Lawrence Berkeley National Laboratory
Recent Work

Title
REFINED IMPULSE APPROXIMATION FOR THE COLLISIONAL EXCITATION OF THE CLASSICAL ANHARMONIC-OSCILLATOR

Permalink
https://escholarship.org/uc/item/1bs0r1h9

Author
Mahan, Bruce H.

Publication Date
1970-02-01

REFINED IMPULSE APPROXIMATION FOR THE COLLISIONAL EXCITATION OF THE CLASSICAL ANHARMONIC OSCILLATOR

Bruce H. Mahan

February 1970

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

Refined Impulse Approximation for the Collisional

Excitation of the Classical Anharmonic Oscillator

Bruce H. Mahan

Department of Chemistry and Inorganic Materials Research
Division of the Lawrence Radiation Laboratory,
University of California, Berkeley, California

A modification of the conventional classical

theory of vibrational-translational energy exchange

is made which leads to an expression of increased

accuracy and which has the proper behavior at high

energy. It is pointed out that the refined impulse

approximation can be used to calculate the energy

transferred to an anharmonic oscillator in configura-

tions where the potential energy curve has positive

curvature. The case in which the oscillator potential

has negative curvature is analysed, and is shown to

lead to energy exchanges which exceed the predictions

of the impulse approximation. Expressions are given

for the energy transferred in grazing collisions

which can be used to estimate total inelastic cross

sections.

The excitation of a harmonic oscillator by collision with an external free particle has been studied extensively using both classical and quantum mechanics.[1] Much less attention has been directed to the collisional excitation of anharmonic oscillators, particularly those already in a state of high excitation. The purpose of this paper is to point out an approximate solution to this problem which may be of value in understanding of the collisional dissociation of molecules, and in analysing energy partitioning in reactive collisions. In addition, an elementary modification of the conventional solution of the excitation of the harmonic oscillator is made, which leads to an expression having the correct behavior at high collision energies.

GENERAL CONSIDERATIONS

We treat the collision in one dimension of a particle A with the diatomic oscillator BC. The coordinates and geometry of the collision are shown in Fig. 1. Before beginning the mathematical manipulation, it is helpful to recognize in a qualitative physical way that a given collision is considered to be inelastic if it induces relative motion of atoms B and C. If B and C are linked by a bond of infinite rigidity, then any force exerted on B as a result of collision with A also acts with the same magnitude and direction on C. The sole consequence of the collision is then to change the velocity of the center of mass of BC, with no energy appearing as relative

translation of B and C. Since the rigidity of a molecule is quantitatively expressed by the bond force constant, molecules with large force constants are difficult to excite vibrationally.

The case in which B and C are free particles is particularly interesting since the inelasticity can be found exactly, and because the situation represents the limiting cases of vanishing molecular force constant or impulsive A-B interaction. If B and C are initially stationary in the laboratory, and A has an initial velocity v_o, then the initial velocity of B relative to the AB center of mass is $v_o M_A/(M_A + M_B)$. The collision is elastic in the AB center of mass system, so the change in the velocity of B after a head-on collision with A is just $2 v_o M_A/(M_A + M_B)$, which is also the laboratory velocity of B after the collision. Consequently, the final energy of relative motion of B and C is

$$\Delta E = \frac{1}{2} \left[M_B M_C/(M_B + M_C) \right] \left[2 M_A v_o/(M_A + M_B) \right]^2$$

If ΔE is to be expressed in terms of E_r, the energy of initial relative motion of A on the center of mass of BC, then

$$\Delta E/E_r = 4 M_A M_B M_C M/(M_A + M_B)^2 (M_B + M_C)^2 \leq 1 \qquad (1)$$

where

$$M = M_A + M_B + M_C$$

We should expect then any classical theory of vibrational excitation should approach this result in the limit of vanishing molecular force constant, or as the A-B interaction time

becomes much smaller than the vibrational period. As has been pointed out,[1] the conventional approximate treatment of vibrational excitation gives a result which does not properly converge to the impulse limit. In what follows, we shall demonstrate why this incorrect limiting behavior occurs, and show that a proper treatment leads to an expression which is correct in the impulse limit.

EXCITATION OF A HARMONIC OSCILLATOR

The derivation of the equations of motion for the one-dimensional collisional excitation of an oscillator is given in the review article of Rapp and Kassal,[1] whose notation we follow. It is necessary to repeat several steps of the well worn derivation in order to establish the nature of the modification which is required. Accordingly, we have the equations of motion

$$\mu \, \ddot{y} + \frac{\partial V}{\partial y} = 0; \quad \tilde{m} \, \ddot{x} + \frac{\partial V}{\partial x} = 0$$

where y, the oscillator coordinate, is the separation of B and C, μ is the oscillator reduced mass $M_B M_C / (M_B + M_C)$, x is the distance between A and the BC center of mass, and $\tilde{m}$ is the reduced mass of A on BC, or $M_A(M_B + M_C)/M$. The potential V is written as the sum of the term pertaining to the free oscillator and an interaction term:

$$V(x, y) = V_o(y) + V'(x,y)$$

For the harmonic oscillator V_o is replaced by $\frac{1}{2} f(y-y_o)^2$, where f is the force constant and y_o is the equilibrium separation. It is usually assumed that V' depends only on the A-B

separation, and has the form

$$V'(x - \gamma y) = A \exp[-(x - \gamma y)/L]$$

where L is a characteristic distance for the A-B interaction, and γ is $M_C/(M_B + M_C)$. Substitution into the equations of motion gives

$$\mu \ddot{y} = - f(y - y_0) - (A\gamma/L) \exp[-(x - \gamma y)/L] \qquad (2)$$

$$\tilde{m} \ddot{x} = (A/L) \exp[-x(x - \gamma y)/L] \qquad (3)$$

In the conventional approximate treatment, it is assumed that the displacement of the oscillator from its equilibrium position is very small during the duration of the collision, and consequently that y can be set equal to y_0 in the exponent of Eqs. (2) and (3) to give

$$\mu \ddot{y} + f(y - y_0) = -(A'\gamma/L) \exp(-x/L) \qquad (4)$$

$$\tilde{m} \ddot{x} = (A'/L) \exp(-x/L) \qquad (5)$$

where

$$A' = A \exp(\gamma y_0/L)$$

The solution of the second of these equations gives x(t), which is then substituted into Eq. (4) to define a driven oscillator problem. Application of Green's method then gives the well-known solution for the change in the relative velocity of B and C. However, it is important to notice that the procedure of setting y equal to y_0 or to any constant in the exponential terms is equivalent to making the impulse approximation. This becomes clear if we note that for a freely vibrating oscillator we have

$$y = y_0 + B \sin(\omega t + \delta)$$

with B nonzero. Setting y equal to a constant during the collision implies that the A-B interaction time is an interval τ short enough that

$$\omega\tau \cong \omega L/v_0 << 1$$

which is the condition for validity of the impulse approximation.

If the A-B interaction is impulsive in the first approximation, then it is not correct to retain $\tilde{m}$ as the mass term in Eq. (5). In the impulse limit, A interacts only with B, and to remain consistent, $\tilde{m}$, the reduced mass of A on BC, should be replaced by the reduced mass of A on B. This change has an important consequence. In evaluating the constant A', it is conventional to argue that at the turning point x_t in the motion of particle A, all the kinetic energy of relative motion is converted to potential energy, and consequently

$$\frac{1}{2} \tilde{m} v_0^2 = A' \exp(-x_t/L) \equiv A''$$

To remain consistent with the impulse approximation, $\tilde{m}$ in this expression should be replaced by $M_A M_B/(M_A + M_B)$, the A-B reduced mass. The conventional use of $\tilde{m}$ in this relation is equivalent to assuming that the BC bond is infinitely rigid, which is the antithesis of the impulse approximation.

Changing to the correct reduced mass makes no difference to the solution of Eq. (5), since the same mass term appears on both sides of the equation. The same is not true for Eq. (4),

however, and when the driven oscillator problem is solved
with the correct reduced mass, the result is

$$\Delta E / E_r = \frac{4 M_A M_B M_C M}{(M_A + M_B)^2 (M_B + M_C)^2} \left(\frac{\pi \omega L}{v_o}\right)^2 \operatorname{csch}^2 (\pi \omega L / v_o) \tag{6}$$

Introduction of the expansion of the hyperbolic cosecant gives

$$\Delta E / E_r = 4 (M_A M_B M_C M) / (M_A + M_B)^2 (M_B + M_C)^2 \left[1 - \sum_1^\infty \frac{2(2^{2k-1}-1)}{(2k)!} B_{2k} \left(\frac{\pi \omega L}{v_o}\right)^{2k}\right] \tag{7}$$

where B_{2k} are the Bernouli numbers. This result shows that
the modified solution converges properly to the impulse approxi-
mation in the limit as $\omega L / v_o$ approaches zero.

It is of interest to note that in their extensive numerical
investigation of the vibrational excitation problem, Kelley
and Wolfsberg[2] found that ΔE_{ap}, the energy change calculated from
the conventional approximation, exceeded the exact energy
change ΔE calculated numerically. Rapp and Kassal[1] give the
approximate relation between ΔE_{ap} and ΔE in the form

$$\Delta E_{ap} / \Delta E \equiv R = \exp[1.685 \, m]$$

where

$$m = M_A M_C / M_B M$$

This expression is most accurate when m is small, which occurs
when M_A or M_C is much less than M_B. The ratio of ΔE_{ap} to
the energy change ΔE_{RIA} calculated by the refined impulse
approximation proposed in this paper (Eq. 6) is

$$\Delta E_{ap}/\Delta E_{RIA} \equiv R' = (M_A + M_B)^2 (M_B + M_C)^2 / M_B^2 M^2$$

When the mass of particle A is relatively small, these two ratios become approximately

$$R \cong 1 + 1.685 \, M_A M_C / [M_B(M_B + M_C)]$$

$$R' \cong 1 + 2 \, M_A M_C / [M_B(M_B + M_C)]$$

When the mass of C is small compared to all others, M_A replaces M_C in the denominators of the second terms in these expressions. The similarity between these two ratios shows that the refined impulse approximation given in this paper is close to the exact result, particularly when the mass of A or C is small compared to that of B. Apparently the failure of the approximate treatment to include energy conservation is not as serious a defect as has been thought.

EXCITATION OF AN ANHARMONIC OSCILLATOR

Once it is recognized that Eq. (6) is a first order refinement of the impulse approximation, a possible extension to the excitation of an anharmonic oscillator becomes clear. While the restoring force for an anharmonic oscillator is a nonlinear function of displacement, it is possible to linearize it approximately by expanding the force $F(y)$ about its value F_a at a particular extension y_a. Thus we can write

$$F(y) \cong F_a + \left(\frac{\partial F}{\partial y}\right)_{y_a} (y - y_a)$$

$$\frac{\partial V_o(y)}{\partial y} \cong - F_a + \left(\frac{\partial^2 V_o}{\partial y^2}\right)_{y_a} (y - y_a)$$

We can use this expression in place of the oscillator restoring force term in Eq. (4) to get

$$\mu \ddot{y} + \left(\frac{\partial^2 V_o}{\partial y^2}\right)_{y_a} (y - y_a) = F_a - (A'\gamma/L) \exp(-x/L) \quad (8)$$

Thus the fact that the collision occurs nearly impulsively allows us to assume that y is always near y_a during the collision, and thereby to reduce the situation approximately to the linear driven oscillator problem. We can conclude that for an anharmonic oscillator, the quantity ω^2 can be regarded as a function of the oscillator coordinate, and Eq. (6) used to calculate the energy transfer to anharmonic oscillators in particular configurations.

It should be noted that a highly excited anharmonic oscillator will spend much of the time in an extended state where y_a exceeds the equilibrium internuclear separation. In such regions the curvature of the oscillator will be smaller than it is near y_o, and in fact will pass through zero and become negative. For example, the curvature of the outer wall of the Morse potential becomes negative when the potential energy exceeds one quarter of the dissociation energy. Thus it is important to consider the solution of Eq. (8) when the potential curvature is negative. We write

$$\ddot{y} - \lambda^2(y - y_a) = F_a/\mu - (A'\gamma/\mu L)\ \exp(-x/L) \qquad (9)$$

where λ^2, a positive constant, is the negative curvature of
the potential divided by the reduced mass, and

$$A' = A\ \exp[-\gamma(y_a - y_o)/L]$$

The solutions to the homogeneous equation are easily
found to be $\sinh\lambda t$ and $\cosh\lambda t$. From these it is possible to
construct[3] the Green's function

$$G(t,s) = \lambda^{-1}\ \sinh\lambda(t-s) \qquad\qquad s < t$$

which satisfies the homogeneous equation, vanishes and has
unit derivative when s equals t. Thus the general solution
to the driven oscillator of negative curvature is

$$y(t) = y_a\ \cosh\lambda t + (\dot{y}_a/\lambda)\ \sinh\lambda t + \frac{1}{\mu}\int_a^t G(t,s)F(s)ds \qquad (10)$$

where $F(s)$ is the time dependent driving force on the oscillator.
For simplicity, we assume $\dot{y}_a$ is zero. In addition, we will
ignore the effect of the oscillator restoring force F_a in the
inhomogeneous term of Eq. (9) since it represents the intrinsic
motion of the oscillator itself, and we wish to calculate only
the effect of the collision on the oscillator. We expand
the hyperbolic sine which occurs in the Green's function,
and restrict the external driving forces to those which are
even functions of time. This gives us

$$y(t) = y_a \cosh\lambda t + (\mu\lambda)^{-1} \sinh\lambda t \int_a^t F(s) \cosh\lambda s \, ds \quad (11)$$

Comparison with Eq. (10) shows that as t approaches infinity, the oscillator velocity acquired as a result of the collision is

$$\dot{y}(\infty) = \mu^{-1} \int_{-\infty}^{\infty} F(s) \cosh\lambda s \, ds$$

and thus the energy increase of the oscillator is

$$\Delta E = (2\mu)^{-1} \left[\int_{-\infty}^{\infty} F(t) \cosh\lambda t \, dt \right]^2 \quad (12)$$

Equation (12) is very similar to the expression which gives the energy transferred to a harmonic oscillator of positive curvature, which involves the cosine transform of the driving force. In fact, since $\cos(ix)$ equals $\cosh x$, the two expressions could be interconverted merely by changing the sign of the curvature of the potential.

For the exponential repulsive potential between particles A and B, the time dependent force[1] is

$$F(t) = \frac{1}{2} \left[M_A M_B / (M_A + M_B) \right] (v_o^2 \gamma / L) \operatorname{sech}^2(v_o t / 2L)$$

Substitution in Eq. (12) leads to a known integral, and after some manipulation we find

$$\Delta E / E_r = \left[4 M_A M_B M_C M / (M_A + M_B)^2 (M_B + M_C)^2 \right] \left[(\pi\lambda L / v_o) \operatorname{cosec}(\pi\lambda L / v_o) \right]^2 \quad (13)$$

$$= \frac{4 M_A M_B M_C M}{(M_A + M_B)^2 (M_B + M_C)^2} \left[1 + \sum_1^{\infty} \frac{2(2^{2k-1} - 1)}{(2k)!} |B_{2k}| (\pi\lambda L / v_o)^{2k} \right]^2 \quad (14)$$

where we must have

$$\lambda L/v_o < 1$$

in both Eqs. (13) and (14).

We see that the energy transferred to an oscillator of negative curvature exceeds the impulse value by an amount which increases as the magnitude of the curvature increases. This result is physically reasonable, since any displacement of one atom of an oscillator with negative curvature of the potential induces a force on the other atom which is in the direction opposite to the displacement, thereby exciting relative motion of the atoms. A somewhat remarkable consequence of the same argument is that the energy transfer increases as the duration of the collision L/v_o increases, as Eq. 14 shows to be true.

Although Eq. (13) is limited to near impulse conditions, its qualitative implications for kinetic processes are very interesting. It seems clear that energy transfer to and from a highly vibrating oscillator can be even more facile than if the particle of the oscillator were not bound at all. In this light, it is easier to understand the fairly large amounts of energy which have been found to be removed by collisions from molecules undergoing unimolecular decomposition after chemical activation.[4] Also, in the area of atom transfer reactions of the type

$$A + BC \rightarrow AB + C$$
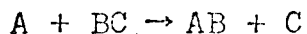
it is of interest to estimate the amount of vibrational energy
which is induced in AB by recoil of atom C. It is now clear
that if this recoil occurs when the AB bond is sufficiently
extended to be in a region of negative curvature, large amounts
of the B-C recoil energy will be incorporated as internal
energy of the new molecule.

ENERGY TRANSFER IN GRAZING COLLISIONS

Since it is clear that if the relative velocity of
collision is large, and the potential curvature small or nega-
tive, the energy transferred to vibrational motion can be large,
it is of interest to examine the energy transferred in grazing
collisions. The coordinates and collisional trajectory appro-
priate for this situation are shown in Fig. 2. It is simplest
to take an "impact parameter" b measured between the centers
of mass of A and B, and assume that A moves with a constant
velocity v_o. The velocity change of B is to be calculated from
the refined impulse approximation. To do this, one must first
recognize that since B is stationary, the force on B parallel
to the trajectory of A is equal and opposite on the incoming
and outgoing legs of the trajectory, and thus does not contribute
to a change in the velocity of B. The A-B force component
perpendicular to trajectory does change the velocity of B,
and contributes both to vibrational and rotational excitation,
depending on the orientation of BC. If the A-B potential is
of the form

$$V_{AB} = A \; e^{-r/L}$$

where r is the A-B separation, then the force which contributes to vibrational excitation is

$$F_{vib} = (\cos\delta)(b/r)(A/L) \; e^{-r/L} \qquad (15)$$

The equation for the trajectory is

$$r = (b^2 + v_o^2 t^2)^{1/2} \qquad (16)$$

We assume first that the oscillator has positive curvature. Then, since the energy transferred to vibration is the absolute square of the Fourier transform of the appropriate force,[1] divided by 2μ, we have

$$\Delta E_v = (2\mu)^{-1}(A/L)^2 \cos^2\delta \left| \int_{-\infty}^{\infty} \exp(i\omega t) \; \exp\left\{-\left[t^2 + (b/v_o)^2\right]^{1/2}\right\} dt \right|^2$$

The transform is known,[6] and the result is

$$\Delta E_v = 2\mu^{-1}(A/L)^2(\cos^2\delta)(b/L)^2 \left[(v/L)^2 + \omega^2\right]^{-1} K_1^2\left[(b/L)(1+\omega^2 L^2/v_o^2)\right] \qquad (17)$$

where K_1 is the first order modified Bessel function. If we make use of the asymptotic expression for the Bessel function valid at large values of the argument, we get after some reduction

$$\Delta E_v = \pi\mu^{-1}A^2(\cos^2\delta)(b/L)v_o^{-2}\exp\left[-(2b/L)(1+L^2\omega^2/v_o^2)^{1/2}\right] \qquad (18)$$

This result shows clearly that the vibrational excitation decreases as the impact parameter increases, as well as when the parameter $L\omega/v_o$ increases. Unlike the head-on collision case, the energy transferred depends explicitly on the pre-exponential factor in the A-B potential.

For an oscillator of negative curvature λ^2, the appropriate expression for the vibrational excitation is

$$\Delta E_v = (2\mu)^{-1}(A/L)^2(\cos^2\delta)\left[\int_{-\infty}^{\infty}e^{-r/L}\cosh\lambda t\ dt\right]^2 \tag{19}$$

with r given as a function of time by Eq. (16). This integral does not appear to be known. However, most of the contribution to the integral comes from values of r near b, and accordingly we write

$$r = b(1 + v_o^2t^2/b^2)^{1/2} \cong b(1 + v_o^2t^2/2b^2)$$

and use this in the exponential term of Eq. (19). The result is

$$\Delta E_v \cong \pi(4\mu)^{-1} A^2(\cos^2\delta)(b/L)v_o^2 \exp\left[-(2b/L)(1 - \lambda^2L^2/2v_o^2)\right] \tag{20}$$

It is clear that this expression is closely related to Eq. (18). However, the energy transferred in the negative curvature case increases with $\lambda L/v_o$, as was found to be true for head-on collisions. Both Eqs. (18) and (20) can be used to find the maximum impact parameter and therefore the cross section for

a vibrational energy excitation of magnitude substantially

smaller than the initial relative kinetic energy.

References

1. D. Rapp and T. Kassal, Chem. Rev., 69, 61 (1969).

2. J. D. Kelley and M. Wolfsberg, J. Chem. Phys. 44, 324 (1966).

3. H. Margenan and G. M. Murphy, "The Mathermatics of Physics and Chemistry," Van Nostrand, Princeton, N.J., 1943.

4. R. E. Harrington, B. S. Rabinovitch, and M. R. Hoare, J. Chem. Phys. 33, 744 (1960).

5. G. H. Kohlmaier and B. S. Rabinovitch, J. Chem. Phys. 38, 1692, 1709 (1963); 39, 490 (1963).

6. G. A. Campbell and R. M. Foster, Fourier Integrals for Practical Applications, Van Nostrand, Princeton, N.J., 1948.

Figure 1. Coordinates used in the treatment of a one-dimensional treatment of the collision of an atom A with an oscillator BC.
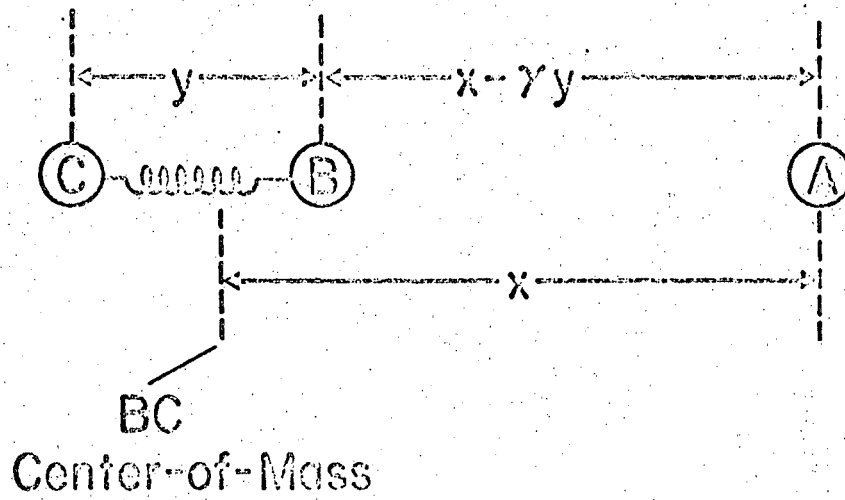
Figure 2. Coordinates and geometry of a grazing collision. The atoms
A and B lie in the plane of the collision. The angle
lies between the BC internuclear line and the line perpendicular
to the trajectory. The distance of closest approach is taken
to be equal to the impact parameter b between A and B.