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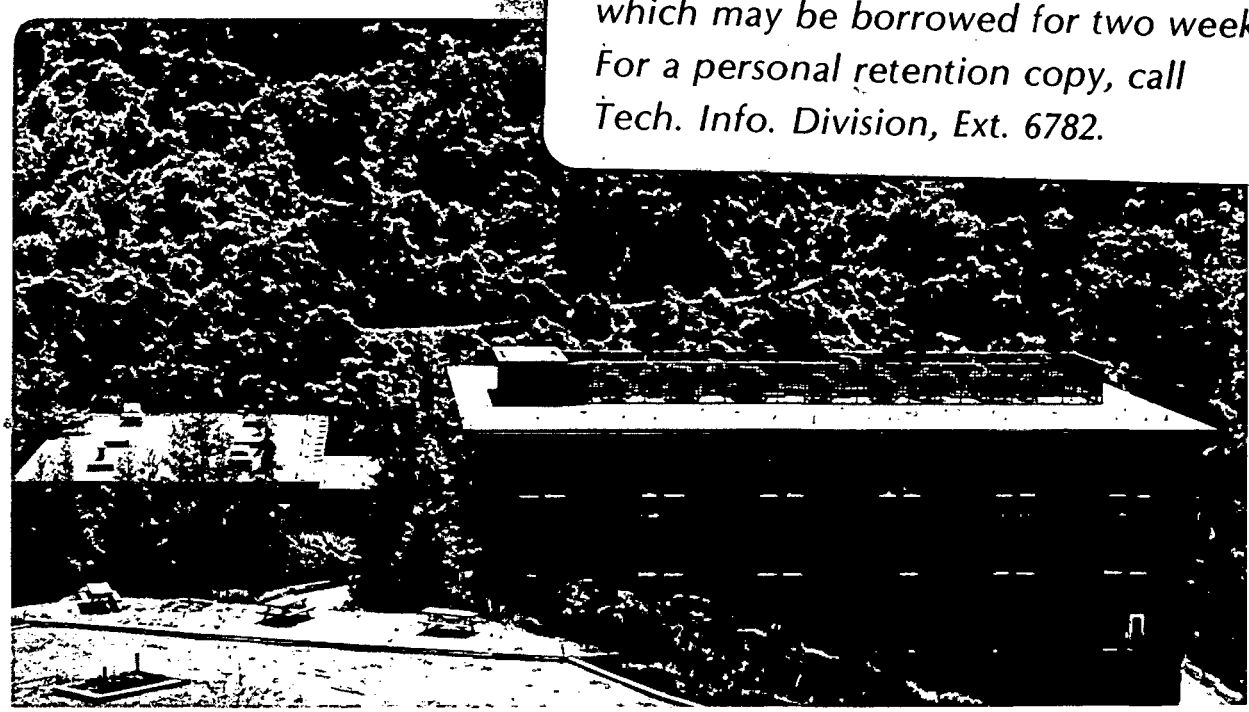

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# Application of the Semiclassical Perturbation (SCP) Approximation to Diffraction and Rotationally Inelastic Scattering of Atoms and Molecules from Surfaces

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## Abstract

The semiclassical perturbation (SCP) approximation of Miller and Smith [Phys. Rev. A 17, 17 (1978] is applied to the scattering of atoms and molecules from crystal surfaces. Specifically, diffraction of He from LiF, and diffraction and rotationally inelastic scattering of $H_2$ from LiF are treated, and the SCP model is seen to agree well with earlier coupled-channel and quantum sudden calculations. These tests of the SCP model are all for "soft" interaction potentials, e.g., of the Lennard-Jones Devonshire variety, but it is also shown that the model behaves correctly in the limit of an impulsive hard-wall potential function. The SCP picture thus appears to have a wide range of validity for describing the dynamics of gas-surface collisions.

## I. Introduction.

The understanding of the gas-surface scattering interaction has been the focus of considerable research recently by both theorists and experimentalists.[1] Experimental techniques have advanced to a point where the energy distribution of the final states of incident gas particles scattering off of a solid surface can be determined, and at least part of the recent theoretical interest can be attributed to the interesting questions generated by such experiments.[2-7] In particular, measurements of rotationally inelastic scattering of polar and nonpolar diatoms off of ionic crystal surfaces[6,7] has provided excellent data on final rotational state distributions from which theoretical interpretation of the form of the interaction potential, as well as the dominant mechanisms for energy transfer, can be made.

Although coupled-channel quantum scattering calculations of diffractive and inelastic gas-solid collisions are obviously the most rigorous theoretical treatment of the problem, they are not feasible except at low collision energy and for the lightest gas species (e.g., He, $H_2$), both qualifications tending to minimize the number of strongly coupled channels. Because of their expense, it is also usually not possible to carry out extensive parameter variation in an assumed potential function in order to fit calculations to experiments.

It is thus desirable to have at hand reliable theoretical models that are relatively easy to apply to a variety of physical systems. Also, it is clear that one must resort to approximate

models if one wishes to include the dynamical effects of surface motion (i.e., phonons). To this end a number of workers[8-11] have recently considered various kinds of sudden approximations to describe the gas-surface collision, and in this paper we consider another simple but often quantitatively reliable dynamical model, the semiclassical perturbation (SCP) approximation as developed by Miller and Smith.[12,13] The SCP approximation is particularly appealing because a large part of the calculation can be carried out analytically, thus providing more insight into the relation between the "input", the potential function, and the "output", the transition probabilities. Application[14-16] of the SCP model to a variety of phenomena in inelastic scattering and other aspects of polyatomic reaction dynamics has shown it to have a wide range of validity.

The purpose of this paper is to demonstrate the extent to which the SCP approach can be useful for describing gas-surface scattering phenomena. The accurate coupled-channel calculations by Wolken[17-19] on diffraction of He from LiF, and diffractive rotationally inelastic scattering of $H_2$ from LiF, provide excellent data for testing the SCP approximation, and these applications are presented in Sections II and III. (This, in fact, is one of the important uses of accurate coupled-channel calculations, namely to produce benchmarks to test and calibrate simpler dynamical models.) The results of the SCP approximation are in general in excellent agreement with Wolken's accurate coupled-channel calculations. Section III also describes the results of SCP

calculations on the $H_2$-LiF system at energies that give significant rotational inelasticity, the same system treated by Gerber *et al.*[10] within the sudden approximation. The results of the SCP model agree well with those of the sudden approximation, which in this case should be accurate. Finally, Section IV concludes and discusses possible further extensions.

## II. Atom-Surface Scattering in the SCP Approximation.

The Hamiltonian for an atom of mass m scattering from a rigid surface is

$$H = \frac{p^2}{2m} + V(x,y,z) \quad , \tag{2.1}$$

and for use of the semiclassical perturbation (SCP) approximation the potential is divided into a zero$^{th}$ order part plus a perturbation,

$$V(x,y,z) = V_0(z) + V_1(x,y,z) \quad . \tag{2.2}$$

(The z coordinate is perpendicular to the surface; i.e., the surface is in the x-y plane.) We choose the potential to be of the form originally proposed by Lennard-Jones and Devonshire[20] and later used by Wolken[17-19] (and by many others) in his coupled-channel calculations. The zero$^{th}$ order potential is a Morse function,

$$V_0(z) = D(e^{-2\alpha z} - 2e^{-\alpha z}) \quad , \tag{2.3}$$

and the perturbation term is

$$V_1(x,y,z) = -2\beta D e^{-2\alpha z}[\cos(\frac{2\pi x}{a_x}) + \cos(\frac{2\pi y}{a_y})] \quad , \tag{2.4}$$

where $a_x$ and $a_y$ are the lattice spacings, D the dissociation energy of $V_0(z)$, and $\beta$ the dimensionless coupling parameter that determines

the strength of the surface corrugation. We have used the same potential parameters as those used by Wolken for the (001) face of the LiF crystal in both the atom (He)[17] and diatom ($H_2$,$D_2$)[18] cases studied here.

The S-matrix element, i.e., amplitude, for scattering to the final diffractive channel characterized by quantum numbers ($n_x$,$n_y$) (channel (0,0) is the specular channel) is given within the SCP approximation by

$$S_{n_x n_y,00} = e^{2i\eta_0}(a_x a_y)^{-1} \int_0^{a_x} dx_0 \int_0^{a_y} dy_0 \; e^{-i\Delta k_x x_0} \; e^{-i\Delta k_y y_0} \; e^{2i\eta_1(x_0,y_0)} \quad , \tag{2.5}$$

where $\Delta k_x$ and $\Delta k_y$ are the changes in the x- and y-momenta (in units of $\hbar$), and are related to the diffraction order quantum numbers by

$$\Delta k_x = 2\pi \; n_x/a_x \quad , \quad \Delta k_y = 2\pi \; n_y/a_y \quad . \tag{2.6}$$

$\eta_0$ is the zero$^{th}$ order WKB (elastic) phase shift determined by the potential $V_0$, and $\eta_1$ is the first order phase shift given by

$$2\eta_1(x_0,y_0) = - \int_{-\infty}^{\infty} dt \, V_1(x(t),y(t),z(t)) \quad . \tag{2.7}$$

In Eq. (2.7) the trajectory (x(t),y(t),z(t)) is that determined by the zero$^{th}$ order potential $V_0$; i.e., z(t) is the inverse function of

$$t(z) = \pm \int_{z_0}^{z} dz' \, \{\frac{2}{m} [E-V_0(z')]\}^{-1/2} \quad , \tag{2.8a}$$

and

$$x(t) = x_0 + \frac{\bar{k}_x}{m} t \tag{2.8b}$$

$$y(t) = y_0 + \frac{\bar{k}_y}{m} t \quad , \tag{2.8c}$$

where $\bar{k}_x$ and $\bar{k}_y$ are the averages of the initial and final values of the momenta.

The above equations take on the more standard form of inelastic scattering within the SCP model if one introduces the angle variables $(q_x, q_y)$ that are conjugate to the quantum numbers $(n_x, n_y)$,

$$q_x = 2\pi x_0/a_x \tag{2.9a}$$

$$q_y = 2\pi y_0/a_y \quad . \tag{2.9b}$$

Equation (2.5) then becomes

$$S_{n_x n_y, 00} = e^{2i\eta_0} \int_0^{2\pi} \frac{dq_x}{2\pi} \int_0^{2\pi} \frac{dq_y}{2\pi} \, e^{-i\Delta n_x q_x} \, e^{-i\Delta n_y q_y} \, e^{2i\eta_1(q_x, q_y)} \quad , \tag{2.10}$$

and if one introduces the explicit form for $V_1$ of Eq. (2.4), the expression for the first order phase shift becomes

$$2\eta_1(q_x,q_y) = -2\beta D \int_{-\infty}^{\infty} dt\, e^{-2\alpha z(t)} \left[\cos(q_x+\omega_x t) + \cos(q_y+\omega_y t)\right] \quad , \qquad (2.11)$$

where

$$\omega_x = 2\pi\bar{k}_x/(a_x m) \qquad (2.12a)$$

$$\omega_y = 2\pi\bar{k}_y/(a_y m) \quad . \qquad (2.12b)$$

We note also that

$$\bar{k}_x = k_x^{\,i} + \tfrac{1}{2}\Delta k_x = k_x^{\,i} + \pi n_x/a_x \qquad (2.13a)$$

$$\bar{k}_y = k_y^{\,i} + \tfrac{1}{2}\Delta k_y = k_y^{\,i} + \pi n_y/a_y \quad , \qquad (2.13b)$$

and that

$$k_x^{\,i} = k \sin\theta \cos\phi \qquad (2.14a)$$

$$k_y^{\,i} = k \sin\theta \sin\phi \quad , \qquad (2.14b)$$

where $E = \hbar^2 k^2/2m$ is the initial translational energy of the atom and $(\theta,\phi)$ the polar angles of the incident beam.

Inserting Eq. (2.11) into Eq. (2.10), it is quite straightforward to show that the probability for transition to the channel $(n_x, n_y)$ is

$$P_{n_x n_y, 00} \equiv |S_{n_x n_y, 00}|^2$$

$$= J_{n_x}(A_x)^2 \, J_{n_y}(A_y)^2 \quad , \tag{2.15}$$

where the arguments, $A_x$ and $A_y$, of the regular Bessel functions are

$$A_x = 2\beta D \int_{-\infty}^{\infty} dt \; e^{-2\alpha z(t)} \cos(\omega_x t) \tag{2.16a}$$

$$A_y = 2\beta D \int_{-\infty}^{\infty} dt \; e^{-2\alpha z(t)} \cos(\omega_y t) \quad . \tag{2.16b}$$

For the Morse potential $V_0(z)$, the integral which defines $z(t)$, Eq. (2.8a), is evaluated to give

$$e^{-\alpha z(t)} = \lambda(\tfrac{E}{D}) / [\cosh(\alpha \bar{v}_z t) - \lambda] \tag{2.17}$$

where $\lambda = (1+E/D)^{-1/2}$, and $\bar{v}_z$ is taken to be the average of the initial and final values of the velocity in the z-direction. With Eq. (2.17), the collision integrals of Eq. (2.16) are evaluated to give

$$A_x = \frac{4\pi\beta}{\alpha\bar{v}_z \sinh(\pi\omega_x/\alpha\bar{v}_z)} \left\{\frac{E\omega_x}{\alpha\bar{v}_z} \cosh\left[\frac{\omega_x}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)\right]\right.$$

$$\left. + \sqrt{DE} \sinh\left[\frac{\omega_x}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)\right]\right\} \quad , \quad (2.18)$$

and similarly for $A_y$ with $\omega_x \to \omega_y$.

Equations (2.15) and (2.18) are the final result of the SCP calculation. For small $\beta$ they give first order diffraction probabilities proportional to $\beta^2$ and are essentially the same as a distorted wave calculation. Similar to a sudden approximation, however, the SCP expression also describes higher order diffraction processes. The sudden approximation, in fact, is obtained if one sets $\omega_x = 0$ in Eq. (2.18) (and $\omega_y = 0$ in the corresponding equation for $A_y$). The SCP result is thus in principle better than the sudden approximation since it allows, in an approximate fashion, for some motion in the x and y directions during the collision.

Figure 1 compares the results given by the SCP model (i.e., Eqs. (2.15) and (2.18)) to Wolken's coupled-channel quantum calculations[17] for specular, first-, second-, and third-order diffraction intensities as a function of the surface corrugation parameter $\beta$. The agreement is quite good over the entire range of $\beta$; this is particularly gratifying with regard to the second and third order diffractive transitions. Figure 2 shows a similar comparison for the four individual first order transitions. The individual components of the first-order diffraction are in good agreement with the exact quantum results.[17] The experimental results of O'Keefe *et al.*,[21]

indicate that the intensity of the (0,±1) peaks are considerably larger than the (-1,0) peak, to which both sets of calculated results agree. Finally, the SCP approximation also predicts decreasing specular intensity with decreasing $\theta_i$, in agreement with the trend predicted by the coupled-channel calculations[17] and the experimental observations.[21]

In concluding our treatment of atom-surface scattering it is interesting to compare the SCP expression, Eqs. (2.15) and (2.18), which has used the "soft" Lennard-Jones Devonshire potential, to the semiclassical expression (which is extremely accurate) for scattering from a hard-wall potential. For the case of normal incidence and high energy, the semiclassical expression for the $n^{th}$ order diffraction probability, for a one-dimensional hard sinusoidal surface is[22]

$$P_{n,0} = J_n(2hk)^2 \quad , \tag{2.19}$$

where $k = mv/\hbar$ and h is the amplitude of the sinusoidal hard-wall potential. This is seen to be the same form as the one-dimensional SCP expression, if one can make the identification

$$A \leftrightarrow 2hk \quad . \tag{2.20}$$

From Eq. (2.18) it is not hard to show that in the high energy limit $A_x \equiv A$ becomes

$$A = 2\,\frac{\beta}{\alpha}\,k + \text{constant} \quad , \tag{2.21}$$

and consistent with higher energy (i.e., large k) one may neglect the constant (which is proportional to the well-depth of the Morse potential). To complete the comparison we identify the hard-wall corrogation parameter h as one half the difference between the classical turning points in the Lennard-Jones Devonshire potential for the on-site and off-site locations; i.e.,

$$h = \frac{1}{2}(z_+ - z_-) \quad , \tag{2.22a}$$

where $z_+$ and $z_-$ are the roots of the equation

$$D[(1\pm 2\beta)e^{-2\alpha z} - 2e^{-\alpha z}] = E \quad . \tag{2.22b}$$

In the limit of high energy and small $\beta$, it is easy to show that Eq. (2.22) gives

$$h = \frac{\beta}{\alpha} \quad ,$$

so that with Eq. (2.21) one has

$$A \simeq 2hk \quad ,$$

and the identification in Eq. (2.20) is indeed established. In addition to working well for soft potentials, one thus sees that the SCP approximation behaves correctly for hard-wall potentials and impulsive dynamics.

## III. Diatom-Surface Diffraction and Translational-Rotational Energy Exchange.

The direct scattering of a diatomic molecule off of a solid surface results in specular reflection, diffraction, and inelastic processes associated with energy exchange between the translational degree of freedom of the incoming particle, the various internal degrees of freedom of the diatom, and the phonon modes of the solid. To illustrate the potential usefulness of the SCP approximation for describing diatom-surface scattering, we consider here the specific case of diffractive and rotationally inelastic scattering of $H_2$ off of a LiF (001) surface, and compare these results with those of two previous theoretical treatments of the same system.[10,18,19] The large amount of experimental and theoretical data available on $H_2$ scattering off of LiF makes it a particularly appealing system for testing our dynamical model.

The results of calculations using the SCP approximation are first compared with the coupled-channel quantum calculations of Wolken, who considered mostly $\Delta j=0$ diffraction intensities of $H_2$ and $D_2$ scattering off of LiF.[18,19] Next, the SCP approximation is tested against the data of Gerber *et al.*,[10] who studied rotationally inelastic $H_2$-LiF scattering using the sudden approximation. Since the first vibrational level of $H_2$ lies well above the energy range of interest in both of these studies, $H_2$ is treated as a rigid rotor. Also, the coupled-channel calculations of Wolken[19] strongly support the argument that exchange of energy between $H_2$ and the phonon modes of the solid is unimportant in reproducing many of the observed experimental results, and thus phonon modes have been neglected

in all of these calculations.

The SCP S-matrix element for a transition from initial rotational state $j_1$, with space-fixed z-axis projection $m_1$, to final rotational state $j_2$ and $m_2$, and final diffraction channel $n_x$ and $n_y$, is given by

$$S_{n_x n_y j_2 m_2 \leftarrow 00 j_1 m_1} = e^{2i\eta_0} \int_0^{2\pi} \frac{dq_x}{2\pi} e^{-iq_x n_x} \int_0^{2\pi} \frac{dq_y}{2\pi} e^{-iq_y n_y} \int_0^{2\pi} \frac{dq_j}{2\pi} e^{-i\Delta j q_j}$$

$$\int_0^{2\pi} \frac{dq_m}{2\pi} e^{-i\Delta m q_m} e^{2i\eta_1} , \qquad (3.1)$$

where, as before, the q's are the t=0 values of the angle variables for the various degrees of freedom, and the first order phase $2\eta_1$ is the time integral of the perturbation. We use the same potential as that used by Wolken for his coupled-channel calculations on the $H_2$-LiF system,[18,19]

$$V(x,y,z,\theta) = V(\theta)\cdot V(x,y,z) = [1+\lambda' P_2(\cos\theta)]\cdot[V_0(z)+V_1(x,y,z)] \ , (3.2)$$

where $V(x,y,z)$ has the same form as in the atom-surface interaction [Eqs. (2.2)-(2.4)] but here describes the portion of the diatom-surface interaction which is averaged over the orientation and the vibrational amplitude of the diatom. $V(\theta)$ describes the orientation dependence of the potential, where $\theta$ is the angle between the z-axis (normal to the surface plane) and the diatom bond, $\lambda$ determines the

strength of the dependence of the potential on the rotational motion of the diatom, and $P_2(\cos\theta)$ is the usual Legendre polynomial. This form of the interaction potential assumes no $\phi$ dependence (azimuthal angle) and thus there can be no change in the component along a space-fixed z-axis of the rotational angular momentum:

$$\int_0^{2\pi} \frac{dq_m}{2\pi} e^{-i\Delta m\, q_m} = \delta_{m_2,m_1} \quad . \tag{3.3}$$

Expanding the product of factors in the potential gives

$$V(x,y,z,\theta) = V_0(z) + V_1(x,y,z) + \lambda' P_2(\cos\theta)\, V_0(z) + \lambda' P_2(\cos\theta)\, V_1(x,y,z); \tag{3.4}$$

the last three terms account for diffraction, rotational inelasticity, and the coupling of diffraction with rotational inelasticity, respectively, and are treated as the perturbation. As in the treatment of atom-surface scattering, the zero$^{th}$ order trajectory is calculated from $V_0(z)$. Identifying $\theta$ as the angle variable $q_j$, the first order phase shift is given by

$$2\eta_1(q_x,q_y,q_j) = -\int_{-\infty}^{\infty} dt\, [V_1(x(t),y(t)z(t)) + \lambda' P_2(\cos q_j(t)) V_0(z(t))$$

$$+ \lambda' P_2(\cos q_j(t))\, V_1(x(t),y(t),z(t))] \quad ; \tag{3.5}$$

x(t), y(t), and z(t) are given as before in Section II, and

$$q_j(t) = q_j + \omega_j t \quad , \tag{3.6}$$

where

$$\omega_j = B(2\bar{j}+1)$$

$$\bar{j} = \frac{1}{2}(j_1+j_2) \quad .$$

Substituting in these trajectory functions gives

$$\begin{aligned} 2\eta_1(q_x,q_y,q_j) &= A_x \cos q_x + A_y \cos q_y + A_j \cos(2q_j) \\ &+ A_{xj}^{+} \cos(q_x+2q_j) + A_{xj}^{-} \cos(q_x-2q_j) \\ &+ A_{yj}^{+} \cos(q_y+2q_j) + A_{yj}^{-} \cos(q_y-2q_j) \quad , \end{aligned} \tag{3.7}$$

where the collision integrals are

$$A_x = (1 + \frac{\lambda'}{4})\, 2\beta D \int_{-\infty}^{\infty} dt\, e^{-2\alpha z(t)} \cos(\omega_x t) \quad , \tag{3.8a}$$

and similarly for $A_y$,

$$A_j = -\frac{3\lambda' D}{4} \int_{-\infty}^{\infty} dt\, [e^{-2\alpha z(t)} - 2e^{-\alpha z(t)}] \cos(2\omega_j t) \quad , \tag{3.8b}$$

$$A^{\pm}_{xj} = \frac{3\lambda'\beta D}{4} \int_{-\infty}^{\infty} dt\ e^{-2\alpha z(t)} \cos(2\omega_j \pm \omega_x)t \quad , \tag{3.8c}$$

and similarly for $A^{\pm}_{yj}$.

Because of the mixed terms in Eq. (3.7)--i.e., the last four terms--the integral giving the S-matrix element,

$$S_{n_x n_y j_2, 00 j_1} = e^{2i\eta_0} \int_0^{2\pi} \frac{dq_x}{2\pi} \int_0^{2\pi} \frac{dq_y}{2\pi} \int_0^{2\pi} \frac{dq_j}{2\pi}\ e^{-in_x q_x}\ e^{-in_y q_y}\ e^{-i\Delta j q_j}$$

$$\times\ e^{2i\eta(q_x, q_y, q_j)} \quad , \tag{3.9}$$

cannot be evaluated to give a simple product of Bessel functions. This can be dealt with by using the trick of Miller and Smith:[12] one defines the following variables

$$Q^x_- = 2q_j - q_x \qquad\qquad Q^x_+ = 2q_j + q_x$$

$$Q^y_- = 2q_j - q_y \qquad\qquad Q^y_+ = 2q_j + q_y \quad ,$$

and inserts for each new variable the following integral representation of the delta function expanded in a Fourier representation,

$$\int_0^{2\pi} \frac{dQ^x_{\pm}}{2\pi} \sum_{k=-\infty}^{\infty} e^{-ik(Q^x_{\pm} - 2q_j \mp q_x)} \quad , \tag{3.10}$$

with a similar additional two integrals for $Q^y_{\pm}$. The S-matrix element for diffraction and rotational inelasticity can then be written as a sum of products of Bessel functions, so that the transition probability is

$$|S_{n_x n_y j_2, 00 j_1}|^2 = |\sum_{k_1} \sum_{k_2} \sum_{k_3} \sum_{k_4} i^{k_1+k_2-k_3-k_4}$$

$$\times J_{n_x+k_1-k_3}(A_x)\, J_{n_y+k_2-k_4}(A_y)\, J_{\frac{\Delta j}{2}-k_1-k_2-k_3-k_4}(A_j)$$

$$\times J_{k_1}(A^-_{x_j})\, J_{k_2}(A^-_{y_j})\, J_{k_3}(A^+_{x_j})\, J_{k_4}(A^+_{y_j})|^2 \quad , \qquad (3.11)$$

where the various collision integrals are given by Eq. (3.8). Evaluation of these integrals gives the following expressions:

$$A_x = \frac{4\pi\beta(1+\frac{\lambda'}{4})}{\alpha\bar{v}_z \sinh(\frac{\pi\omega_x}{\alpha\bar{v}_z})} \{ (\frac{\omega_x E}{\alpha\bar{v}_z}) \cosh[\frac{\omega_x}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)] + \sqrt{ED} \sinh[\frac{\omega_x}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)]\} \qquad (3.12a)$$

(similary for $A_y$)

$$A_j = \frac{3\pi\lambda'}{2\alpha\bar{v}_z \sinh(\frac{2\pi\omega_j}{\alpha\bar{v}_z})} \{\sqrt{ED} \sinh[\frac{2\omega_j}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)] - (\frac{2\omega_j E}{\alpha\bar{v}_z}) \cosh[\frac{2\omega_j}{\alpha\bar{v}_z}(\pi-\cos^{-1}\lambda)]\} \qquad (3.12b)$$

$$A^{\pm}_{xj} = \frac{3\pi\lambda'}{2\alpha\bar{v}_z \sinh\left(\frac{\pi(2\omega_j \pm \omega_x)}{\alpha\bar{v}_z}\right)} \left\{\frac{(2\omega_j \pm \omega_x)E}{\alpha\bar{v}_z} \cosh\left[\frac{2\omega_j \pm \omega_x}{\alpha\bar{v}_z}(\pi - \cos^{-1}\lambda)\right] + \sqrt{ED}\right.$$

$$\left. \sinh\left[\frac{2\omega_j \pm \omega_x}{\alpha\bar{v}_z}(\pi - \cos^{-1}\lambda)\right]\right\} \quad , \qquad (3.12c)$$

(similarly for $A^{\pm}_{yj}$). The four infinite sums in Eq. (3.11) may appear formidable, but one can easily show that only the 0, ±1 terms contribute significantly. Thus, Eq. (3.11) provides an extremely efficient means for calculating intensities of rotational and diffractive transitions.

Figure 3 shows the intensity of the specular, first-, second-, and third-order diffraction channels (with $\Delta j=0$) as a function of the surface corrugation parameter $\beta$. The parameter $\lambda'$, which determines the strength in the potential of the orientation dependence of the diatom, is kept constant at 0.24.[18] The calculations were performed assuming an initial distribution of ortho to para hydrogen of 3:1. Also, the SCP results were normalized such that $R_0 = 1$ at $\beta=0$. Comparison of the results of the SCP approximation with the coupled-channel calculations of Wolken[19] shows quite good agreement with, as in the He/LiF comparison, the deviation between the two sets of results less than 5%, except at the very largest values of $\beta$. The effect of increasing the strength of the perturbation is also shown quite clearly in Figure 3, where the deviation between the SCP versus the coupled-channel results for $R_I$ and $R_{II}$ increases with $\beta$.

Table I compares the SCP calculations with the coupled-channel

calculations of Wolken[19] on $H_2$ versus $D_2$ scattering from LiF at $\beta = 0.003$. These calculations were performed at the same de Broglie wave length for each isotope, with an incident energy of $D_2$ at half the incident energy of $H_2$. As can be seen, all of the differences between $H_2$ and $D_2$ observed in the experiments of O'Keefe, et al.,[21] and predicted by the calculations of Wolken,[18,19] are reproduced (at comparable accuracies) in the SCP approximation (e.g., increase in higher order diffraction with decrease in specular reflection for $D_2$ compared to $H_2$). In both the $H_2$ and $D_2$ calculations at $\beta = 0.03$, the SCP approximation predicts a larger value for $R_0$ than the exact quantum calculations, with a concomitant lower value for $R_I$. It should be noted, however, that this particular $\beta$ value was chosen by Wolken such that the exact quantum calculations matched the experimental data for $R_I$. The bottom of Table 1 compares SCP and exact quantum for the one rotationally inelastic transition intensity reported in reference 19. The increase in rotational inelasticity of $D_2$ over $H_2$ is seen to be not quite as dramatic as predicted by the exact quantum calculations, but it is still significant.

Finally, we focus on the accuracy of the SCP approximation in predicting rotational inelasticity. The report by Gerber, et al., on rotationally inelastic molecule-surface scattering in the sudden approximation discusses the separability of rotational and diffractive transitions for a potential with low corrugation (small $\beta$) and weak dependence on orientation of the diatom (small $\lambda'$).[10] Their tabulated data showing $\Delta j$ transitions for different diffraction channels demonstrated a reasonably strong independence of the relative

rotational distribution on the diffraction channel, at the particular energies (0.5-0.9 eV) and $\beta$ values (0.005-0.03) used in their calculations. At these particularly small values of $\beta$, the term in the potential which couples the orientation dependence with the dependence on surface corrugation (i.e., the term which contains the product $\beta\lambda'$), can be neglected. In this case, Eq. (3.11) reduces to

$$|S_{n_x n_y j_2 \leftarrow 00 j_1}|^2 = J^2_{n_x}(A_x)\, J^2_{n_y}(A_y)\, J^2_{\frac{\Delta j}{2}}(A_j) \quad , \tag{3.13}$$

where the only modification of the collision integrals of Eq. (3.8) is that $\lambda'$ is set to zero in Eq. (3.8a). Equation (3.13) shows explicitly the decoupling of rotational inelasticity and diffraction.

Figure 4 shows the probability for rotational transitions, $P_{j_2 \leftarrow j_1}$, summed over all diffraction channels $n_x$ and $n_y$, as a function of final rotation number $j_2$, where

$$P_{j_2 \leftarrow j_1} = \sum_{n_x, n_y} |S_{n_x n_y j_2 \leftarrow 00 j_1}|^2 \quad , \tag{3.14}$$

and $S_{n_x n_y j_2 \leftarrow 00 j_1}$ is calculated using Eq. (3.13). The results of the SCP approximation are compared with those of the sudden approximation as formulated by Gerber, et al.,[10] at two different energies (0.5 and 0.7 eV) and three different $\beta$ values (0.03, 0.01 and 0.005).

Rotational inelasticity for the diffraction summed rotational probabilities is seen to increase as $\beta$ is decreased. This is primarily due to the dominant individual rotationally inelastic transition

probabilities for the $n_x=n_y=0$ diffraction spot, which increases with increasing $\beta$. We do observe, however, that for $n_x,n_y\neq 0$, rotational inelasticity decreases with decreasing $\beta$, in agreement with the observation by Gerber, et al.[10] The agreement between the SCP and the sudden approximation is slightly better at 0.5 eV than at 0.7 eV. As energy is increased, more probability is shifted into the higher order diffraction channels as more of these channels become open. The same set of diffraction channels was consistently used at all energies in the calculations based on the sudden approximation,[10] and we have used the same set here to facilitate comparison of the results. At least part of the discrepancy at higher energies is due to neglect of some of these higher order channels. Also, one would expect the SCP approximation to increase in accuracy as the probability for rotational inelasticity (and thus the perturbation) decreases, which is the observed trend for decreasing energy. Increasing $\beta$ also decreases the probability for diffractive summed rotational inelasticity, which is one reason why the agreement between the SCP and sudden approximations is seen to get better with increasing $\beta$, at all energies.

## IV. Concluding Remarks.

The purpose of this paper has been to show the usefulness of the SCP approximation in describing gas-surface dynamics. The results presented in Section II are in excellent agreement with coupled-channel quantum calculations which describe specular and diffractive scattering for a particular atom-surface system. Section III has extended the atom-surface description to include the rotational degree of freedom of a diatom-surface scattering event, which is valid when the diatom can be treated as a rigid rotor. As in the atom-surface case, comparison with experimental observation and previous calculations for a particular scattering system show both qualitative and quantitative agreement. These results imply that the SCP approximation can be useful on a predictive basis.

It is clear how the model can be easily generalized to include the vibrational degree of freedom of a diatomic molecule, but more challenging is the generalization to include vibrational degrees of freedom of the surface atoms, i.e., phonons. Work is in progress with this specific goal, and to the extent that it is successful we plan to apply the SCP approach in conjunction with the semiclassical multichannel branching model[16] to describe sticking probabilities and accommodation coefficients, i.e., phenomena that involve energy transfer between the surface and the gas molecules. The dynamics of surface phenomena is sufficiently complex that we believe simple models of the SCP variety have much to offer to the understanding of these processes.

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Table 1. Calculated and observed intensities for the $H_2(D_2)$/LiF(001) scattering system at $\beta$ = 0.03.

$H_2$ (ortho:para=3:1)
$\theta$=50°, Incident Energy=104 meV

| | SCP | Exact Quantum[b] | Relative to $R_0$=1.0 SCP | Exact Quantum[b] | Observed[c] |
|---|---|---|---|---|---|
| $R_0$ | 0.526 | 0.469 | 1.0 | 1.0 | 1.0 |
| $R_{10}$ | 0.023 | 0.021 | 0.043 | 0.045 | -- |
| $R_{-10}$ | 0.049 | 0.060 | 0.092 | 0.129 | 0.22 |
| $R_{0\pm1}$ | 0.161 | 0.189 | 0.306 | 0.402 | 0.38 |
| $R_I$ | 0.394 | 0.459 | 0.744 | 0.978[a] | 0.98 |
| $R_{II}$ | 0.062 | 0.067 | 0.118 | 0.140 | 0.60 |

$D_2$ (ortho:para=2:1)
$\theta_i$=50°, Incident Energy=52 meV

| | SCP | Exact Quantum[b] | Relative to $R_0$=1.0 SCP | Exact Quantum[b] | Observed[c] |
|---|---|---|---|---|---|
| $R_0$ | 0.254 | 0.176 | 1.0 | 1.0 | 1.0 |
| $R_{10}$ | 0.025 | 0.048 | 0.098 | 0.273 | -- |
| $R_{-10}$ | 0.048 | 0.114 | 0.189 | 0.647 | 0.72 |
| $R_{0\pm1}$ | 0.220 | 0.221 | 0.866 | 1.257 | 0.72 |
| $R_I$ | 0.513 | 0.604 | 2.020 | 3.430 | 2.16 |
| $R_{II}$ | 0.187 | 0.185 | 0.736 | 1.050 | 1.32 |

Same conditions as above except $\beta$ = 0.05.

| | $H_2$ SCP | $H_2$ Exact Quantum[b] | $D_2$ SCP | $D_2$ Exact Quantum[b] |
|---|---|---|---|---|
| $R_I(0\rightarrow2)$ | 0.026 | 0.014 | 0.059 | 0.086 |

[a]Wolken adjusted $\beta$ parameter to fit this number to experimental data.

[b]Reference 19.

[c]Reference 21.

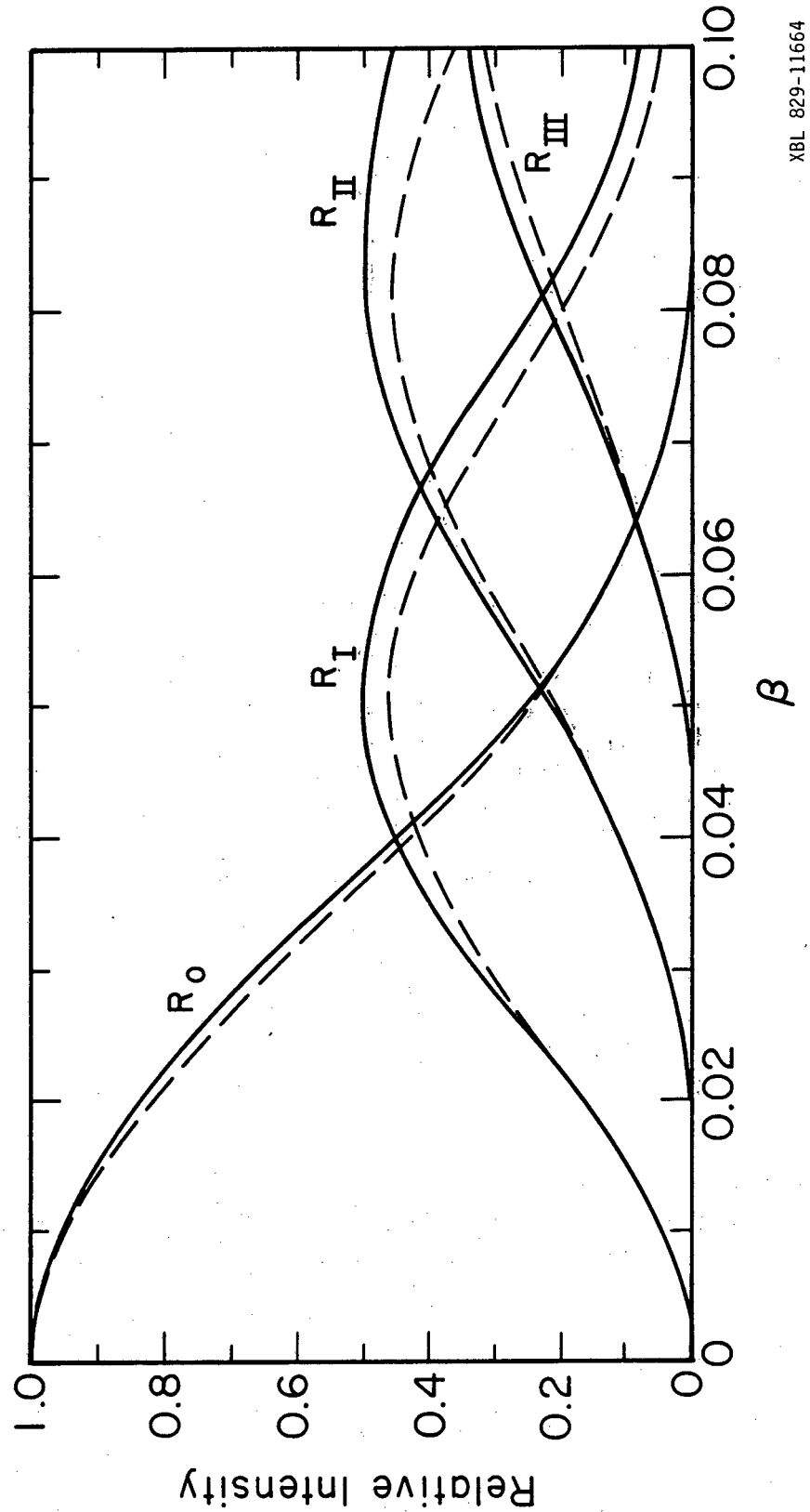
## Figure Captions

Figure 1. Specular, first-, second-, and third-order diffraction intensities as a function of $\beta$ for He scattering off of a LiF(001) surface: $E = 20$ meV, $\theta_i = 30°$. (___ exact quantum,[17] ... SCP).

Figure 2. Intensity scattered into the four first-order diffraction spots as a function of $\beta$, with the same conditions as given in Figure 1. (___ exact quantum,[17] ... SCP).

Figure 3. Specular, first-, second-, and third-order diffraction intensities as a function of $\beta$ for $H_2$ scattering off of a LiF(001) surface: $E = 104$ meV, $\theta_i = 50°$, $\Delta j = 0$, ortho:para $H_2$ = 3:1. (___ exact quantum,[19] ... SCP).

Figure 4. Rotationally inelastic transition probabilities (summed over all diffractive channels) for $H_2$ scattering off LiF, for three different values of $\beta$. (a) $E = 0.7$ eV, $\theta_i = 0°$, $j_1 = 1$, (b) $E = 0.7$ eV, $\theta_i = 0°$, $j_1 = 0$, (c) $E = 0.5$ eV, $\theta_i = 0°$, $j_1 = 0$. (... quantum sudden, ___ SCP).




XBL 829-11664

Figure 1

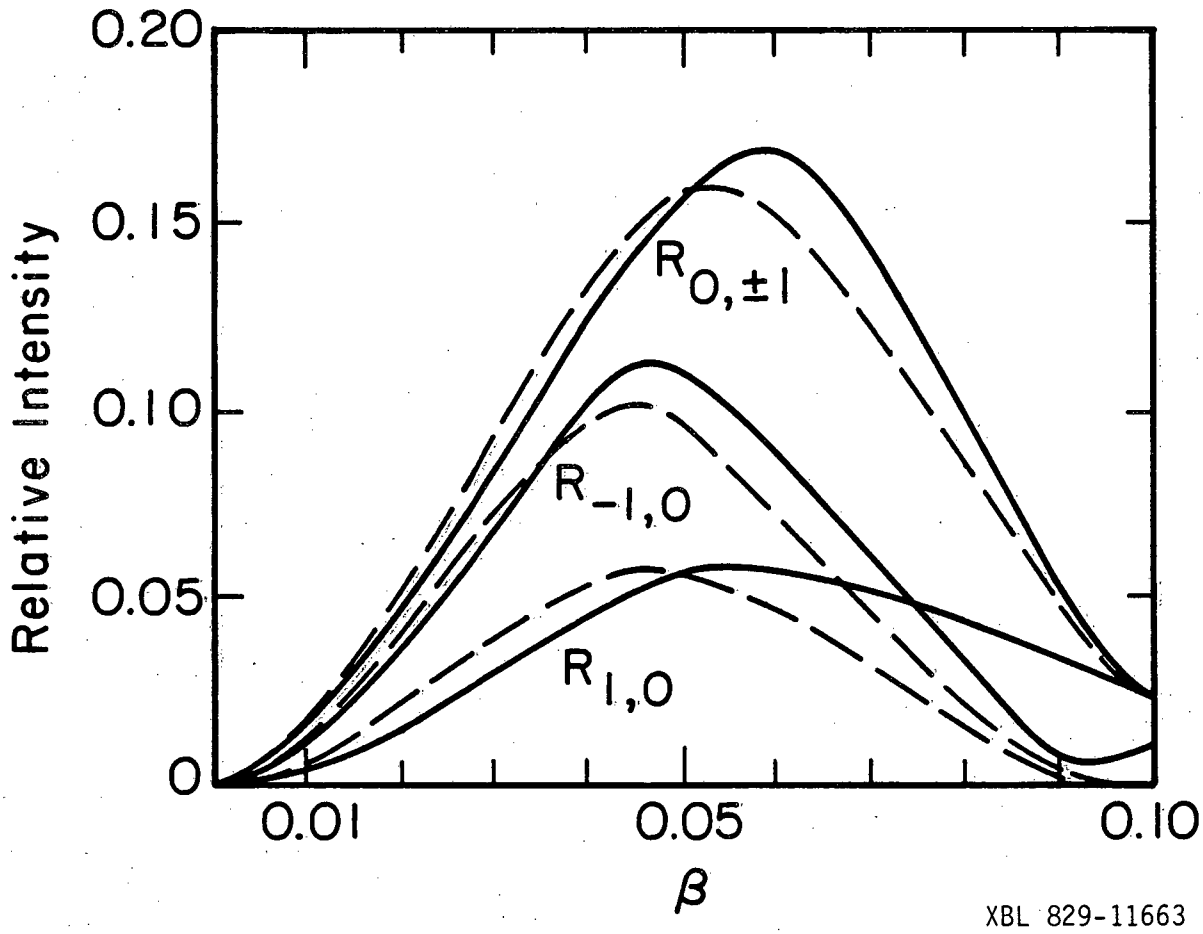

0.20
0.15
0.10
0.05
0
Relative Intensity
$R_{0,\pm 1}$
$R_{-1,0}$
$R_{1,0}$
0.01
0.05
0.10
$\beta$
XBL 829-11663

Figure 2

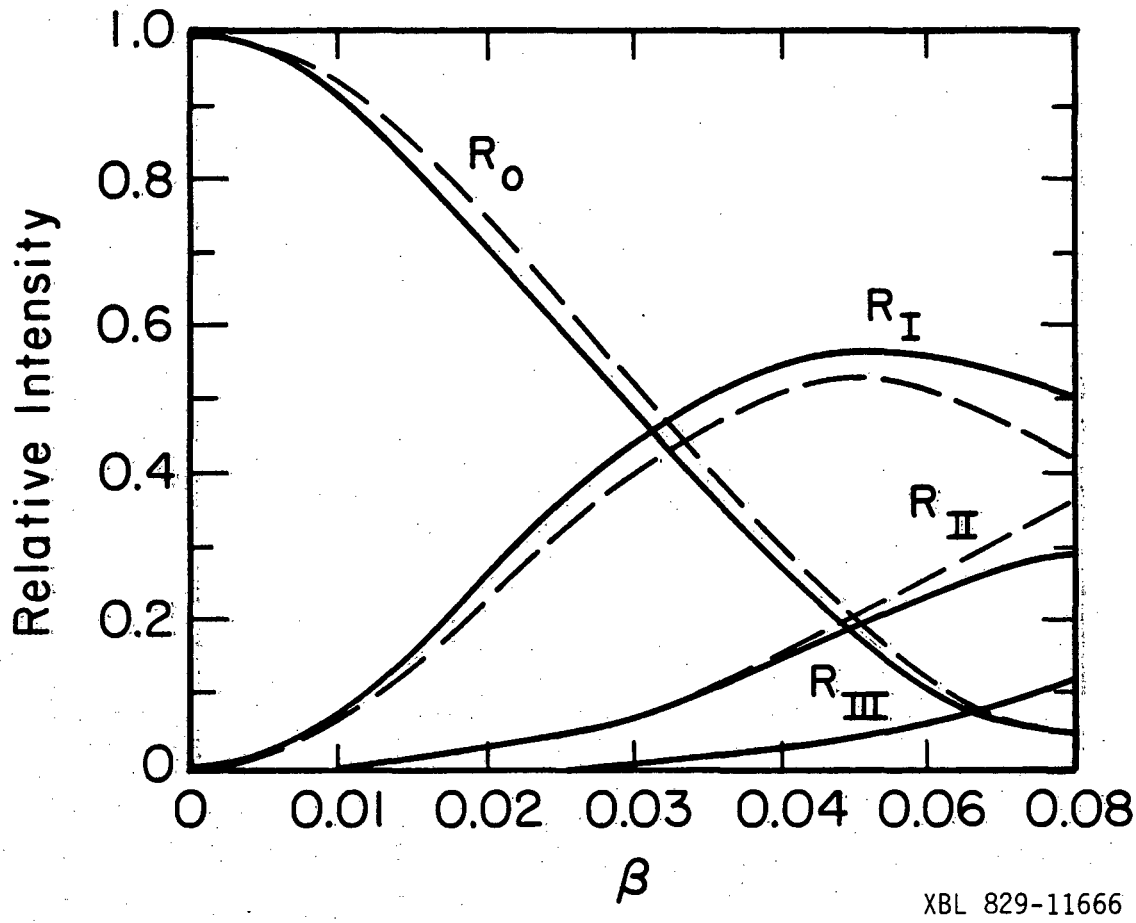

1.0
0.8
0.6
0.4
0.2
0
Relative Intensity
$R_o$
$R_I$
$R_{II}$
$R_{III}$
0
0.01
0.02
0.03
0.04
0.06
0.08
$\beta$
XBL 829-11666

Figure 3

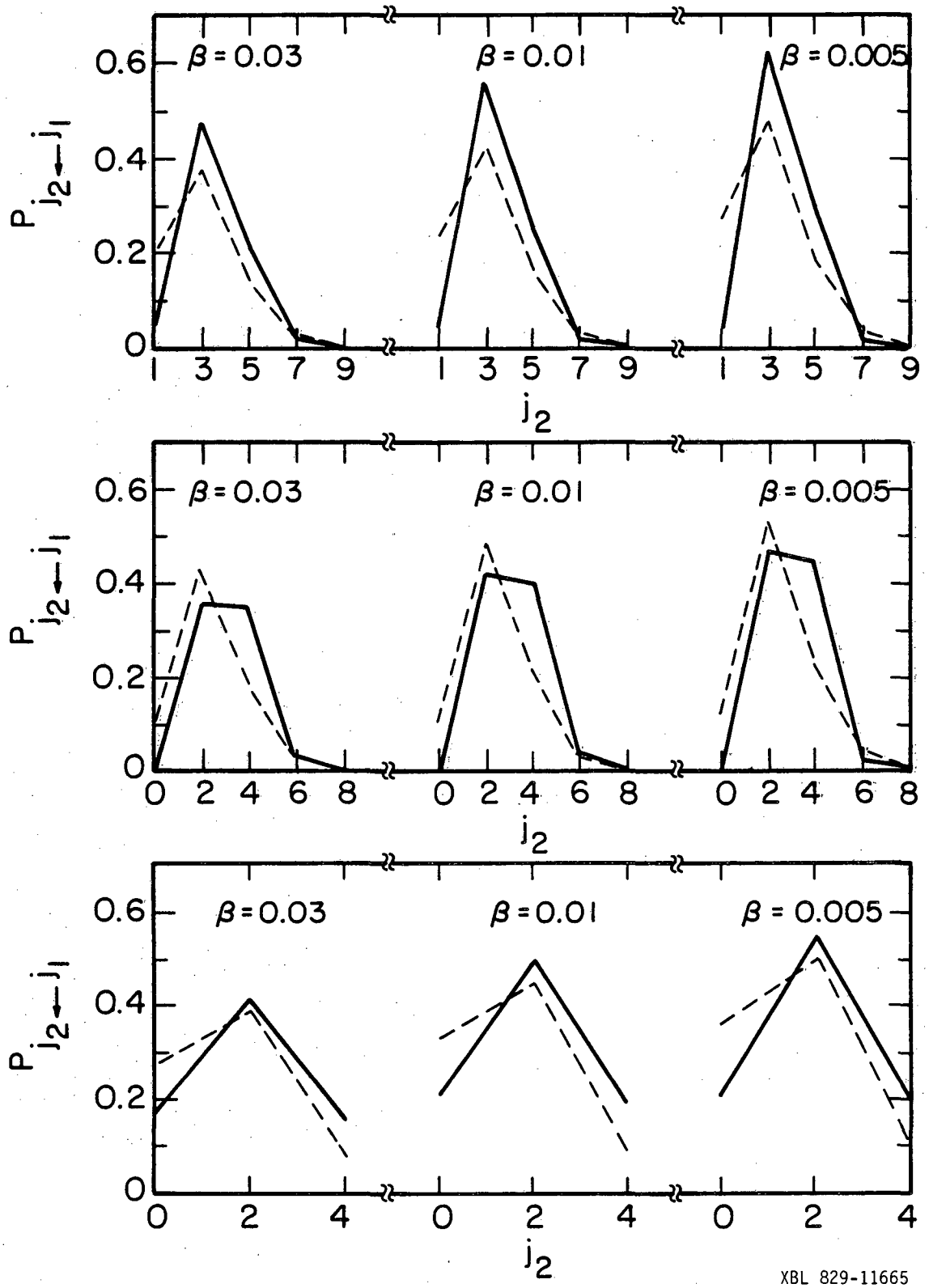

β = 0.03
β = 0.01
β = 0.005
0.6
0.4
0.2
0
$P_{j_2 \leftarrow j_1}$
1 3 5 7 9
$j_2$
0 2 4 6 8
0 2 4
XBL 829-11665

Figure 4

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