_{\ell,m=1}^{F-1} Z_{\ell m} \sin[q_s - (q_\ell+q_m) + \beta_{\ell m}] \tag{III-64a}$$

with

$$Z_{\ell m} = \sqrt{(2n_\ell+1)(2n_m+1)\,\omega_\ell\omega_m}\, \frac{(1-\lambda^2)^{1/2}}{4\alpha} \frac{\sin\frac{\omega_s-(\omega_\ell+\omega_m)}{2} t}{\omega_s-(\omega_\ell+\omega_m)}$$

$$\times \left\{ \sum_{i,j\neq s} [-(\frac{\partial g_{ij}}{\partial x_s})_{x=0} (L^{-1})^{\dagger}_{i\ell}(L^{-1})^{\dagger}_{jm} + (\frac{\partial g_{is}}{\partial x_j})_{x=0} L_{j\ell}(L^{-1})^{\dagger}_{im} \frac{\omega_s}{\omega_\ell g_{ss}}] \right\} , \tag{III-64b}$$

and $$\beta_{\ell m} = \frac{\pi}{2} + \frac{\omega_s - (\omega_\ell + \omega_m)}{2} t ; \tag{III-64c}$$

$$III \simeq \sum_{\ell,m,n=1}^{F-1} Y_{\ell mn} [A_1 \sin(q_n - q_\ell + q_m + \gamma_1) + A_2 \sin(q_n + q_\ell - q_m + \gamma_2)$$

$$+ A_3 \sin(q_n - q_\ell - q_m + \gamma_3) , \tag{III-65a}$$

with

$$A_1 = \frac{\sin(\frac{\omega_n - \omega_\ell + \omega_m}{2} t)}{\omega_n - \omega_\ell + \omega_m} , \quad \gamma_1 = \pi - \frac{\omega_n - \omega_\ell + \omega_m}{2} t, , \tag{III-65b}$$

$$A_2 = \frac{\sin(\frac{\omega_n + \omega_\ell - \omega_m}{2} t)}{\omega_n + \omega_\ell - \omega_m} , \quad \gamma_2 = \pi - \frac{\omega_n + \omega_\ell - \omega_m}{2} t , \tag{III-65c}$$

and

$$A_3 = \frac{\sin(\frac{\omega_n - \omega_\ell - \omega_m}{2} t)}{\omega_n - \omega_\ell - \omega_m}, \quad \gamma_3 = \pi - \frac{\omega_n - \omega_\ell - \omega_m}{2} t . \tag{III-65d}$$

In many cases Eqs.(III-62) can be simplifed further. For example, if the local mode frequency is close to the frequencies of the normal modes, the the term I in Eq.(III-62c) provides the dominant contibution. So that the correlation function C(t) takes the form

$$C(t) \simeq \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{d\mathbf{q}}{(2\pi)^{F-1}} \prod_{\ell=1}^{F-1} \exp[-iW_\ell \sin(q_s - q_\ell + \delta_\ell)] . \tag{III- 66}$$

Introducing a new variable

$$Q_\ell = q_s - q_\ell \tag{III- 67}$$

and using the identity

$$1 = \int_0^{2\pi} \frac{dQ_\ell}{2\pi} \sum_{k_\ell=-\infty}^{\infty} e^{ik_\ell(Q_\ell - q_s + q_\ell)} \tag{III- 68}$$

one can perform the integrals in Eq.(III-66) and obtain a very simple, analytical expression for C(t)

$$C(t) = \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{\ell} \sum_{k_\ell=-\infty}^{\infty} e^{-ik_\ell(q_s-q_\ell+\delta_\ell)} J_{k_\ell}(W_\ell) = \prod_{\ell=1}^{F-1} J_o(W_\ell) \ , \qquad \text{(III- 69)}$$

where the relation

$$\int_0^{2\pi} \frac{dq}{2\pi} e^{iqn} = \delta_{n,0} \qquad \text{(III- 70)}$$

has been used and J_{k_ℓ}, J_o are the regular Bessel functions. Similarly, if the local mode frequency is about twice those of the normal modes, then the dominant term II gives

$$C(t) \simeq \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{\ell,m=1}^{F-1} \exp[-iZ_{\ell m}\sin(q_s - q_\ell - q_m + \delta_{\ell m})]$$

$$= \prod_{\ell,m=1}^{F-1} J_o(Z_{\ell m}) \ , \qquad \text{(III- 71)}$$

where the same trick as that above has been used.

III.f) Sample calculation: the CH(CD) stretch local mode overtone spectra of benzene(perdeuterobenzene C_6D_6).

To demonstrate the use of the SCP kinetic coupling model the CH(DH) stretch local mode overtone spectra of benzene(perdeuterobenzene C_6D_6) have been studied. Benzene is one of the very well studied molecules. The normal mode fundamental frequencies and the force constants are available in the literature[47,49,50]. In benzene, as in most of

hydrocarbons, the hydrogen atoms vibrate along the direction of the CH bonds fairly uncoupled to the other motions in the molecule. So to a good approximation the hydrogen vibrational motions along the CH bonds can be treated as local modes. Besides, since the six CH bonds do not have common atoms, the direct kinetic couplings between the six CH stretch local mode motions are zero and it is also conceivable that the quadratic off-diagonal terms between the six CH stretch motions in the potential energy in terms of internal coordinates are negligible. So that to a good approximation the six CH stretch local modes can be treated as the six uncoupled anharmonic Morse oscillators with Morse potential $V(x_s) = D[1-\exp(-\alpha x_s)]^2$, where D is the CH bond dissociation energy and α is the scaling parameter. Furthermore, the benzene molecule has the D_{6h} symmetry and the six CH bonds are equivalent. Thus the problem can be further simplified to considering only a single CH oscillator interacting with the ring modes. Then, the Hamiltonian for the problem of the CH local mode overtone reads

$$H = H_o + H_1 \tag{III-72a}$$

with

$$H_o = \frac{1}{2} g_{CH} P_{CH}^2 + D\,[1 - \exp(-\alpha x_{CH})] + \frac{1}{12} \sum_{\ell=1}^{15} (\dot{Q}_\ell^2 + \omega_\ell^2 Q_\ell^2) \,, \tag{III-72b}$$

and

$$g_{CH} = \frac{1}{\mu_H + \mu_C} \,, \quad \mu_H = \frac{1}{m_H} \,, \quad \mu_C = \frac{1}{m_C} \,, \tag{III-72c}$$

where m_H and m_C are the masses of atom H and atom C, respectively. Here only the fifteen in-plane normal ring modes are included, since there are no coupling between the CH stretch local mode and the out- of-plane normal modes. H_1 consists of only the second term in Eq.(III-62c), i.e., the kinetic coupling between the CH stretch x_{CH} and the in-plane

internal coordinates, due to the fact that because of the small mass of the hydrogen atom, the CH stretch mode has the frequeney ($\sim 3000 cm^{-1}$), considerably higher than the other modes ($600 \sim 1600 cm^{-1}$). The in-plane internal coordinates which are kinetically coupled with the CH stretch x_{CH} are: the extension of the CC stretch coordinates x_1, x_6 and the in-plane CCH wag $x_w \equiv X_{CHo}\beta \equiv X_{CHo}(\phi_6-\phi_1)/2$, where ϕ_1 and ϕ_6 are the CCH bond angles and x_{CHo} is the equilibrium length of the CH bond [see Fig.(III-3)]. By using the general formulae for the Wilson G matrix elements in Table VI-1 of Ref.(47) the kinetic coupling H_1 reads (for the details, see the Appendix C)

$$H_1 \simeq B_1 x_{CH} P_w^2 + B_2 x_{CH} (P_6-P_1) P_w + B_3 x_w (P_6-P_1) P_{CH} \qquad \text{(III-73a)}$$

with

$$B_1 = -\left(\frac{\mu_H}{X_{CHo}} + \frac{\mu_C}{X_{CHo}} + \frac{\mu_C}{2X_{CHo}}\right), \quad B_2 = -\sqrt{3}/(4X_{CHo})\mu_C, \quad B_3 = \sqrt{3}/(4X_{CHo})\mu_c, \qquad \text{(III-73b)}$$

where P_w, P_1 and P_6 are the momenta conjugate to x_w, x_1 and x_6, respectively. With the interaction Hamiltonian H_1 given by Eqs.(III-73) the SCP correlation function Eq.(III-71) takes the form

$$C(t) = \prod_{\ell,m=1}^{10} J_o(Z_{\ell m}) \qquad \text{(III-74a)}$$

with

$$Z_{\ell m} = \{B_1 (L^{-1})^{\dagger}_{w\ell} (L^{-1})^{\dagger}_{wm} + B_2 (L^{-1})^{\dagger}_{wm} [(L^{-1})^{\dagger}_{6\ell} - (L^{-1})^{\dagger}_{1\ell}] + B_3 \frac{\omega_{CH}}{g_{CH}\omega_m} L_{wm}$$

$$\times [(L^{-1})^{\dagger}_{6\ell} - (L^{-1})^{\dagger}_{1\ell}]\} \sqrt{(2n_\ell+1)(2n_m+1)\omega_\ell \omega_m} \; \frac{(1-\lambda^2)^{1/2} \sin\left(\frac{\omega_{CH}-\omega_\ell-\omega_m}{2} t\right)}{2\alpha\,(\omega_{CH}-\omega_\ell-\omega_m)}, \qquad \text{(III-74b)}$$

$$\omega_{CH} = \alpha\sqrt{2Dg_{CH}}\,\lambda \quad \text{and} \quad \lambda = 1-(n_{CH}+1)\alpha \,/\, (2D/g_{CH})^{1/2}, \qquad \text{(III-74c)}$$

where the Morse potential paremeters D=0.199(0.218)a.u. and α=0.9386(0.898)a.u. for benzene(perdeuterobenzene C_6D_6) are determined such that the energy eigenvalues for the CH(CD) stretch Morse oscillator $h_{CH}(n_{CH}) = -D\lambda^2$ fit the experimental CH(CD) overtone spacing listed in Table III-2, the transformation matrix elements $(L^{-1})^{\dagger}_{w\ell}$, $[(L^{-1})^{\dagger}_{6\ell}-L^{-1})^{\dagger}_{1\ell}$, and L_{wm}, $\ell,m=1,\ldots,10$ are given in Table III-3, and the fact that only ten modes have different frequencies (five modes are doubly degenerated) has been used. The overtone spectrum of the CH(CD) stretch local mode $I_{n_{CH},o}(\omega)$, then, can be determined by Fourier transform of the correlation function C(t). Since $Z_{\ell m}(t)\sim\sin[(\omega_{CH}-\omega-\omega_m)t/2]$ is an odd funcion of time t and $J_o(Z_{\ell m})$ is a even function of $Z_{\ell m}$. Consequently, the spectra given by Eq.(III-62a) is symmetric.

The results for the CH stretch local mode overtones, n=5-9, in benzene C_6H_6 are shown as the solid line curves in Figs.III.5-III.7. For comparison the experimental results[33] are presented in Fig.III.4. In Fig.III.5 the square of absolute value of the correlation function $|C(t)|^2$ plotted as a function of t. The $\log|C(t)|^2$ as a function of t is plotted in Fig.III.6. The calculated absorption spectra of benzene are given in Fig.III.7. In Fig.III.6 it is seen that $|C(t)|^2$ does not decay simply exponentially and there are recurrences. However, as shown in Fig.III.7, except for the n=6 CH stretch overtone the spectra are structureless. It seems that the recurrences are not so substantial as to effect the major feature of the spectra. In order to see to what extent the recurrences effect the features of spectra, in Figs.III.5-III.7 we have also plotted the curves (dashed line) for $|\tilde{C}(t)|^2$, $\log|\tilde{C}(t)|^2$ and the corresponding spetra $\tilde{I}(\omega)/\tilde{I}(\omega)$, where $\tilde{C}(t)$ is defined by

$\tilde{C}(t) = C(t)$ for $0<t<t_F$ and $\tilde{C}(t) = \exp(-t/\tau_F)$ for $t>t_F$

with (III-75a)

$$\tau_F = -t_F/\log[C(t_F)] \ . \qquad \text{(III-75b)}$$

Here the time t_F indicated by the arrows in Figs.III.5-III.7 is the time at which the $|C(t)|^2$ has decayed to about 0.01 (except for n=6, for which t_F is about the end time of the initial rapid decay). In Fig.III.7 it is seen that except for n=6,the dashed line very closely follows the solid line. Thus, it seems that the initial rapid decay of $|C(t)|^2$ dominates the main features of the absorption spectrum as along as $|C(t)|^2$ is small ($\sim<0.01$) for later time. For n=6 CH stretch overtone there are strong recurrences. As a consequence, the absorption spectrum has some structure. The dashed line is different from the solid one. The former is close to being the envelope of the latter.

Similarly, the results for C_6D_6 are shown in Figs.III.8-III.10. Fig.III.8 and Fig.III.9 show that for CD stretch overtone n=5 of C_6D_6 the $|C(t)|^2$ hardly has any decay. Consequently, the spectra have an extremely narrow sharp peak. The $|C(t)|^2$ for CD stretch overtones n=6,7 and 8 initially decay approximately exponentially (but with much slower decay rate than that for CH overtone), then strong recurrences occur.

The line widths of the CH(CD) overtones of $C_6H_6(C_6D_6)$ taken from calculated spectra are listed in Table III.4 where the experimental results are also included.

The comparison shows that the present SCP kinetic coupling model gives semi-quantitively good results. For C_6H_6 the calculated line width of the CH stretch overtone n=5 is the largest while the line width of

the CH overtone n=9 is the smallest. The calculation reproduced the experimentally observed narrowing trend in the high overtone lineshapes. The line width calculated by the present model are systematically smaller than the experimental results. However, this is what might be expected from the fact that in this model only the linear terms of anharmonic kinetic couplings between the local mode and the ring normal modes are included. Taking into account the higher order terms in kinetic couplings and the other couplings such as the potential coupling, the couplings between the ring normal modes, and Coriolis coupling, etc., certainly will increase the decay rate of the overtone states, so that the lineshape will become broader.

For perdeuterobenzene C_6D_6 the results of the present work have the general features of the line shape of the CD overtone, i.e., the line widths are narrower than those of the CH overtones. Unfortunately, the calculated line widths for CD overtones are too narrow. Certainly, this is due to the lack of considering the other couplings which might be important since the kinetic coupling is so weak for CD overtone.

III.g) Remarks

The SCP reaction path model and the SCP kinetic coupling model lead to the extremely simple, explicit formulas for the dynamic quantities of interest. They provide us with very practical, although approximate, ways to deal with the dynamic problem for polyatomic systems. The sample calculations show that these methods are semi-quantitative. The SCP reaction path model seems applicable to a variety of problems in polyatomc dynamics[41], while the SCP kinetic coupling model is useful mainly in the study of the intramolecular energy transfer, which

certainly is a very important aspect of polyatomic dynamics. From a practical point of view the SCP kinetic coupling model seems more attractive. In this model the only input imformation needed is the harmonic force field of the molecule in the equilibrium geometry which can be obtained either by efficient ab initio quantum chemistry calculation[51], or by fitting the experimentally measured spectroscopic data[52]. From this input it is a simple matter to obtain the imformation about the energy transfer between the modes, and about the spectrum of the local mode, since we have a simple expression for that. It seems very promising that the SCP kinetic coupling model will find wide use in the theoretical study of the intramolecular dynamics of polyatomic system.

IV. A new semiclassical approach to the molecular dynamics--label variable classical mechanics.

IV.a) Introduction

In the light of difficulty with solving Schrödinger's equation and the failure of classical mechanics to account for the quantum effects prevailing in molecular dynamics, a great deal of effort have been devoted to developing a hybrid approach, semiclassical mechanics, by which simple classical mechanics could be used to obtain quantum imformation. The well known classical S-matrix theory(27) and the time-dependent wave-packet approach(53) are among the successfully developed semiclassical methods.

In a series of papers on continuous represention theory by Klauder(54), an interesting point of view on the correspondence between quantum mechanics and classical mechnics is presented. If one establishes a correspondence between the unit vector $|\Phi\rangle$ in Hilbert space Ξ, which describes the states of a system, and the sets of labels ℓ in an abstract label variable space $\mathcal{L}$ by a unitary mapping $M(\ell)$: $\ell \in \mathcal{L} \rightarrow |\Phi(\ell)\rangle \in \Xi$, then, it has been shown(54) that under certain restrictions the label variables formally follow the laws of classical mechanics. So that the evolution of the state vector in Hilbert space can be (in general, approximately) determined by calculating the time development of the label variables classically. In this chapter, based on this idea as an alternative semiclassical approach, the formalism for calculating the transition probabilities of inelastic scattering is developed.

IV.b) The classical mechanics of label variables--the basic idea.

It is illustrative to consider first the case of a single, nonrelativistic particle free moving in only one dimension. One begins with choosing a unit vector $|\Phi_o\rangle$ in the Hilbert space Ξ of the system as a reference vector. Thus,

$$\langle\Phi_o|\Phi_o\rangle = 1 \qquad \text{(IV-1)}$$

In principle the reference vector $|\Phi_o\rangle$ can be any proper vector in Hilbert space. A pair of self-adjoint oprtators acting in the Hilbert space are denoted by $\hat{Q}$ and $\hat{P}$; for example, $\hat{Q}$ and $\hat{P}$ might be the position and momentum operator, respectively. These operators obey the canonical commutation relation

$$[\hat{Q},\hat{P}] = i\,\hbar \quad . \qquad \text{(IV-2)}$$

Using these operators one can generate a two-parameter, unitary family of operators

$$\hat{U}[p,q] \equiv e^{-iq\hat{P}/\hbar}\, e^{ip\hat{Q}/\hbar} \qquad \text{(IV-3)}$$

that satisfy the composition law

$$\hat{U}[p,q]\ \hat{U}[p',q'] = e^{ipq'/\hbar}\ \hat{U}[p+p',q+q'],$$

as well as the basic relation

$$\hat{U}^{-1}[p,q] = \hat{U}^{\dagger}[p,q] = e^{-iq\hat{P}/\hbar}\, e^{ip\hat{Q}/\hbar} = e^{ipq}\ \hat{U}[-p,-q] \ . \qquad \text{(IV-5)}$$

Here p and q denote two arbitrary complex parameters. By acting on the reference vector $|\Phi_o\rangle$ with the unitary operartor $\hat{U}[p,q]$ one defines the unit vector

$$|\Phi[p,q]\rangle \equiv \hat{U}[p,q]|\Phi_o\rangle, \tag{IV-6}$$

which is labeled by p and q. It can be shown[55] that the set of these vectors $|\Phi[p,q]\rangle$ for all p and q form a continuous basis G of the Hilbert space Ξ in the sense that we can resolve the identity operator as

$$I = \int |\Phi[p,q]\rangle \frac{dp\ dq}{2\pi h} \langle\Phi[p,q]| \ ; \tag{IV-7}$$

therfore, an arbitrary vector $|\psi\rangle \in \Xi$ can be expressed in terms of the set of these vectors

$$|\psi\rangle = \int |\Phi[p,q]\rangle \frac{dp\ dq}{2\pi h} \psi(p,q) \ , \tag{IV-8}$$

where $\psi(p,q) \equiv \langle\Phi[p,q]|\psi\rangle$ is a representation of the vector $|\psi\rangle$ in this continuous basis G. Now if one imposes on the reference vector $|\Phi_o\rangle$ the restictions

$$\langle\Phi_o|\hat{P}|\Phi_o\rangle = 0 \text{ and } \langle\Phi_o|\hat{Q}|\Phi_o\rangle = 0, \tag{IV-9}$$

i.e., the mean values of $\hat{P}$ and $\hat{Q}$ in the reference atate are zero, then it is easy to show that

$$\langle\Phi[p,q]|\hat{P}|\Phi[p,q]\rangle = p \text{ and } \langle\Phi[p,q]|\hat{Q}|\Phi[p,q]\rangle = q. \tag{IV-10}$$

This means that, for such a choice of the reference vector, the label variables p and q acquire a physical significance, i.e., p and q now are the mean values of the operator $\hat{P}$ and $\hat{Q}$ in state $|\Phi[p,q]\rangle$, respectively. Eqs.(IV-9) and (IV-10) immediately lead to the following canonical kinematical form

$$i\hbar\langle\Phi[p,q]|\dot{\Phi}[p,q]\rangle = \langle\Phi[p,q]|\, e^{-ipP/\hbar}\, [\dot{q}\hat{P}-\dot{p}\hat{Q}]\, e^{ip\hat{Q}/\hbar}|\Phi_o\rangle$$

$$= \langle\Phi_o|[\dot{q}(\hat{P}+p) - \dot{p}\hat{Q}]\,|\Phi_o\rangle = p\dot{q}\ , \qquad \text{(IV-11)}$$

where the dot denotes the time derivative.

Consider now the equation of motion for evolution of the label variables p and q. As is well known in quantum mechanics[56], the time evolution of a state obeys the Schrödinger's equation

$$i\hbar\frac{d|\psi\rangle}{dt} = \hat{H}\,|\psi\rangle\ , \qquad \text{(IV-12)}$$

where $\hat{H}$ is the Hamiltonian of the system. The solution of this equation can be formally written as

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle\ , \qquad \text{(IV-13)}$$

if $\hat{H}$ does not depend on time t explicitly. The schrödinger's equation can be deduced by extremizing of the quantum action functional

$$I = \int [\langle\psi|i\hbar\dot{\psi}\rangle - \langle\psi|\hat{H}|\psi\rangle]\, dt \qquad \text{(IV-14)}$$

under unrestricted variation of the vector $|\psi(t)\rangle$. The unrestricted variation means that the vector $|\psi(t)\rangle$ can be any vector in the whole Hilbert space Ξ. Among all the vectors in Hilbert space only the vector which causes the action functional I to have an extreme value will correspond to a real state of the system. Suppose now the variation of the vector $|\psi\rangle$ is limited to a fairly restricted set of unit vectors such as the basis set vectors $|\Phi[p,q]\rangle$ just defined. In other words, one uses $|\Phi[p,q]\rangle$ instead of $|\psi\rangle$ in the expression of the action functional in Eq.(IV-14), and with the help of Eq.(IV-11) one obtains

$$I' = \int dt \{i\hbar\langle\Phi[p,q]|\dot{\Phi}[p,q]\rangle - \langle\Phi[p,q]|\hat{H}|\Phi[p,q]|\rangle\}$$

$$= \int dt\ (p\dot{q} - H) \qquad \text{(IV-15)}$$

with

$$H \equiv \langle\Phi[p,q]|\hat{H}|\Phi[p,q]\rangle\ . \qquad \text{(IV-16)}$$

One immediately recognizes that formally this is a classical action functional. The extremal variation of I' with respect to arbitrary variation of p and q yields the classical Hamilton's equations of motion

$$\dot{q} = \partial H/\partial p \quad , \dot{p} = -\ \partial H/\partial q\ . \qquad \text{(IV-17)}$$

There are two reasons why we have used the word "formally" here. First, H(p,q) is not equal to the classical Hamiltonian $H_{cl}(p,q)$ which has the functional form of the quantum mechanical Hamiltonian with explicit p and q substitution for the operators $\hat{P}$ and $\hat{Q}$, respectively. There is an

additional term $O(\hbar,\Phi_o,p,q)$[54],

$$H(p,q) \equiv \langle\Phi[p,q]|\hat{H}|\Phi[p,q]\rangle = \langle\Phi_o|\hat{H}(\hat{P}+p,\hat{Q}+q)|\Phi_o\rangle$$

$$= H_{cl}(p,q) + O(\hbar,\Phi_o,p,q) \qquad \text{(IV-18)}$$

For nonpathological Hamiltonians O depends only on the positive powers of $\hbar$. Hence, in this case

$$\lim_{\hbar\to 0} O(\hbar,\Phi_o,p,q) = 0 \ .$$

That is, in the classical limit $\hbar\to 0$, one has $H(p,q)=H_{cl}(p,q)$ so that Eq.(IV-17) becomes the conventional classical equation of motion. Since classical mechanics arises only in the formal sense, one can just as well adopt H(p,q) itself as the "classical" Hamiltonian. Second, in classical mechanics p and q refer to the momentum and coordinate of a particle. Here, however, p and q just represent label variables for the state vector $\Phi[p,q]$. The physical significance of p and q depends on the choice of the reference vector $|\Phi_o\rangle$ and the unitary operetor $\hat{U}[p,q]$.

This essentially finishes the general description of the approach. The practical scheme is as follows: Suppose that the system initially is in a state $|\Phi(0)\rangle=|\Phi[p(0),q(0)]\rangle$, i.e., the initial values p(0) and q(0) of p and q are known. Then, integrating the equation of motion Eq.(17) for p and q one obtains the values of p and q at time t, i.e., p(t) and q(t). Hence, the state of the system at time t can be determined as

$$|\Phi(t)\rangle = |\Phi[p(t),q(t)]\rangle \ . \qquad \text{(IV-19)}$$

In general if the system initially in a state which is not in the basis set G, then we can expand it in terms of the basis set states

$$|\psi(0)\rangle = \int |\Phi[p_o,q_o]\rangle \frac{dp_o dq_o}{2\pi\hbar} \langle\Phi[p_o,q_o]|\psi(0)\rangle \qquad \text{(IV-20)}$$

and at later time t we have

$$|\psi(t)\rangle = \int |\Phi[p_o(t),q_o(t)]\rangle \frac{dp_o dq_o}{2\pi\hbar} \langle\Phi[p_o,q_o]|\psi(0)\rangle \ , \qquad \text{(IV-21)}$$

where $|\Phi[p_o(t),q_o(t)\rangle$ can be evaluated by using the procedure just described above.

The crucial thing we have done during the derivation is the restricted variation of the functional. That is, we limited ourselves to considering only the vectors within the basis set G. It implies that we have assumed that if initially the system is in the state $|\Phi(0)\rangle = |\Phi[p(0),q(0)]\rangle$ belonging to the basis set G, then later on the state vector $|\Phi(t)\rangle$ for the system would be within the basis set G all the time and never goes beyond the basis set G. Mathematically it means if

$$|\Phi(0)\rangle = |\Phi[p(0),q(0)]\rangle \in G \text{ for } t=0$$

then

$$|\Phi(t)\rangle = e^{-iHt/\hbar}|\Phi(0)\rangle = \Phi|[p(t),q(t)]\rangle \in G \qquad \text{(IV-22)}$$

for all t. In general, this is not true. The validity of this approximation depends on the choice of the reference vector $|\Phi_o\rangle$ and on the Hamiltonian operaror $\hat{H}$. For example, if the Hamiltonian is linear or quadratic in $\hat{P}$ and $\hat{Q}$, it would be exact[54].

It is straightforward to generalize the above formalism to a system of N degrees of freedom. All that is needed is the replace the scalar label variables with the vector label variables

$$q \rightarrow \mathbf{q} \qquad , \; p \rightarrow \mathbf{p} \; , \tag{IV-23}$$

scalar operators with the vector operators

$$\hat{Q} \rightarrow \hat{\mathbf{Q}} \; , \quad \hat{P} \rightarrow \hat{\mathbf{P}} \; , \tag{IV-24}$$

and consequently the scalar product with the vector inner product

$$q\hat{P} \rightarrow \mathbf{q}\cdot\hat{\mathbf{P}} \; , \; p\hat{Q} \rightarrow \mathbf{p}\cdot\hat{\mathbf{Q}} \; . \tag{IV-25}$$

Here $\mathbf{q}$ and $\mathbf{p}$ denote the sets of labels $\{q_i\}$ and $\{p_i\}$, $i=1,2,\ldots,N$, $\hat{\mathbf{Q}}$ and $\hat{\mathbf{P}}$ signify the sets of the operators $\{\hat{Q}_i\}$ and $\{\hat{P}_i\}$, $i=1,2,\ldots,N$, which satisfy the commutation relation

$$[\hat{Q}_i,\hat{P}_j] = i\hbar\delta_{ij} \; , \; [\hat{Q}_i,\hat{Q}_j] = 0, \; [\hat{P}_i,\hat{P}_j] = 0 \; , \tag{IV-26}$$

where δ_{ij} is the Kronecker delta function.

IV.c) Application to the collinear inelastic scattering of A+BC.

To illustrate the application of the general results obtained above, it is useful to consider the simplest nontrivial example of a collision system that possesses an internal degree of freedom in

addition to translation. The Hamiltonian of the system is

$$H(\hat{P},\hat{R},\hat{p},\hat{r}) = H_o(\hat{P},\hat{R},\hat{p},\hat{r}) + V(\hat{r},\hat{R}) \quad , \tag{IV-27a}$$

with

$$H_o(\hat{P},\hat{R},\hat{p},\hat{r}) = \frac{\hat{P}^2}{2\mu} + \frac{\hat{p}^2}{2m} + v(\hat{r}) \ , \tag{IV-27b}$$

where $\hat{R}$ and $\hat{P}$ are the cartesian coordinate and momentum for translation of A relative to the center of mass of BC, and $\hat{r}$ and $\hat{p}$ are the cartesian variables for the vibration of BC.

One must first choose the reference vector. It is obvious that one should take the initial state as the reference state if it is possible, since it corresponds to the zero initial value of label variables and there would be no ambiguity in deciding the initial condition. However, as a reference state it must be a proper vector, and things will be much easier if the expectation values of $\hat{P}$ and $\hat{R}$ are zero as required by Eq.(IV-9). In the present case, the initial vibrarional state corresponds to a proper vector in Hilbert space and can be chosen as a reference vector for the vibrational motion. However, in general it does not fulfill the conditions of Eq.(IV-9)

$$\langle n_i|\hat{p}|n_i\rangle = \bar{p} \neq 0, \ \langle n_i|\hat{r}|n_i\rangle = \bar{r} \neq 0 \quad , \tag{IV-28}$$

where $|n_i\rangle$ is the initial vibrational state of molecule BC. But if the new pair of self-adjoint operators $\hat{p}'$and $\hat{r}'$

$$\hat{p}' = \hat{p} - \bar{p} \ , \ \hat{r}' = \hat{r} - \bar{r} \tag{IV-29}$$

are used as the generator of unitary mappong, one will have

$$[\hat{r}',\hat{p}'] = i\hbar \ , \langle n_i|\hat{p}'|n_i\rangle = 0, \text{ and } \langle n_i|\hat{r}'|n_i\rangle = 0 \ . \qquad \text{(IV-30)}$$

In contrast, the initial momentum eigenstate for translation is not a localized state, i.e., is not a proper vector, so it cannot be chosen as a reference vector. Instead a Gaussian wave packet state $|\Phi_{ot}\rangle$ is chosen, which has the representation in positon representation

$$\langle R|\Phi_{ot}\rangle = \frac{1}{(\pi\xi)^{1/4}} \exp(-\frac{R^2}{2\xi^2}) \quad , \qquad \text{(IV-31a)}$$

and in momentum representation

$$\langle P|\Phi_{ot}\rangle = \sqrt{\xi/\hbar}\ \frac{1}{(\pi)^{1/4}} \exp(-\frac{\xi^2}{2\hbar^2} P^2) \ , \qquad \text{(IV-31b)}$$

where subscript t refers to translational motion, and ξ is a paremeter characterizing the width of the wave packet. $|\Phi_{ot}\rangle$ satisfies the condition of Eq.(IV-9)

$$\langle\Phi_{ot}|\hat{P}|\Phi_{ot}\rangle = 0 \text{ and } \langle\Phi_{ot}|\hat{R}|\Phi_{ot}\rangle = 0 \qquad \text{(IV-32)}$$

The direct product of these two reference vectors constitutes the reference vector for the complete system

$$|\Phi_o\rangle = |n_i\rangle|\Phi_{ot}\rangle \qquad \text{(IV-33)}$$

The unitary mapping operator is then defined by

$$\hat{U}(P_R,q_R,p_r,q_r) = e^{-iq_R\hat{P}/\hbar}\, e^{-iq_r\hat{p}'/\hbar}\, e^{ip_R\hat{R}/\hbar}\, e^{ip_r\hat{r}'/\hbar} , \qquad \text{(IV-34)}$$

where p_R, q_R, p_r and q_r are label variables, and the unit vector is given by

$$|\Phi[p_R(t),q_R(t),p_r(t),q_r(t)]\rangle = \hat{U}[p_R(t),q_R(t),p_r(t),q_r(t)]|\Phi_o\rangle$$

$$= e^{-iq_R(t)\hat{P}/\hbar}\, e^{-q_r(t)\hat{p}'/\hbar}\, e^{ip_R(t)\hat{R}/\hbar}\, e^{ip_r(t)\hat{r}'/\hbar}|n_i\rangle|\Phi_{ot}\rangle$$

$$= |\Phi_t[p_R(t),q_R(t)]\rangle\, |\Phi_v[p_r(t),q_r(t)]\rangle , \qquad \text{(IV-35)}$$

where

$$|\Phi_t[p_R(t),q_R(t)]\rangle \equiv e^{-iq_R(t)\hat{P}/\hbar}\, e^{ip_R(t)\hat{R}/\hbar}|\Phi_{ot}\rangle \qquad \text{(IV-36a)}$$

and

$$|\Phi_v[p_r(t),q_r(t)]\rangle \equiv e^{-iq_r(t)\hat{p}'/\hbar}\, e^{ip_r(t)\hat{r}'/\hbar}|n_i\rangle . \qquad \text{(IV-36b)}$$

If at t=0 one has

$$|\Phi[p_R(0),q_R(0),p_r(0),q_r(0)\rangle = |\Phi_t[p_R(0),q_R(0)]\rangle|n_i\rangle , \qquad \text{(IV-37)}$$

then, from Eqs.(IV-35) and (IV-36), it is clear that

$$p_r(0) = 0 \text{ and } q_r(0) = 0 \qquad \text{(IV-38)}$$

or

$$|\Phi_v[p_r(0),q_r(0)]\rangle = |\Phi_v[0,0]\rangle = |n_i\rangle \qquad \text{(IV-39)}$$

and

$$|\Phi_t[p_R(0),q_R(0)]\rangle = e^{-iq_R(0)\hat{P}/\hbar}\, e^{ip_R(0)\hat{R}/\hbar}|\Phi_{ot}\rangle \qquad \text{(IV-40)}$$

According to Eq.(IV-18), with help of Eq.(IV-35), it follows that

$$H(p_r,p_r q_R,q_r) \equiv \langle\Phi[p_R,p_r,q_R,q_r]|H(\hat{P},\hat{R},\hat{p},\hat{q}\ )|\Phi[p_R,p_r,q_R,q_r]\rangle$$

$$= \langle\Phi[p_R,p_r,q_R,q_r]|H'(\hat{P},\hat{R},\hat{p}',\hat{r}')|\Phi[p_R,p_r,q_R,q_r]\rangle$$

$$= \langle\Phi_o|H'(\hat{P}+p_R,\hat{R}+q_R,\hat{p}'+p_r,\hat{r}'+q_r)|\Phi_o\rangle$$

$$= \frac{P_R^{\ 2}}{2\mu} + \frac{(p_r+\bar{p})^2}{2m} + \bar{v}(q_r,\bar{r}) + \bar{V}(q_R,q_r,\bar{r}) + 0_P \qquad \text{(IV-41)}$$

where

$$0_P = \langle n_i|\frac{(\hat{p}')^2}{2m}|n_i\rangle + \langle\Phi_{ot}|\frac{\hat{P}^{\ 2}}{2\mu}|\Phi_{ot}\rangle$$

$$= \langle n_i|\frac{\hat{p}^{\ 2}}{2m}|n_i\rangle - \frac{\bar{p}^{\ 2}}{2m} + \langle\Phi_{ot}|\frac{\hat{P}^{\ 2}}{2\mu}|\Phi_{ot}\rangle = \text{const.} \quad , \qquad \text{(IV-42)}$$

and

$$\bar{v}(q_r,\bar{r}) = \langle n_i|v(\hat{r}+q_r)|n_i\rangle \quad , \qquad \text{(IV-43a)}$$

$$\bar{V}(q_r,\bar{r},q_R) = \langle\Phi_{ot}n_i|V(\hat{R}+q_R,\hat{r}+q_r)|\Phi_{ot}n_i\rangle \quad . \qquad \text{(IV-43b)}$$

Similarly one has

$$H_o(p_R,p_r q_R,q_r) \equiv \langle\Phi[p_R,p_r,q_R,q_r]|H_o(\hat{P},\hat{R},\hat{p},\hat{r})|\Phi[p_R,p_r,q_R,q_r]\rangle$$

$$= \frac{P_R^{\ 2}}{2\mu} + \frac{(p_r+\bar{p})^2}{2m} + \bar{v}(q_r,\bar{r}) + 0_P \quad . \qquad \text{(IV-44)}$$

From the scattering theory [57] it is well known that

$$|\text{out}\rangle = \hat{S}|\text{in}\rangle = \lim_{t_1 \to -\infty, t_2 \to +\infty} e^{i\hat{H}_o t_2/\hbar} e^{-i\hat{H} t_2/\hbar} e^{i\hat{H} t_1/\hbar} e^{-i\hat{H}_o t_1/\hbar} |\text{in}\rangle \quad , \tag{IV-45}$$

where $|\text{out}\rangle$ and $|\text{in}\rangle$ are out-asymptote and in-asymptote, respectively, and $\hat{S}$ is the scattering operator. Mathematically, as expressed in Eq.(IV-45), t_1 should tend to $-\infty$ and t_2 tend to $+\infty$. But in practice it is sufficient that $|t_1| = |t_{1f}|$ and $t_2 = t_{2f}$ be large enough so that one has

$$e^{-i\hat{H}t/\hbar} |\Phi\rangle \simeq e^{-i\hat{H}_o t/\hbar} |\text{in}\rangle \text{ for } t < t_1 = -|t_{1f}| \ , \tag{IV-46a}$$

and

$$e^{-i\hat{H}t/\hbar} |\Phi\rangle \simeq e^{-i\hat{H}_o t/\hbar} |\text{out}\rangle \text{ for } t > t_2 = t_{2f} \quad . \tag{IV-46b}$$

With this understanding one can rewrite the Eq.(IV-45) as

$$|\text{out}\rangle = \hat{S}|\text{in}\rangle = \hat{\Omega}_3 \hat{\Omega}_2 \hat{\Omega}_1 |\text{in}\rangle \quad , \tag{IV-47}$$

with

$$\hat{\Omega}_1 \equiv e^{i\hat{H}_o |t_{1f}|/\hbar} \ , \ \hat{\Omega}_2 \equiv e^{-i\hat{H}(t_{2f}+|t_{1f}|)/\hbar} \ , \ \hat{\Omega}_3 \equiv e^{i\hat{H}_o t_{2f}/\hbar} \ . \tag{IV-48}$$

This form suggests that the out-asymptote $|\text{out}\rangle$ is obtained from the in-asymptote by following its evolution during 3 separate time periods: in period 1 from $t=0$ to $t=t_{1f}$ the evolution of state is generated by the Hamiltonian $\hat{H}_o$, or, equivalently, $(-\hat{H}_o)$ generates the evolution from $t=0$ to $t=|t_{1f}|$; in period 2 the state is evolved from t_{1f} to t_{2f} according to Hamiltonian $\hat{H}$; and, finally, in period 3 the state is evolved from $t=t_{2f}$ back to $t=0$ by $\hat{H}_o$.

If one now identifies $|\text{in}\rangle = |n_1\rangle \ |\Phi_{ot}[p_R(0), q_R(0)]\rangle$, then by virtue of our approximation Eq.(IV-22) one has

$$|\text{out}\rangle = |\Phi[p_R(t_f),p_r(t_f),q_R(t_f),q_r(t_f)]\rangle$$

$$= |\Phi_v[p_r(t_f),q_r(t_f)]\rangle|\Phi_t[p_R(t_f),q_r(t_r)]\rangle$$

$$= e^{-iq_R(t_f)\hat{P}/\hbar}\, e^{-iq_r(t_f)\hat{p}'/\hbar}\, e^{ip_R(t_f)\hat{R}/\hbar}\, e^{ip_r(t_f)\hat{r}'/\hbar}\, |n_i\rangle|\Phi_{ot}\rangle \quad , \tag{IV-49}$$

where $p_R(t_f),q_R(t_f),p_r(t_f)$ and $q_r(t_f)$ are correspondingly determined by classical trajectory calculation as follows. One first integrates the classical equations of motion Eqs.(IV-50) corresponding to $H_o(p_R,p_r,q_R,q_r)$ from $t=0$ to $t=t_{1f}$

$$\frac{dq_R(t)}{dt} = \frac{p_R(t)}{\mu} \quad , \quad \frac{dq_r(t)}{dt} = \frac{p_r + \bar{p}}{m} \quad , \tag{IV-50a}$$

$$\frac{dp_R(t)}{dt} = 0 \quad , \quad \frac{dp_r(t)}{dt} = -\frac{\partial\bar{v}(q_r,\bar{r})}{\partial q_r} \quad , \tag{IV-50b}$$

with initial conditions

$$q_R = q_R(0) \ , \ p_R = p_R(0) \ , \ q_r = 0 \ , \text{ and } p_r = 0 \ , \quad \text{at } t=0 \quad , \tag{IV-51}$$

then continuously integrates Eqs.(IV-52) corresponding to $H(p_R,p_r,q_R,q_r)$ from $t=t_{1f}$ to $t=t_{2f}$

$$\frac{dq_R(t)}{dt} = \frac{p_R(t)}{\mu} \quad , \quad \frac{dq_r(t)}{dt} = \frac{p_r + \bar{p}}{m} \quad , \tag{IV-52a}$$

$$\frac{dp_R(t)}{dt} = -\frac{\partial\bar{V}(q_r,\bar{r},q_R)}{\partial q_R} \quad , \quad \frac{dp_r(t)}{dt} = -\frac{\partial\bar{v}(q_r,\bar{r})}{\partial q_r} - \frac{\partial\bar{V}(q_r,\bar{r},q_R)}{\partial q_r} \quad , \tag{IV-52b}$$

and finally integrates Eq.(IV-50) from $t=t_2$ back to $t=0$.

The projection of $|\text{out}\rangle$ on the final state $|n_t P^f\rangle$ then can be readily calculated

$$\langle n_f P^f | \text{out}\rangle = \langle n_f | \Phi_v[p_r(t_f), q_r(t_f)]\rangle \langle P^f | \Phi_t[p_R(t_f), q_R(t_f)]\rangle \quad , \tag{IV-53}$$

where

$$\langle P^f | \Phi_t[p_R(t_f), q_R(t_f)]\rangle = \langle P^f | \, e^{-iq_R(t_f)P/\hbar} \, e^{ip_R(t_f)R/\hbar} | \Phi_{ot}\rangle$$

$$= \sqrt{\xi/\hbar} \, \frac{1}{(\pi)^{1/4}} \exp\{-\frac{i}{\hbar} q_R(t_f)P^f - \frac{\xi^2}{2\hbar^2}[P^f - p_R(t)]^2\} \quad . \tag{IV-54}$$

and

$$\langle n_f | \Phi_v[p_r(t_f), q_r(t_f)]\rangle = \langle n_f | \, e^{iq_r(t_f)\hat{p}'/\hbar} \, e^{-ip_r(t_f)\hat{r}'/\hbar} | n_i\rangle$$

$$= e^{iq_r(t_f)\bar{p}/\hbar} \, e^{-ip_r(t_f)\bar{r}/\hbar} \int_{-\infty}^{\infty} dr \langle n_f | r\rangle \, e^{ip_r(t_f)[r - q_r(t_f)]/\hbar} \langle r - q_r(t_f) | n_i\rangle \tag{IV-55}$$

Here $|n_f\rangle$ and $|P^f\rangle$ are final vibrarional state and translational momentum eigenstate, respectively.

On the other hand, one has

$$\langle n_f P^f | \text{out}\rangle = \langle n_f P^f | \hat{S} | \text{in}\rangle = \langle n_f P^f | \hat{S} | n_i\rangle | \Phi_t(p_R(0), q_R(o)]\rangle$$

$$= \int \frac{dP}{2\pi\hbar} \langle n_f P^f | \hat{S} | n_i P\rangle \langle P | \Phi_t[p_R(0), q_R(0)]\rangle = S_{n_f \leftarrow n_i}(E) \int \frac{\mu}{2\pi\hbar P} dE \, \delta(E - E_o)$$

$$\times \frac{2\pi\hbar}{\mu}(PP^f)^{1/2} \langle P | \Phi_t[p_R(0), q_R(0)]\rangle = \left(\frac{P^f}{P^i}\right)^{1/2} \langle P^i | \Phi_t[p_R(0), q_R(0)]\rangle S_{n_f \leftarrow n_i}(E) \quad ,$$

or

$$S_{n_f \leftarrow n_i}(E) = \left(\frac{P^i}{P^i}\right)^{1/2} \frac{\langle n_f P^f | \text{out}\rangle}{\langle P^i | \Phi_t[p_{RT}(0), q_R(0)]\rangle} \quad , \tag{IV-56}$$

with

$$P^i = \sqrt{2\mu(E - \varepsilon_{n_i})}, \qquad P^f = \sqrt{2\mu(E - \varepsilon_{n_f})} \quad , \tag{IV-57}$$

and

$$\langle P^i|\Phi_t[p_R(0),q_R(0)]\rangle=\sqrt{\xi/\pi}\,\frac{1}{(\pi)^{1/4}}\exp\{[-\frac{i}{\hbar}q_R(0)P^i]-[\frac{\xi^2}{2\hbar^2}(P^i-p_R(0)^2]\}\ . \tag{IV-58}$$

Here ε_n is the vibrarional energy of molecule BC in the state n and E_o is the total energy of the whole system. Eq.(IV-56) is exact. Now if an approximation Eq.(IV-53) is used, then by virtue of Eq.(IV-54) and Eq.(IV-55) it is obtained that

$$S_{n_f\leftarrow n_i}(E) = (\frac{P^i}{P^f})^{1/2}\frac{\langle P^f|\Phi_t[p_R(t),q_R(t)]\rangle}{\langle P^i|\Phi_t[p_R(0),q_R(0)]\rangle}\langle n_f|\Phi_v[p_r(t_f),q_r(t_f)]\rangle$$

$$=\frac{\sqrt{P^i}}{\sqrt{P^f}}e^{-i\gamma(t_f)/\hbar}e^{\frac{-\xi^2}{2\hbar^2}B(t_f)}\int_{-\infty}^{\infty}dr\langle n_f|r\rangle e^{ip_r(t_f)[r-q_r(t_f)]/\hbar}\langle r-q_r(t_f)|n_i\rangle\ , \tag{IV-59}$$

where

$$\gamma(t_f) = q_R(t_f)P^f - q_R(0)P^i + p_r(t_f)\bar{r} - q_r(t_f)\bar{p}\quad , \tag{IV-60a}$$

$$B(t_f) = [P^f - p_R(t_f)]^2 - [P^i - p_R(0)]^2\quad . \tag{IV-60b}$$

Thus, the transition probability can be calculated

$$P_{n_f\leftarrow n_i} = |S_{n_f\leftarrow n_i}(E)|^2 = \frac{P^i}{P^f}\ e^{-(\frac{\xi}{\hbar})^2 B(t_f)}$$

$$\times\left|\int_{-\infty}^{\infty}dr\ \langle n_f|r\rangle\ e^{ip_r(t_f)[r-q_r(t_f)]/\hbar}\langle r-q_r(t_f)|n_i\rangle\right|^2\quad , \tag{IV-61}$$

where $p_R(t_f),q_R(t_f),p_r(t_f)$ and $q_r(t_f)$ are determined by calculating one classical trajectory.

IV.d) Example: The vibrationally inelastic scattering of collinear

$He+H_2$.

To test the potential usefulness of this new approach a calculation for the Secrest-Johnson model[32] of collinear $He+H_2$ vibrationally inelastic scattering has been carried out. In the usual dimensionless coordinate system the Hamiltonian reads

$$H(P,R,p,r) = \frac{\hat{P}^2}{2\mu} + \frac{\hat{p}^2}{2} + \frac{\hat{r}^2}{2} + \exp[-\alpha(\hat{r}-\hat{R})] \quad , \tag{IV-62}$$

with

$$\mu = \frac{2}{3} \quad \text{and} \quad \alpha = 0.3 \quad . \tag{IV-63}$$

In this case the vibration states $|n\rangle$ are the eigenstates of harmonic oscillator, so that

$$\langle n_i|\hat{P}|n_i\rangle = \bar{p} = 0 \quad , \langle n_i|\hat{r}|n_i\rangle = 0 \quad . \tag{IV-64}$$

Also, the "classical" hamiltonian has the form

$$H_o = \frac{p_R^2}{2\mu} + \frac{p_r^2}{2} + \frac{q_r^2}{2} + 0_p + 0_v \quad , \tag{IV-65}$$

with

$$0_p = \langle n_i|\frac{\hat{p}^2}{2}|n_i\rangle + \langle\Phi_{ot}|\frac{\hat{p}^2}{2}|\Phi_{ot}\rangle = \text{const.} \quad \text{and} \quad 0_v = \langle n_i|\frac{\hat{r}^2}{2}|n_i\rangle = \text{const.} \quad , \tag{IV-66}$$

and

$$H = H_o + A\exp[\alpha(q_r - q_R)] \quad , \tag{IV-67}$$

with

$$A = \langle n_i|e^{\alpha\hat{r}}|n_i\rangle\langle\Phi_{ot}|e^{-\alpha\hat{R}}|\Phi_{ot}\rangle = \text{const.} \quad . \tag{IV-68}$$

It immediately follows that the equations of motion for the label variables are:

for H_o

$$\frac{dq_R}{dt} = \frac{p_R}{\mu}, \quad \frac{dq_r}{dt} = p_r, \quad \frac{dp_R}{dt} = 0, \text{ and } \frac{dp_r}{dt} = -q_r \quad , \tag{IV-69}$$

and for H

$$\frac{dq_R}{dt} = \frac{p_R}{\mu} \quad , \quad \frac{dq_r}{dt} = p_r \quad ,$$

$$\frac{dp_R}{dt} = A\ \alpha \exp \alpha(q_r - q_R) \ , \quad \frac{dp_r}{dt} = -q_r - A\ \alpha \exp \alpha(q_r - q_R) \quad . \tag{IV-70}$$

In this example the matrix element Eq.(IV-55) has a simple analytic expression. In order to see this let us first make the following transformation:

$$\hat{a} \equiv (\hat{r} + i\ \hat{p})/\sqrt{2} \quad , \quad \hat{a}^\dagger \equiv (\hat{r} - i\hat{p})/\sqrt{2} \quad , \tag{IV-71}$$

and

$$Z(t) \equiv [q_r(t) + ip(t)]/\sqrt{2} \quad , \text{ and } \quad \theta(t) \equiv \tan^{-1} \frac{p_r(t)}{q_r(t)} \tag{IV-72}$$

It then follows that (for the details, see the appendix D)

$$\langle n_f | e^{-iq_r(t_f)\hat{p}} e^{ip_r\hat{r}} | n_f \rangle = e^{-i\frac{1}{2}|Z(t_f)|^2 \sin 2\theta(t_f)} e^{-\frac{1}{2}|Z(t_f)|^2}$$

$$\times \langle n_f | e^{\hat{a}^\dagger Z(t_f)} e^{-\hat{a}Z^*(t_f)} | n_i \rangle$$

$$= e^{-i\frac{1}{2}|Z(t_f)|^2 \sin 2\theta(t_f)} e^{\frac{|Z(t_f)|^2}{2}} e^{i(n_f - n_i)\theta(t_f)}$$

$$\times \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i!\,n_f!}\,|Z(t_f)|^{n_f - n_i + 2k}}{k!(n_i - k)!(n_f - n_i + k)!} \ , \tag{IV-73}$$

where $Z^*(t_f) = [q_r(t_f)-ip_r(t_f)]/\sqrt{2}$ and $|Z| = (ZZ^*)^{1/2}$. By virture of Eq.(IV-73), the transition probability Eq.(IV-61) becomes

$$P_{n_f \leftarrow n_i} = \frac{P^i}{P^f} \exp\{-\frac{\xi^2}{2}[(P^f-p_R(t_f))^2 - (P^i-p_R(0))^2]\}\exp-|Z(t_f)|^2$$

$$\times \left| \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i!n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} |Z(t_f)|^{n_f-n_i+2k} \right|^2 . \qquad \text{(IV-74)}$$

If this theory gave $|out\rangle = \hat{S}|n_i\rangle|\Phi_{ot}[p_R(0),q_R(0)]\rangle$ exactly, the transition amplitude $S_{n_f \leftarrow n_i}(E)$ obtained by using Eq.(IV-56) would be independent of the choice of $p_R(0)$ and $q_R(0)$. Since it is an approximation, though, the results of a calculation do depend on the choice of $p_R(0)$. Since $p_R(0)$ is the average value of the momentum $\hat{p}$ in the initial wave packet state $|\Phi_f[p_R(0),q_R(0)]\rangle$ with initial and final vibrational states $|n_i\rangle$ and $|n_f\rangle$ and total energy E_o specified, physical intuition suggests that the usual semiclassical choice of $p_R(0)$ should be reasonable

$$p_R(0) = [2\mu(E_o - \frac{\varepsilon_{n_i} + \varepsilon_{n_f}}{2})]^{1/2} . \qquad \text{(IV-75)}$$

The choice of $q_k(0)$ is more and less arbitrary. It only affects the determination of t_{1f} and t_{2f}. So long as the conditions Eq.(IV-46) are satisfied, $q_R(0)$ can be any value. Furthermore, from Eq.(IV-70) and Eq(IV-71) one can see that the parameter ξ which characterizes the reference vector $|\Phi_{ot}\rangle$ do not have any dynamic effect on the classical motion of label variables. That is, the initial conditions and the final values of $p_R(t)$ and $|Z(t)|$ are independent of ξ. Therefore, one can

freely choose ξ. However, ξ appears in expression Eq.(IV-74) for the probability $P_{n_f \leftarrow n_i}$. In order to eliminate this ξ dependence we use the microreversibility condition

$$P_{n_f \leftarrow n_i} = P_{n_i \leftarrow n_f} \quad , \tag{IV-76}$$

and notice that for the semiclassical choice of $p_R(0)$[see Eq.(IV-75)], one has

$$P_{n_f \leftarrow n_i} = \frac{P^i}{P^f} \exp\{-\frac{\xi^2}{2}[(P^f - p_R(t_f))^2 - (P^i - p_R(o))^2] F_{f \leftarrow i}(|Z(t_f)|)\}$$

$$= \frac{P^f}{P^i} \exp\{-\frac{\xi^2}{2}[(P^i - p_R(t_f))^2 - (P^f - p_R(0))^2 F_{i \leftarrow f}(|Z(t_f)|)\} = P_{n_i \leftarrow n_f} \quad , \tag{IV-77}$$

where

$$F_{f \leftarrow i}(|Z(t_f)|) = \exp[-|Z(t_f)|^2] \left| \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! n_f!}\ |Z(t_f)|^{n_f - n_i + 2k}}{k!(n_i - k)!(n_f - n_i + k)!} \right|^2$$

and

$$F_{i \leftarrow f}(|Z(t_f)|) = e^{-|Z(t_f)|^2} \left| \sum_{k=0}^{n_f} (-1)^k \frac{\sqrt{n_i! n_f!}\ |Z(t_f)|^{n_i - n_f + 2k}}{k!(n_f - k)!(n_i - n_f + k)!} \right|^2 . \tag{IV-78}$$

It is easy to show that

$$F_{f \leftarrow i} = F_{i \leftarrow f} .$$

Thus, Eq.(IV-77) becomes

$$\frac{P^i}{P^f} \exp\{-\frac{\xi^2}{2}[(P^f - p_R(t_f))^2 - (P^i - p_R(0))^2]\}$$

$$= \frac{P^f}{P^i} \exp\{-\frac{\xi^2}{2}[(P^i - p_R(t_f))^2 - (P^f - p_R(0))^2]\} . \tag{IV-79}$$

rearranging Eq.(IV-79) gives

$$\frac{P^i}{P^f}\exp\{-\frac{\xi^2}{2}[(P^i-p_r(0\ ))^2-(P^f-p_R(t_f))^2]\}=\exp\{\frac{p_R(0)-p_R(t_f)}{P^f-P^i}\ln\frac{P^f}{P^i}\}\quad, \tag{IV-80}$$

then, one obtains

$$P_{n_f\leftarrow n_i}=B\ \exp[-|Z(t_f)|^2]\left|\sum_{k=0}^{n_i}(-1)^k\frac{\sqrt{n_f!n_i!}}{k!(n_i-k)!(n_f-n_i+k)!}|Z(t_f)|^{n_f n_i+2k}\right|^2 ,$$

with (IV-81a)

$$B=\exp\{\frac{p_R(0)-p_R(t_f)}{P^f-P^i}\ln\frac{P^f}{P^i}\}\quad . \tag{IV-81b}$$

It is very interesting to notice that Eq.(IV-81a) is identical to the semiclassical probability expression obtained from the forced quantum oscillator method[58-61] except for the extra factor B which is close to one. We can see this, if one makes a substitution $k\rightarrow(n_i-k)$ and realizes that $|Z(t_f)|^2$ is just the classical energy transfer associated with the one trajectory being integrated.

The results from Eqs.(IV-81) are given in table IV.1 where for comparison the exact quantum mechanical results of Ref.(32) are also included. In Fig.IV.1 we pictorially present the results for total energy, E_o=4,6. and 10 in units of $\hbar\omega$. For a given total energy E_o and an initial vibrational state n_i only one classical trajectory needs to be calculated to determine the transition probability to a final vibrational state n_f.

The comparision in Table IV.1 and Fig.IV.1 shows that the present approach describes the inelastic scattering process encouragingly well.

One obtains reasonably good results over a wide range of energies for a great variety of Δn transitions.

IV.e) T-V and V-V energy transfer in collinear collision of two diatomic molecules—an application of label variable classical mechanics.

The above example shows the validity of this approach for the calculation of the absolute value of the S-matrix elements since the phase of the S-matrix elements is irrelevant in this example. For more complex collision processes a coherent sum of S-matrix elements is often involved, so the phase of the S-matrix elements, then, plays an important role. Therefore, any useful approximate method must be able to give the correct relative phase factors as well as the absolute value of the transition amplitude.

In order to test how well the label variable classical mechanics method handles the phase problem, we consider the T-V and V-V energy transfer in collinear collisions of two identical harmonic oscillators, where quantum resonance phenomina are pronounced. A certain amount of work on this subject has been done using different approaches[63-71] It is a little surprising that only a few full quantum mechanical calculations[63-65] have been done.

The Hamiltonian for the collinear collision of two diatomic molecules AB + BC, after separaring out the motion of the center of mass, has the form

$$\tilde{H} = \frac{\tilde{P}^2}{2\mu} + \frac{\tilde{p}_1^{\,2}}{2m_1} + \frac{\tilde{p}_2^{\,2}}{2m_2} + v_1(\tilde{x}_1) + v_2(\tilde{x}_2) + V(\tilde{x}_1,\tilde{x}_2,\tilde{X}) \qquad \text{(IV-82)}$$

with

$$m_1 = \frac{m_A m_B}{m_A+m_B} \ , \ m_2 = \frac{m_C m_D}{m_C+m_D} \ , \ \mu = \frac{(m_A+m_B)(m_C+m_D)}{M} \ \text{and} \ M = m_A+m_B+m_C+m_D \ , \tag{IV-83}$$

where m_A, m_B, m_C, and m_D are the masses of the atoms A,B,C, and D, respectively, $\tilde{X}$ and $\tilde{P}$ are the Cartesian coordinate and momentum for the relative translational motion between the centers of mass of two molecules, and $\tilde{x}_1, \tilde{p}_1$ and $\tilde{x}_2, \tilde{p}_2$ are the Cartesian coordinates and momenta for vibrational motion of two diatomic molecules, respectively. If one describes the molecules as two identical harmonic oscillators and uses the nearest atom approximation[72,73] for the interaction potential, i.e., one assumes that the interaction potential $V(\tilde{x}_1, \tilde{x}_2, \tilde{X})$ varies only with the distance between the two rearest atoms of the molecules; then the Hamiltonian, in dimensionless units, can be written as

$$\hat{H} = \frac{\hat{P}^2}{2\mu} + \frac{\hat{p}_1^2}{2} + \frac{\hat{r}_1^2}{2} + \frac{\hat{p}_2^2}{2} + \frac{\hat{r}_2^2}{2} + V[\hat{R}-(\hat{r}_1+\hat{r}_2)] \ , \tag{IV-84}$$

with

$$\hat{R} = \left(\frac{m\omega}{\hbar}\right)^{1/2} \frac{m_C+m_D}{m_D} \tilde{X} \ , \ \hat{P} = \left(\frac{1}{m\omega\hbar}\right)^{1/2} \frac{m_D}{m_C+m_D} \tilde{P} \ ,$$

$$\hat{H} = \frac{\tilde{H}}{\hbar\omega} \ , \quad \mu = \frac{m_D(m_A+m_B)}{m_C(m_A+m_B+m_C+m_D)}$$

and

$$\hat{r}_1 = \left(\frac{m\omega}{\hbar}\right)^{1/2} (\tilde{x}_1 - \tilde{x}_o) \ , \ \hat{r}_2 = \left(\frac{m\omega}{\hbar}\right)^{1/2} (\tilde{x}_2 - \tilde{x}_o) \ , \ \hat{p}_1 = \left(\frac{1}{\hbar\omega m}\right)^{1/2} \tilde{p}_1 \ , \ \text{and} \ \hat{p}_2 = \left(\frac{1}{\hbar\omega m}\right)^{1/2} \tilde{p}_2 \ , \tag{IV-85}$$

where $\tilde{x}_o$, m and ω are respectively the equilibrium position, mass and the frequency of the harmonic osillators, and $m_B = m_C$ has been assumed. One now introduces the following variable transformations

$$\hat{p}_+ = \frac{1}{\sqrt{2}}(\hat{p}_1 + \hat{p}_2) \ , \ \hat{p}_- = \frac{1}{\sqrt{2}}(\hat{p}_1 - \hat{p}_2) \ , \ \hat{r}_+ = \frac{1}{\sqrt{2}}(\hat{r}_1 + \hat{r}_2) \ , \ \text{and} \ \hat{r}_- = \frac{1}{\sqrt{2}}(\hat{r}_1 - \hat{r}_2) \ . \tag{IV-86}$$

It is easy to show that $\hat{p}_+$, $\hat{r}_+$ and $\hat{p}_-$, $\hat{r}_-$ satisfy the canonical commutation relation, i.e.,

$$[\hat{r}_+,\hat{p}_+] = i \quad , \quad [\hat{r}_-,\hat{p}_-] = i \quad , \qquad \text{(IV-87)}$$

so that the Hamiltonian can be rewritten as

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{p}_+^2}{2} + \frac{\hat{r}_+^2}{2} + \frac{\hat{p}_-^2}{2} + \frac{\hat{r}_-^2}{2} + V(\hat{R}-\sqrt{2}\,\hat{r}_+)$$

$$= \frac{\hat{p}^2}{2\mu} + \hat{h}_+ + \hat{h}_- + V(\hat{R}-\sqrt{2}\,\hat{r}_+) = \hat{H}_+ + \hat{h}_- \quad , \qquad \text{(IV-88)}$$

with

$$\hat{h}_+ = \frac{\hat{p}_+^2}{2} + \frac{\hat{r}_+^2}{2} \quad , \quad \hat{h}_- = \frac{\hat{p}_-^2}{2} + \frac{\hat{r}_-^2}{2} \quad , \quad H_+ = \frac{\hat{p}^2}{2\mu} + \hat{h}_+ + V(\hat{R}-\sqrt{2}\hat{r}_+) \; . \qquad \text{(IV-89)}$$

One immediately notices that the system now consists of the pseudo oscillators (+) and (−); and that the oscillator (−) couples neither with oscilator (+) nor with relative translation. In other words, the operator $\hat{h}_-$ commutes with the total Hamiltonian $\hat{H}$, and consequently commutes with transition operator $\hat{S}$. Therefore, the S matrix is diagonal in the representation of the eigenstates of $\hat{h}_-$, i.e., if

$$\hat{h}_+|n_+\rangle = \varepsilon_+|n_+\rangle \quad , \quad \text{and} \quad \hat{h}_-|n_-\rangle = \varepsilon_-|n_-\rangle \quad , \qquad \text{(IV-90)}$$

then

$$\delta(E^f-E^o)\, S_{n_+^f n_-^f \leftarrow n_+^i n_-^i} = \langle E_+^f n_-^f n^f \,|\hat{S}|\, E_+^o n_-^i n^i \rangle = \delta(E^f-E^o)\, \delta_{n_-^f, n_-^i}\, S^{n_-^i}_{n_+^f \leftarrow n_+^i} \quad ,$$

or

$$S_{n_+^f n_-^f \leftarrow n_+^i n_-^i}(E_o) = \delta_{n_-^f \leftarrow n_-^i}\, S^{n_-^i}_{n_+^f \leftarrow n_+^i}(E_o - \varepsilon_-^i) \quad , \qquad \text{(IV-91)}$$

where E^o and E^f are the initial and final total energy of the system,

and $S^{n_-^i}_{n_+^f \leftarrow n_+^i}$ is the transition matrix for the pseudo atom-oscillator(+) collision system described by the Hmiltonian $\hat{H}_+$, which can be calculated by using Eqs(IV-58),(IV-54) and (IV-73),

$$S_{n_+^f \leftarrow n_+^i}(E_o - \varepsilon_-) = \sqrt{B}\, e^{i\gamma(t_f)} \exp[-|Z_+(t_f)|^2/2]$$
$$\times \sum_{k=0}^{n_+^i} (-1)^k \frac{\sqrt{n_+^i!\, n_+^f!}}{k!(n_+^i-k)!(n_+^f-n_+^i+k)!} |Z_+|^{n_+^f-n_+^i+2k} \quad . \qquad \text{(IV-92)}$$

The real problem, however, is to calculate the transition amplitudes $S_{n_2^f n_1^f \leftarrow n_2^i n_1^i}(E)$, so one must establish the relation between $S_{n_2^f n_1^f \leftarrow n_2^i n_1^i}(E)$ and $S_{n_+^f n_-^f \leftarrow n_+^i n_-^i}(E)$. In order to do this, the following creation and annihilation operators are introduced:

$$\hat{a}_1 \equiv (\hat{r}_1 + i\hat{p}_1)/\sqrt{2} \ , \ \hat{a}_1^\dagger \equiv (\hat{r}_1 - i\hat{p}_1)/\sqrt{2} \ , \ \hat{a}_2 \equiv (\hat{r}_2 + i\hat{p}_2)/\sqrt{2} \ , \ \hat{a}_2^\dagger \equiv (\hat{r}_2 - i\hat{p}_2)/\sqrt{2} \quad ,$$

and (IV-93)

$$\hat{a}_+ \equiv (\hat{r}_+ + i\hat{p}_+)/\sqrt{2} \ , \ \hat{a}_+^\dagger \equiv (\hat{r}_+ - i\hat{p}_+)/\sqrt{2} \ , \ \hat{a}_- \equiv (\hat{r}_- + i\hat{p}_-)/\sqrt{2} \ , \ \hat{a}_-^\dagger \equiv (\hat{r}_- - i\hat{p}_-)/\sqrt{2} \quad .$$

(IV-94)

These operators satisfy the canonical commutation relations

$$[\hat{a}_i, \hat{a}_j] = 0 \quad , \ [\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij} \quad , \ i,j = 1,2 \quad , \qquad \text{(IV-95)}$$

and

$$[\hat{a}_\ell, \hat{a}_m] = 0 \quad , \ [\hat{a}_\ell, \hat{a}_m^\dagger] = \delta_{\ell m} \ , \quad \ell, m = + \ , \ - \quad . \qquad \text{(IV-96)}$$

From their definition it is straightforward to show that

$$\hat{a}_1=(\hat{a}_+ + \hat{a}_-)/\sqrt{2}\ ,\ \hat{a}_2=(\hat{a}_+ - \hat{a}_-)/\sqrt{2}\ ,\ \hat{a}_1^\dagger=(\hat{a}_+^\dagger + \hat{a}_-^\dagger)/\sqrt{2}\ ,\ \hat{a}_2^\dagger=(\hat{a}_+^\dagger - \hat{a}_-^\dagger)/\sqrt{2}\quad ,$$

and (IV-97a)

$$|n_1=0,n_2=0\rangle = |n_+=0,n_-=0\rangle \quad , \tag{IV-97b}$$

where $|n_1 n_2\rangle$ and $|n_+ n_-\rangle$ are the direct product states of the eigenstates of $\hat{h}_1,\hat{h}_2$ and $\hat{h}_+,\hat{h}_-$ respectively, with $\hat{h}_1=(\hat{p}_1^2+\hat{r}_1^2)/2$ and $\hat{h}_2=(\hat{p}_2^2+\hat{r}_2^2)/2$ Therefore one has

$$|n_2 n_1\rangle = \frac{\hat{a}_1^\dagger{}^{n_1}\,\hat{a}_2^\dagger{}^{n_2}}{\sqrt{n_1!n_2!}}\,|n_2=0,n_1=0\rangle = \frac{(\hat{a}_+^\dagger+\hat{a}_-^\dagger)^{n_1}(\hat{a}_+^\dagger-\hat{a}_-^\dagger)^{n_2}}{\sqrt{2}^{(n_1+n_2)}\sqrt{n_1!n_2!}}|n_+=0,n_-=0\rangle$$

$$=\frac{\sqrt{n_1!n_2!}}{\sqrt{2}^{(n_1+n_2)}}\sum_{k_1=0}^{n_1}\sum_{k_2=0}^{n_2}(-1)^{k_2-k_2}\frac{(\hat{a}_+^\dagger)^{k_1+k_2}(\hat{a}_-^\dagger)^{(n_1+n_2)-(k_1+k_2)}}{k_1!k_2!(n_1-k_1)!(n_2-k_2)!}\quad |n_+=0,n_-=0\rangle$$

$$=\frac{\sqrt{n_1!n_2!}}{\sqrt{2}^{(n_1+n_2)}}\sum_{k_1=0}^{n_1}\sum_{k_2=0}^{n_2}(-1)^{n_2-k_2}\frac{\sqrt{n_+!n_-!}}{k_1!k_2!(n_1-k_1)!(n_2-k_2)!}|n_+,n_-\rangle \quad , \tag{IV-98a}$$

with

$$n_+ = k_1+k_2\ ,\qquad n_- = n_1+n_2-n_+ \quad . \tag{IV-98b}$$

Consequently, it follows that

$$\langle E^f n_2^f n_1^f|\hat{S}|n_1^i n_2^i E^o\rangle = \delta(E^f-E^o)\ S_{n_2^f n_1^f \leftarrow n_2^i n_1^i}$$

$$=\frac{\sqrt{n_1^f!n_1^f!n_2^i!n_2^i!}}{G}\sum_{k_1^i=0}^{n_1^i}\sum_{k_1^f=0}^{n_1^f}\sum_{k_2^i=0}^{n_2^i}\sum_{k_2^i=0}^{n_2^i}\frac{\sqrt{n_+^i n_+^f n_-^i n_-^f}}{k_1^i!k_1^f!\ k_2^i!k_2^f!(n_1^i-k_1^i)!(n_1^f-k_1^f)!}$$

$$\times \frac{(-1)^{n_2^i+n_2^f-k_2^i-k_2^f}}{(n_2^i-k_2^i)!(n_2^f-k_2^f)!} \delta(E^f-E^o)\, S_{n_+^f n_-^f \leftarrow n_+^i n_-^i}(E^o) \quad , \qquad \text{(IV-99A)}$$

With

$$G = (n_1^i + n_1^f + n_2^i + n_2^f)/2 \quad . \qquad \text{(IV-99b)}$$

Hence, after the quantities $q_R(t_f)$, $p_R(t_f)$, $p_+(t_f)$, and $q_+(t_f)$ are determined by a classical trajectory calculation according to the procedure described in Sections IV.c and IV.d, the transition probability $P = \left|S_{n_2^f n_1^f \leftarrow n_2^i n_1^i}\right|^2$ can be easily evaluated in accordance with Eqs.(IV-99), (IV-91) and (IV-92).

IV.f) Example: the collinear collision of $H_2 + H_2$.

To illustrate the methodology described in the last section the collinear collision of $H_2 + H_2$ with a exponential repulsive interaction has been considered. The Hamiltonian for the system, in dimensionless units, reads

$$\hat{H} = \frac{\hat{p}_R^2}{2\mu} + \frac{\hat{p}_1^2}{2} + \frac{\hat{r}_1^2}{2} + \frac{\hat{p}_2^2}{2} + \frac{\hat{r}_2^2}{2} + \exp\{-\alpha[\hat{R}-(\hat{r}_1+\hat{r}_2)]\}$$

$$= \frac{\hat{p}_R^2}{2\mu} + \frac{\hat{p}_+^2}{2} + \frac{\hat{r}_+^2}{2} + \frac{\hat{p}_-^2}{2} + \frac{\hat{r}_-^2}{2} + \exp\{-\alpha[\hat{R}-\sqrt{2}\,\hat{r}_+]\} \quad , \qquad \text{(IV-100)}$$

with

$$\mu = 0.5 \quad , \quad \alpha = 0.2973 \quad . \qquad \text{(IV-101)}$$

The "classical" Hamiltonian is

$$H = \frac{p_R^2}{2\mu} + \frac{p_+^2}{2} + \frac{q_+^2}{2} + A\exp[-\alpha(q_R-\sqrt{2}\,q_+)] + \frac{p_-^2}{2} + \frac{q_-^2}{2} + 0_P + 0_V \ , \qquad \text{(IV-102)}$$

where

$$A = C \cdot D \quad \text{with } C = \langle \Phi_{ot} | e^{-\alpha \hat{R}} | \Phi_{ot} \rangle = \text{const.} \ , \ D = \langle n_+^i | e^{\alpha \hat{r}} | n_+^i \rangle = \text{const.} \ , \tag{IV-103a}$$

and

$$0_p = \langle \Phi_{ot} | \frac{\hat{p}_R^2}{2\mu} | \Phi_{ot} \rangle + \langle n_+^i | \frac{\hat{p}_+^2}{2} | n_+^i \rangle + \langle n_-^i | \frac{\hat{p}_-^2}{2} | n_-^i \rangle = \text{const.} \quad , \tag{IV-103b}$$

$$0_v = \langle n_+^i | \frac{\hat{r}_+^2}{2} | n_+^i \rangle + \langle n_-^i | \frac{\hat{r}_-^2}{2} | n_-^i \rangle = \text{const.} \quad . \tag{IV-103c}$$

The constants 0_p and 0_v have no dynamic effect since they do not enter the equations of motion for the label variables, so they need not be calculated. The constant A, or more precisely, the constant D plays a crucial role in determining the transition probability, since it , as we will see later, determines the relative phase between the terms in the coherent sum for the transition S matrix elements. It is a simple exercise to show that the constant D has the following analytic expression

$$\langle n_+^i | e^{\sqrt{2}\alpha \hat{r}_+} | n_+^i \rangle = \langle n_+^i | e^{\alpha(\hat{a}_+^\dagger + \hat{a}_+)} | n_+^i \rangle$$

$$= e^{1/2\, \alpha^2} \langle n_+^i | e^{\alpha \hat{a}_+^\dagger} e^{\alpha \hat{a}_+} | n_+^i \rangle = e^{1/2\, \alpha^2} \sum_{k=0}^{n_+^i} \alpha^{2k} \frac{n_+^i!}{(k!)^2 (n_+^i - k)!} \quad . \tag{IV-104}$$

Acoording to Eq.(IV-99) the transition probabilities for the T-V and V-V energy fransfer are given by the following expressions:

i) 1-quantum T-V energy fransfer

$$S_{n_1=0\to1,\ n_2=0\to0} = S_{n_1=0\to0,\ n_2=0\to1} = \frac{1}{\sqrt{2}}\ S_{n_+=0\to1,\ n_-=0\to0} \quad , \qquad \text{(IV-105)}$$

$$S_{n_1=0\to1,\ n_2=1\to1} = S_{n_1=1\to1,\ n_2=0\to1} = \frac{1}{2}\ S_{n_+=0\to2,\ n_-=0\to0} \quad , \qquad \text{(IV-106)}$$

$$S_{n_1=0\to0,n_2=1\to2} = S_{n_1=1\to2,n_2=0\to0} = \frac{1}{2\sqrt{2}}(S_{n_+=1\to2,n_-=0\to0} + \sqrt{2}S_{n_+=0\to1,n_-=1\to1}) \ ,$$

and (IV-107)

$$S_{n_1=0\to2,n_2=1\to0} = S_{n_1=1\to0,n_2=0\to2} = \frac{1}{2\sqrt{2}}(S_{n_+=1\to2,n_-=0\to0} - \sqrt{2}S_{n_+=0\to1,\ n_-=1\to1}); \qquad \text{(IV-108)}$$

ii) 2-quanta T-V energy transfer

$$S_{n_1=0\to1,\ n_2=0\to1} = \frac{1}{\sqrt{2}}\ S_{n_+=0\to2,\ n_-=0\to0} \quad , \qquad \text{(IV-109)}$$

$$S_{n_1=0\to2,\ n_2=0\to0} = S_{n_1=0\to0,\ n_2=0\to2} = \frac{1}{\sqrt{2}}\ S_{n_+=0\to2,\ n_-=0\to0} \quad ; \qquad \text{(IV-110)}$$

iii) 1-quantum V-V energy transfer

$$S_{n_1=1\to0,\ n_2=0\to1} = \frac{1}{2}\ (S_{n_+=1\to1,\ n_-=0\to0} - S_{n_+=0\to0,\ n_-=1\to1}) \quad , \text{(IV-111)}$$

$$S_{n_1=0\to1,\ n_2=2\to1} = \frac{1}{2\sqrt{2}}\ (S_{n_+=2\to2,\ n_-=0\to0} - S_{n_+=0\to0,\ n_-=2\to2}) \ ; \text{(IV-112)}$$

iv) 2-quanta V-V energy transfer

$$S_{n_1=0\to2,n_2=2\to0} = \frac{1}{4}\ S_{n_+=2\to2,n_-=0\to0} + \frac{1}{4}\ S_{n_+=0\to0,n_-=2\to2} - \frac{1}{2}\ S_{n_+=1\to1,n_-=1\to1} \ . \qquad \text{(IV-113)}$$

From the above expressions, one sees that the evaluation of a given transition probability consists of the calculation of a number of transition amplitudes for a pseudo system. The corresponding initial

values of the label variables are the same for all the calculations. However, the corresponding "classical" potential terms are different. It is the difference in the constant D that gives rise to the different phases of the terms in the coherent sum for a transition probability. The results obtained by using the Eqs.(IV-105)-(IV-113) are presented in Tables IV.2-IV-6 along with the results of quantum mechanical calculations[64] and some other approximate calculations[70].

From the comparisons in Tables IV.2-IV.6 it is seen that the results of present work are in good agreement with the quantum mechanical calculation except for the transitions 01→11, 01→20, and 01→02 in 1-quantum T-V energy transfer (shown in Table IV.3) and 2-quanta T-V energy transfer (shown in Table IV.4). But as the earlier work of Clarkr and Thiele[70] has pointed out, the quantum calculations[64] are in error at least for 2-quanta T-V energy transfer. Since Equations (IV-105) and (IV-110) show that the exact transition probabilities $P_{n_1=0\to0,n_2=0\to2}$ and $P_{n_1=0\to1,n_2=0\to1}$ must be in the ratio 1 to 2, the quantum results, however, are not in this expected ratio (see Table IV.4). Besides, as noted by Clarke and Thiele[70], the quantum calculation[64] included only states $|ij\rangle$ for which i and j were no larger than 2. Therefore, their results for 01→11, 01→20 and 01→20 transitions are questionable. Clarke and Thiele[70] have empirically corrected their numerical results, but unfortunately they have no way to correct the phase, which is very important in the present case. Therefore their results for transitions 01→11, 01→20 and 01→20 are also unlikely to be reliable.

In contrast, the present calculation has neither the empirical correction nor the inaccuracy due to the choice of the basis set of

states. Since our results agree with the reliable parts of the quantum mechanical calculation[64] very well (shown in Table IV.2 IV.5 and IV.6), it might be not incongruous to expect that the present method has yielded reasonably reliable results as a whole. It would be interesting if a more complete full quantum calculation could be done to provide a more reliable result for further comparison.

IV.g) Discussion.

The principle idea of the present semiclassical approach has been to use classical mechanics in a formal sense to determine the time evolution of the state vector. In the above applications one may recognize some similarities to time-dependent wave packet methods[53], but in fact there are significant differences. The wave packet methods are essentially a combination of time-dependent Hartree-Fock theory and Ehrenfest's theorem; and an important aspect of them are the classical parameters, i.e., the coordinates and momenta of the particles. The actual equations of motion that characterize the wave packet, however, are nonclassical. In contrast, the present approach stems from the restricted variation of the action functional. This leads to a set of classical Hamilton's equation of motion for the label variables, which may or may not have a direct physical interpretation. The "classical" Hamiltonian, which is the expectation value of quantum Hamiltonian in the reference state, is, in general, not identical to the classical Hamiltonian, while the wave-packet methods use the classical Hamiltonian with the potential energy approximated by the quadratic expansion at the average position of the wave-packet.

Also, as seen in the example treated above, the present approach deals equally well with translational wave functions (as a Gaussian wave packet) and with stationary states. Thus one can easily use initially excited vibrational states, whereas the usual wave packet methods must represent excited states as linear combinations of Gaussians. It is also clear that the present approach can deal equally well with quantum systems that have no classical analog, e.g., spin systens[54].

Finally, an important and practical feature of the present approach is its simplicity since for a given transition only one (in the example 1) or a few (in the example 2) classical trajectories need to be calculated

However, the present approach is an approximate method. The accuracy will depend on the nature of the system investigated and the choice of the reference vector. It is sufficiently promising, though, that its generalization to three-dimensional systems and also to polyatomic dynamics seems worthwhile.

V. Concluding remarks

In this thesis we explored several new quantum and semiclassical approaches in the attempt to improve the efficiency of dynamic calculations for molecular, especially polyatomic, systems. This certainly contributes in the effort to reach the goal of doing quantitatively meaningful, really *ab initio* calculations in practice for polyatomic systems. However, it is our feeling that if one could not make any revolutionary break through, it would seem unlikely to reach this goal even by resorting to the supercomputer.

In Chapter IV of this work, with the motivation of getting rid of the traditional semiclassical idea, i.e., using simple classical mechanics to describe the motion of the particle itself, we have tried to develop a new semiclassical idea based on unitary mapping. The approach , certainly, is still in a primitive stage and should be pursued further at least in the spirit of doing something new.

Appendex A: Green's function matrix $G(R,R')$

The Green's function matrix $\mathbf{G}(R,R')$ considered here is defined to be the solution of the following matrix equation

$$[-(\hbar^2/2\mu)\,\mathbf{I}\,(d^2/dR^2) - (\mathbf{E} - \mathbf{V}(R))]\,\mathbf{G}(R,R') = \delta(R,R')\,\mathbf{I} \quad , \tag{A--1}$$

with the boundary conditions

$$\mathbf{G}(0,R') = 0 \ , \ \mathbf{G}'(\infty,R')\,\mathbf{G}^{-1}(\infty,R') = [\,\mathbf{G}'(\infty,R')\,\mathbf{G}^{-1}(\infty,R')]^{\dagger} \quad , \tag{A--2}$$

where dagger ($\dagger$) denotes the complex conjugate transpose, the prime denotes the derivative with respect to R, $\mathbf{I}$ is the unit matrix , $\mathbf{E}$ is a diagonal matrix, and $\mathbf{V}(R)$ is a Hermitian matrix. We demand $\mathbf{G}(R,R')$ be a continuous function. One labels

$$\mathbf{G}(R,R') = \mathbf{G}_1(R) \qquad \text{for } 0 < R < R' \quad , \tag{A--3}$$

and

$$\mathbf{G}(R,R') = \mathbf{G}_2(R) \qquad \text{for } R' < R < \infty \quad . \tag{A--4}$$

Then, we have

$$[-(\hbar^2/2\mu)\,\mathbf{I}\,(d^2/dR^2) - (\mathbf{E} - \mathbf{V}(R))]\,\mathbf{G}_1(R) = 0 \quad \text{for } 0 < R < R' \quad , \tag{A-5a}$$

$$[-(\hbar^2/2\mu)\,\mathbf{I}\,(d^2/dR^2) - (\mathbf{E} - \mathbf{V}(R))]\,\mathbf{G}_2(R) = 0 \quad \text{for } R' < R < \infty \ , \tag{A-5b}$$

with the boundary conditions

$$G_1(0) = 0 \quad , \; G_2'(\infty)\, G_2^{-1}(\infty) = [G_2'(\infty)\, G_2^{-1}(\infty)]^{\dagger} \quad , \tag{A-6a}$$

and

$$G_1(R') = G_2(R') \; . \tag{A-6c}$$

Integrating both sides of Eq.(A-1) from $R'-\varepsilon$ to $R'+\varepsilon$ and taking the limit $\varepsilon \to 0$, one obtains

$$(- \hbar^2/2\,\mu)[\, G'(R,R')|_{R'+0} - G'(R,R')|_{R'-0} = I \quad , \tag{A-6c}$$

or

$$G_1'(R') - G_2'(R') = (2\mu\,/\hbar^2)\; I \quad . \tag{A-6d}$$

Now let $f(R)$ be a regular solution of the equation

$$[\, - (\hbar^2/2\mu)\; I\; (d^2\,/dR^2) - (E - V(R))]\; f(R) = 0 \quad , \tag{A--7}$$

which satisfies the boundary condition

$$f(R) = 0 \; , \tag{A--8}$$

and $g(R)$ be a irregular solution of the same equation

$$[- (\hbar^2/2\mu)\; I\; (d^2\,/dR^2) - (E - V(R))]\; g(R) = 0 \; , \tag{A--9}$$

Which satisfies the boundary condition

$$g'(\infty)\; g^{-1}(\infty) = [\; g'(\infty)\; g^{-1}(\infty)]^{\dagger} \quad , \tag{A-10}$$

and is linearlly indepedent of $\mathbf{f}(R)$, then the solutions $\mathbf{f}(R)$ and $\mathbf{g}(R)$ have following properties:

(i)

$$\mathbf{w}_r \equiv \mathbf{g}^\dagger(R)\ \mathbf{f}'(R) - \mathbf{g}'^\dagger(R)\ \mathbf{f}(R) = \text{const. matrix} \quad , \tag{A-11}$$

(ii)

$$\mathbf{Y}_g(R) \equiv \mathbf{g}'(R)\mathbf{g}^{-1}(R) = [\mathbf{g}^{-1}(R)]^\dagger\ [\mathbf{g}'(R)]^\dagger = [\mathbf{g}'(R)\ \mathbf{g}^{-1}(R)]^\dagger = \mathbf{Y}_g^\dagger(R) \ ,$$

(iii) (A-12)

$$\mathbf{Y}_f(R) = \mathbf{f}'(R)\mathbf{f}^{-1}(R) = [\mathbf{f}^{-1}(R)]^\dagger\ [\mathbf{f}'(R)]^\dagger = [\mathbf{f}'(R)\ \mathbf{f}^{-1}(R)]^\dagger = \mathbf{Y}_f^\dagger(R), \tag{A-13}$$

where $\mathbf{w}_r$ is the Wronskian matrix of two solution $\mathbf{f}(R)$ and $\mathbf{g}(R)$, and $\mathbf{Y}_f$, $\mathbf{Y}_g$ are the log-derivative matrices for the regular solution $\mathbf{f}(R)$ and the irregular solution $\mathbf{g}(R)$, respectively. Now first let us prove the property (i). Taking the complex conjugate transpose of Eq.(A-9) gives

$$(-\hbar^2/2\mu)\ \mathbf{g}''(R) - \mathbf{g}^\dagger(R)\ (\mathbf{E} - \mathbf{V}) = 0 \quad , \tag{A-14}$$

where the Hermitian property of matrix $\mathbf{V}$ has been used, and the double prime denotes the second derivative with respect to R. Multiplying Eq.(A-14) from right by $\mathbf{f}(R)$, Eq.(A-7) from left by $\mathbf{g}^\dagger(R)$ and subtracting term by term, one obtains

$$\mathbf{g}^{\dagger\prime\prime}(R)\mathbf{f}(R) - \mathbf{g}^\dagger(R)\ \mathbf{f}''(R) = 0 \quad ,$$

or

$$\frac{d}{dR}[\ \mathbf{g}^\dagger(R)\ \mathbf{f}'(R) - \mathbf{g}^{\dagger\prime}(R)\ \mathbf{f}(R)] = 0 \quad .$$

Thus

$$\mathbf{w}_r \equiv \mathbf{g}^\dagger(R)\ \mathbf{f}'(R) - \mathbf{g}^{\dagger\prime}(R)\ \mathbf{f}(R) = \text{const.} \quad . \tag{A-15}$$

Similarly it can be shown that

$$f^{\dagger}(R)\ f'(R) - f^{\dagger\prime}(R)\ f(R) = \text{const.}\ , \tag{A-16a}$$

and

$$g^{\dagger}(R)\ g'(R) - g^{\dagger\prime}(R)\ g(R) = \text{const.}\ . \tag{A-16b}$$

To prove properties (ii) and (iii) using boundary condition Eq. (A-8) gives

$$f^{\dagger}(R)\ f'(R) - f^{\dagger\prime}(R)\ f(R) = f^{\dagger}(0)\ f'(0) - f^{\dagger\prime}(0)\ f(0) = 0 \quad ,$$

or

$$Y_f \equiv f'(R)\ f^{-1}(R) = [\ f'(R)\ f^{-1}(R)]^{\dagger} = Y_f^{\dagger}\ . \tag{A-17}$$

By virture of boundary condition Eq.(A-10), Eq.(A-16b) leads to

$$g^{\dagger}(R)\ g'(R) - g^{\dagger\prime}(R)\ g(R) = g^{\dagger}(\infty)\ g'(\infty) - g^{\dagger\prime}(\infty)\ g(\infty) = 0 \quad ,$$

or

$$Y_g \equiv g'(R)\ g^{-1}(R) = [\ g'(R)\ g^{-1}(R)\ ]^{\dagger} = Y_g^{\dagger} \quad . \quad . \tag{A-18}$$

From comparing Eq.(A-5) and Eq.(A-6) with Eq.(A-7)-Eq.(A-10) it is obvious that one may take

$$G(R,R') = \begin{cases} G_1(R) = f(R)\ A & 0 < R < R' \quad , \\ \\ G_2(R) = g(R)\ B & R' < R < \infty \quad . \end{cases} \tag{A-19}$$

The continuity at $R = R'$ (Eq.(A-6-c) requires

$$f(R')\ A = g(R')\ B \quad . \tag{A-20}$$

The discontinuity in the first derivative (Eq.(A-6-d) becomes

$$f'(R') \mathbf{A} - g'(R') \mathbf{B} = \frac{2\mu}{\hbar^2} \mathbf{I} \quad . \tag{A-21}$$

Solving the Eqs.(A-20) and (A-21) for **A** and **B** we have

$$\mathbf{A} = -\frac{2\mu}{\hbar^2} [\, g'(R') \, g^{-1}(R') \, f(R') - f'(R') \,]^{-1}$$

$$= \frac{2\mu}{h^2} \mathbf{w}_r^{-1} g^{\dagger}(R') \ , \tag{A-22}$$

and

$$\mathbf{B} = -\frac{2\mu}{\hbar^2} [\, g'(R') - f'(R') \, f^{-1}(R') \, g(R') \,]^{-1}$$

$$= \frac{2\mu}{\hbar^2} (\, \mathbf{w}_r^{\dagger})^{-1} f^{\dagger}(R') \ . \tag{A-23}$$

where the Eqs.(A-11)-(A-13) have been used. Eq.(A-22) and Eq.(A-23) shows that if the determinant of the Wronskian matrix $\mathbf{w}_r$ is not equal to zero, then one has

$$\mathbf{G}\,(R,R') = \begin{cases} \mathbf{G}\,(R) = \dfrac{2\mu}{\hbar^2} f(R) \, \mathbf{w}_r^{-1} \, g^{\dagger}(R') & \text{for } 0 < R < R' \ , \\[2ex] \mathbf{G}\,(R) = \dfrac{2\mu}{\hbar^2} \, g(R) \, (\, \mathbf{w}_r^{\dagger})^{-1} \, f^{\dagger}(R') & \text{for } R' < R < \infty \ . \end{cases} \tag{A-24}$$

It is well known that the nonvanishing of the determinant of the Wronskian matrix $\mathbf{w}_r$ is a necessary condition for linear independence of f(R) and g(R). From Eq.(A-24) it is obvious that

$$\mathbf{G}\,(R,R') = \mathbf{G}^{\dagger}(R,R') \quad . \tag{A-25}$$

<u>Appendix</u> B: Numerical calculation of Green's function matrix **G** (R,R')

At first glance it seems easy to calculate the Green's function matrix $G(R,R')$, since according to Eq.(A-24) what one needs to do is solve homogeneous equations Eq.(A-7) and Eq.(A-9) for the regular solution $f(R)$ and the irregular one $g(R)$. In practice, however, it is extremely difficult to obtain $f(R)$ and $g(R)$ with enough accuracy for calculating accurate $G(R,R')$, because $f(R)$ and $g(R)$ both involve exponential functions. In order to avoid the difficulty with directly calculating the regular solution $f(R)$ and irregular solution $g(R)$ one rewrite the Green's function matrix $G(R,R')$ in the following form

$$G(R,R') = \begin{cases} (2\mu/\hbar^2)\, f(R)\, f^{-1}(R')\, [\, Y_f(R') - Y_g(R')]^{-1} & \text{for } 0 < R < R', \\ (2\mu/\hbar^2)\, g(R)\, g^{-1}(R')\, [\, Y_f(R') - Y_g(R')]^{-1} & \text{for } R' < R < \infty, \end{cases} \tag{B -1}$$

where Eq.(A-19), Eq.(A-20), Eq.(A-22) and Eq.(23) has been used. In this form the $G(R,R')$ can be accurately and efficiently calculated by using renormalized Numerov method. The matrix renormalized Numerov algorithm[7] is an efficient method that can be used to obtain the numerical solution $u(R)$ of Eq.(A-7) or Eq.(A-9). The basic formula is the three term recurrence relation

$$F_n\, u_n - (12\, I - 10\, F_{n-1})\, u_{n-1} + F_{n-2}\, u_{n-2} = 0\ , \tag{B -2}$$

where

$$F_n = I - T_n\ , \tag{B -3}$$

and

$$T_n = (\Delta/12)\left(\frac{2\mu}{\hbar^2}\right)(E - V(R_n)]\ . \tag{B -4}$$

Here $\mathbf{I}$ is a unit matrix and Δ is the spacing between the N equally spaced grid points R_o, R_1, $R_2, \ldots,$ R_N, with point N being in the asymptotic region. Now we introduce the ratio matrix

$$\mathbf{R}_n = \mathbf{u}_{n-1}\, \mathbf{u}_n^{-1} \qquad , n = 1,2,\ldots, N \,. \tag{B -5}$$

Using Eq.(B-2) and Eq.(B-5) one obtains

$$\mathbf{F}_n\, R_n = 12\, \mathbf{I} - 10\, \mathbf{F}_{n-1} - \mathbf{F}_{n-2}\, \mathbf{R}_{n-1}. \tag{B -6}$$

Then for regular solution we have

$$\mathbf{R}_n^f = (12\, \mathbf{I} - 10\, \mathbf{F}_{n-1} - \mathbf{F}_{n-2}\, \mathbf{R}_{n-1}^f\,)^{-1}\, \mathbf{F}\,, \tag{B-7a}$$

or

$$(\,\mathbf{R}_n^{\,f})^{-1} = \mathbf{F}_n^{-1}\, (12\, \mathbf{I} - 10\, \mathbf{F}_{n-1} - \mathbf{F}_{n-2}\, \mathbf{R}_{n-1}^f\,) \quad , \tag{B-7b}$$

and the initial value of $\mathbf{R}_1^f$ is

$$\mathbf{R}_1^f = 0\,, \tag{B-8a}$$

since we have

$$f_o = f(R_o) = 0 \text{ and } f_1 = f\,(R_1) \neq 0 \quad . \tag{B-8b}$$

Starting from $\mathbf{R}_1^f$ and propagating the solution of Eq.(B-7) outwards one obtains

$$\mathbf{R}_2^f\,,\ \mathbf{R}_3^f, \ldots,\ \mathbf{R}_n^f, \ldots,\ \mathbf{R}_N^f \quad .$$

For the irregular solution one has

$$(\mathbf{R}_{n-1}^g)^{-1} = [\ 12\, \mathbf{I} - 10\, \mathbf{F}_{n-1} - \mathbf{F}_n (\mathbf{R}_n^g\,)^{-1}]^{-1} \mathbf{F}_{n-2}\,, \tag{B-9a}$$

or

$$\mathbf{R}^g_{n-1} = (\mathbf{F}_{n-2})^{-1}(12\ \mathbf{I} - 10\ \mathbf{F}_{n-1} - \mathbf{F}_n(\mathbf{R}^g_n)^{-1}\ )^{-1}\ . \tag{B-9b}$$

Beginning with the asymptotic boundary condition $(\mathbf{R}^g_N)^{-1} = g_N/g_{N-1}$ one can solve Eq.(B-9) iterativly to obtain

$$(\mathbf{R}^g_{N-1})^{-1},\ (\mathbf{R}^g_{N-2})^{-1},\ \ldots,\ (\mathbf{R}^g_n)^{-1},\ \ldots,\ (\mathbf{R}^g_1)^{-1}\ .$$

To calculate the log-derivetive matrix $\mathbf{Y}_n$ we use the matrix version of Blatts[74] formula, i.e.,

$$\mathbf{u}'_n = \Delta^{-1}[(\ 0.5\ \mathbf{I} - \mathbf{T}_{n+1})\ \mathbf{u}_{n+1} - (0.5\ \mathbf{I} - \mathbf{T}_{n-1}\ )\ \mathbf{u}_{n-1}\ ]\ . \tag{B-10}$$

Thus,

$$\mathbf{Y}_n = \mathbf{u}'_n\ \mathbf{u}^{-1}_n = \Delta^{-1}\ [(0.5\ \mathbf{I} - \mathbf{T}_{n+1})\ \mathbf{R}^{-1}_{n+1} - (0.5\ \mathbf{I} - \mathbf{T}_{n-1})\ \mathbf{R}_n]\ . \tag{B-11}$$

It is straightforward to show that

$$\mathbf{u}_n\ \mathbf{u}^{-1}_{n'} = \begin{cases} \mathbf{R}_{n+1}\mathbf{R}_{n+2}\cdots\cdot\ \mathbf{R}_{n'} & \text{for } n < n' \\ \mathbf{I} & \text{for } n = n' \\ \mathbf{R}^{-1}_n\ \ \mathbf{R}^{-1}_{n-1}\ \cdots\cdot\ \mathbf{R}^{-1}_{n'+1} & \text{for } n > n' \end{cases}\ , \tag{B-12}$$

since according to Eq.(B-5) one has

$$\mathbf{u}_n = \mathbf{R}_{n+1}\ \mathbf{R}_{n=2}\ \cdots\cdot\ \mathbf{R}_N\ \mathbf{f}_N\ . \tag{B-13}$$

Now we are ready to express the numerical solution of $\mathbf{G}(R,R'\ )$ in terms of $\mathbf{R}_n$'s

$$\mathbf{G}\ (n\ ,\ n'\ ) = \begin{cases} \dfrac{2\mu}{\hbar^2}\ \mathbf{R}^f_{n+1}\cdots\cdot\ \mathbf{R}^f_{n'}\ (\ \mathbf{Y}^f_{n'} - \mathbf{Y}^f_{n'}) & \text{for } n < n', \\ \dfrac{2\mu}{\hbar^2}\ (\ \mathbf{Y}^f_{n'} - \mathbf{Y}^g_{n'}\ )^{-1} & \text{for } n = n', \\ \dfrac{2\mu}{\hbar^2}\ (\mathbf{R}^g_n)^{-1}\cdots\cdot\ (\mathbf{R}^g_{n'+1})^{-1}\ (\mathbf{Y}^f_{n'} - \mathbf{Y}^g_{n'}) & \text{for } n > n', \end{cases} \tag{B-14}$$

where Eqs.(B-1) and (B-12) have been used, and

$$\mathbf{Y}^f_{n'} = \Delta^{-1}[(0.5\ \mathbf{I} - \mathbf{T}_{n'+1})\ (\mathbf{R}^f_{n'+1})^{-1} - (\ 0.5\ \mathbf{I} - \mathbf{T}_{n'-1})\ \mathbf{R}^f_{n'}]\ , \tag{B-15a}$$

$$\mathbf{Y}^g_{n'} = \Delta^{-1}[(0.5\ \mathbf{I} - \mathbf{T}_{n'+1})\ (\mathbf{R}^g_{n'+1})^{-1} - (0.5\ \mathbf{I} - \mathbf{T}_{n'-1})\ \mathbf{R}^g_{n'}\ ]. \tag{B-15b}$$

There are couple advantages of using formula Eq.(B-14) to calculate Green's function matrix $\mathbf{G}\ (\mathbf{R},\mathbf{R}')$. First, by using Eq.(B-5) one can efficiently generate the all matrices $\mathbf{R}_n$, n=1,2,..., N. Secondly, since matrices $\mathbf{R}_n$, n=1,2,..., N, are the ratio matrices there is no difficulty with the exponentially growing or decaying wavefunctions for closed channels.

Appendix C: The first derivatives of Wilson G matrix elements.

For the internal coordinates of benzene defined in Fig.III.1 the relevant Wilson G matrix elements can be determined from Table VI-1 of Ref.(45):

$$g_w = g_{\beta\beta} X^2_{CHo} = X^2_{CHo}\ [\frac{\mu_H}{s} + (\frac{1}{s^2} + \frac{1}{sX_o} + \frac{3}{4X_o})\ \mu_C]\ , \tag{C -1}$$

$$g_{wt_6} = \frac{X_{CHo}}{2}\ (g_{\phi_1 t_6} - g_{\phi_6 t_6}) = \frac{\mu_C X_{CHo}}{2}[\frac{\sqrt{3}}{s} + \frac{3/4}{X_o}]\ , \tag{C -2}$$

$$g_{wt_1} = \frac{X_{CHo}}{2}\ (g_{\phi_1 t_1} - g_{\phi_6 t_1}) = -\frac{\mu_C X_{CHo}}{2}\ [\ \frac{\sqrt{3}}{s} + \frac{3/4}{X_o}\ ]\ , \tag{C -3}$$

$$g_{t_6 s} = \mu_C \cos(\phi_6 - \beta),\ g_{t_1 s} = \mu_C \cos(\phi_1 + \beta),\ g_{s\alpha} = \frac{\mu_C}{X_o}\sqrt{3}\ [\cos(\phi_1+\beta) + \cos(\phi_6-\beta)]\ ,$$

with (C -4)

$$\mu_C = \frac{1}{m_C}\ ,\ \mu_H = \frac{1}{m_H}\ ,\ s = X_{CHo} + x_{CH}\ , \tag{C -5}$$

where m_C and m_H are the masses of atom C and atom H. Then the relevant derivatives are

$$\frac{\partial g_w}{\partial x_{CH}}\Big|_{\mathbf{x}=0} = -\ [2(\frac{\mu_H}{X_{CHo}} + \frac{\mu_C}{X_{CHo}}) + \frac{\mu_C}{X_o}]\ , \tag{C -6}$$

$$\frac{\partial g_{wt_6}}{\partial x_{CH}}\Big|_{\mathbf{x}=0} = -\frac{\sqrt{3}\mu_C}{2X_{CHo}}\ , \qquad \frac{\partial g_{wt_1}}{\partial x_{CH}}\Big|_{\mathbf{x}=0} = \frac{\sqrt{3}}{2}\frac{\mu_C}{X_{CHo}}\ , \tag{C -7}$$

$$\frac{\partial g_{t_6 s}}{\partial x_w}\Big|_{\mathbf{x}=0} = \frac{\sqrt{3}}{2}\frac{\mu_C}{X_{CHo}}\ , \quad \frac{\partial g_{t_1 s}}{\partial x_w}\Big|_{\mathbf{x}=0} = -\frac{\sqrt{3}}{2}\frac{\mu_C}{X_{CHo}}\ , \quad \frac{\partial g_{s\alpha}}{\partial x_w}\Big|_{\mathbf{x}=0} = 0\ . \tag{C -8}$$

Appendix D:

Let $\hat{P}$ and $\hat{Q}$ be a pair of self-adjoint operators which satisfy the canonical commutation relation

$$[\hat{Q},\hat{P}] = i\hbar\ . \tag{D-1}$$

Introduce a unitary operator

$$\hat{U}[p,q] \equiv \exp\ (-iq\hat{P}/\hbar)\ \exp(ip\hat{Q}/\hbar) \tag{D -1}$$

where p and q are the parameters. Now let us do the lollowing tranformations:

$$\hat{a} \equiv (\hat{Q}+i\hat{P})/\sqrt{2\hbar}\ ,\ \hat{a}^\dagger \equiv (\hat{Q}-i\hat{P})/\sqrt{2\hbar}\ ,\ \ Z \equiv (q+ip)/\sqrt{2\hbar}\ ,\ \text{and}\ \theta \equiv \tan^{-1}\frac{p}{q} \tag{D -2}$$

Here $\hat{a}$ and $\hat{a}^\dagger$ are well known annihilation and creation operators. Then

it follows that

$$i(-q\hat{P} + p\hat{Q})/\hbar = \hat{a}^{\dagger}Z - z^{*}\hat{a} \quad , \quad [\hat{a},\hat{a}^{\dagger}] = 1 \quad , \tag{D -3}$$

$$\hat{a}^{k}|n\rangle = [\frac{n!}{(n-k)!}]^{1/2}|n-k\rangle \quad , \quad |n\rangle = \frac{(\hat{a}^{\dagger})^{n}}{\sqrt{n!}}|0\rangle \quad , \tag{D -4}$$

and

$$-pq = \frac{i\hbar}{2}(Z+Z^{*})(Z-Z^{*}) = \frac{i\hbar}{2}(Z^{2}-Z^{*2}) = -\hbar|Z|^{2}\sin 2\theta \quad , \tag{D -5}$$

where $|n\rangle$ is the eigenstate of harmonic oscillator. Using Eq.(D-3) and Eq.(D-5) gives

$$\langle n_f|\exp[-iq\hat{P}/\hbar)\exp(ip\hat{Q}/\hbar)|n_i\rangle = \exp(-ipq/2\hbar)\langle n_f|\exp[-iq\hat{P}/\hbar+ip\hat{Q}/\hbar]|n_i\rangle$$

$$=e^{-i\frac{|Z|^2}{2}\sin 2\theta}\langle n_f|e^{\hat{a}^{\dagger}Z-z^{*}\hat{a}}|n_i\rangle = e^{-i\frac{|Z|^2}{2}\sin 2\theta}e^{\frac{|Z|^2}{2}}\langle n_f|e^{\hat{a}^{\dagger}Z}\sum_{k=0}^{\infty}\frac{(-Z^{*})^{k}}{k!}\hat{a}^{k}|n_i\rangle \ . \tag{D -6}$$

With help of Eqs.(D-4) one has

$$\langle n_f|\exp(\hat{a}Z)\sum_{k=0}^{\infty}\frac{(-Z^{*})^{k}}{k!}\hat{a}^{k}|n_i\rangle = \langle n_f|e^{\hat{a}^{\dagger}Z}\sum_{k=0}^{n_i}(-1)^{k}(Z^{*})^{k}\frac{\sqrt{n_i!}}{k!\sqrt{(n_i-k)!}}|n_i-k\rangle \quad ,$$

$$= \sum_{k=0}^{n_i}\langle n_f|e^{\hat{a}^{\dagger}Z}[\frac{n_i!}{(n_i-k)!}]^{1/2}(-1)^{k}(Z^{*})^{k}\frac{\hat{a}^{\dagger(n_i-k)}}{\sqrt{k!(n_i-k)}}|0\rangle = \sum_{k=0}^{n_i}(-1)^{k}(Z^{*})^{k}\frac{\sqrt{n_i!}}{k!(n_i-k)!}$$

$$\times\langle n_f|(\hat{a}^{\dagger})^{n_i-k}e^{\hat{a}^{\dagger}Z}|0\rangle = \sum_{k=0}^{n_i}(-1)^{k}(Z^{*})^{k}\frac{\sqrt{n_i!n_f!}}{k!(n_i-k)!}\frac{\exp(|Z|^{2}/2)}{\sqrt{(n_f-n_i+k)!}}\langle n_f-n_i+k|Z\rangle$$

$$= \sum_{k=0}^{n_i} (-1)^k (Z^*)^k \frac{\sqrt{n_i!\,n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} Z^{n_f-n_i+k}$$

$$= \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_f!\,n_i!}}{k!(n_i-k)!(n_f-n_i+k)!} |Z|^{n_f-n_i+2k} \exp[i(n_f-n_i)\theta] \quad , \qquad \text{(D -7)}$$

where $|Z\rangle \equiv \exp(\hat{a}^\dagger Z)\ |0\rangle \exp(-|Z|^2/2)$ is the well known coherent state[62] which is an eigenstate of the operator $\hat{a}$ such that

$$\hat{a}|Z\rangle = Z|Z\rangle \quad \text{and} \quad \langle n|Z\rangle = \exp(-|Z|^2/2)\ \frac{Z^n}{\sqrt{n!}} \quad . \qquad \text{(D -8)}$$

Substituting Eq.(D-7) into Eq.(D-6) yields

$$\langle n_f|\exp(-iq\hat{P}/\hbar)\exp(ip\hat{Q}/\hbar)|n_i\rangle = \exp(-i\frac{|Z|^2}{2}\sin 2\theta)$$

$$\times \exp[-i(n_f-n_i)\theta]\exp(-\frac{|Z|^2}{2}) \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i!\,n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} |Z|^{n_f-n_i+2k} \quad . \qquad \text{(D -9)}$$

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Table II.1 . DWBA reaction probabilities for collinear $H+H_2$ on the Porter-Karplus potential surface

Total[a] energy(ev)	No. of channels 1	3	4	6	8	14	Exact[b] QM
0.3028	2.92-10[c]	7.61-10	7.74-10	7.75-10	7.75-10		7.76-10
0.3128	4.07-9	1.08-8	1.10-8	1.10-8	1.10-8		1.07-8
0.3228	3.43-8	9.28-8	9.44-8	9.45-8	9.45-8		9.33-8
0.3428	1.03-6	2.89-6	2.994-6	2.95-6	2.95-6		2.88-6
0.3628	1.43-5	4.24-5	4.32-5	4.33-5	4.33-5		4.37-5
0.3828	1.19-4	3.78-4	3.87-4	3.90-4	3.90-4		3.89-4
0.4028	6.90-4	2.39-3	2.47-3	2.50-3	2.51-3		2.46-3
0.4276	4.20-3	1.64-2	1.73-2	1.77-2	1.77-2	1.74-2	1.74-2
0.4334	6.00-3	2.46-2	2.61-2	2.68-2	2.68-2	2.66-2	2.65-2
0.4428	1.06-2	4.57-2	4.90-2	5.07-2	4.97-2		4.90-2
0.4465	1.31-2	5.77-2	6.21-2	6.45-2	6.42-2	6.45-2	6.17-2
0.4546	2.01-2	9.34-2	1.02-1	1.06-1	9.32-2	1.06-1	1.00-1
0.4628	3.04-2	1.48-1	1.63-1	1.71-1	8.94-2		1.56-1
0.4768	5.79-2	3.06-1	3.41-1	3.43-1	3.76-1	4.09-2	2.97-1
0.4826	7.40-2	3.99-1	4.49-1	4.28-1	5.40	1.12+1	3.70-1
0.4898	9.44-2	5.45-1	6.15-1	5.07-1	1.20-1	8.90-1	4.65-1
0.50	1.43-1	8.14-1	9.08-1	4.09-1	1.31-1		6.01-1
0.60	1.46+1	9.95-1	8.41-1	8.74-2	2.87-1		1.00

a. The zero of energy is the bottom of the reactant diatom potential.

b. Reference(18).

c. 2.92-10 $\equiv 2.92\times10^{-10}$.

Table II.2. Exact quantum reaction for collinear $H+H_2$ on the Porter-Karplus potential surface

Total[a] energy(ev)	No. of channels 1	2	3	4	5	6	Other[b] QM
0.3128	4.10-9[e]	8.30-9	9.65-9	9.84-9	1.32-8	1.45-8	1.07-8
0.3628	1.46-5	3.31-5	3.86-5	4.01-5	4.87-5	4.67-5	4.37-5
0.4028	7.23-4	1.91-3	2.26-3	2.36-3	2.63-3	2.61-3	2.46-3
0.4334	6.55-3	2.02-2	2.43-2	2.52-2	2.73-2	2.69-2	2.65-2
0.4546	2.26-2	7.73-2	9.28-2	9.00-2	1.02-1	1.01-1	1.00-1
0.4826	8.56-2	3.02-1	3.50-1	3.68-1	3.70-1	3.70-1	3.70-1
0.5000	1.64-1	5.22-1	5.78-1	5.97-1	6.01-1	6.01-1	6.01-1
0.6000	8.34-1	9.97-1	9.97-1	1.00	1.00	1.00	1.00
0.7000	9.91-1	9.93-1	9.92-1	9.91-1	9.91-1	9.90	9.91-1
0.8000[c]	9.96-1	9.68-1	9.47-1	9.5-1	9.51-1	9.49-1	9.95-1
0.8706	9.78-1	8.56-1	2.72-1	1.78-1	1.88-1	1.66-1	1.83-1
0.8976	9.72-1	4.95-1	6.28-1	6.78-1	6.59-1	6.70-1	6.62-1
1.2026	8.27-1	3.52-1	2.08-1	2.33-1	2.13-1	2.28-1	2.29-1
1.3966[d]	7.07-1	1.73-1	1.42-1	1.36-1		1.32-1	1.31-1
1.6466	5.44-1	3.37-2	8.08-2	7.86-2		7.39-2	8.00-2

a.The zero of energy is the bottom of the reactant diatom potential well.

b.Reference 18

c.Two channels are opened.

d.Three channels are opened.

e.See c of Table II.1.

Table III.1. Vibrational transition probabilities

$E_o(\hbar\omega)$		10		8		6		4		3	
$n_1 \rightarrow n_2$		QM[a]	SCP[b]	QM	SCP	QM	SCP	QM	SCP	QM	SCP
0	0	0.060	0.025	0.204	0.225	0.538	0.573	0.892	0.882	0.978	0.964
	1	0.218	0.181	0.434	0.334	0.394	0.254	0.108	0.064	0.022	0.014
	2	0.366	0.237	0.291	0.148	0.064	0.029	1.2-3	7.1-4		
	3	0.267	0.120	0.071	0.025						
	4	0.089	0.028								
1	0	0.218	0.181	0.434	0.334	0.394	0.254	0.108	0.064	0.022	0.014
	1	0.286	0.081	0.034	0.020	0.244	0.422	0.850	0.905	0.977	0.987
	2	9.0-3	0.064	0.220	0.314	0.345	0.237	0.042	0.025	9.0-4	1.5-3
	3	0.170	0.232	0.261	0.139	0.037		0.0139			
	4	0.240	0.114	0.051	0.014						
	5	0.071	0.018								
2	0	0.366	0.237	0.291	0.148	0.068	0.029	1.2-3	7.0-4		
	1	0.009	0.064	0.220	0.314	0.345	0.237	0.042	0.025		
	2	0.207	0.109	0.039	0.025	0.347	0.579	0.955	0.982		
	3	0.018	0.075	0.250	0.336	0.233	0.141	1.3-3	2.0-3		
	4	0.169	0.236	0.189	0.086	6.0-3	2.7-3				
	5	0.194	0.077	0.016	0.004						
	6	0.034	6.9-3								

a. The exact quantum results of Ref.(32).

b. The results of the SCP reaction path model.

Table III.2 Energy spacings between successive CH and CD overtones in C_6H_6 and C_6D_6 respectively.

	$\Delta\nu_{n-1,n}$ (cm^{-1})	
n	CH[a]	CD[b]
1	3043	2294
2	2929	2209
3	2814	2153
4	2700	2097
5	2586	2040
6	2472	1984
7	2358	1928
8	2245	1871
9	2129	1815

a. Calculated by using the formula for the observed spacing in the CH stretch overtone spectrum[33]:

$$\bar{\nu}\ (cm^{-1}) = 3157.1\ (n + \tfrac{1}{2}) - 57.1\ (n + \tfrac{1}{2})^2$$

b. Calculated by using the formula for the observed spacing in the CD stretch overtone spectrum[33]:

$$\bar{\nu}\ (cm^{-1}) = 2322.3\ (n + \tfrac{1}{2}) - 28.2\ (n + \tfrac{1}{2})^2 \quad .$$

Table III.3. The ring normal modes of C_6H_6 and C_6D_6 and the coefficients in Eqs(III-74)[a]

symmetry	$\bar{\nu}(cm^{-1})$		$(L^{-1})^{\dagger}_{wi}$ (b)		$(L^{-1})^{\dagger}_{6i}-(L^{-1})^{\dagger}_{1i}$ (b)		L_{wi} (c)	
	C_6H_6	C_6D_6	CH	CD	CH	CD	CH	CD
A_{1g}	993	945	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
A_{2g}	1350	1059	0.3644	0.4685	0.0000	0.0000	0.4574	0.3557
E_{2g}	606	579	0.0874	0.2314	1.7068	1.4389	0.0784	0.1041
$E_{2gb'}$	1599	1557	-.1828	0.1157	-1.609	1.8256	-.3894	0.2687
E_{2gb}	1178	869	-.5430	0.7773	-1.621	-1.825	-.4699	0.3565
B_{1u}	1010	970	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
B_{2u}	1309	1282	0.1656	0.0637	1.2968	1.549	0.2738	0.1488
B_{2u}	1146	824	0.3740	-.5759	-1.100	0.8446	0.3229	-.2730
E_{1ub}	1037	814	-.4140	-.7258	0.8338	0.8023	-.2533	-0.289
E_{1ub}	1482	1333	0.3892	0.3098	0.3588	0.5746	0.5865	0.3949

a. Results taken from Ref.(44).

b. In square root of atomic weight mass unit.

c. In (1/square root of atomic weight mass) unit.

Table III.4. Line width of CH(CD) stretch overtone of benzene(perdeuterobenzene C_6D_6).

n_{CH}	FWHM(cm^{-1}) CH Exp.[a]	CH SCPKC[b]	CD Exp[a]	CD SCPKC[b]
5	111	82	50	
6	95	23-60	37	>7
7	90	60	~35 >	>8
8	100	56	65	>6
9	56	32		

a.Reference (33).

b.Present work--SCP kinetic coupling model.

Table IV.1 The transition probabilities for collinear $He+H_2$ vibrationally inelastic scattering.

$E_o(\hbar\omega)$		10		8		6		4		3	
$n_1 \rightarrow n_2$		QM[a]	LVCM[b]	QM	LVCM	QM	LVCM	QM	LVCM	QM	LVCM
0	0	0.060	0.099	0.204	0.253	0.538	0.531	0.892	0.851	0.978	0.955
	1	0.218	0.279	0.434	0.393	0.394	0.333	0.108	0.102	0.022	0.023
	2	0.366	0.306	0.291	0.212	0.064	0.057	1.2-3	1.6-3		
	3	0.267	0.168	0.071	0.050						
	4	0.089	0.050								
1	0	0.218	0.279	0.434	0.393	0.394	0.333	0.108	0.102	0.022	0.023
	1	0.286	0.144	0.034	0.001	0.244	0.248	0.850	0.847	0.977	0.983
	2	9.0-3	0.015	0.220	0.251	0.345	0.327	0.042	0.045		
	3	0.170	0.214	0.261	0.229	0.037	0.040				
	4	0.240	0.195	0.051	0.049						
	5	0.071	0.062								
2	0	0.366	0.306	0.291	0.212	0.068	0.057	1.2-3	1.6-3		
	1	0.009	0.015	0.220	0.251	0.345	0.327	0.042	0.045		
	2	0.207	0.188	0.039	0.012	0.347	0.349	0.955	0.971		
	3	0.018	1.7-5	0.250	0.257	0.233	0.243	1.3-3	2.0-3		
	4	0.169	0.191	0.189	0.190	6.0-3	8.9-3				
	5	0.194	0.181	0.016	0.022						
	6	0.034	0.043								

a.The exact quantum results of Ref. (32).

b.The results of the lable variable classical mechanics.

Table IV.2. Transition probabilities for 1-quantum T-V energy transfer

Transition $n_1^i n_2^i \to n_1^f n_2^f$	$E/\hbar\omega$	QM[a]	LVCM[b]	Adiabatic[c] (corrected)	PDK[d]
00 → 01	2.05	1.69-6[e]	1.61-6	1.69-6	3.13-6
	2.25	7.84-5	7.64-5	7.84-5	1.49-4
	2.50	6.50-4	6.29-4	6.50-4	1.23-3
	2.75	2.31-3	2.24-3	2.31-3	4.39-3
	3.05	6.41-3	6.27-3	6.41-3	1.24-2
	3.50	1.74-2	1.75-2	1.74-2	3.47-2
	3.95	3.26-2	3.49-2	3.26-2	6.83-2

a. The quantum mechanical results of Reference (64).

b. The results of the label variable classical mechanics.

c. The results of the first order adiabatic approximation corrected against QM[a] results in Reference (70).

d. The results of the first order distorted wave T-matrix method (partially decoupled T matrix) of Reference (70).

e. See c of table II.1.

Table IV.3. Transition probabilities for 1-quantum T-V energy transfer[a]

Transition $n_1^i n_2^i \rightarrow n_1^f n_2^f$	$E/\hbar\omega$	QM[a]	LVCM[b]	Adiabatic[c] (corrected)	PDK[d]
01→11	3.05	1.95-6[b]	1.60-6	1.54-6	2.98-6
	3.50	2.86-4	6.28-4	5.68-4	1.15-3
	3.95	6.53-3	4.59-3	3.82-3	8.16-3
01→02	3.05	1.11-6	3.22-6	3.12-6	5.93-6
	3.50	1.52-4	1.24-3	1.12-3	2.21-3
	3.95	4.44-4	8.80-3	7.74-3	1.54-2
01→20	3.05	5.60-8	8.21-9	1.13-7	1.89-7
	3.50	4.55-5	2.04-5	9.93-5	1.71-4
	3.95	4.13-4	4.28-4	1.22-3	1.85-3

a. See Table IV.1 for an axplanation of the different results.

b. See c of Table II.1.

Table IV.4. Transition probabilities for 2-quanta T-V energy transfer[a]

Transition $n_1^i n_2^i \to n_1^f n_2^f$	$E/\hbar\omega$	QM[a]	LVCM[b]	Adiabatic[c] (corrected)	PDK[d]
00→11	3.05	1.50-8[b]	1.05-8	9.98-9	3.74-8
	3.50	2.24-5	1.15-5	9.89-6	4.14-5
	3.95	3.97-4	1.73-4	1.20-4	6.11-4
00→02	3.05	3.50-9	5.28-9	4.94-9	1.87-8
	3.50	1.89-6	5.75-6	4.94-6	2.07-5
	3.95	1.81-5	8.63-5	5.99-5	3.05-4
Ratio of transition probabilities $P_{00\to11}/P_{00\to02}$	3.05	4.3	2	2	2
	3.50	11.85	2	2	2
	3.95	21.9	2	2	2

a. See Table IV.1 for an explanation of the different results.

b. See c of Table II.1

Table IV.5. Transition probabilities for 1-quantum V-V energy transfer[a]

Transition $n_1^i n_2^i \to n_1^f n_2^f$	$E/\hbar\omega$	QM[a]	LVCM[b]	Adiabatic[c] (corrected)	PDK[d]
01→10	2.05	4.1-3[b]	4.49-3	4.10-3	4.00-3
	2.25	2.11-2	2.02-2	2.09-2	2.02-2
	2.50	4.38-2	4.00-2	4.29-2	4.00-2
	2.75	6.81-2	5.96-2	6.55-2	5.94-2
	3.05	9.89-2	8.23-2	9.32-2	8.18-2
	3.50	0.146	0.113	0.137	0.113
	3.95	0.188	0.139	0.178	0.137

Table IV.6. Transition probabilities for 2-quantum V-V energy transfer[a]

Transition $n_1^i n_2^i \to n_1^f n_2^f$	$E/\hbar\omega$	QM[a]	LVCM[b]	Adiabatic[c] (corrected)	PDK[d]
02→11	3.05	7.82-3	7.76-3	7.84-3	7.76-3
	3.50	7.61-2	7.40-2	7.88-2	7.39-2
	3.95	0.132	0.134	0.148	0.132
02→20	3.05	1.70-5	1.67-5	1.71-5	1.67-5
	3.50	1.57-3	1.50-3	1.71-3	1.49-3
	3.95	5.17-3	5.23-3	6.51-3	5.15-3

a. See Table IV.1 for an explanation of the different results.

b. See c of Table II.1.

Figure Captions

Figure II.1 Relative coordinates pertaining to the A+BC → AB+C (AC+B) reaction.

Figure III.1 A countour plot of the potential surface [Eq.(III-34)] in mass-weighted coordinates [Eq.(III-35)]. Also shown are the reaction path, and the gradient paths starting from different initial points high up on the potential wall.

Figure III.2 Vibrational transition probabilities $P_{n_2,n_1}(E)$ as a function of final vibrational quantum number n_2, for $n_1=0,1,2,\ldots$ and three different values of the total energy E_o.

Figure III.3. Numbering of in-plane internal coordinates which are kinetically coupled with CH stretch x_{CH} : $s=x_{CH}+X_{CHo}$ is CH bond length; $t_1=x_1+X_o$ and $t_6=x_6+X_o$ are CC bond lengths; $\beta=(\phi_6-\phi_1)/2$, where ϕ_6 and ϕ_1 are CCH bond angles; α is CCC bond angles; X_o and X_{CHo} are equilibrium bond lengths of CC bond and CH bond, respectively.

Figure III.4. The experemental absorption spectra of $C_6H_6(C_6D_6)$ of Ref.(33) .Each panel contains: spectral assignments where n indicates the number of quanta of CH(CD) stretch exitation, positions of band maxima or band centers($\bar{\nu}_o$in cm^{-1}), and FWHM band widths in cm^{-1} (less certain bandwidths are given in parentheses). Ordinates are absorption cross sections (σ values, in millibarms ($mb=10^{-27}cm^2$) and abscissa are spectral shifts relative to the band maxima.

Figure III.5. The square of absolute value of the correlation function $|c(t)|^2$ for CH stretch local mode overtones n=5-9 in C_6H_6 as a function of time. The dashed line corresponds to $\tilde{c}(t)$ defined by Eqs.(III.75).

Figure III.6. The logarithm of $|c(t)|^2$ as a function of time for CH stretch local mode overtones n=5-9 in C_6H_6. The dashed line corresponds to $\tilde{c}(t)$ defined by Eqs.(III-75).

Figure III.7. The absorption spectra $I(\Delta\nu)/I(\nu_o)$ for CH stretch local mode overtones n=5-9 in C_6H_6. The dashed line corresponds to $\tilde{c}(t)$ defined by Eqs.(III-75).

Figure III.8. The square of absolute value of the correlation function $|c(t)|^2$ for CD stretch local mode overtones n=5-8 in C_6D_6 as a function of time.

Figure III.9. The logarithm of $|c(t)|^2$ as a function of time for CD stretch local mode overtones n=5-8 in C_6D_6.

Figure III.10. The absorption spectra $I(\Delta\nu)/I(\nu_o)$ for CD stretch local mode overtones n=5-8 in C_6D_6.

Figure IV.1 Transition probabilities for the collinear $He+H_2$ vibrationally inelastic scattering.

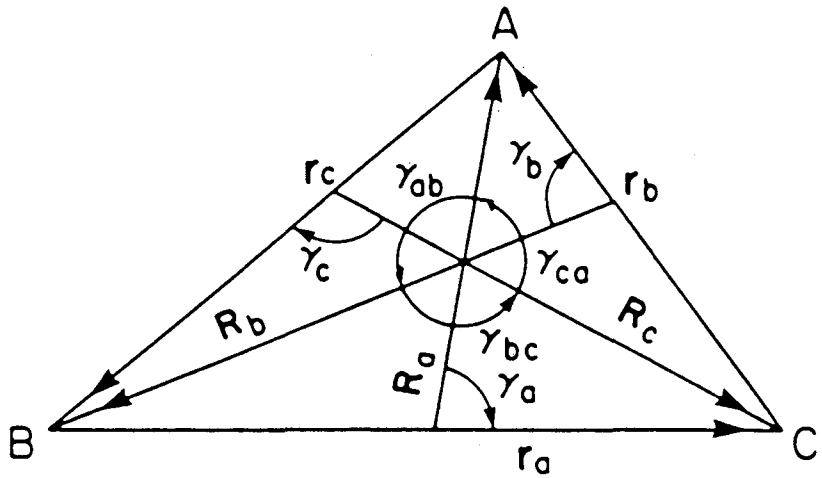
A
B
C
r_c
r_b
r_a
γ_{ab}
γ_b
γ_c
γ_{ca}
γ_{bc}
γ_a
R_b
R_c
R_a

Figure II.1

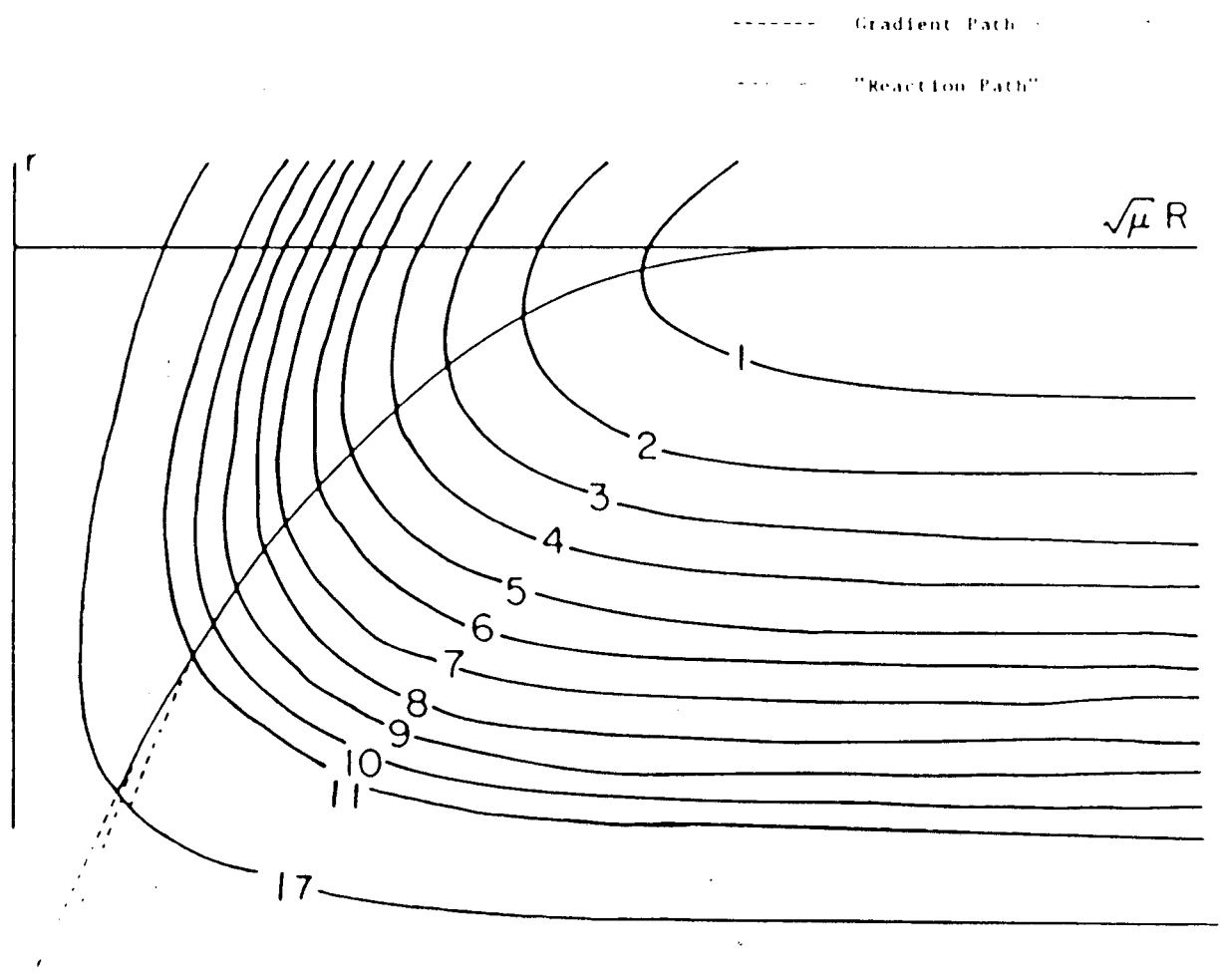

Figure III.1

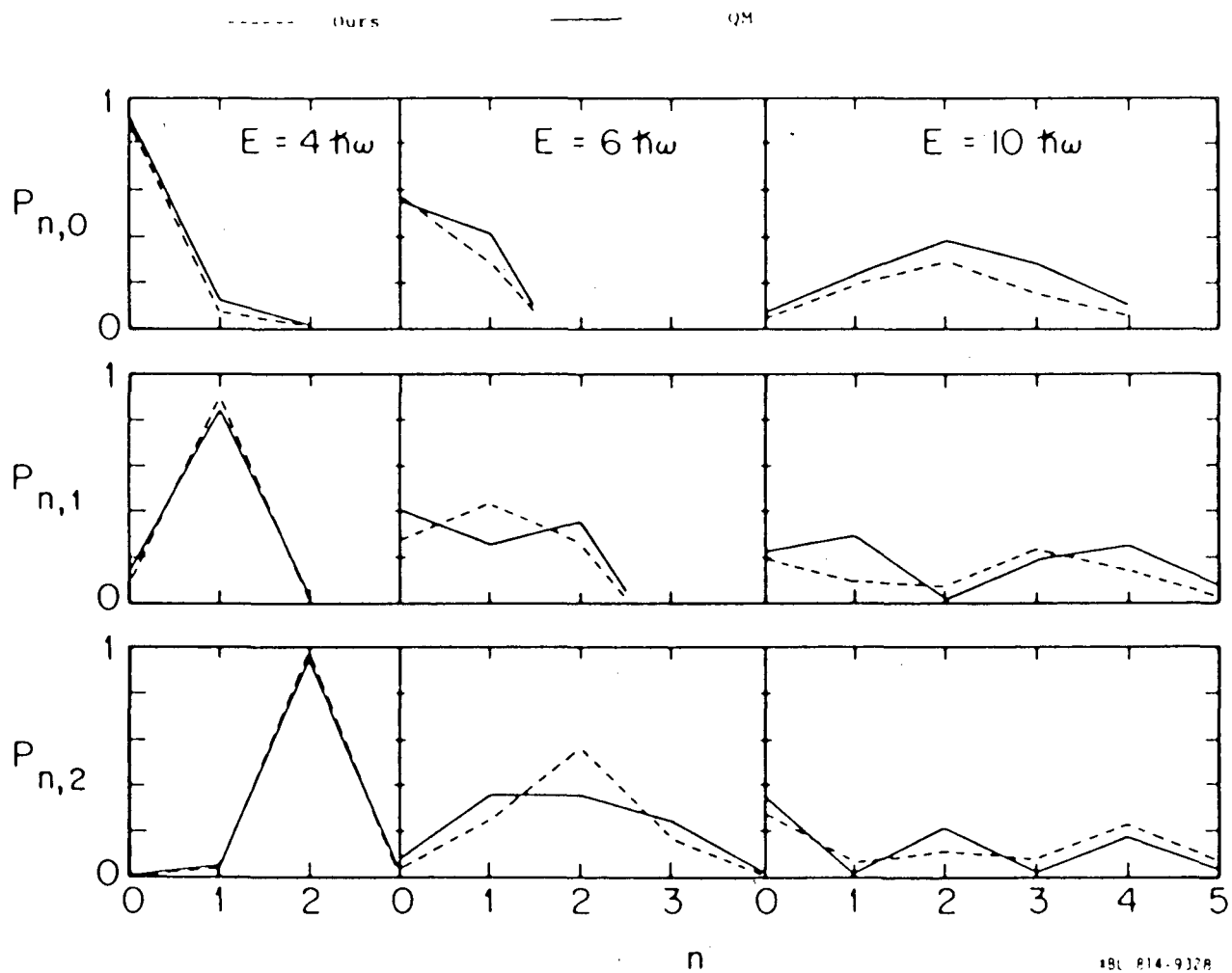
Ours
QM
E = 4 ħω
E = 6 ħω
E = 10 ħω
P n,0
P n,1
P n,2
1
0
0 1 2
0 1 2 3
0 1 2 3 4 5
n
ISL 814-9328

Figure III.2

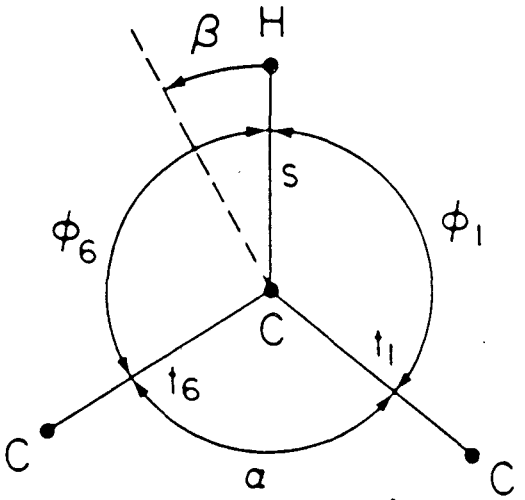

Figure III.3

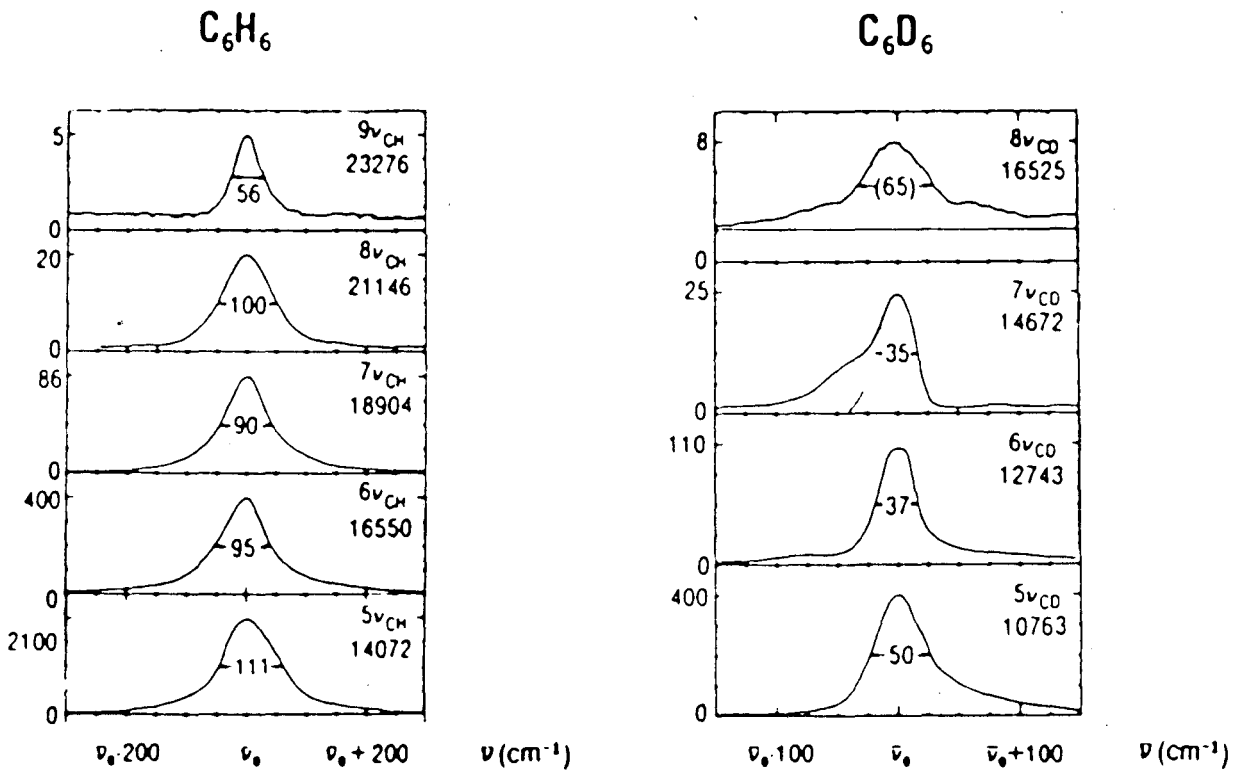
C6H6
C6D6
9νCH
23276
56
8νCH
21146
100
7νCH
18904
90
6νCH
16550
95
5νCH
14072
111
8νCD
16525
(65)
7νCD
14672
35
6νCD
12743
37
5νCD
10763
50
ν0-200
ν0
ν0+200
ν(cm-1)
ν0-100
ν0
ν0+100
ν(cm-1)

Figure III.4

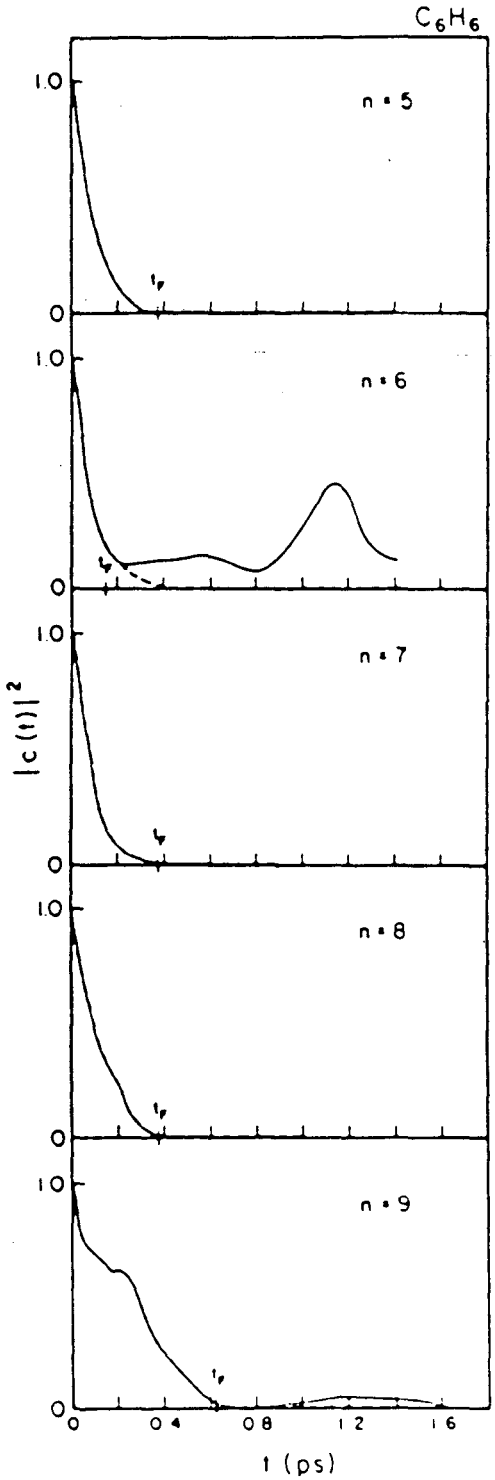

Figure III.5

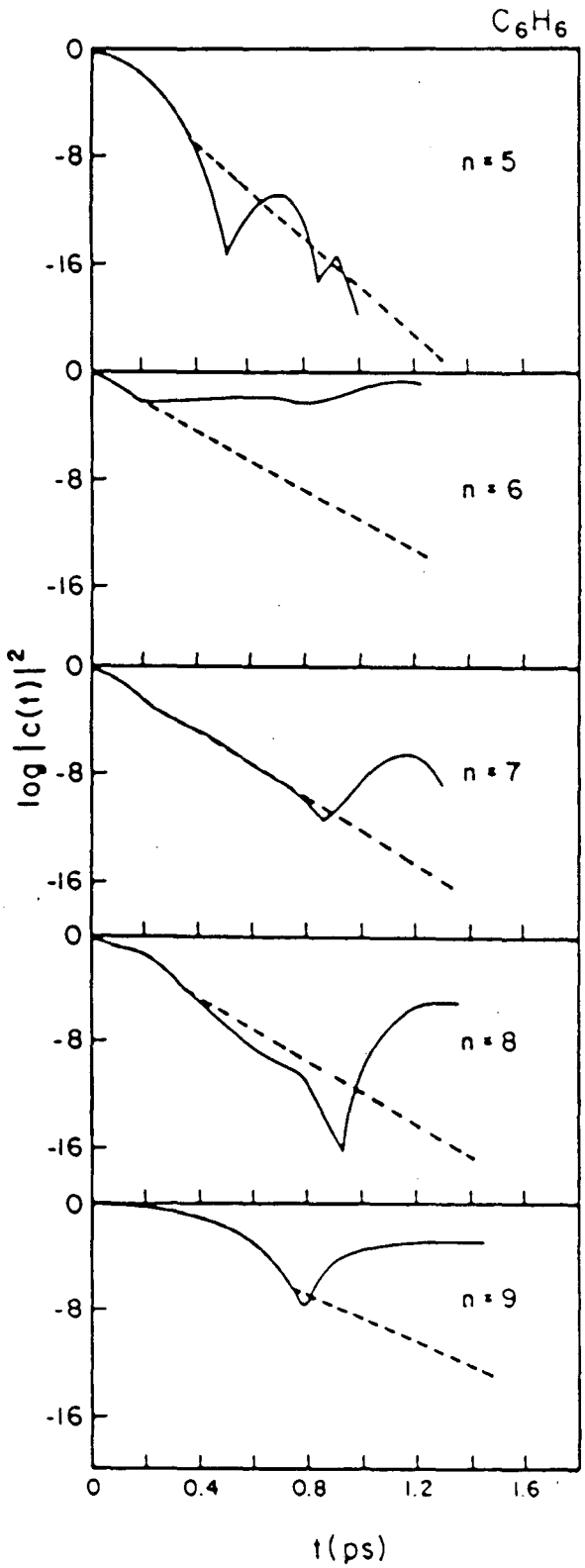

Figure III.6

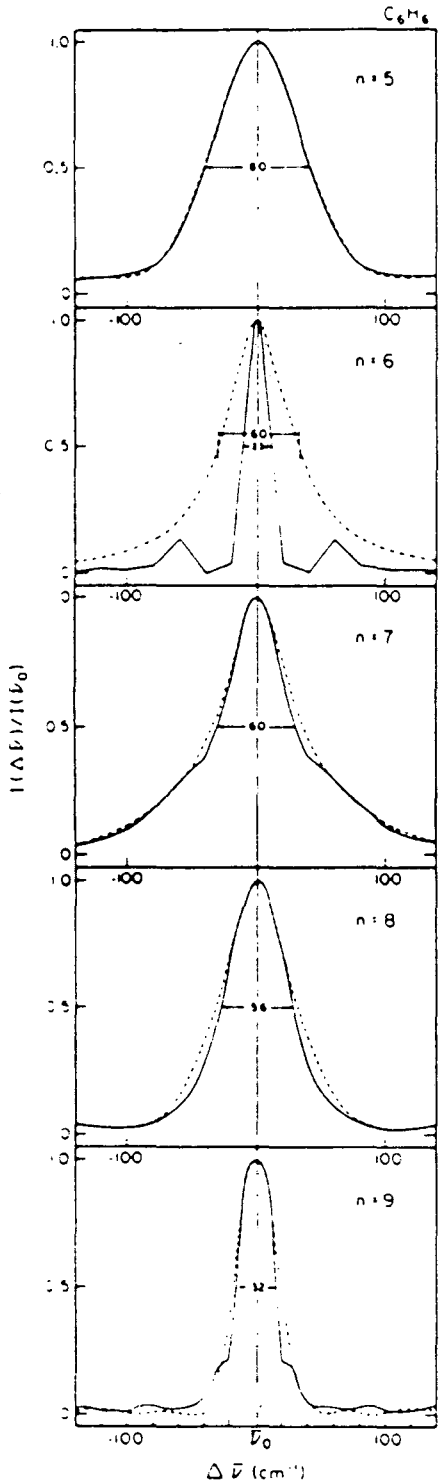

Figure III.7

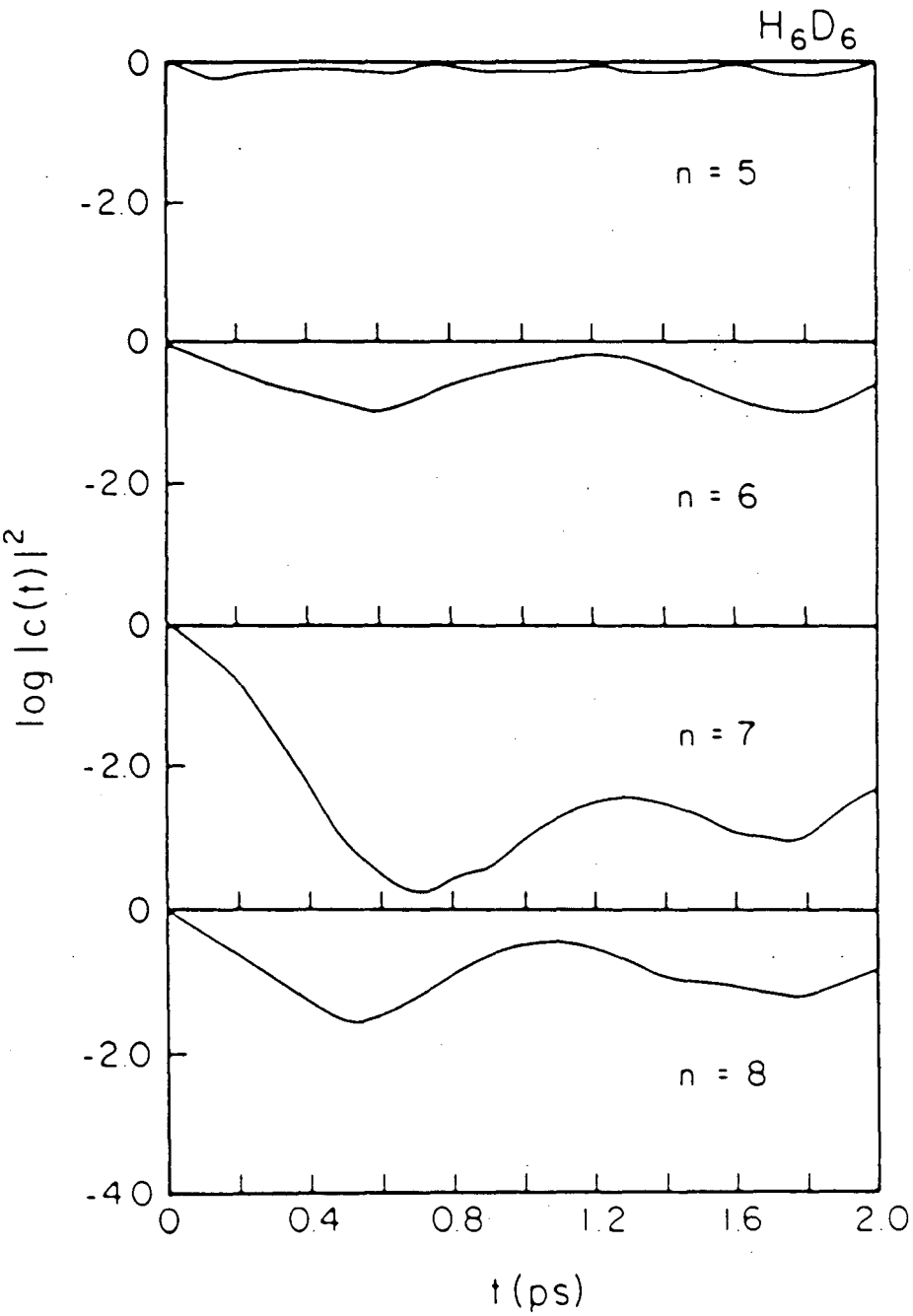

Figure III.8

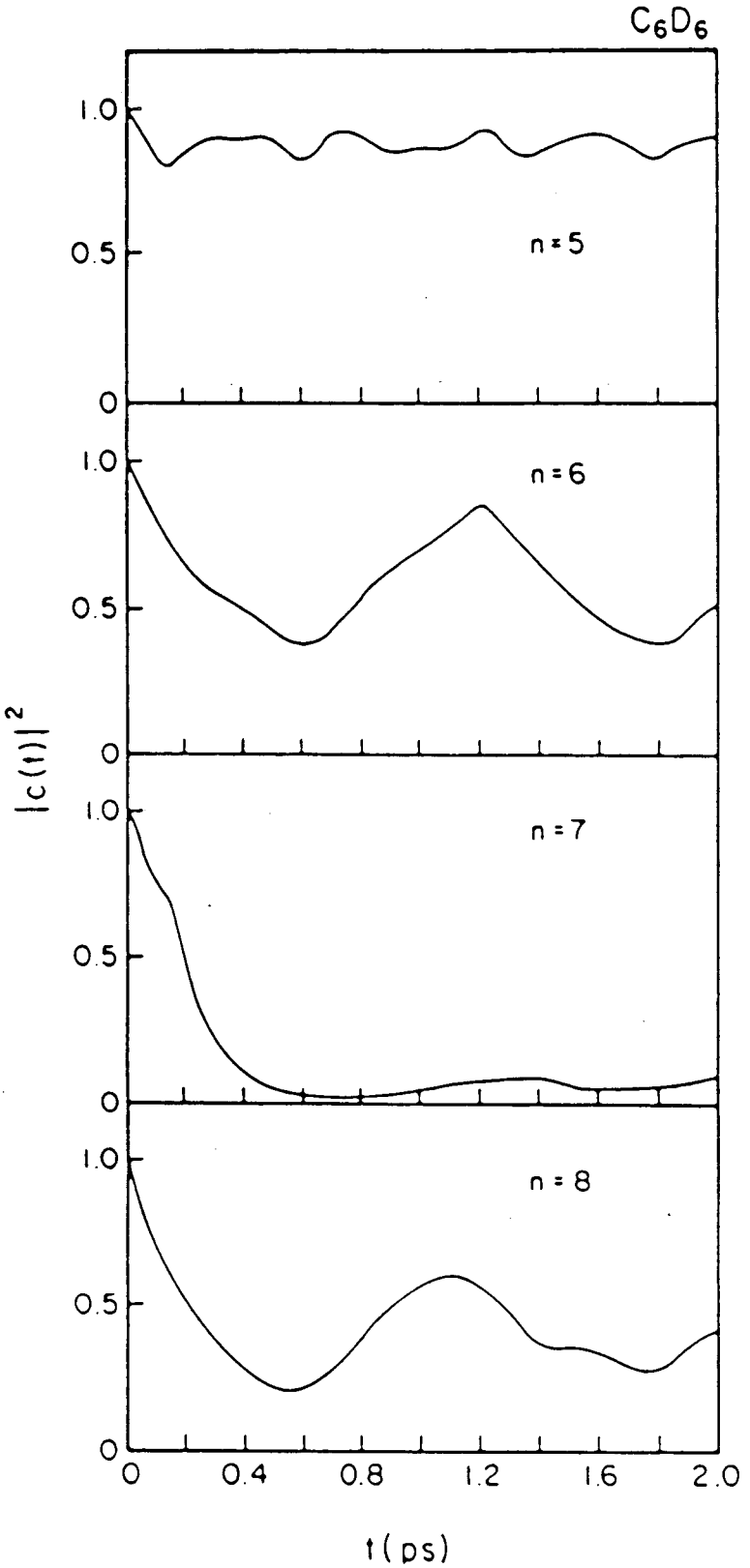

Figure III.9

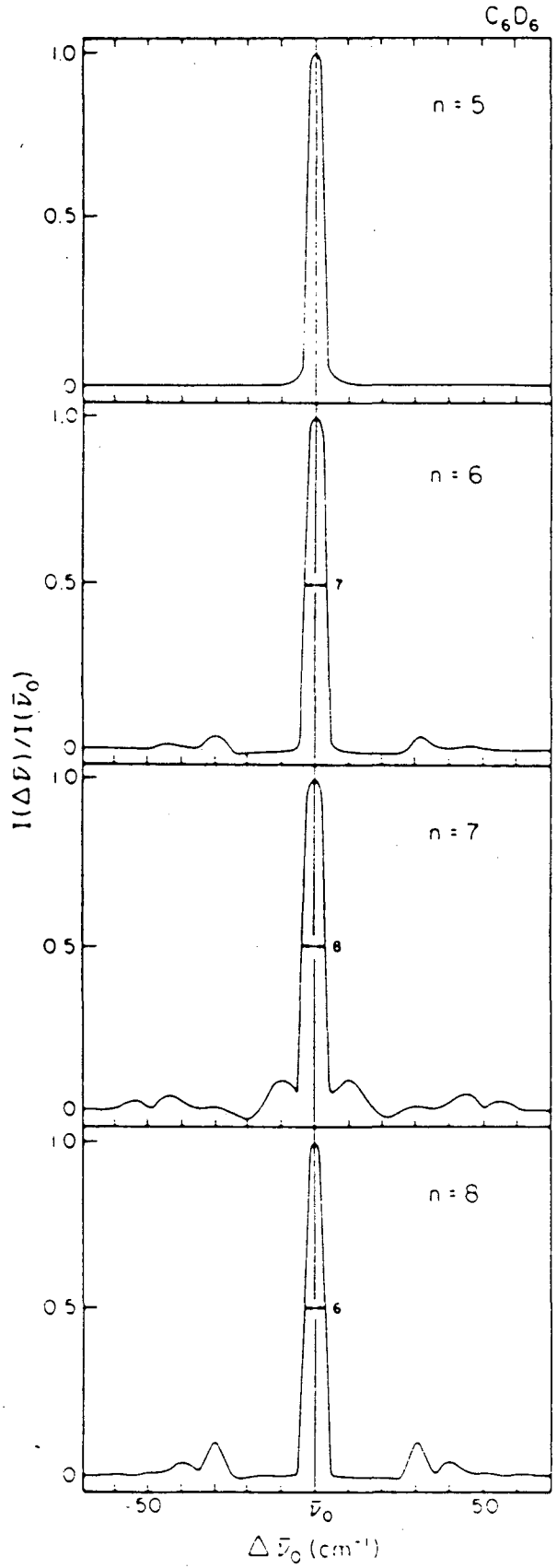

Figure III.10

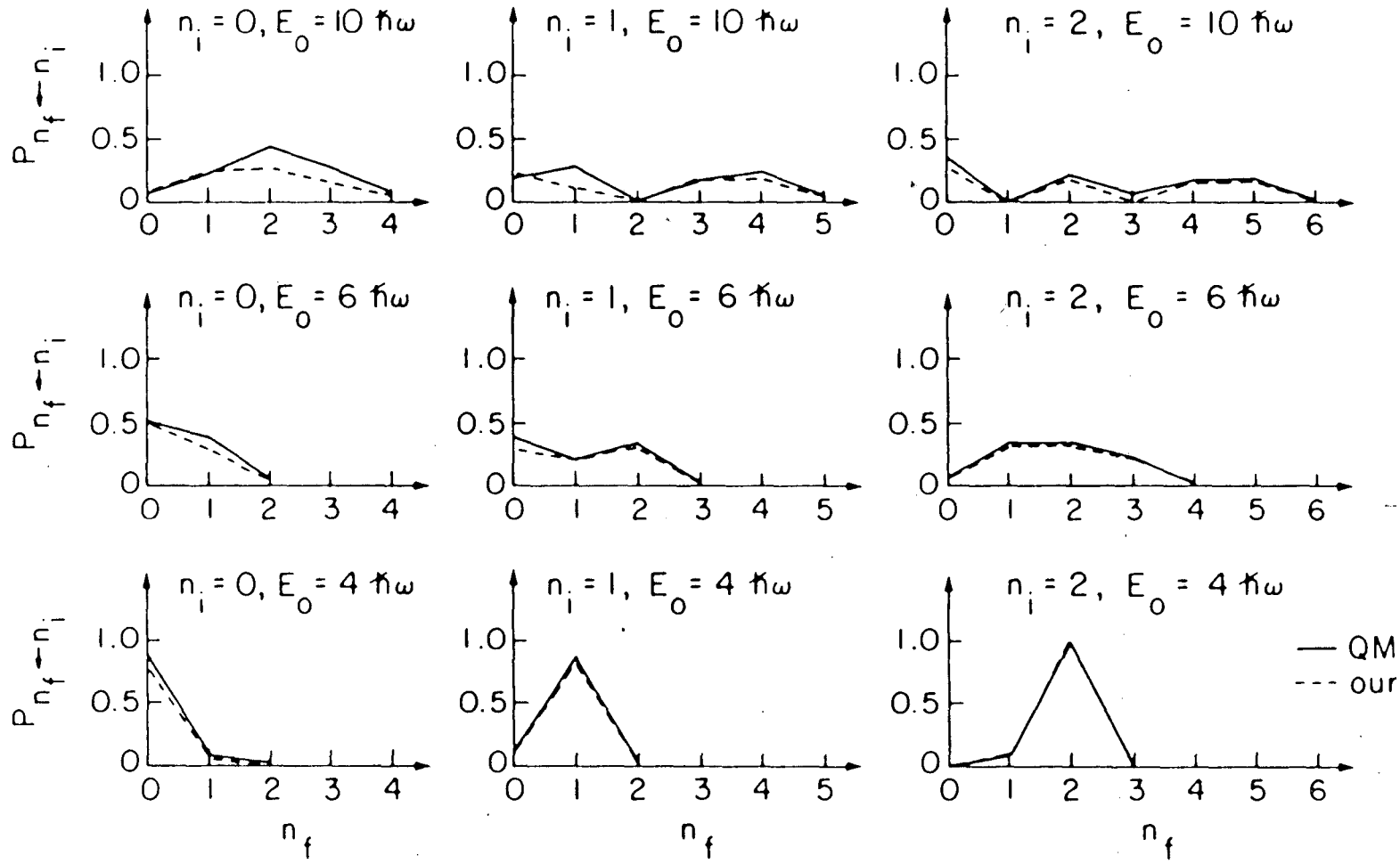
$n_i = 0, E_0 = 10\ \hbar\omega$
$n_i = 1, E_0 = 10\ \hbar\omega$
$n_i = 2, E_0 = 10\ \hbar\omega$
$n_i = 0, E_0 = 6\ \hbar\omega$
$n_i = 1, E_0 = 6\ \hbar\omega$
$n_i = 2, E_0 = 6\ \hbar\omega$
$n_i = 0, E_0 = 4\ \hbar\omega$
$n_i = 1, E_0 = 4\ \hbar\omega$
$n_i = 2, E_0 = 4\ \hbar\omega$
$P_{n_f \leftarrow n_i}$
n_f
QM
our

Figure IV.1

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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