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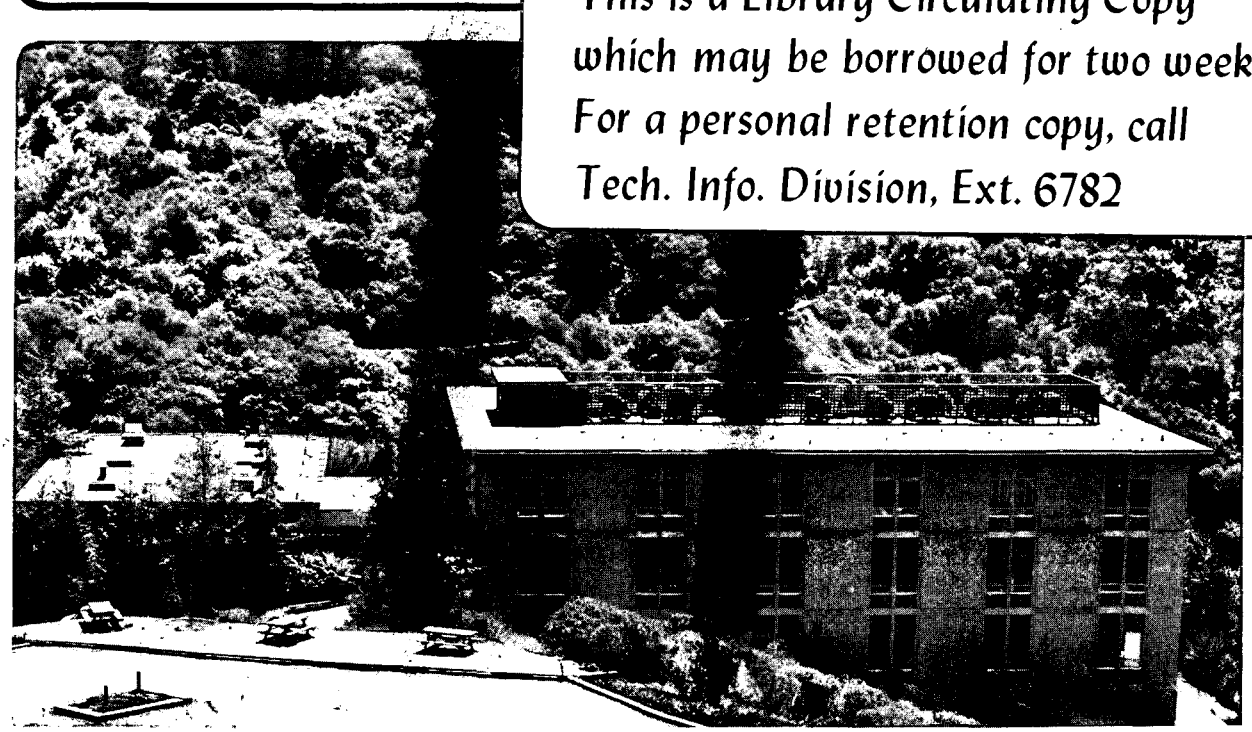

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UNIFIED SEMICLASSICAL PERTURBATION AND INFINITE ORDER SUDDEN APPROXIMATION, WITH APPLICATION TO THE REACTION PATH HAMILTONIAN MODEL

By

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Abstract

It is shown how two popular approximate dynamical models--the semiclassical perturbation (SCP) approximation and the infinite order sudden (IOS) approximation--can be combined in a consistent way that includes the correct features of both. Application of this unified SCP-IOS approximation to the reaction path Hamiltonian model of Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)] leads to extremely simple, explicit formulae for the reactive S-matrix, product state distributions, etc., which can be readily applied to polyatomic systems. Initial numerical tests on a simple model problem indicate that the model is of useful accuracy.

I. Introduction

Although rigorous, numerically exact calculations for inelastic and reactive molecular collision processes are becoming increasingly feasible nowadays,[1] there is still the obvious desire to devise simple approximate theoretical models that are as quantitatively reliable as possible. This is particularly true when one is dealing with the dynamics of polyatomic systems, for which rigorous approaches become unfeasible. This paper considers two such approximate models that are currently receiving some attention--the infinite order sudden (IOS) approximation[2] and the semiclassical perturbation (SCP) approximation[3]--and shows how they can be combined into a "unified" model that reproduces both of them in the appropriate limits. (The SCP approximation is also essentially equivalent to the "strong-coupling correspondence principle" of Percival and Richards,[4] which is essentially equivalent to a semiclassical approximation of Levine and Johnson,[5] which is essentially equivalent to approximations developed earlier by Cross.[6])

Section II first summarizes the SCP and IOS approximations in a consistent notation, and Section III describes their synthesis. Section IV shows that application of this unified SCP-IOS approximation to the reaction path Hamiltonian model[7] for polyatomic reaction dynamics leads to exceptionally simple expressions for product state distributions, tunneling probabilities, etc. Results of calculations using this approximation are described in Section V, and one sees that the model is capable of a reasonable level of accuracy.

II. Summary of the SCP and IOS Approximations

A. Semiclassical Perturbation Approximation

The notation here follows that of reference 3, where the SCP result is derived as a first-order perturbation approximation to the initial value representation of classical S-matrix theory.[8] As noted in the Introduction, though, there are other routes to the resulting expressions.

Consider the classical Hamiltonian describing a general inelastic collision process for a system of F degrees of freedom:

$$H(P,R,\underset{\sim}{n},\underset{\sim}{q}) = \frac{P^2}{2\mu} + \varepsilon(\underset{\sim}{n}) + V(R,\underset{\sim}{n},\underset{\sim}{q}) \quad ; \tag{2.1}$$

(R,P) are the coordinate and momentum for relative translation, and $(\underset{\sim}{n},\underset{\sim}{q},) = (n_i,q_i)$, i=1, ..., F-1 are the action-angle variables for the F-1 internal degrees of freedom of the collision partners. $\varepsilon(\underset{\sim}{n})$ is the internal energy of the collision partners as a function of the action variables (i.e., the quantum numbers), and V is the interaction potential. The interaction potential is divided into a zero$^{\underline{th}}$ order term that is independent of the angles $\underset{\sim}{q}$ and can thus cause no inelastic transitions, plus a perturbation which can,

$$V(R,\underset{\sim}{n},\underset{\sim}{q}) = V_0(R,\underset{\sim}{n}) + \Delta V(R,\underset{\sim}{n},\underset{\sim}{q}) \quad . \tag{2.2}$$

In applications V_0 is often assumed to be independent of the internal action variables $\underset{\sim}{n}$. The most generally correct way of

choosing V_0 is as the phase average of the full interaction potential,

$$V_0(R,\underset{\sim}{n}) = (2\pi)^{-(F-1)} \int_0^{2\pi} d\underset{\sim}{q}\ V(R,\underset{\sim}{n},\underset{\sim}{q}) \qquad ; \tag{2.3}$$

this is equivalent to the distorting potential of the distorted wave Born approximation in quantum mechanics.[9] In applications, though, V_0 is often chosen by a simpler prescription.

The S-matrix element for the $\underset{\sim}{n}_1 \rightarrow \underset{\sim}{n}_2$ transition is given within the SCP approximation by[3]

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = \frac{e^{2i\eta_0}}{(2\pi)^{F-1}} \int_0^{2\pi} d\underset{\sim}{q}_0 \quad \exp[-i\Delta\underset{\sim}{n}\cdot\underset{\sim}{q}_0 \ -i \int_{-\infty}^{\infty} dt\ \Delta V(R(t),\underset{\sim}{n},\underset{\sim}{q}_0+\underset{\sim}{\omega}t)] \quad , \tag{2.4}$$

where (with $\hbar$=1 everywhere)

$$\Delta\underset{\sim}{n} = \underset{\sim}{n}_2-\underset{\sim}{n}_1 \tag{2.5a}$$

$$\underset{\sim}{n} = \frac{1}{2}\ (\underset{\sim}{n}_1+\underset{\sim}{n}_2) \qquad . \tag{2.5b}$$

R(t) is the zero$^{\underline{th}}$ order translational trajectory determined from H_0,

$$H_0(P,R,\underset{\sim}{n}) = \frac{P^2}{2\mu} + \varepsilon(\underset{\sim}{n}) + V_0(R,\underset{\sim}{n}) \qquad ; \tag{2.6a}$$

i.e., R(t) is the inverse function of

$$t(R) = \pm \int_{R_<}^{R} dR' \left\{\frac{2}{\mu}\left[E-\varepsilon(\underset{\sim}{n})-V_0(R',\underset{\sim}{n})\right]\right\}^{-1/2} \quad , \tag{2.6b}$$

where E is the total energy. η_0 is the WKB elastic phase shift determined by V_0:

$$\eta_0 = \lim_{R\to\infty}\left[-kR + \int_{R_<}^{R} dR' \quad \sqrt{2\left[E-\varepsilon(\underset{\sim}{n})-V_0(R',\underset{\sim}{n})\right]}\right] \tag{2.7a}$$

$$k = \sqrt{2\mu[E-\varepsilon(\underset{\sim}{n})]} \quad . \tag{2.7b}$$

Equation (2.4) has the form of a Fourier transform in the angle variables $\underset{\sim}{q}_0$ of an exponential of a time integral of the perturbation ΔV, where the time dependence of ΔV is determined by the zero$^{\underline{th}}$ order Hamiltonian H_0; i.e., R(t) is given by Eq. (2.6), and

$$\underset{\sim}{n}(t) = \underset{\sim}{n} \quad \text{(constant)} \tag{2.8a}$$

$$\underset{\sim}{q}(t) = \underset{\sim}{q}_0 + \underset{\sim}{\omega}t \quad , \tag{2.8b}$$

where

$$\underset{\sim}{\omega} = \frac{\partial\varepsilon(\underset{\sim}{n})}{\partial\underset{\sim}{n}} \quad .$$

Approximations based on Eq. (2.4) have included rotational excitation of polar molecules by electrons,[3] rotational excitation in atom-rigid rotor collisions,[10] and also vibrational excitation[11] in molecular collisions, and the results obtained have in general been quite encouraging. Even though the model is based on first

order perturbation dynamics, the exponential form of the semiclassical expression for the S-matrix elements means that the perturbation is incorporated, at least approximately, to infinite order, as is characteristic of other exponentiated first order theories.[12]

B. Infinite Order Sudden Approximation

The semiclassical version of the sudden approximation (SA) results from Eq. (2.4) by setting $\underset{\sim}{\omega}=0$ in ΔV; i.e., it is assumed that the internal motion is frozen during the translational motion;

$$S^{SA}_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = \frac{e^{2i\eta_0}}{(2\pi)^{F-1}} \int_0^{2\pi} d\underset{\sim}{q}_0 \exp[-i\Delta\underset{\sim}{n}\cdot\underset{\sim}{q}_0 - i\int_{-\infty}^{\infty} dt\ \Delta V(R(t),\underset{\sim}{n},\underset{\sim}{q}_0)] \quad , \tag{2.9}$$

or this can be written more suggestively as

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = (2\pi)^{-(F-1)} \int_0^{2\pi} d\underset{\sim}{q}_0 \exp[-i\Delta\underset{\sim}{n}\cdot\underset{\sim}{q}_0+2i\eta(\underset{\sim}{q}_0,\underset{\sim}{n})] \quad , \tag{2.10}$$

where

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = \eta_0 - \frac{1}{2}\int_{-\infty}^{\infty} dt\ \Delta V(R(t),\underset{\sim}{n},\underset{\sim}{q}_0) \quad . \tag{2.11}$$

The <u>infinite order</u> sudden approximation can be obtained by identifying Eq. (2.11) as the first two terms of a Taylor's series and then "unexpanding" the series. Using the fact that the elastic trajectory R(t) is the same for t<0 and t>0,

and changing the integration variable in Eq. (2.11) from t to R, gives

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = -kR + \int_{R_<}^{R} dR' \sqrt{2\mu[E-\varepsilon(\underset{\sim}{n})-V_0(R',\underset{\sim}{n})]}$$

$$- \int_{R_<}^{R} dR' \frac{\mu\ \Delta V(R',\underset{\sim}{n},\underset{\sim}{q}_0)}{\sqrt{2\mu[E-\varepsilon(\underset{\sim}{n})-V_0(R',\underset{\sim}{n})]}} \quad , \tag{2.12}$$

with $R\to\infty$. To lowest order in ΔV one observes that Eq. (2.12) is equivalent to

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = -kR + \int_{R_<}^{R} dR' \sqrt{2\mu[E-\varepsilon(\underset{\sim}{n})-V_0(R',\underset{\sim}{n})-\Delta V(R',\underset{\sim}{n},\underset{\sim}{q}_0)]} \quad , \tag{2.13}$$

which is the infinite order WKB phase function to which Eq. (2.12) is the expansion to first order in ΔV; i.e., $\eta(\underset{\sim}{q}_0)$ is the WKB phase shift for the translational motion computed with the internal motion frozen. This is emphasized even more clearly by noting that Eq. (2.13) is the translational phase integral,

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = -kR + \int_{R_<}^{R} dR'\ P(R') \quad , \tag{2.13'}$$

where the translational momentum P(R) is determined by energy conservation using the total Hamiltonian with $\underset{\sim}{n}$ and $\underset{\sim}{q}$ held fixed,

$$E = H(P,R,\underset{\sim}{n},\underset{\sim}{q}_0) = \frac{P^2}{2\mu} + \varepsilon(\underset{\sim}{n}) + V_0(R,\underset{\sim}{n}) + \Delta V(R,\underset{\sim}{n},\underset{\sim}{q}_0) \quad . \tag{2.14}$$

The IOS corresponds to using Eq. (2.13) in Eq. (2.10).

III. The Unified Approximation

The advantage of the IOS approximation over the SCP is that it includes the "perturbation" to infinite order in the phase function η, and if the collision is indeed sudden--i.e., if the internal motion is infinitely slow compared to the change in the translational momentum--then ΔV is included correctly to infinite order. The SCP approximation is more correct, on the other hand, by including (approximately) the effect of motion of the internal degrees of freedom during the collision. The IOS is thus best for collisions involving "hard wall" interaction potentials, where the duration of the collision itself is small compared to a period of the internal motion, while the SCP is better when the interaction is effective over an extended range and motion of the internal degrees of freedom thus an important consideration (e.g., in resonance energy transfer). The goal here is to combine these two models in such a way to incorporate the correct features of both of them.

A way of doing this is rather obvious from the way they have been presented in Section II: in the IOS expression, Eqs. (2.10) and (2.13), one simply re-introduces the zero$^{\underline{th}}$ order of motion of the internal degrees of freedom, i.e., makes the replacement

$$\underset{\sim}{q}_0 \rightarrow \underset{\sim}{q}_0 + \underset{\sim}{\omega} t \tag{3.1}$$

in the integrand of Eq. (2.13). Equation (2.10) still applies, but now the phase function is

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = -kR + \int_{R_<}^{R_>} dR' \sqrt{2\mu[E-\varepsilon(\underset{\sim}{n})-V(R',\underset{\sim}{n},\underset{\sim}{q}_0+\underset{\sim}{\omega}t(R'))]} \quad , \tag{3.2}$$

where $V = V_0+\Delta V$, and where $t(R)$ is determined by the zero$^{\underline{th}}$ order Hamiltonian, i.e., by Eq. (2.6). It is clear that Eq. (3.2) incorporates the IOS limit if $\underset{\sim}{\omega} \to 0$ and also the SCP limit if Eq. (3.2) is expanded to first order in ΔV.

This unified SCP-IOS model, i.e., Eqs. (2.10) and (3.2), could be applied to the rotationally and/or vibrationally inelastic collision processes that have been treated either by the IOS or SCP approximations, with little increase in difficulty. An even more sophisticated version of this approach, and presumably more accurate (but also more complicated to apply), would be to use numerically computed classical trajectories to determine the time dependence of $\underset{\sim}{q}(t)$. In this case the phase function $\eta(\underset{\sim}{q}_0,\underset{\sim}{n})$ would be given by

$$\eta(\underset{\sim}{q}_0,\underset{\sim}{n}) = -PR \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\, \dot{R}(t)\, P(t) \tag{3.3a}$$

$$= -\int_{t_1}^{t_2} dt\, R(t)\, \dot{P}(t) \quad , \tag{3.3b}$$

with $t_1 \to -\infty$, $t_2 \to +\infty$, and where $R(t)$, $P(t)$ are determined by the classical trajectory generated by the full Hamiltonian of Eq. (2.1), with the initial conditions

$$\underset{\sim}{q}(0) = \underset{\sim}{q}_0 \tag{3.4a}$$

$$\underset{\sim}{n}(0) = \underset{\sim}{n} \tag{3.4b}$$

$$R(0) = R_< \text{ (the classical turning point)} \tag{3.4c}$$

$$P(0) = 0 \quad . \tag{3.4d}$$

The S-matrix elements are still given in terms of η by Eq. (2.10).

It would be interesting to explore the accuracy of the above approximation for rotationally and/or vibrationally inelastic collisions of atom-diatom or diatom-diatom systems and for collisions of atoms and diatoms with solid surfaces.

IV. Application to the Reaction Path Hamiltonian

Application of the SCP-IOS approximation of the previous section leads to particularly simple results for the S-matrix if the reaction path Hamiltonian model of Miller, Handy and Adams[7] is used to describe the dynamics. The reaction path model is an extension of ideas introduced first by Hofacker[13] and by Marcus[14] for describing a chemical reaction as motion along a reaction path. If the reaction is dominated by a single saddle point region--i.e., a transition state--then the reaction path[15] is conveniently defined as the steepest descent path (if mass-weighted cartesian coordinates are used) through the saddle point leading from reactants to products (cf. the "intrinsic reaction coordinate" of Fukui, et al.[16]). In terms of the reaction coordinate s, the mass-weighted distance along the reaction path, and the normal coordinates $\{Q_k\}$, k=2,..., F, for vibrational motion normal to the reaction path, and their conjugate momenta, (p_s, P_k), k=2,..., F, the explicit form of the classical Hamiltonian derived by Miller et al.[7] is

$$H(p_s, s, \underset{\sim}{P}, \underset{\sim}{Q}) = \frac{\frac{1}{2}\left[p_s - \sum_{k,k'=2}^{F} Q_k P_{k'} B_{k,k'}(s)\right]^2}{\left[1 + \sum_{k=2}^{F} Q_k B_{k,1}(s)\right]^2} + V_0(s)$$

$$+ \sum_{k=2}^{F} \left[\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2\right] \quad . \tag{4.1}$$

$V_0(s)$ is the potential energy along the reaction path, $\{\omega_k(s)\}$ the frequencies of transverse vibrational modes, $B_{k,k'}(s)$ coriolis

coupling functions which couple vibrational mode k to vibrational mode k', and $B_{k,1}(s)$ curvature coupling functions which couple vibrational mode k to the reaction coordinate (which is labeled as mode k=1). Eq. (4.1) applies to the case of zero total angular momentum, so that F = 3N-6 where N is the number of atoms of the system; the Hamiltonian for non-zero total angular momentum has also been given,[7] but is more complicated.

To cast this Hamiltonian in the form of that in Sections II and III, one transforms from the vibrational coordinates and momenta (Q_k, P_k), k=2,..., F to their action-angle variables (n_k, q_k),

$$Q_k = \sqrt{\frac{2n_k+1}{\omega_k(s)}} \quad \sin q_k \tag{4.2a}$$

$$P_k = \sqrt{(2n_k+1)\omega_k(s)} \quad \cos q_k \quad , \tag{4.2b}$$

and the reaction path Hamiltonian becomes

$$H(p_s, s, \underset{\sim}{n}, \underset{\sim}{q}) = \frac{\frac{1}{2}\left[p_s - \sum_{k,k'=2}^{F} B_{k,k'}(s)\sqrt{(2n_k+1)(2n_{k'}+1)}\sqrt{\frac{\omega_{k'}(s)}{\omega_k(s)}}\sin q_k \cos q_{k'}\right]^2}{\left[1 + \sum_{k=2}^{F} B_{k,1}(s)\sqrt{\frac{2n_k+1}{\omega_k(s)}} \sin q_k\right]^2}$$

$$+ V_0(s) + \sum_{k=2}^{F} (n+\tfrac{1}{2})\, \omega_k(s) \quad . \tag{4.3a}$$

(Here the diagonal elements $B_{k,k}(s)$ are defined by

$$B_{k,k}(s) = -\frac{\omega_k'(s)}{2\,\omega_k(s)} \quad .) \tag{4.3b}$$

In the present case the reaction coordinate s plays the role of the translational coordinate R of Sections II and III, and it varies from $-\infty$ to $+\infty$ during a reactive collision. Thus the expression for the S-matrix element for the reaction from state $\underset{\sim}{n}_1$ of reactants to $\underset{\sim}{n}_2$ of products which is equivalent to Eqs. (2.10) and (3.2) is

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = (2\pi)^{-(F-1)} \int_0^{2\pi} d\underset{\sim}{q}_0 \quad \exp[-i\Delta\underset{\sim}{n}\cdot\underset{\sim}{q}_0 + i\phi(\underset{\sim}{q}_0,\underset{\sim}{n})] \quad , \tag{4.4}$$

where

$$\phi(\underset{\sim}{q}_0,\underset{\sim}{n}) = -p_s(s)s \Big|_{s_1}^{s_2} + \int_{s_1}^{s_2} ds \; p_s(s) \quad , \tag{4.5}$$

and $s_1 \to -\infty$, $s_2 \to +\infty$. $p_s(s)$ is determined by energy conservation,

$$H(p_s,s,\underset{\sim}{n},\underset{\sim}{q}) = E \quad ,$$

and with the Hamiltonian of Eq. (4.3) this gives

$$p_s(s) = \sqrt{2[E-V_a(s)]} \left[1 + \sum_{k=2}^{F} B_{k,1}(s)\sqrt{\frac{2n_k+1}{\omega_k(s)}} \; \sin q_k(s)\right]$$

$$+ \sum_{k,k'=2}^{F} B_{k,k'}(s) \sqrt{(2n_k+1)(2n_{k'}+1)} \sqrt{\frac{\omega_{k'}(s)}{\omega_k(s)}} \sin q_k(s) \; \cos q_{k'}(s) \tag{4.6a}$$

where V_a is the vibrationally adiabatic potential

$$V_a(s) = V_0(s) + \sum_{k=2}^{F} (n_k + \tfrac{1}{2})\, \omega_k(s) \quad . \tag{4.6b}$$

To complete the model one must specify the s-dependence of the angle variables, and the simplest assumption is that it is the vibrationally adiabatic phase determined by the following zero$^{\underline{th}}$ order Hamiltonian,

$$H_0(p_s, s, \underset{\sim}{n}) = \frac{1}{2}\, p_s^{\,2} + V_a(s) \quad ;$$

this gives

$$q_k(s) = q_k(0) + \delta_k(s) \quad , \tag{4.7a}$$

where

$$\delta_k(s) = \int_0^s ds' \; \frac{\omega_k(s')}{\sqrt{2[E-V_a(s')]}} \quad . \tag{4.7b}$$

The variables $\{q_k(0)\}$, k=2,..., F are the integration varibles $\underset{\sim}{q}_0$ of Eq. (4.4).

The S-matrix given by Eqs. (4.4)-(4.7) takes an especially simple form if one neglects the coriolis coupling elements $B_{k,k'}(s)$. (They are often less significant than the curvature couplings $B_{k,l}(s)$, and in any event it will be discussed below how they can be included.) The expression is

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = \frac{e^{i\phi_0}}{(2\pi)^{F-1}} \int_0^{2\pi} d\underset{\sim}{q}_0 \quad \exp\{-i\Delta\underset{\sim}{n}\cdot\underset{\sim}{q}_0$$

$$+ i \int_{-\infty}^{\infty} ds \sqrt{2[E-V_a(s)]} \sum_{k=2}^{F} B_{k,1}(s)\sqrt{\frac{2n_k+1}{\omega_k(s)}} \sin[q_k(0)+\delta_k(s)]\}$$

$$= e^{i\phi_0} \prod_{k=2}^{F} (2\pi)^{-1} \int_0^{2\pi} dq_k(0) \quad \exp\{-i\Delta n_k \; q_k(0)$$

$$+ i \int_{-\infty}^{\infty} ds \sqrt{2[E-V_a(s)]} \quad B_{k,1}(s)\sqrt{\frac{2n_k+1}{\omega_k(s)}} \quad \sin[q_k(0)+\delta_k(s)]\} \quad .$$

(4.8)

Each factor in Eq. (4.8) is a phase factor times a Bessel function of order Δn_k, and the resulting transition probability is thus given by

$$P_{n_2,n_1}(E) = |S_{\underset{\sim}{n}_2,n_1}(E)|^2$$

$$= \prod_{k=2}^{F} J_{\Delta n_k}(|\gamma_k|)^2 \quad , \qquad (4.9a)$$

where

$$\gamma_k = \int_{-\infty}^{\infty} \sqrt{2[E-V_a(s)]} \quad B_{k,1}(s)\sqrt{\frac{2n_k+1}{\omega_k(s)}} \; e^{i\delta_k(s)} \quad .(4.9b)$$

Equation (4.9) provides an extremely simple estimate of the distribution of final quantum states resulting from the reaction

provided, of course, that one has the necessary properties of the reaction path, i.e., $V_0(s)$,$\{\omega_k(s)\}$, and $\{B_{k,1}(s)\}$. Equation (4.9) also has a simple relation to the classical mechanics of the problem: $|\gamma_k|$ is the average classical change in the classical action variable $n_k(t)$, i.e.,

$$\langle \Delta n_k \rangle_{\text{classical}} = |\gamma_k| \quad , \tag{4.10}$$

and as a function of Δn_k, the Bessel function $J_{\Delta n_k}(|\gamma_k|)^2$ has its maximum value at $\Delta n_k = |\gamma_k|$. The most probable change in the quantum number n_k is thus the average classical value.

The quadratic coupling elements, i.e., $B_{k,k'}$, of Eq. (4.6) can be taken into account using the trick of Miller and Smith.[3] This is illustrated by considering here the case F=2, i.e., the collinear A + BC → AB + C reaction. Equation (4.6a) reads

$$p_s(s) = \sqrt{2[E-V_a(s)]}\ \left[1+\kappa(s)\sqrt{\frac{2n+1}{\omega(s)}}\ \sin q(s)\right]$$

$$- \frac{\omega'(s)}{4\omega(s)}\ (2n+1)\ \sin 2q(s) \quad , \tag{4.11}$$

where $\kappa(s) = B_{2,1}(s)$ is the curvature of the reaction path, and the reactive S-matrix element is thus given by

$$S_{n_2,n_1}(E) = \frac{e^{i\phi_0}}{2\pi}\int_0^{2\pi} dq_0\ \exp\{-i\Delta n q_0 + i\int_{-\infty}^{\infty} ds\ \sqrt{2[E-V_a(s)]}\ \kappa(s)\sqrt{\frac{2n+1}{\omega(s)}}$$

$$\times\ \sin[q_0+\delta(s)]\ -i\int_{-\infty}^{\infty} ds\ \frac{\omega'(s)}{4\omega(s)}\ (2n+1)\ \sin[2q_0+2\delta(s)]\}\ . \tag{4.12}$$

The difficulty here is the appearance of a first and second harmonic of q_0 in the exponent of the integrand, and the way to deal with it is to introduce a new integration variable and a delta function to compensate for it:

$$\int_0^{2\pi} dq_0 \rightarrow \int_0^{2\pi} dq_0 \int_0^{2\pi} dq_1 \quad \delta(q_1-2q_0) \quad .$$

The delta function is expanded in a Fourier representation,

$$\delta(q_1-2q_0) = \frac{1}{2\pi} \sum_{k=-\infty}^{\infty} e^{-ik(q_1-2q_0)} \quad ,$$

so that Eq. (4.12) becomes

$$S_{n_2,n_1}(E) = e^{i\phi_0} \sum_{k=-\infty}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} dq_0 \; \exp\{-i(\Delta n-k)q_0$$

$$+ i \int_{-\infty}^{\infty} ds \sqrt{2[E-V_a(s)]}\, \kappa(s) \sqrt{\frac{2n+1}{\omega(s)}} \sin[q_0+\delta(s)]\} \frac{1}{2\pi} \int_0^{2\pi} dq_1 \; \exp\{-ikq$$

$$- i \int_{-\infty}^{\infty} ds \frac{\omega'(s)}{4\omega(s)} (2n+1) \sin[q_1+2\delta(s)]\} \quad . \qquad (4.13)$$

Each of the two integrals is now a Bessel function, the price being paid is that one now has a sum of such terms. The explicit result for the transition probability is

$$P_{n_2,n_1}(E) = |S_{n_2,n_1}(E)|^2$$

$$= \left| \sum_{k=-\infty}^{\infty} e^{ik(2\eta_1-\eta_2)} J_{\Delta n-2k}(|\gamma_1|)\, J_k(|\gamma_2|)\right|^2 \tag{4.14a}$$

where

$$\gamma_1 = \int_{-\infty}^{\infty} ds\, \sqrt{2[E-V_a(s)]}\, \kappa(s)\sqrt{\frac{2n+1}{\omega(s)}}\; e^{i\delta(s)} \tag{4.14b}$$

$$\gamma_2 = -\int_{-\infty}^{\infty} ds\, \frac{\omega'(s)}{4\omega(s)}\,(2n+1)\; e^{2i\delta(s)} \tag{4.14c}$$

$$\eta_k = \arg(\gamma_k)\ ,\ k=1,\ 2 \qquad . \tag{4.14d}$$

If the ω' term is neglected, then $\gamma_2=0$, so that only the term k=0 contributes to the sum, and the simpler result is regained:

$$\lim_{\gamma_2\to 0} P_{n_2,n_1} = J_{\Delta n}(|\gamma_1|)^2 \qquad . \tag{4.15a}$$

Conversely, if the reaction path is approximately straight, so that $\gamma_1=0$, then the only term which contributes to the sum is $k = \frac{\Delta n}{2}$, so that Δn is required to be even , and

$$\lim_{\gamma_1\to 0} P_{n_2,n_1} = J_{\frac{\Delta n}{2}}(|\gamma_2|)^2 \qquad ; \tag{4.15b}$$

i.e., without reaction path curvature, there is a selection rule $\Delta n=0,\ \pm 2,\ \pm 4,\ \ldots$.

This trick can be used in general to evaluate integrals involving first and second harmonics of the angle variables that appear in Eqs. (4.4)-(4.6).

As a final note, it is interesting to see that the present model can also be used to determine tunneling probabilities if the energy E is below the maximum of the vibrationally adiabatic potential $V_a(s)$. Equations (4.4)-(4.8) still apply but with the modifications that the factor $\sqrt{2[E-V_a(s)]}$ is imaginary,

$$\sqrt{2[E-V_a(s)]} \rightarrow i\sqrt{2[V_a(s)-E]} \quad ,$$

over the region of s for which $E < V_a(s)$. This introduces imaginary terms into the phase factors, which are effectively the tunneling probabilities. The imaginary part of the zero$^{\underline{th}}$ order phase ϕ_0 of Eq. (4.8), for example, is the vibrationally adiabatic barrier penetration integral,

$$\mathrm{Im}\ \phi_0 = \int_{s_<}^{s_>} \sqrt{2[V_a(s)-E]} \quad ,$$

so that the factor $\exp(i\phi_0)$ gives rise to the vibrationally adiabatic zero curvature tunneling probability.[17] The remaining factors in the expression for the S-matrix thus provide corrections to the vibrationally adiabatic tunneling approximation.

V. Example: Collinear Vibrational Excitation

To illustrate the potential usefulness and expected degree of accuracy of the SCP-IOS approximation to the reaction path Hamiltonian model, calculations have been carried out with it for one of the standard inelastic scattering benchmarks, namely the Secrest-Johnson[18] collinear model of He-H_2 vibrational excitation. This is a non-reactive process, but it is nevertheless possible to treat it via the reaction path model.

In the usual reduced units the Secrest-Johnson[18] Hamiltonian is

$$H(P,R,p,r) = \frac{P^2}{2\mu} + \frac{p^2}{2} + \frac{1}{2} r^2 + e^{\alpha(r-R)} \quad , \tag{5.1}$$

and $\mu = \frac{2}{3}$, $\alpha = 0.3$ for the He-H_2 case. Figure 1 shows a contour plot of the potential surface V,

$$V(r,R) = \frac{1}{2} r^2 + e^{\alpha(r-R)} \quad , \tag{5.2}$$

in the mass-weighted cartesian coordinates

$$x = \sqrt{\mu}\, R \tag{5.3a}$$

$$y = r \quad . \tag{5.3b}$$

Also shown is the reaction path which was determined by following the gradient of V (in the mass-weighted cartesian coordinates) down from a position high up on the repulsive wall; different initial points were tried until a path was obtained that was essentially independent of the initial point over the energy

region of interest.

The only modification needed of Eq. (4.14) for the vibrational transition probability is for the fact that the non-reactive trajectory in s is from $s=+\infty$ to 0 (defined as the classical turning point) back to $+\infty$, rather than $s=-\infty \rightarrow +\infty$ as for the reactive case. It is not hard to show that the appropriate modifications of the collision integrals γ_1 and γ_2 are

$$\gamma_1 = \int_0^\infty ds\ \sqrt{2[E-V_a(s)]}\ \kappa(s) \sqrt{\frac{2n+1}{\omega(s)}}\ e^{-i\delta(s)} \qquad \text{(incoming part)}$$

$$+ \int_0^\infty ds\ \sqrt{2[E-V_a(s)]}\ \kappa(s) \sqrt{\frac{2n+1}{\omega(s)}}\ e^{i\delta(s)} \qquad \text{(outgoing part)} \quad ,$$

or

$$\gamma_1 = 2 \int_0^\infty ds\ \sqrt{2[E-V_a(s)]}\ \kappa(s) \sqrt{\frac{2n+1}{\omega(s)}}\ \cos\delta(s) \quad , \qquad (5.4a)$$

and

$$\gamma_2 = + \int_0^\infty ds\ \frac{\omega'(s)}{4\omega(s)}\ (2n+1)\ e^{-2i\delta(s)} \qquad \text{(incoming part)}$$

$$- \int_0^\infty ds\ \frac{\omega'(s)}{4\omega(s)}\ (2n+1)\ e^{2i\delta(s)} \qquad \text{(outgoing part)} \quad ,$$

or

$$\gamma_2 = -2i \int_0^\infty ds \; \frac{\omega'(s)}{4\omega(s)} \; (2n+1) \; \sin 2\delta(s) \quad . \tag{5.4b}$$

The vibrational transition probability is thus given by

$$P_{n_2,n_1}(E) = \left| \sum_{k=-\infty}^{\infty} i^k \, J_{\Delta n-2k}(|\gamma_1|) \; J_k(|\gamma_2|) \right|^2 \quad , \tag{5.5a}$$

with γ_1 and γ_2 given by Eq. (5.4). For the present application $|\gamma_2|$ is so small that only the term k=0 makes a significant contribution to the sum in Eq. (5.5a), so that one in effect has

$$P_{n_2,n_1}(E) \simeq J_{\Delta n}(|\gamma_1|)^2 \; J_0(|\gamma_2|)^2$$

$$\simeq J_{\Delta n}(|\gamma_1|)^2 \quad ; \tag{5.5b}$$

i.e., it is the coupling due to the curvature of the reaction path which causes the vibrational excitation, and for this example the coupling due to the variation of $\omega(s)$ has neglible effect.

The results of Eq. (5.5) are given in Table I, along with the exact quantum mechanical results of reference 18. Some of these results are also shown pictorially in Figure 2. The SCP-IOS approximation to the reaction path model is seen to provide a reasonable, semi-quantitative description of the vibrationally inelastic process over a wide range of energies and also for large Δn transitions. Its attractiveness, of course, is its applicability to systems of considerably higher dimensionality, both reactive and nonreactive, and the degree of accuracy produced for this example gives some confidence that the results obtained for these more general applications will be usefully accurate.

VI. Concluding Remarks

The purpose of this paper has been to show how the semiclassical perturbation approximation can be combined in a simple and consistent way with the infinite order sudden approximation, and then to apply this "unified" SCP-IOS approximation to the reaction path Hamiltonian of Miller, Handy, and Adams. The approximation will be correct in both the sudden limit, i.e., when the motion of the internal degrees of freedom is slow compared to the translational motion, and in the limit that adiabatic perturbation theory is valid, i.e., when the motion of the internal degrees of freedom is much faster than the translational motion. Since it is correct in these two opposite limits, it is reasonable to expect it to have useful accuracy in fairly general circumstances. The results of the calculations described in Section V tend to bear this out.

Our interest in the overall approach described in this paper is that, given the necessary quantum chemistry information about the reaction path, it can be easily applied to model the dynamics of truly polyatomic systems. A variety of applications are in progress.

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Figure Captions

1. A contour plot of the potential surface of Eq. (5.2) in mass-weighted coordinates [Eq. (5.31)]. Also shown is the reaction path.

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.

References

1. See, for example, (a) W. A. Lester, Jr., Dynamics of Molecular Collisions Part A (Vol. 1 of Modern Theoretical Chemistry), ed. W. H. Miller, Pelnum, N.Y., 1976, p. 1; (b) J. C. Light, Atom-Molecule Collision Theory, ed. R. B. Bernstein, Plenum, N.Y., 1979, p. 239; (c) D. Secrest, ibid., pp. 265, 377.
2. See, for example, the survey and references in D. J. Kouri, Atom-Molecule Collision Theory, ed. R. B. Bernstein, Plenum, N.Y., p. 301.
3. W. H. Miller and F. T. Smith, Phys. Rev. A 17, 939 (1978).
4. I. C. Percival and D. Richards, J. Phys. B 3, 1035 (1970).
5. R. D. Levine and B. R. Johnson, Chem. Phys. Lett. 7, 404 (1970); see also G. L. Hofacker and R. D. Levine, Chem. Phys. Lett. 9, 617 (1971).
6. R. J. Cross, Jr., J. Chem. Phys. 49, 1753 (1968); 58, 5178 (1973).
7. W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. 72, 99 (1980).
8. W. H. Miller, J. Chem. Phys. 53, 1949 (1970); Adv. Chem. Phys. 25, 69 (1974).
9. See, for example, N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions, Oxford U.P., 1965, p. 349.
10. A. P. Clark, A. S. Dickinson, and D. Richards, Adv. Chem. Phys. 36, 63 (1977).
11. J. C. Farantos and J. N. Murrell, Int. J. Quant. Chem. 19, 95 (1981).

12. See, for example, R. D. Levine, Chem. Phys. Lett. 2, 76 (1968); G. G. Balint-Kurti and R. D. Levine, Chem. Phys. Lett. 7, 107 (1970).

13. G. L. Hofacker, Z. f. Naturforsch 18a, 607 (1963); S. F. Fischer, G. L. Hofacker, and R. Seiler, J. Chem. Phys. 51, 3951 (1969).

14. R. A. Marcus, J. Chem. Phys. 45, 4493, 4500 (1966); 49, 2610 (1968).

15. H. F. Schaefer, Chem. Brit. 11, 227 (1975).

16. K. Fukui, S. Kato, and H. Fujimoto, J. Am. Chem. Soc. 97, 1 (1975).

17. D. G. Truhlar and A. Kuppermann, J. Chem. Phys. 56, 2232 (1972).

18. D. Secrest and B. R. Johnson, J. Chem. Phys. 45, 4556 (1966).

Table I. Vibrational Transition Probabilities[a]

		E = 10		E = 8		E = 6		E = 4		E = 3	
n_1	n_2	QM[b]	SCP[c]	QM	SCP	QM	SCP	QM	SCP	QM	SCP
0	0	0.060	0.0249	0.204	0.2254	0.538	0.573	0.892	0.8818	0.978	0.964
	1	0.218	0.1813	0.434	0.334	0.394	0.254	0.108	0.0635	0.0221	0.0141
	2	0.366	0.2366	0.291	0.148	0.064	0.0288	0.00122	0.00071		
	3	0.267	0.120	0.071	0.0246						
	4	0.089	0.0275								
1	0	0.218	0.1813	0.434	0.334	0.394	0.254	0.108	0.0635	0.0221	0.0141
	1	0.286	0.0805	0.034	0.0197	0.244	0.422	0.850	0.905	0.977	0.987
	2	0.009	0.0641	0.220	0.314	0.345	0.237	0.0418	0.0248	0.000898	0.0015
	3	0.170	0.232	0.261	0.139	0.037	0.0139				
	4	0.240	0.1141	0.051	0.0143						
	5	0.071	0.0184								
2	0	0.366	0.237	0.291	0.1477	0.068	0.0288	0.00122	0.00071		
	1	0.009	0.064	0.220	0.314	0.345	0.237	0.0418	0.0248		
	2	0.207	0.109	0.0388	0.0248	0.347	0.579	0.955	0.982		
	3	0.018	0.075	0.250	0.336	0.233	0.1411	0.00133	0.002		
	4	0.169	0.236	0.189	0.0858	0.006	0.0027				
	5	0.0239	0.0766	0.016	0.00397						
	6	0.0064	0.0069								

References for Table I.

[a] The quantities listed are the vibrational transition probabilities $P_{n_2,n_1}(E)$ for the model problem described in Section V.

[b] The exact quantum mechanical results of reference 18.

[c] The results of the present SCP-IOS approximation to the reaction path model.

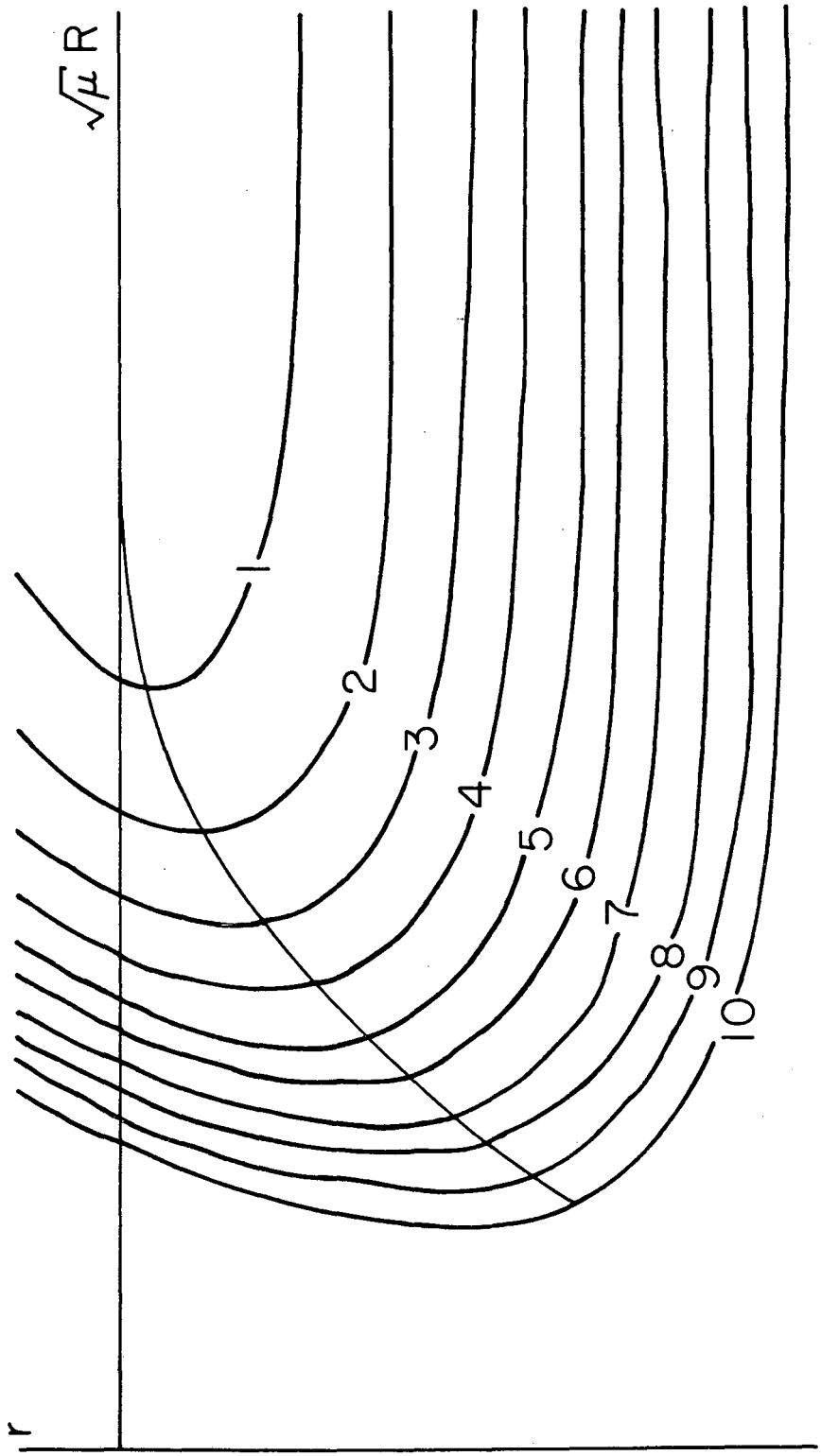

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Figure 1

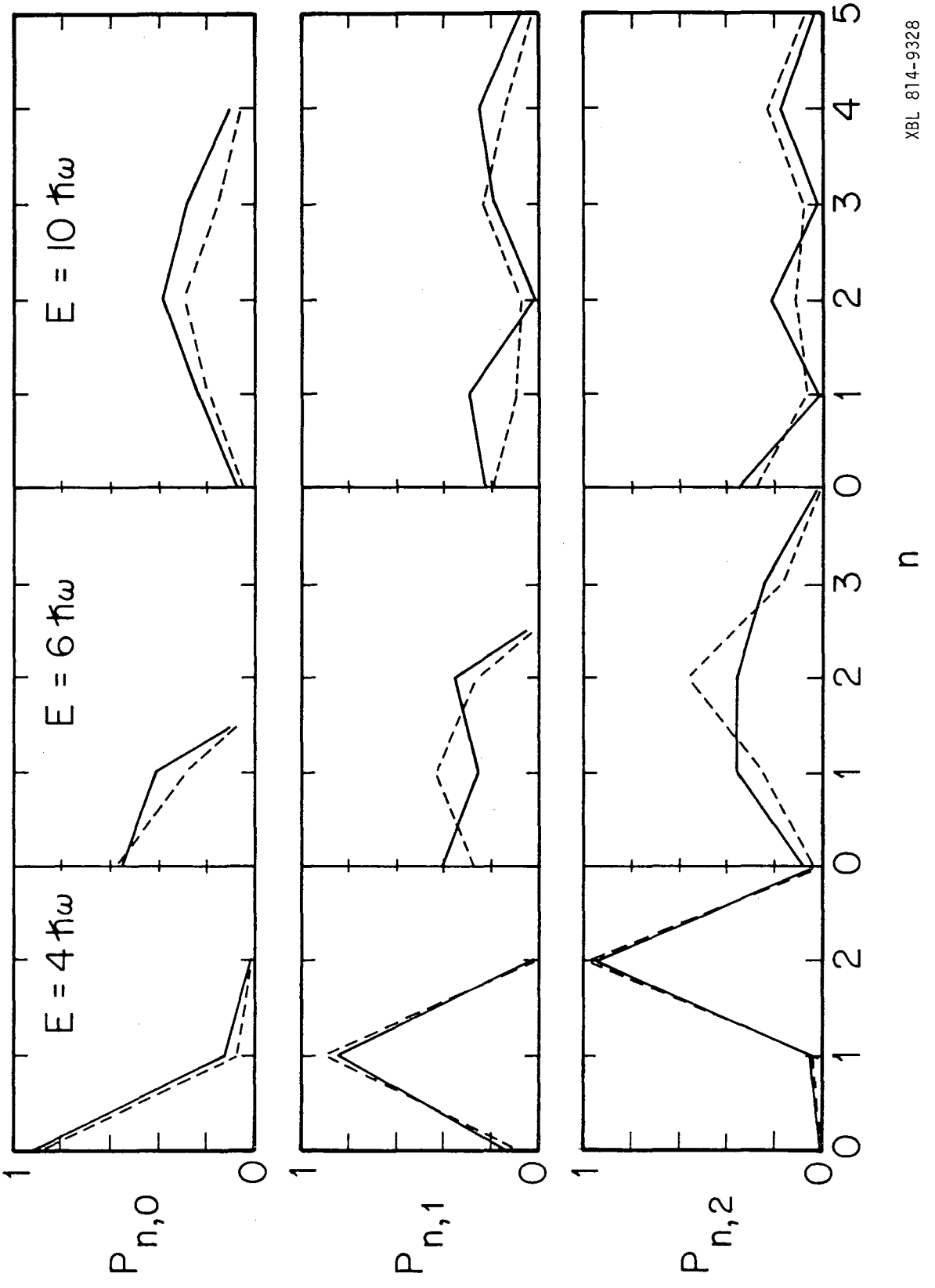

Figure 2

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