

Vibrational Energy Exchange in Quantum and Classical Mechanics

DONALD RAPP

Lockheed Missiles and Space Company, Palo Alto, California

(Received 6 January 1964)

The probability of vibrational energy exchange in a molecular collision can be calculated using (1) a wave-mechanical treatment using the method of "distorted waves," (2) a semiclassical time-dependent perturbation procedure in which the perturbation energy is obtained as a function of time from the classical collision trajectory, and (3) a purely classical calculation of the energy transferred to a classical vibrator. These methods are reviewed, related, and compared.

I. INTRODUCTION

IN a previous paper,¹ it was shown that a small perturbation calculation using purely classical mechanics gave the same result for the average vibrational energy transferred in a molecular collision as the wave-mechanical small perturbation result, when certain approximations were made. This presentation did not make clear how the various approximations entered into the wave-mechanical treatment and an adequate discussion of the relationships between the classical method, the time-independent wave-mechanical method, and the time-dependent wave-mechanical method was not given. The purpose of this paper is to enlarge upon these aspects of the problem for the case of a small perturbation and small transition probabilities.

Landau and Teller² first performed the calculation using the classical method. Unfortunately, they wrote the symbol ν to mean what we now generally write as $\omega = 2\pi\nu$, and this led to some misunderstanding³ in making comparisons with the quantum theory,^{4,5} as has been pointed out previously.⁶⁻⁹ When wave mechanics was first discovered, there was a tendency to completely discard classical mechanics in the rush to apply the new mechanics to as wide a range of problems as possible. It is understandable then that Landau and Teller chided previous workers who used methods of great sophistication and rigor which were not necessary in this problem.

The requirements that must be met in a molecular collision involving a transition from one state to

another, in order for classical mechanics to be a good approximation for some or all of the motions, are difficult to define. One usually relies on the general statement that when the de Broglie wavelength is "small" compared to the distance over which the potential varies significantly, classical mechanics should be a good approximation. However, a more precise formulation based on a WKB treatment gives the requirement

$$(d/dx)(\lambda/2\pi) \ll 1.$$

The factor 2π in this expression is important and should not be overlooked. As we shall see presently, when the potential varies with a coordinate as $e^{-x/L}$, one finds that if terms like $\exp(-4\pi^2 L/\lambda)$ are small compared to unity, the quantum result reduces to the classical result. We therefore gain a more precise meaning for the word "small." If $4\pi^2 L/\lambda \cong 3$, one only incurs errors of the order of 3% by using the classical method.

II. WAVE-MECHANICAL PROBLEM

We deal with a linear arrangement of three atoms (Fig. 1). Initially, A and the diatomic molecule B-C are separated by an infinite distance and have relative velocity v_i . If the positions of A, B, and C are specified by the respective distances ξ_A , ξ_B , and ξ_C from some origin on the line passing through A, B, and C, the Schrödinger equation has the form

$$-\frac{\hbar^2}{2} \left(\frac{1}{m_A} \frac{\partial^2 \Psi}{\partial \xi_A^2} + \frac{1}{m_B} \frac{\partial^2 \Psi}{\partial \xi_B^2} + \frac{1}{m_C} \frac{\partial^2 \Psi}{\partial \xi_C^2} \right) + V\Psi = E\Psi. \quad (1)$$

An orthogonal transformation can then be made to coordinates \tilde{m}^1x , μ^1y , and M^1R , where

$$\tilde{m} = [m_A(m_B + m_C)] / (m_A + m_B + m_C),$$

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

$$M = m_A + m_B + m_C,$$

$$x = [(m_B \xi_B + m_C \xi_C) / (m_B + m_C)] - \xi_A,$$

$$y = \xi_C - \xi_B,$$

$$R = (m_A \xi_A + m_B \xi_B + m_C \xi_C) / M,$$

and

¹ D. Rapp, J. Chem. Phys. **32**, 735 (1960).

² L. Landau and E. Teller, Physik Z. Sowjetunion **10**, 34 (1936).

³ In Refs. 4 and 5, Herzfeld identifies L of the classical theory with $2\pi L$ of the wave-mechanical theory because of this misunderstanding.

⁴ K. F. Herzfeld, "Relaxation Phenomena in Gases," in *Thermodynamics and Physics of Matter*, edited by F. Rossini (Princeton University Press, Princeton, New Jersey, 1955).

⁵ K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959).

⁶ T. L. Cottrell and N. Ream, Trans. Faraday Soc. **51**, 1453 (1955).

⁷ D. Rapp, M. S. thesis, Princeton University, 1956.

⁸ R. C. Amme and S. Legvold, J. Chem. Phys. **30**, 163 (1959).

⁹ B. Stevens and M. Boudart, Ann. N.Y. Acad. Sci. **67**, 570, (1957).

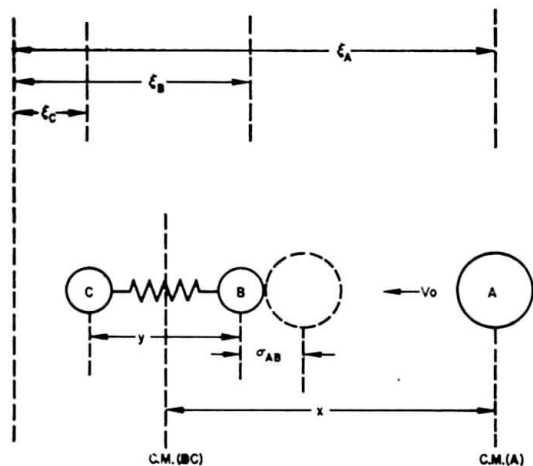


FIG. 1. Collision coordinates.

The coordinates x , y , and R refer to motion of A, relative to the center of mass of BC, relative motion of B with respect to C, and motion of the center of mass of A+B+C. The Schrödinger equation then transforms to

$$-\frac{\hbar^2}{2} \left(\frac{1}{M} \frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{\tilde{m}} \frac{\partial^2 \Psi}{\partial x^2} + \frac{1}{\mu} \frac{\partial^2 \Psi}{\partial y^2} \right) + V \Psi = E \Psi. \quad (2)$$

The potential energy V is independent of the center of mass of A+B+C, so $V = V(x, y)$ is independent of R . If we then write $E = E_T + E_I$, and $\Psi = \Psi_T(R) \Psi_I(x, y)$, where T refers to translational motion of the center of mass of A+B+C, and I refers to internal relative motion, we obtain

$$\Psi_T \propto \exp[i(2ME_T)^{1/2}R/\hbar]$$

and

$$-\frac{\hbar^2}{2} \left(\frac{1}{\tilde{m}} \frac{\partial^2 \Psi_I}{\partial x^2} + \frac{1}{\mu} \frac{\partial^2 \Psi_I}{\partial y^2} \right) + V(x, y) \Psi_I = E_I \Psi_I. \quad (3)$$

Equation (3) is perfectly general for any three-body linear collision. The application to vibrational energy transfer obtains when a particular choice of the form of Ψ_I and $V(x, y)$ is made.

The function $V(x, y)$ is of the form $V^{(BC)}(y) + V'(x, y)$ in which $V^{(BC)}(y)$ is the binding potential of the diatomic molecule B-C (in our case approximately a harmonic oscillator) and $V'(x, y)$ is the interaction of A with B-C. As $x \rightarrow \infty$, $V'(x, y) \rightarrow 0$. As a result, Ψ_I has the asymptotic form for large x

$$\Psi_I \sim \sum_n \Psi_n^{(A)}(x) \Psi_n^{(BC)}(y), \quad (4)$$

where $\Psi_n^{(BC)}(y)$ is a solution of the equation

$$[-(\hbar^2/2\mu)(d^2/dy^2) + V^{(BC)}(y) - \epsilon_n] \Psi_n^{(BC)}(y) = 0, \quad (5)$$

and $\Psi^{(A)}(x)$ become plane waves as $x \rightarrow \infty$. In particular, for a unit flux of A incident on B-C in the initial

state i , the asymptotic form is

$$\begin{aligned} \Psi_i^{(A)}(x) &\sim \exp(-ik_i x) + a_i \exp(ik_i x), \\ \Psi_n^{(A)}(x) &\sim a_n \exp(ik_n x) \quad (n \neq i), \end{aligned} \quad (6)$$

and the probability of transition to the state n is $|a_n|^2 k_n/k_i$.

Following Jackson and Mott,¹⁰ we next assume that asymptotic Eq. (4) can be used for all x , with the $\Psi_n^{(BC)}(y)$ still solutions of Eq. (5), but the $\Psi^{(A)}(x)$ are not plane waves when $V'(x, y)$ is appreciable. We see that the appropriate $\Psi^{(A)}(x)$ to pick are the "distorted" wavefunctions corresponding to elastic scattering from $V'(x, y)$. If we insert Eq. (4) into Eq. (3) and use Eq. (5) to simplify, we obtain

$$\left[-\frac{\hbar^2}{2\tilde{m}} \frac{d^2}{dx^2} - \frac{\hbar^2 k_n^2}{2\tilde{m}} - V'(x, y) \right] \Psi_n^{(A)}(x) \Psi_n^{(BC)}(y) = 0, \quad (7)$$

where $\hbar^2 k_n^2/2m = E - \epsilon_n$. We then multiply Eq. (7) by $\Psi_j^{(BC)}(y)$ and integrate over all y , to obtain

$$-(\hbar^2/2m) \left[(d^2/dx^2) + k_j^2 \right] \Psi_j^{(A)}(x) + \sum_n V_{jn}'(x) \Psi_n^{(A)}(x) = 0, \quad (8)$$

in which we have used the orthogonality of the $\Psi^{(BC)}(y)$, and

$$V_{jn}'(x) = \int_{-\infty}^{+\infty} \Psi_j^{(BC)}(y) V'(x, y) \Psi_n^{(BC)}(y) dy. \quad (9)$$

If the probability of a change of state of B-C is small, we can take $a_i^{(0)} \approx 1$. Then, to zero order,

$$\Psi_i^{(A)}(x) = f_i^{(0)}, \quad \Psi_n^{(A)}(x) = 0, \quad (n \neq i).$$

To first order,

$$\begin{aligned} \Psi_i^{(A)}(x) &= f_i^{(0)} + f_i^{(1)} \\ \Psi_n^{(A)}(x) &= f_n^{(1)} \quad (n \neq i). \end{aligned} \quad (10)$$

We must next establish the order of the integrals. We use the potential function previously described¹

$$V'(x, y) = V(x) \{1 + [m_C/(m_B + m_C)](Y/L)\}, \quad (11)$$

where $Y = y - y_0$, and y_0 is the equilibrium rest value of y . We therefore find

$$V_{jj}'(x) = V(x), \quad (12)$$

$$V_{jn}'(x) = V(x) [m_C/(m_B + m_C)](Y_{jn}/L), \quad (j \neq n) \quad (13)$$

where

$$Y_{jn} = \int_{-\infty}^{\infty} \Psi_j^{(BC)}(Y) Y \Psi_n^{(BC)}(Y) dY.$$

The order of the transition probability is dependent on the order of the small quantity Y_{jn}/L . We therefore define V_{jj}' to be zero order and V_{jn}' to be first order.

¹⁰ J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703 (1932).

If we then put Eq. (10) into Eq. (8) and set the sum of terms of each order equal to zero, we obtain

$$-(\hbar^2/2\tilde{m})[(d^2/dx^2) + k_i^2]f_i^{(0)} + V_{ii}'f_i^{(0)} = 0, \quad (14)$$

$$-(\hbar^2/2\tilde{m})[(d^2/dx^2) + k_j^2]f_j^{(1)} + V_{jj}'f_j^{(1)} + V_{ij}'f_i^{(0)} = 0, \quad (15)$$

where i is again the initial state and j is any other state.

If we now regard Eq. (14) as a purely mathematical entity, we define the solution for arbitrary subscript j as $F_j(x)$, and choose that solution which goes to zero as $x \rightarrow -\infty$ [since $V(x) \rightarrow \infty$], and which has the asymptotic form

$$F_j(x) \sim \cos(k_j x + \eta) \quad (16)$$

as $x \rightarrow +\infty$. Because of Eq. (6), and since $a_i^{(0)} = 1$, we must take

$$2F_i = f_i^{(0)}. \quad (17)$$

We now solve Eq. (15) by making the substitution $f_j^{(1)} = gF_j$, and multiplying through by F_j to obtain

$$-\frac{\hbar^2}{2\tilde{m}} \left[\frac{d}{dx} \left(F_j^2 \frac{dg}{dx} \right) \right] + 2V_{ij}' F_i F_j = 0, \quad (18)$$

in which we have used Eq. (14) to simplify. If Eq. (18) is integrated, using the fact that $F_j \rightarrow 0$ as $x \rightarrow -\infty$, we obtain

$$F_j^2 \frac{dg}{dx} = \left(\frac{m_C}{m_B + m_C} \right) \frac{Y_{ij}}{L} \frac{4\tilde{m}}{\hbar^2} \int_{-\infty}^x F_i V(x) F_j dx. \quad (19)$$

For large x , the integral in Eq. (19) is a constant, namely.

$$\int_{-\infty}^{\infty} F_i V(x) F_j dx,$$

and we obtain

$$\lim_{x \rightarrow \infty} (g) = \left[\left(\frac{m_C}{m_B + m_C} \right) \frac{Y_{ij}}{L} \frac{4\tilde{m}}{\hbar^2} \int_{-\infty}^{\infty} F_i V(x) F_j dx \right] \times [\tan(k_j x + \eta) + \text{const.}] \quad (20)$$

We must now choose the constant in Eq. (20) so that $f_i^{(1)} = gF_i$ has the same asymptotic form as Eq. (6). If the constant is chosen as $-i/k_j$, we obtain

$$\lim_{x \rightarrow \infty} f_j^{(1)} = \left[-i \left(\frac{m_C}{m_B + m_C} \right) \frac{Y_{ij}}{L} \frac{4\tilde{m}}{\hbar^2 k_j} \int_{-\infty}^{\infty} F_i V(x) F_j dx \right] \times \exp[i(k_j x + \eta)], \quad (21)$$

so that

$$|a_j|^2 = \left(\frac{m_C}{m_B + m_C} \right)^2 \frac{Y_{ij}^2 (4\tilde{m})^2}{L^2 (\hbar^2 k_j)} \left| \int_{-\infty}^{\infty} F_i V(x) F_j dx \right|^2, \quad (22)$$

and

$$P_{i \rightarrow j} = \left(\frac{m_C}{m_B + m_C} \right)^2 \frac{Y_{ij}^2 (4\tilde{m})^2}{L^2 (\hbar^2)} \frac{1}{k_i k_j} \left| \int_{-\infty}^{\infty} F_i V(x) F_j dx \right|^2. \quad (23)$$

Here, F_i and F_j are once again the solutions of Eq. (14) which have the asymptotic form Eq. (16) as $x \rightarrow \infty$, and which go to zero as $x \rightarrow -\infty$. This result can be generalized to any unperturbed B-C wavefunctions $\Psi_j^{(BC)}(Y)$ and any potential of the form $V'(x, Y) = V^{(A)}(x) V^{(BC)}(Y)$, in which $V^{(BC)}(Y) = 1 + f(Y)$, and $f(Y) \ll 1$. The result can then be written

$$P_{i \rightarrow j} = \left| \int_{-\infty}^{+\infty} F_i V^{(A)}(x) F_j dx \right|^2 \times \left| \int_{-\infty}^{\infty} \Psi_i^{(BC)}(Y) f(Y) \Psi_j^{(BC)}(Y) dY \right|^2 \left(\frac{4\tilde{m}}{\hbar^2} \right)^2 \frac{1}{k_i k_j}. \quad (24)$$

III. CONNECTION WITH SEMICLASSICAL TIME-DEPENDENT PERTURBATION THEORY

Zener¹¹ was the first to apply this method to the present problem. We consider a molecule B-C which is initially in vibrational state $\Psi_i^{(BC)}(Y)$ with energy ϵ_i and wish to compute the probability of finding it in state $\Psi_j^{(BC)}(Y)$ with energy ϵ_j if a time-dependent perturbation is applied in the form of a molecular collision. In the usual way [analogous to Eq. (4)], we write the total wavefunction as

$$\Psi = \sum_n a_n(t) \Psi_n^{(BC)}(Y) \exp(i\omega_n t), \quad (25)$$

where $\omega_n = \epsilon_n/\hbar$. The use of this wavefunction in the time-dependent wave equation

$$(H_0 + V')\Psi = \hbar i (\partial \Psi / \partial t), \quad (26)$$

where

$$H_0 \Psi_n^{(BC)} = \epsilon_n \Psi_n^{(BC)}(Y), \quad \text{gives} \\ da_n/dt = (\hbar i)^{-1} \sum_j a_j(t) V_{nj}' \exp(i\omega_{jn} t), \quad (27)$$

where $V_{nj}'(t)$ is the V_{nj}' of Eq. (9) and the classical $x(t)$ converts x to t . If we let $a_i(-\infty) = 1$, the probability of transition to State j is $|a_j(\infty)|^2$. In analogy to Eqs. (9) and (10), we let $a_i \approx 1$ for all t , assuming $|a_i|^2 \gg |a_j|^2$ for $i \neq j$ and obtain

$$P_{i \rightarrow j} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} V_{ij}'(t) \exp(i\omega_{ij} t) dt \right|^2. \quad (28)$$

The time-dependent perturbation result is

$$P_{i \rightarrow j} = \left| \int_{-\infty}^{\infty} V(t) \exp(i\omega_{ij} t) dt \right|^2 \times \left| \int_0^{\infty} \Psi_i^{(BC)}(Y) f(Y) \Psi_j^{(BC)}(Y) dY \right|^2 \frac{1}{\hbar^2}, \quad (29)$$

in which $V(t)$ is obtained by using the classical $x(t)$ in $V^{(A)}(x)$.

The correspondence between this and Eq. (24) is

$$\int_{-\infty}^{\infty} F_i V^{(A)}(x) F_j dx = \frac{\hbar(k_i k_j)^{1/2}}{2\tilde{m}} \int_0^{\infty} V(t) \cos(\omega_{ij} t) dt \quad (30)$$

¹¹ C. Zener, Proc. Cambridge Phil. Soc. **29**, 136 (1932).

in the classical limit. To show this correspondence, we use the quasiclassical wavefunctions given in the Appendix for $x > a_n$, and neglect the classically forbidden region of x .¹² We then have

$$F_i F_j = \frac{1}{2} \left[\frac{(k_i k_j)}{[k_i(x) k_j(x)]} \right]^{\frac{1}{2}} \times \left\{ \cos \left[\int_{a_i}^x k_i(x') dx' + \int_{a_j}^x k_j(x') dx' - \frac{\pi}{2} \right] + \cos \left[\int_{a_i}^x k_i(x') dx' - \int_{a_j}^x k_j(x') dx' \right] \right\}. \quad (31)$$

The first cosine term in Eq. (31) oscillates much more rapidly than the second cosine term if $|(k_i - k_j)| \ll |(k_i + k_j)|$ (as is necessary for the use of the classical trajectory). Since these cosines are to be multiplied by the slowly varying function $V^{(A)}(x)$ and integrated, the integral involving the rapidly oscillating cosine can be neglected.

We then make the approximation

$$\tilde{m} dx / \hbar [k_i(x) k_j(x)]^{\frac{1}{2}} = dt \quad (32)$$

in which an average velocity is used because $k_i \approx k_j$, and neglect the difference between a_i and a_j for the same reason, to obtain

$$\int_{-\infty}^{\infty} F_i V^{(A)}(x) F_j dx = \frac{\hbar}{2\tilde{m}} (k_i k_j)^{\frac{1}{2}} \times \int_0^{\infty} V(t) \left\{ \cos \int_0^X [k_i(X') - k_j(X')] dX' \right\} dt, \quad (33)$$

in which $X = x - a$.

But by conservation of energy,

$$k_i(X) - k_j(X) = \frac{\omega_{ij}}{\frac{1}{2}[v_i(X) + v_j(X)]},$$

and since $v_i \approx v_j$, we obtain Eq. (30) with

$$t = \int_0^X \frac{dX'}{\frac{1}{2}[v_i(X') + v_j(X')]} \quad (34)$$

The assumption of Eq. (32) is not a critical one; it does nothing more than require $k_i \approx k_j$. The assumption of Eq. (34) is more restrictive; it requires that the velocity used in converting $V^{(A)}(x)$ to $V(t)$ must be

considered as the arithmetic mean of v_i and v_j , the velocities in the initial and final quantum states. Zener¹¹ has called attention to this point previously.

IV. PURELY CLASSICAL LIMIT

In the preceding sections, it is shown that in the classical limit for motion in coordinate x , the wave-mechanical method becomes identical with the time-dependent perturbation method (using the classical collision trajectory to obtain the perturbation energy as a function of time). The classical collision trajectory is obtained for a collision of constant energy $E_0 = \frac{1}{2} \tilde{m} v_0^2$ in a potential field $V(x)$, and it turns out that one must equate v_0 to $(v_i + v_j)/2$, the average of velocities before and after transfer of a quantum of energy. In each case the motion in y was quantized and no classical approximations were used.

The first treatment of this problem in the classical limit for both x and y was given by Landau and Teller,² who only calculated the exponential dependence of the energy transfer on collision velocity. This approach has been extended to include the pre-exponential terms by Rapp,¹ and by Parker.¹³ In this method, the classical collision trajectory $X(t)$ is used to obtain the transient driving force on the oscillator

$$F(t) = -(\partial/\partial Y)[V(X, Y)]_{X(t)}.$$

For the potential given in Eq. (11),

$$F(t) = -[mc/(m_B + m_C)](L)^{-1}V(t). \quad (35)$$

A purely classical oscillator initially oscillating with phase δ and amplitude A , when acted upon by a transient driving force $F(t)$ acquires the net motion¹⁴

$$\lim_{t \rightarrow \infty} Y(t) = A \sin(\omega t + \delta) + \frac{1}{\mu \omega} \int_{-\infty}^t F(s) \sin[\omega(t-s)] ds, \quad (36)$$

in which the first term is the initial oscillation before collision, and the second term is the change due to the transient force. If $F(s)$ is an even function, that part of the integral involving

$$\int_{-\infty}^{\infty} F(s) \sin \omega s ds$$

is zero, and one has

$$\lim_{t \rightarrow \infty} Y(t) = \left[A \cos \delta + \frac{1}{\mu \omega} \int_{-\infty}^{\infty} F(s) \cos \omega s ds \right] \sin \omega t + A \sin \delta \cos \omega t. \quad (37)$$

Then defining $|Y(t)|^2$ as the square of the amplitude,

¹² J. G. Parker, Phys. Fluids **2**, 449 (1959).

¹⁴ J. C. Slater and N. H. Frank, *Mechanics* (McGraw-Hill Book Company, Inc., New York, 1947).

¹² The proof given was also worked out independently by R. A. Allen and P. Feuer (private communication). It is interesting to speculate whether one could use the WKB wavefunctions directly in Eq. (23) to obtain a simple result which is intermediate in range of validity between the wave-mechanical and semiclassical results. This author has been unable to effect the integration of the matrix element with these wavefunctions. However, Landau [L. Landau and E. Lifshitz, *Quantum Mechanics* (Pergamon Press, London, 1958), pp. 178-183] has arrived at a principle [see also B. Widom, Discussions Faraday Soc. **33**, 37 (1962)] which allows one to evaluate the exponential part of the matrix element. Landau's procedure is roughly equivalent to the following discussion given in this paper, although the details are somewhat nebulous to this author.

we find

$$\Delta E_{\text{vib}} = \frac{1}{2} \mu \omega^2 [|Y(\infty)|^2 - |Y(0)|^2] \\ = \frac{\mu \omega^2}{2} \left[\frac{2A}{\mu \omega} \cos \delta \int_{-\infty}^{\infty} F(s) \cos \omega s ds + \frac{1}{\mu^2 \omega^2} \left| \int_{-\infty}^{\infty} F(s) \cos \omega s ds \right|^2 \right], \quad (38)$$

in which ΔE_{vib} is the vibrational energy transferred to the oscillator. Since all possible values of the initial phase δ are equally probable between 0 and 2π , the average energy transferred is

$$\langle \Delta E_{\text{vib}} \rangle_{\text{av}} = \frac{1}{2\mu} \left| \int_{-\infty}^{\infty} F(s) \cos \omega s ds \right|^2, \quad (39)$$

as has been shown previously by Rapp¹ for the case $A=0$.¹⁵ Now the picture that one must adopt is that this $\langle \Delta E_{\text{vib}} \rangle_{\text{av}}$ is transferred in every collision, and that $\langle \Delta E_{\text{vib}} \rangle_{\text{av}} \ll h\nu$. In the semiclassical or wave-mechanical methods, an entire quantum is transferred only now and then with probability $P_{i \rightarrow j}$. Although these pictures of the process are radically different, if one considers the net energy transfer to the oscillator averaged over many collisions, the two results become identical. By considering the relationship between the classical and semiclassical calculations described by Rapp,¹ one may show the correspondence between the methods. Rapp¹⁶ and especially Takayanagi¹⁷ have more clearly shown this correspondence. Following Takayanagi,¹⁷ we see that the semiclassical result Eq. (29) for the potential in Eq. (11), takes the form

$$P_{i \rightarrow j} = \frac{Y_{ij}^2}{\hbar^2} \left| \int_{-\infty}^{\infty} F(s) \cos \omega s ds \right|^2, \quad (40)$$

and the net energy transferred to the oscillator is

$$(\Delta E_{\text{vib}})_{sc} = h\nu \left| \int_{-\infty}^{\infty} F(s) \cos \omega s ds \right|^2 \hbar^{-2} \left(\frac{mc}{m_B + mc} \right)^2 L^{-2} \\ \times [Y^2_{i,i+1} - Y^2_{i,i-1}]. \quad (41)$$

Rapp^{1,16} has shown that when $i=0$, Eq. (41) is the same as Eq. (39). Takayanagi¹⁷ and Gilbey¹⁸ have shown that the same holds true for any value of i . The reason that a net energy is transferred to the oscillator is that by supposition the collision velocity is high enough that $\hbar v^2/2 \gg h\nu$ in order to use the classical trajectory. Therefore the semiclassical and purely

classical methods give identical results as far as the energy transferred is concerned.

V. DISCUSSION

The calculation of energy exchange to an oscillator depends on two coordinates, the external coordinate X , and the vibrational amplitude Y . The calculation can be carried out completely wave mechanically, semi-classically in which Coordinate X is treated classically, or purely classically in which both coordinates are classical. At high velocities, the net energy transferred to the oscillator is identical for all three methods.

The procedure to follow for any potential $V(X)$ is as follows. In the wave-mechanical method, Eq. (14) must be solved for the F_i functions, and these must be used to calculate the matrix element in Eq. (22). In the semiclassical method, one must neglect vibrations and calculate the unperturbed trajectory $X(t)$ from

$$dX/dt = \{ (2/\tilde{m}) [E - V(X)] \}^{1/2}.$$

One then puts the $X(t)$ into $V(X)$ to obtain $V(t)$ to use in Eq. (28). In the purely classical method, one uses the $V(t)$ in Eqs. (35) and (39).

These procedures have been carried out for an exponential repulsive potential in the wave-mechanical approach by Jackson and Mott,¹⁰ Schwarz and Herzfeld,^{4,5} and Takayanagi¹⁹; in the semiclassical approach by Zener,¹¹ Rapp,¹ and Takayanagi;¹⁹ and the purely classical method by Rapp¹ and Parker.¹³ The correspondence between the results has been demonstrated by Rapp¹⁶ and by Takayanagi.¹⁷

The same procedures have also been carried out for a Morse potential interaction, in the wave-mechanical approach by Devonshire,²⁰ and Takayanagi,²¹ in the semiclassical approach by Cottrell and Ream,⁶ Takayanagi,²¹ and by Zener,¹¹ and in the purely classical approach by Turner and Rapp.²² Inconsistencies between these results have been eliminated by Takayanagi¹⁷ and by Allen and Feuer.²³

In most applications, the semiclassical result is sufficiently accurate. However, the limiting factor in the entire calculation is the basic assumption that $|Y| \ll L$. For high vibrational states this is no longer a reasonable approximation, and one cannot use the unperturbed classical trajectory neglecting vibrations (nor can one use the distorted wave approach in the wave-mechanical case) as a reasonable model. For very high collision

¹⁹ K. Takayanagi, Progr. Theoret. Phys. (Kyoto) **8**, 111 (1952); K. Takayanagi and T. Kishimoto, *ibid.* **9**, 578 (1953); K. Takayanagi, J. Phys. Soc. Japan **14**, 75 (1959).

²⁰ A. F. Devonshire, Proc. Roy. Soc. (London) **A158**, 269 (1937).
²¹ K. Takayanagi and Y. Miamoto, Sci. Rept. Saitama University AIII, 101 (1959).

²² R. E. Turner and D. Rapp, J. Chem. Phys. **35**, 1076 (1961). The algebraic error contained in this paper is such that one should not introduce the factor m^* , but retain v^* . Thus only the modifications (i) and (iii) should be retained in that paper. Thus as $E_0 \gg e$, the probability calculated with a Morse potential goes asymptotically to the probability with a simple exponential potential. The numerical changes in Table I are completely negligible.

²³ R. A. Allen and P. Feuer, J. Chem. Phys. **40**, 2810 (1964). (preceding paper).

¹⁵ I am indebted to K. Takayanagi for the clear enunciation of this proof when $A \neq 0$ in his recent review article on energy transfer (not yet published).

¹⁶ D. Rapp, "Vibrational Energy Transfer in Quantum and Classical Mechanics," LMSC Rept. 6-90-61-14 (1961), Lockheed Missiles & Space Company, Palo Alto, California.

¹⁷ K. Takayanagi, "Vibrational and Rotational Transitions in Molecular Collisions" (review paper to be published, Department of Physics, Saitama University, Japan).

¹⁸ D. M. Gilbey, Phys. Chem. Solids **23**, 1453 (1962).

velocities where the transition probabilities can be large even though $|Y| \ll L$, one cannot use the perturbation approximation.²⁴

APPENDIX. WKB CLASSICAL LIMIT FOR THE SOLUTIONS OF EQ. (14)

Equation (23) is a strictly wave-mechanical result. The only limitation on this calculation is that the vibrational amplitude of B-C must be small compared to the range of intermolecular forces L and the transition probability must be small. It is interesting to consider whether the semiclassical result can be obtained directly from Eq. (23) by use of the WKB expressions for the F_i . In order to do this, we require the appro-

priate expressions for the solutions of Eq. (14), which are

$$F_n = \left\{ \frac{k_n}{[k_n(x)]} \right\}^{\frac{1}{2}} \cos \left[\int_{a_n}^x k_n(x') dx' - \frac{\pi}{4} \right] \quad (x > a_n),$$

$$F_n = \left\{ \frac{k_n}{[k_n(x)]} \right\}^{\frac{1}{2}} \exp \left[\int_{a_n}^x k_n(x') dx' \right] \quad (x < a_n),$$

with a_n the classical turning point, and $k_n = k_n(\infty)$, corresponding to State n in Eq. (4). Rapp¹⁶ has evaluated these expressions for an exponential potential and shown that they are just the asymptotic forms of the true solution for large positive and negative $x - a$. These expressions are used in Eq. (31) of the text.

²⁴ D. Rapp and T. E. Sharp, J. Chem. Phys. **38**, 2641 (1963).