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SEMICLASSICAL ANALYSIS OF WEAKLY INELASTIC MOLECULAE COLLISIONS

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MOLECULAR COLLISIONS

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SEMICLASSICAL ANALYSIS OF WEAKLY INELASTIC  
MOLECULAR COLLISIONS

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# Semiclassical Analysis of Weakly Inelastic Molecular Collisions

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## Abstract

This paper applies semiclassical analysis to vibrationally and rotationally inelastic molecular collisions. The deflection angles for weak transitions are shown to be simply related to the classical deflection angles for elastic scattering conditions. The position of the crossing-point, at which the values of the initial and final Lagrangian are equal plays an important role in the discussion, and expressions are derived for these points for different types of transition. Allowance is made for the fact that the effective translational potential energy may depend on the vibrational states of the members of the system.

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## Introduction

This paper attempts to provide some physical insight into the mechanism which gives rise to inelastic behavior during an intermolecular collision. We restrict attention to collisions between an atom A and a diatomic molecule BC; they will be termed inelastic if BC changes its rotational or vibrational state. Furthermore we shall suppose the collisions so weakly inelastic that perturbation theory is applicable. With this restriction, any treatment of the problem is complicated by two factors. First, all translational waves are represented by infinite sums of partial waves and secondly one must be able to calculate radial integrals involving continuum wave functions. Both these difficulties can, of course, be surmounted with the help of high-speed computers, but in this paper they are tackled by analytical methods.

Following the established correspondence between the classical and quantum-mechanical theories of elastic scattering,<sup>1</sup> we recognize that each partial wave in the infinite sum loosely represents the behavior of a particle with a certain impact parameter. Very few partial waves therefore actually contribute to the scattering amplitude at any given angle. We use semi-classical arguments to approximate the radial integrals responsible for coupling the incident "initial" partial waves to different "final" waves. The most important integrals are those for which, at some classically accessible point R, the value of the Lagrangian (kinetic energy minus potential energy)

of the initial wave is equal to that of the final wave. In these cases the Landau-Zener formula can be applied. It turns out that the deflection angle for an inelastic collision may be found by following the classical trajectory for elastic scattering under the initial condition as far as the crossing point and then changing to the classical path appropriate to the final conditions.

The general theory is developed in section 2 and section 3 is devoted to calculating the crossing points for different types of inelastic collision. In calculating the crossing points for vibrationally inelastic collisions we recognize that, at least for potentially reactive systems, the effective translational potential energy may depend on the vibrational state of BC and we show how this may be allowed for on the basis of a simple model. Finally we note that when applied to the results of a recent molecular beam experiment on the system  $K + HBr$ ,<sup>2</sup> with some reservations this theory supports a remark made by the authors to the effect that the apparently markedly inelastic behavior at high scattering angles is unlikely to be due to rotational inelasticity.

## 2. General Theory

The Hamiltonian for the system illustrated in Fig. 1 takes the form

$$H = -\frac{\hbar^2}{2\mu} \nabla_p^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V(r, \rho, \chi), \quad (1)$$

and the potential energy  $V(r, \rho, \chi)$  can be conveniently expanded in Legendre polynomials

$$V(r, \rho, \chi) = V_0(r, \rho) + V_1(r, \rho)P_1(\cos \chi) + \dots \quad (2)$$

In this formulation the overall motion of the centre of mass has been neglected. The reduced masses  $m$  and  $\mu$  are defined by the expressions

$$m = \frac{m_A(m_B+m_C)}{m_A+m_B+m_C}, \quad \mu = \frac{m_B m_C}{m_B+m_C} \quad (3)$$

Following a procedure adopted by Bates and others<sup>3</sup> in discussing electronic transitions, at given  $r$  we first find internal (vibrational-rotational) states  $|1\rangle$  which satisfy

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_\rho^2 + V_0(r, \rho) - W_1(r) \right] |1\rangle = 0, \quad (4)$$

and then take the total wave function in the form

$$\Psi = \sum_1 \psi_1(\underline{r}) |1\rangle. \quad (5)$$

$\psi_1(\underline{r})$  therefore represents the relative motion of A and G when BC is in the internal state  $|1\rangle$ . The Schrodinger equation

$$(H - E)\Psi = 0, \quad (6)$$

then leads to the following set of coupled equations for the  $\psi_1(\underline{r})$ :

$$[\nabla_r^2 + k_1^2 - U_1(r)]\psi_1(\underline{r}) = \sum_1 X_{1j}(\underline{r})\psi_j(\underline{r}), \quad (7)$$

where

$$k_1^2 = \frac{2m}{\hbar^2}[E - W_1(\infty)], \quad U_1(r) = \frac{2m}{\hbar^2}[W_1(r) - W_1(\infty)],$$

and

$$X_{ij}(\underline{r}) = \langle i | \nabla_r^2 - \frac{2m}{\hbar^2} [V(r, \rho, \chi) - V_0(r, \rho)] | j \rangle + \langle i | \nabla_r | j \rangle \nabla_r \quad (8)$$

from the variation with  $r$ , of the internal energy of BC. This variation may well be considerable in potentially reactive systems.

In this work it is assumed that the coupling terms  $X_{ij}$  are so small that solutions to equation (7) can be found by the distorted wave perturbation method.<sup>1</sup> (One should realize that this condition does not automatically follow from the experimental observation that the inelastic scattering cross-section for a given system is small. Each partial wave must be considered separately and this cross-section would be small if a very few initial partial waves were strongly coupled to some final ones. The strongly coupled waves could not then be treated by perturbation theory.) It is supposed that the system can be represented almost entirely by an elastically scattered wave,<sup>4</sup> with unit incident intensity

$$\psi_0(\underline{r}) = \sum_{l_0=0}^{\infty} (2l_0+1) i^{l_0} e^{i\eta_{l_0}^0} \frac{u_{l_0}^0(r)}{k_0 r} P_{l_0}^0(\cos\theta), \quad (9)$$

together with an appropriate initial internal state  $|0\rangle$ . The functions  $u_{l_0}^0(r)$  satisfy

$$\left[ \frac{d^2}{dr^2} + k_0^2 - U_0(r) - l_0 \frac{(l_0+1)}{r^2} \right] u_{l_0}^0(r) = 0, \quad (10)$$

with the following boundary condition at infinity,

$$u_{l_0}^0(r) \sim \sin(k_0 r - l\pi/2 + \eta_{l_0}^0);$$

$u_{l_0}^0(r)$  clearly contains both incoming and outgoing waves. The remaining  $\psi_1(r)$  are chosen to satisfy

$$\left[ \nabla_r^2 + k_1^2 - U_1(r) \right] \psi_1(r) = X_{O1}(r) \psi_0(r) \quad (11)$$

with boundary condition  $\psi_1(r) \sim e^{ik_1 r}$ . Writing

$$\psi_1(r) = \sum_{l_1=0}^{\infty} \frac{v_{l_1}^1(r)}{r} P_{l_1}^m(\cos\theta) e^{im\phi} \quad (12)$$

and following the standard procedure<sup>1</sup> leads to

$$v_{l_1}^1(r) \sim \frac{e^{ik_1 r}}{k_0 k_1} \sum_{l_0=0}^{\infty} (2l+1) i^{l_0 - l_1} e^{i(\eta_{l_0}^0 + \eta_{l_1}^1)} I_{O1}(l_0^0; l_1^m), \quad (13)$$

where

$$I_{O1}(l_0^0; l_1^m) = \int u_{l_0}^0(r) P_{l_0}^0(\cos\theta) X_{O1}(r) u_{l_1}^1(r) P_{l_1}^m(\cos\theta) e^{im\phi} \frac{d\tau}{r^2} \quad (14)$$

and  $u_{l_1}^1(r)$  and  $\eta_{l_1}^1$  are defined by an equation like (10). In evaluating the radial parts of the integrals  $I_{O1}(l_0^0; l_1^m)$ , we follow a semiclassical argument given by Landau<sup>5</sup> and note that the rapid fluctuations in  $u_{l_0}^0(r)$  and  $u_{l_1}^1(r)$  lead to almost complete cancellation unless at some point R

$$k_1^2 - U_1(R) - \frac{l_1(l_1+1)}{R^2} = k_0^2 - U_0(R) - \frac{l_0(l_0+1)}{R^2}; \quad (15)$$

we shall therefore concentrate on those cases for which such a

crossing point exists. It is convenient to distinguish between the cases in which the crossing point is and is not classically accessible. In both cases the important range of integration lies immediately around the crossing point (see for instance §51 of Landau and Lifshitz<sup>6</sup>).

In the first case, using the semiclassical expressions

$$u_{l_1}^1(r) = \frac{k_1}{\left[ k_1^2 - U_1(r) - \frac{l_1(l_1+1)}{r^2} \right]^{1/4}} \cos \left\{ \int_{a_1}^r \left[ k_1^2 - U_1(r) - \frac{l_1(l_1+1)}{r^2} \right]^{1/2} dr + \frac{\pi}{4} \right\}, \quad (16)$$

for  $r > a_1$ , and following Landau directly we find that

$$I_{O_1}(l_0; l_1^1 m^1) = J_{l_0, l_1}^{1m}(R) \cos(\xi_{l_0}^0 - \xi_{l_1}^1 + \frac{\pi}{4}) \quad (17)$$

where, if

$$k(R) = \sqrt{k_0^2 - U_0(R) - \frac{l_0(l_0+1)}{R^2}} = \sqrt{k_1^2 - U_1(R) - \frac{l_1(l_1+1)}{R^2}}$$

and

$$F_1 = \frac{\partial}{\partial r} \left[ U_1(r) + \frac{l_1(l_1+1)}{r^2} \right] \Big|_{r=R}$$

$$J_{l_0, l_1}^{1m}(R) = \sqrt{\frac{2\pi k_0 k_1}{k(R) |F_0 - F_1|}} \int_0^{2\pi} d\phi \int_{-1}^1 d\cos\theta P_{l_0}^0(\cos\theta) X_{O_1}(r) P_{l_1}^m(\cos\theta) e^{im\phi}$$

and

$$\xi_{l_1}^1 = \int_{a_1}^R \left[ k_1^2 - U_1(r) - \frac{l_1(l_1+1)}{r^2} \right]^{1/2} dr.$$

In general, the case when R occurs in the classically inaccessible region is rather less easy to deal with, but Landau and Lifshitz show that in this case

$$I_{01}(l_0 0; l_1 m) \propto \exp \left\{ - \left| \int_{a_1}^R \left[ U_1(r) + \frac{l_1(l_1+1)}{r^2} - k_1^2 \right]^{\frac{1}{2}} dr - \int_{a_0}^R \left[ U_0(r) + \frac{l_0(l_0+1)}{r^2} - k_0^2 \right]^{\frac{1}{2}} dr \right| \right\}, \quad (18)$$

implying that the integral will be smaller the further R lies inside the classically inaccessible region. Equations (17) and (18) are derived on the assumption that the crossing point lies sufficiently far from the classical turning points that the motion is semiclassical in its neighborhood.

We now return to Eqs. (12) and (13). First we recognize that a given final partial wave will generally be made up of contributions from a rather small number of initial partial waves; in other words, for given  $l_1$ , the actual sum in (13) will be quite short. In order to calculate its length one would expand  $X_{01}(\underline{r})$  in the form

$$X_{01}(\underline{r}) = \sum_{l=1}^L \sum_{m=-l}^l X_{01}^{lm}(r) P_l^m(\cos\theta) e^{im\phi}, \quad (19)$$

where L is the last term for which  $X_{01}^{lm}(r)$  is appreciable. The sum in (13) would then have  $2L+1$  terms. We therefore write

$$v_1(\underline{r}) = - \frac{e^{i(k_1 r + m\phi)}}{r} \sum_{l=-L}^L S_{l}^{im}(\theta) \quad (20)$$

and evaluate the sums

$$S_{l}^{im} = \sum_{l_1=0}^{\infty} \frac{1}{k_0 k_1} (2l_0+1) i^{\delta l} e^{i(\eta_{l_0}^0 + \eta_{l_1}^1)} I_{01}(l_0 0; l_1 m_1) P_{l_1}^m(\cos\theta) \quad (21)$$

$l_0 = l_1 + \delta l,$

by the stationary phase approximation.<sup>1</sup> For  $|l_1\theta| \gg 0$ ,  
 $|l_1(\pi-\theta)| \gg 0$  and  $l_1 \gg m$ , ( $m$  cannot exceed  $L$ )<sup>7</sup>

$$F_{l_1}^m(\cos\theta) \approx \sqrt{\frac{2}{(l_1 + \frac{1}{2})\pi \sin\theta}} (l_1 + \frac{1}{2})^m \cos\left[(l_1 + \frac{1}{2})\theta + m\frac{\pi}{2} - \frac{\pi}{4}\right]. \quad (22)$$

Hence, for the case when  $R$  is classically accessible

$$S_{\delta l}^{1m}(\theta) = \int_0^\infty \frac{1}{k_0 k_1} \sqrt{\frac{1}{2\pi \sin\theta}} i^{\delta l} (l_1 + \frac{1}{2})^{m_1 + \frac{1}{2}} j_{l_1 + \delta l, l_1}^{1m}(R) \left[ e^{i\phi_{++}} + e^{i\phi_{+-}} + e^{i\phi_{-+}} + e^{i\phi_{--}} \right] dl, \quad (23)$$

where

$$\phi_{\pm\pm} = \eta_{l_0}^0 + \eta_{l_1}^1 \pm (\xi_{l_0}^0 - \xi_{l_1}^1 + \frac{\pi}{4}) \pm \left[ (l_1 + \frac{1}{2}) \pm m\frac{\pi}{2} - \frac{\pi}{4} \right]. \quad (24)$$

At given  $\theta$  we now look for those values of  $l_1$  for which

$(\partial\phi_{\pm\pm}/\partial l_1 = 0)$ , since at all other values the rapid fluctuations in  $e^{i\phi_{\pm\pm}}$  will cause almost complete cancellation. For an attractive potential only  $\phi_{++}$  and  $\phi_{-+}$  have such turning points,  $l_+$  and  $l_-$  say, at which

$$\frac{\partial}{\partial l_1} \left[ (\eta_{l_0}^0 + \xi_{l_0}^0) + (\eta_{l_1}^1 - \xi_{l_1}^1) \right]_{l_1=l_+} = \theta_+$$

and

$$\frac{\partial}{\partial l_1} \left[ (\eta_{l_0}^0 - \xi_{l_0}^0) + (\eta_{l_1}^1 + \xi_{l_1}^1) \right]_{l_1=l_-} = \theta_- . \quad (25)$$

Similar formulae hold for a repulsive potential, for which only  $\phi_{+-}$  and  $\phi_{--}$  have turning points. In both cases  $S_{\delta l}^{1m}(\theta)$  is the

sum of contributions from two branches. The physical reason for the two branches is quite simple. There is a well-known connection between the W.K.B. semiclassical expression for the phase shift.

$$\eta_{l_1}^1 = \int_{a_1}^{\infty} \left[ k_1^2 - U_1(r) - \frac{l_1(l_1+1)}{r^2} \right]^{\frac{1}{2}} dr - \int_{b_1}^{\infty} \left[ k_1^2 - \frac{l_1(l_1+1)}{r^2} \right]^{\frac{1}{2}} dr \quad (26)$$

and the classical deflection angle for elastic scattering, namely

$$\frac{\partial \eta_{l_1}^1}{\partial l_1} = \Theta_1(-\infty, a_1) = \Theta_1(a_1, \infty), \quad (27)$$

$\Theta_1(-x_1, x_2)$  and  $\Theta_1(x_1, x_2)$  in equation (27) are the angles between the radii at points  $r = x_1$  and  $x_2$  on the trajectories for incoming and outgoing motion under  $l_1$ ,  $k_1$  and  $U_1$ , respectively. This notation was adopted to make clear the implications of the following formulae for  $\theta_+$  and  $\theta_-$ , which are derived from Eqs. (25) by similar methods,

$$\begin{aligned} \theta_+ &= \Theta_0(-\infty, a_0) + \Theta_0(a_0, R) + \Theta_1(R, \infty) \\ \theta_- &= \Theta_0(-\infty, -R) + \Theta_1(-R, a_1) + \Theta_1(a_1, \infty). \end{aligned} \quad (28)$$

When the crossing point lies in the classically accessible region the particle must pass through it twice. The two branches arise because the particle may make the transition from  $|0\rangle$  to  $|1\rangle$  on either occasion. Equation (28) shows that as far as its path is concerned, the particle simply follows the classical trajectory appropriate to the initial state  $(k_0, l_0, U_0)$  until it makes the transition, after which it follows

the appropriate "final" trajectory. The case when R is classically inaccessible is treated in a similar fashion. Since the formula (18) for  $I_{01}(l_0, 0_1, l_1, m)$  contains no fluctuating factors like the term  $\cos(\xi_{l_0}^0 - \xi_{l_1}^1 + \frac{\pi}{4})$  in (17), the scattered wave has only one branch. In the notation of Eqs. (27) and (28) the deflection angle is given by

$$\theta = \Theta_0(-\infty, a_0) + \Theta_1(a_1, \infty).$$

These two possibilities are illustrated in figure 2. In the lower diagram the zig-zag line  $\sphericalangle$  is meant to denote quantum-mechanical tunnelling from  $a_0$  to R and then back to  $a_1$ . It is interesting to find that the scattering angles for given  $\delta l$  are independent of  $m$ . The strength of a given transition however is determined by the angular integrals  $J_{l_0 l_1}^{1m}(R)$  which do depend on  $m$ .

For given  $\theta$ ,  $S_{\delta l}^{1m}(\theta)$  in Eq. (23) may be evaluated by standard methods. Consider a + branch for instance. Near  $l_1 = l_+$ ,  $\phi_{++}$  may be expanded in the form

$$\phi_{++} = \phi_{++}^{(0)} + \frac{1}{2} \phi_{++}^{(2)} (l_1 - l_+)^2 \quad (29)$$

and if the integral over the rest of the range of  $l_1$  is essentially zero

$$\begin{aligned}
 & \int_0^l (l_1 + \frac{1}{2})^{m+\frac{1}{2}} J_{l_0, l_1}^{1m}(R) e^{i\phi_{++}} dr \\
 & \approx (l_+ + \frac{1}{2})^{m+\frac{1}{2}} J_{l_+ + \delta l, l_+}^{1m}(R) e^{i\phi_{++}^{(0)}} \int_0^\infty e^{\frac{1}{2} \phi_{++}^{(2)} (l-l_+)^2} dl \\
 & = (l_+ + \frac{1}{2})^{m+\frac{1}{2}} J_{l_+ + \delta l, l_+}^{1m}(R) e^{i\phi_{++}^{(0)}} \sqrt{\pi / |(\partial\theta_+ / \partial l)_{l=l_+}|} \quad (30)
 \end{aligned}$$

since according to Eqs. (24) and (25),

$$\phi_{++}^{(2)} = \left( \frac{\partial^2 \phi_{++}}{\partial l^2} \right)_{l=l_+} = \left( \frac{\partial \theta_+}{\partial l} \right)_{l=l_+} \quad (31)$$

$S_{\delta l}^{1m}(\theta)$  may therefore be written in the form

$$S_{\delta l}^{1m}(\theta) = f_{\delta l_+}^{1m}(\theta) e^{i\alpha_{\delta l_+}^{m1}} + f_{\delta l_-}^{1m}(\theta) e^{i\alpha_{\delta l_-}^{m1}} \quad (32)$$

where the quantities

$$f_{\delta l_{\pm}}^{1m}(\theta) = \frac{1}{k_0 k_1} \left[ \frac{(l_1 + \frac{1}{2})^{m+\frac{1}{2}}}{\sqrt{2 \sin \theta (\partial\theta_{\pm} / \partial l_1)}} J_{l_0, l_1}^{1m}(R) \right]_{l_1=l_{\pm}} \quad (33)$$

represent the scattering amplitudes into the  $\pm$  branches of the final  $\delta l$  wave.

Finally, it is important to appreciate the approximation on which these formulae are based. We have assumed

(i) that the coupling terms  $X_{1j}(\underline{r})$  in Eq. (8) are sufficiently small to act as small perturbations;

(ii) that  $R$  lies sufficiently far inside the classically accessible region that the particle behaves semiclassically there. For some values of  $\delta l$  of course the crossing point may

be classically inaccessible, in which case the particle must tunnel past the classical turning point to reach it. The corresponding scattering amplitude will therefore be rather small;

(iii) that Eq. (22) is valid for the values of  $l_{\pm}$ ,  $\theta$  and  $m$  under consideration. This analysis will therefore breakdown for scattering at very small angles and probably also at very large angles because  $l_{\pm}$  are then very small; and

(iv) that  $(\partial\theta_{\pm}/\partial l)$  in Eq. (30) does not vanish. (i.e.,  $\theta_{\pm}$  is not a rainbow angle for the  $\pm$  branch.)

The semiclassical analysis of rainbow angle elastic scattering, recently published by Ford and Wheeler<sup>8</sup> can however be applied to each branch separately around the points where  $\partial\theta_{\pm}/\partial l = 0$ .

### 3. Calculation of Crossing Points

In view of the importance of the position of the crossing point R, defined by Eq. (15), it is interesting to investigate its behavior for different types of inelastic collision. We begin by considering purely rotational excitations.

In this case  $U_1(r) = U_0(r)$  and at the crossing point

$$k_0^2 - \frac{l_0(l_0+1)}{R^2} = k_1^2 - \frac{l_1(l_1+1)}{R^2}, \quad (34)$$

where

$$k_1^2 = \frac{2mE}{\hbar^2} - \frac{m}{\mu R^2} j_1(j_1+1). \quad (35)$$

$\mu\rho_v^2$  is the effective moment of inertia of BC in the given vibrational state. Hence

$$R^2 = - \frac{(l_1 - l_0)(l_1 + l_0 + 1)}{(j_1 - j_0)(j_1 + j_0 + 1)} \left( \frac{\mu\rho_v^2}{m} \right). \quad (36)$$

R therefore exists only when  $l_1 > l_0$  and  $j_1 < j_0$  (or vice versa), which implies a weak selection rule on the allowed angular momentum changes; transitions for which  $l$  increases and  $j$  decreases (or vice versa) are strongly preferred. It remains the question whether R is classically accessible or not.

Consider first the artificial case with  $U_0(r) = U_1(r) = 0$ . The classical turning point  $b_0$  is then given by

$$b_0^2 = \frac{l_0(l_0 + 1)}{k_0^2} \quad (37)$$

and according to Eqs. (34) and (37)  $R^2 > b^2$  only when

$$\frac{l_0(l_0 + 1)k_1^2 - l_1(l_1 + 1)k_0^2}{(k_0^2 - k_1^2)} > 0. \quad (38)$$

Equation (38) therefore puts a rough upper limit on the ratio  $[l_1(l_1 + 1)]/[l_0(l_0 + 1)]$  for strong transitions, namely

$$\frac{l_1(l_1 + 1)}{l_0(l_0 + 1)} = \frac{k_1^2}{k_0^2}. \quad (39)$$

In general, of course,  $U(r) \neq 0$ , and one cannot give a simple general expression for the classical turning point  $a_0$ . But  $a_0^2$  will still increase roughly quadratically with  $l_0$  whereas, according to (36),  $R^2$  depends only linearly on  $l_0$  (for a given type of transition  $l_1 - l_0$  is constant). There will therefore

again be an upper limit on  $l_0$  (and hence on the initial classical impact parameter) above which  $\delta l = l_0 - l_1$  transitions are very improbable. The critical value may even be  $l_0 = 0$ , in which case one would expect very little rotational excitation at all.

It is worthwhile noticing that according to Eq. (36)  $R$  will be large, and therefore more likely to be classically accessible when  $\mu$  is large and  $m$  is small. In other words collisions between a light atom  $A$  and a molecule  $BC$  with high moment of inertia are most likely to lead to rotational inelasticity.

In this context it is interesting to examine the results of a recent molecular beam experiment on the collision between  $K$  and  $HBr$ .<sup>2</sup> The authors assume an exp-6 form for the spherical part  $V(r)$  of the translational potential

$$V(r) = \frac{\epsilon}{1-(6/\alpha)} \left\{ \frac{6}{\alpha} \exp \left[ \alpha \left( 1 - \frac{r}{r_m} \right) \right] - \left( \frac{r_m}{r} \right)^6 \right\}. \quad (40)$$

With the values  $\epsilon = 0.55$  kcal/mole,  $\alpha = 12$ ,  $r_m = 4.5$  Å chosen to fit the low angle scattering, the crossing point for rotational transitions always lies in the classically inaccessible region. The apparently inelastic behavior reported for high angle scattering could not therefore be attributed to rotational transitions. This conclusion supports the view of the authors. It is not clear, however, that this form for  $V(r)$  is the only one which would give rise to the reported low angle scattering and this point cannot be definitely settled

without more detailed information about the state of the system after the collision.

We now turn to the more general possibility that both vibrational and rotational state may change during the collision. The main complication is that the vibrational energy of BC may change with  $r$  in different ways for different vibrational states.

For a simple model of the potential  $V_0(r, \rho)$  in Eqs. (2), consider the form

$$V_0(r, \rho) = V(r) + D(r) \left[ e^{-2\beta(\rho - \rho_m)} - 2p(r)e^{-\beta(\rho - \rho_m)} \right] \quad (41)$$

At given  $r$ , the vibrational potential  $V_0(r, \rho) - V(r)$  then has a minimum energy  $-p^2(r)D(r)$  at

$$\rho = \rho_m + \frac{1}{\beta} \ln \frac{1}{p(r)}. \quad (42)$$

If  $p(\infty) = 1$ ,  $V(\infty) = 0$  and  $D(\infty)$  is the dissociation energy of BC,  $V_0(\infty, \rho)$  is a Morse function. At every  $r$ , the vibrational eigenfunctions  $V_n(r, \rho)$  and characteristic energies  $\lambda_n(r)$  must satisfy

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{d\rho^2} + D \left[ e^{-2\beta(\rho - \rho_m)} - 2pe^{-\beta(\rho - \rho_m)} \right] - \lambda_n \right\} V_n(\rho) = 0. \quad (43)$$

For brevity we shall temporarily omit the reminders that  $D$ ,  $p$  and  $\lambda_n$  depend parametrically on  $r$ . The substitutions

$$z = \left( \frac{2\sqrt{2mD}}{\beta\hbar} \right) e^{-\beta(\rho - \rho_m)} \quad \text{and} \quad v_n(r) = e^{-z/2} z^{\alpha_n/2} F_n(z)$$

where

$$\alpha_n^2 = -\frac{8\mu\lambda_n}{\beta^2 n^2},$$

throw (43) into the form

$$\frac{d^2 F_n}{dz^2} + \left(\frac{1+\alpha_n}{z} - 1\right) \frac{dF_n}{dz} + \left(\frac{\sqrt{2\mu D}}{\beta n} p - \frac{1+\alpha_n}{2}\right) F_n = 0. \quad (44)$$

The bound solutions of (44) are confluent hypergeometric functions

$$F(-n, 1+\alpha; z) = \text{const} \times e^z z^{-\alpha} \frac{d^n}{dz^n} (e^{-z} z^{\alpha+n}). \quad (45)$$

where

$$n = \frac{\sqrt{2\mu D}}{\beta n} p - \frac{1+\alpha_n}{2} \quad (46)$$

must be an integer. This implies that  $\lambda_n$  is restricted to the values

$$\lambda_n = -[p - (n + \frac{1}{2})q]^2 D, \quad (47)$$

where  $q = \beta n / \sqrt{2\mu D}$ . Hence in Eq. (4)

$$W_1(r) = V(r) + \lambda_1(r) = V(r) - [p(r) - (1 + \frac{1}{2})g(r)]^2 D(r). \quad (48)$$

It now follows from Eqs. (7) and (15), that the crossing point for a vibrational-rotational transition from  $|i\rangle$  to  $|j\rangle$  is given by

$$k_1^2 - k_j^2 = \frac{l_1(l_1+1) - l_j(l_j+1)}{R^2} - (1-j) \{ 2[p(R)q(R)D(R) - p(\infty)q(\infty)D(\infty)] - (1+j+1)[q^2(R)D(R) - q^2(\infty)D(\infty)] \} \frac{2m}{n^2}. \quad (49)$$

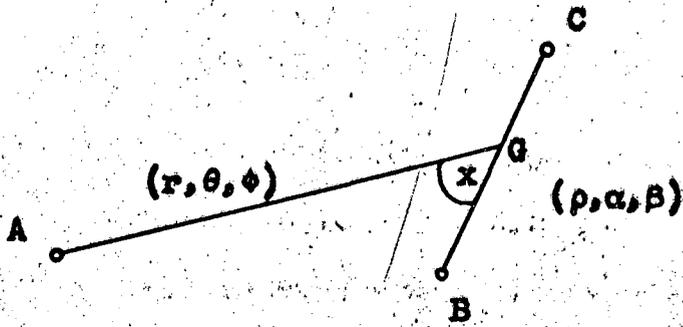
When more is known about the way in which the vibrational potential functions  $V_0(r, \rho) - V(r)$  vary with  $r$  for different actual physical systems Eq. (49) may be useful in deciding whether vibrational-rotational transitions are very likely or not.

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G is the center of mass of BC

Figure 1

Figure 2

(attached )

Sketches to illustrate the trajectory of a particle suffering an inelastic collision when the "crossing-point" R is classically (a) accessible and (b) inaccessible. The zig-zag line  $\sim\sim$  in (b) denotes quantum mechanical tunnelling via R from one "elastic" trajectory to the other. x is the scattering center.

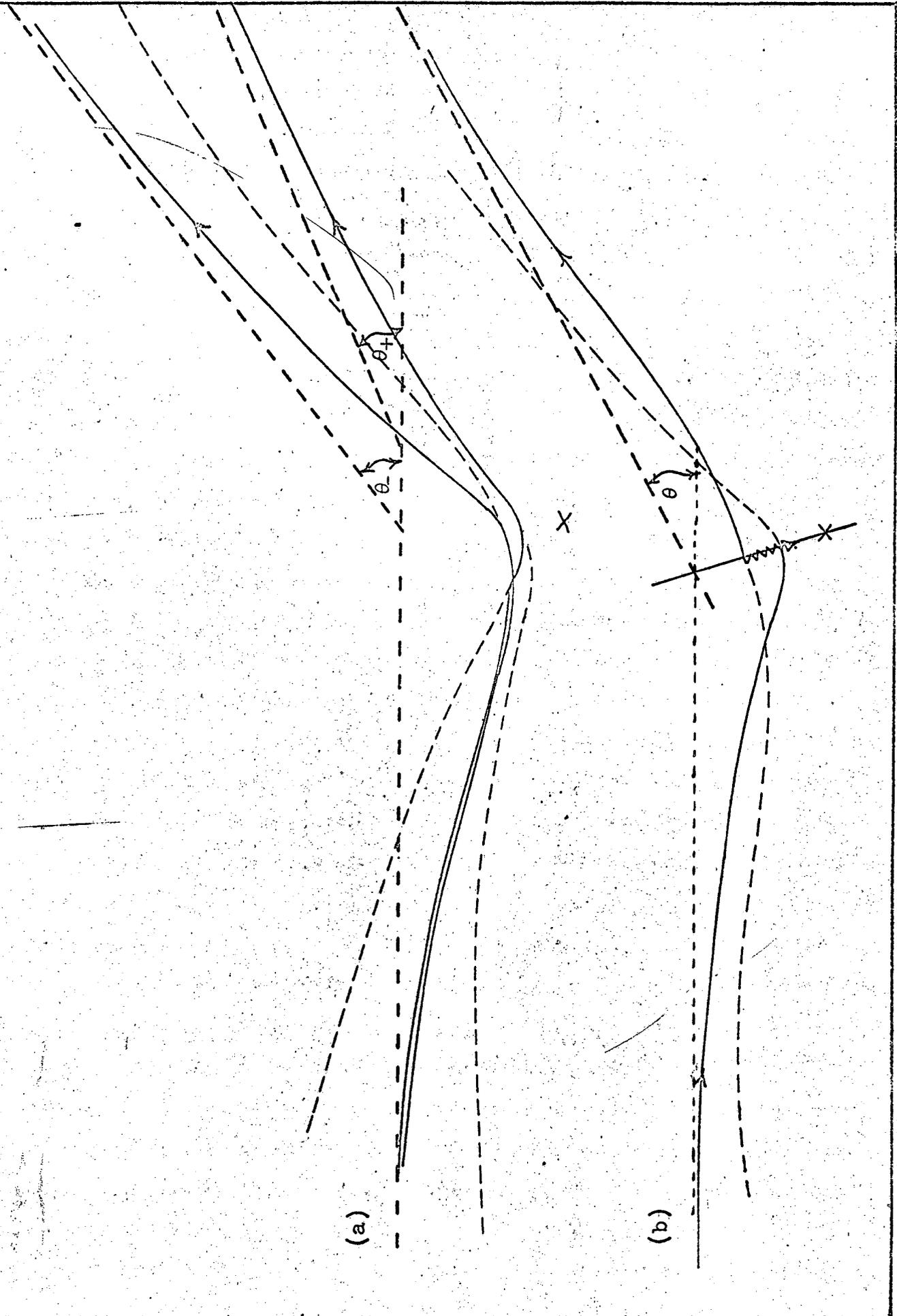


Fig. 2

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