

# Collisionally Induced Vibrational Energy Transfer

[Draft]

David F. Hakala

Rensselaer Polytechnic Institute

December 1974

## INTRODUCTION

Suppose we are looking at a system consisting of an oscillator AB and collision partner C. The oscillator may in general be diatomic or polyatomic and the collision partner could be monatomic, diatomic, or polyatomic. At infinite separation between AB and C the interparticle forces are assumed to go to zero, and the Hamiltonian for the system can be expressed as

$$(1) H^0 = T_{AB} + T_C + V_{AB}^{int} + V_C^{int}$$

where  $T_{AB} = -\frac{\hbar^2}{2\mu_{AB}} \nabla_{AB}^2$  is the kinetic energy operator for AB.

$T_C = -\frac{\hbar^2}{2\mu_C} \nabla_C^2$  is the kinetic energy operator for C.

$V_{AB}^{int}$  = internal potential energy operator for AB.

And  $V_C^{int}$  = internal potential energy operator for C.

Suppose that we allow  <sup>$\mu$</sup>  AB and C to approach each other to a point where the intermolecular forces are no longer negligible. We can represent this energy interaction operator by  $H'$ , and must include this term in our Hamiltonian. The collision process occurs, and as the particles recede  $H' \rightarrow 0$ , leaving us with our pre-collision form of the Hamiltonian. This problem seems ideally suited for treatment by time-dependent perturbation methods, and this will be done now.

## TIME DEPENDENT EQUATIONS

The time-dependence of the Schrödinger equation can be expressed

by

$$i\hbar\dot{\Psi} = H\Psi$$

where  $\Psi$  is the total, time-dependent wave function and  $H$  is the total, time-dependent Hamiltonian. We can express  $H$  as the sum of a time-independent and time dependent term

$$H = H^0 + H'$$

where  $H'$  will be called the time-dependent perturbation. The Schrodinger equation can now be written as

$$i\hbar\dot{\Psi} = (H^0 + H')\Psi.$$

We can express the wave function  $\Psi$  as an expansion in the time-independent wave functions  $\phi_n$  which are solutions to the equation  $H^0\phi_n = E_n\phi_n$ , as follows:

$$\Psi = \sum_n C_n(t)\phi_n e^{-\frac{iE_n t}{\hbar}}$$

and the time dependence is carried in the expansion coefficients  $C_n(t)$ .

Furthermore, we then have

$$\dot{\Psi} = -\frac{i}{\hbar} \sum_n C_n(t)\phi_n e^{-iE_n t/\hbar} E_n + \sum_n \dot{C}_n(t)\phi_n e^{-iE_n t/\hbar}$$

Substituting into the time dependent Schrödinger equation we see the following

$$\sum_n C_n(t)E_n\phi_n e^{-iE_n t/\hbar} + i\hbar \sum_n \dot{C}_n(t)\phi_n e^{-iE_n t/\hbar} = \sum_n C_n(t)E_n\phi_n e^{-iE_n t/\hbar} + \sum_n C_n(t)H'\phi_n e^{-iE_n t/\hbar}$$

or

$$i\hbar \sum_n \dot{C}_n(t)\phi_n e^{-iE_n t/\hbar} = \sum_n C_n(t)H'\phi_n e^{-iE_n t/\hbar}$$

suppose we define the angular frequency  $\omega_{kn}$  as

$$\omega_{kn} = \frac{E_k - E_n}{\hbar}$$

The complete set of  $\phi_n$ 's possesses the property of orthonormality and if we multiply both sides of the equation by  $\phi_k^*$  we obtain

$$i\hbar \dot{C}_k(t) e^{-iE_k t/\hbar} = \sum_n C_n(t) \left( \int \phi_k^* H' \phi_n d\tau \right) e^{-iE_n t/\hbar}$$

$$\dot{C}_k(t) = \frac{1}{(i\hbar)} \sum_n \left[ C_n(t) \left( \int \phi_k^* H' \phi_n d\tau \right) e^{i\omega_{kn} t} \right]$$

It should be noted that the expansion is over a complete set of eigenfunctions, where discrete they can be summed, where continuous they must be integrated.

In this above treatment integration over any continuous eigenfunction necessary to insure completeness of the set has been implicitly assumed.

Returning to the problem, suppose that we replace the perturbation  $H'$  by  $\lambda H'$  and express the coefficients as a power series in  $\lambda$

$$C_n(t) = \sum_{j=0}^{\infty} C_n^{(j)}(t) \lambda^j.$$

This series is assumed to be a continuous and analytic function of  $\lambda$  for  $\lambda \in (0,1)$ . We can substitute the above expression, equate like powers of  $\lambda$ , and then set  $\lambda = 1$  to obtain the following results:

$$\dot{C}_k^{(0)}(t) = 0$$

$$\dot{C}_k^{(j+1)}(t) = (i\hbar)^{-1} \sum_n \left[ \left( \int \phi_k^* H' \phi_n d\tau \right) C_n^{(j)}(t) e^{i\omega_{kn} t} \right]$$

So that we can in principle perform successive integrations to obtain approximate solutions to any desired order in the perturbation. By not doing so infinitely we introduce the first approximation to the treatment.

That  $\dot{C}_k^{(0)}$  is zero implies the  $C_k^{(0)}$ 's to be constant in time.

We shall assume the system to be in a precisely defined state initially, so

that all  $C_k^{(0)}$  are zero except for the one describing the specified state.

Integration of the first order equation gives the following result:

$$C_k^{(1)}(t) = (i\hbar)^{-1} \int_{-\infty}^t (\int \phi_k^* H'(t') \phi_m d\tau) e^{i\omega_{km} t'} dt'$$

where the wave function  $\phi_m$  describes the initial state and  $\phi_k$  the final one.

The constant of integration and limits have been chosen such that

$$C_k^{(1)}(-\infty) = 0.$$

The probability of the system being in the state  $m$  is given by  $|C_m^* C_m|$  and is initially equal to 1. The probability of the system being in the state  $k$  after a time  $t$  under the influence of the perturbation  $H'$  is given by

$$|C_k^*(t) C_k(t)|.$$

Since we have a particle colliding that was initially at  $t = -\infty$  and we are going to  $t = +\infty$ , the probability of going from an initial state  $i$  to a final state  $f$  is given by

$$P_{i,f} = |C_f(\infty)|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} [\int \phi_f^* H' \phi_i d\tau] e^{i\omega_{fi} t'} dt' \right|^2$$

This gives us the first-order perturbation result if we could find an expression for  $H'$  as a function of time.

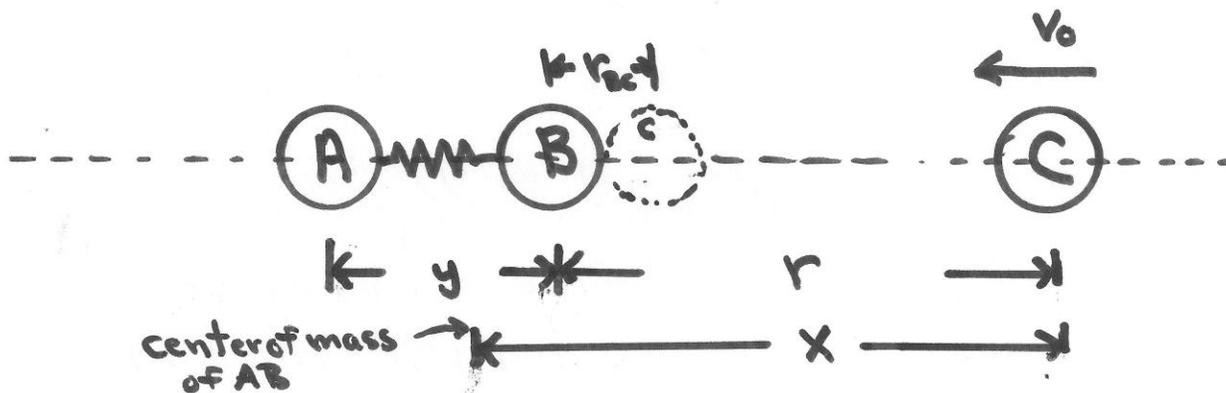
#### SEMI-CLASSICAL APPROACH

Suppose we set up our model as follows:

- (1) AB is the oscillator and has its center of mass at a fixed position.
- (2) C is approaching AB along the vibration coordinate with a relative kinetic

of approach (at infinite separation).

$$\epsilon_k = \frac{\mu v_0^2}{2}$$



The potential energy of the system is assumed to be in the form of  $V = V_0 e^{-\alpha r}$  where  $\alpha$  is some force constant and  $r$  is the distance between AB and C. This distance  $r$  will be given as

$$r = x - \left(\frac{M_A}{M_A + M_B}\right)y$$

for C colliding with B (and

$$r = x - \left(\frac{M_B}{M_A + M_B}\right)y$$

for C colliding with A). Let  $V_0 = 1$  and we can write

$$V(x, y) = \exp\{-\alpha[x - (M_A/M_A + M_B)y]\}$$

At the distance of closest approach ( $r_{BC}$ ) we have therefore

$$V(x_0, y_0) = \epsilon_k = \exp\{-\alpha r_{BC}\}$$

$$r_{BC} \approx x_0 - \left(\frac{M_A}{M_A + M_B}\right)y_0$$

where  $y_0$  = equilibrium value of the harmonic oscillator coordinate  $y$ .

We can rewrite the potential energy in the following way:

$$\begin{aligned} V(x,y) &= \epsilon_k \exp\{-\alpha[x - (\frac{M_A}{M_A + M_B})y - r_{BC}]\} \\ &= \epsilon_k \exp\{-\alpha[(x - x_0) - (y - y_0)(\frac{M_A}{M_A + M_B})]\} \end{aligned}$$

$$\text{or } V(X,Y) = \epsilon_k e^{-\alpha X} e^{\alpha Y (M_A / (M_A + M_B))}$$

where  $X = x - x_0$ ,  $Y = y - y_0$

$$\therefore V(X,Y) = V(X)V(Y)$$

Suppose that  $V(Y) \approx 1$  in order to assign a collision trajectory.

$$V(X,Y) \approx V(X) = \epsilon_k e^{-\alpha X}$$

The total energy of the system (discounting internal energy) is

$$\epsilon_k = V(X) + \frac{\mu v(X)^2}{2}$$

where  $v(X) = \frac{dX}{dt}$ . We can rearrange the above equation to give the following

$$\int_{x_0}^{x_t} \left[ \frac{2\epsilon_k}{\mu} (1 - e^{-\alpha X}) \right]^{1/2} dX = \int_0^t dt.$$

The solution to position as a function of time is implicit in the relation:

$$e^{-\alpha X} = \operatorname{sech}^2\left(\frac{\alpha v_0 t}{2}\right)$$

which results on integration of the above equation. Since the potential



does not depend strongly on  $Y$  (that is to say  $\alpha Y \ll 1$ ) we can write

$$V(Y) = e^{\alpha Y (M_A/M_A + M_B)} \approx \left\{ 1 + \left( \frac{M_A}{M_A + M_B} \right) \alpha Y \right\}.$$

The potential  $V(X,Y)$  can now be written in the form  $V(Y,t)$  as follows:

$$V(Y,t) = \epsilon_k \left\{ 1 + \alpha Y \left( \frac{M_A}{M_A + M_B} \right) \right\} \operatorname{sech}^2 \left( \frac{\alpha v_0 t}{2} \right)$$

This expression gives us the perturbation energy as a function of time,  $t$ , and displacement from the oscillators equilibrium position  $Y$ . If our total wave function is separable into a product of electronic, vibrational, translational, and rotational wavefunctions

$$\Psi = \phi_{\text{elect}} \phi_{\text{vib}} \phi_{\text{rot}} \phi_{\text{trans}}$$

then (assuming they are properly normalized) all will factor out and integrate to unity with the exception of the vibrational wave function, which can be expressed as a function of  $Y$ . The matrix element can be factored into a time dependent and time independent part as follows:

$$H_{if}^{\dagger}(t) = F(t) \int_0^{\infty} \phi_f^*(Y) Y \phi_i(Y) dY$$

where  $F(t) = \partial/\partial Y \{V(Y,t)\}$

$$= \alpha \epsilon_k \left( \frac{M_A}{M_A + M_B} \right) \operatorname{sech}^2 \left( \frac{\alpha v_0 t}{2} \right).$$

From our perturbation theory result we can write for our probability of transition

$$P_{i,f} = \frac{\alpha^2 \epsilon_k^2}{\hbar^2} \left( \frac{M_A}{M_A + M_B} \right)^2 \left| \int_0^{\infty} \phi_f^* Y \phi_i dY \right|^2 \left| \int_{-\infty}^{+\infty} \operatorname{sech}^2 \left( \frac{\alpha v_0 t}{2} \right) e^{i\omega_{fi} t} dt \right|^2$$

The time integral squared has the value of

$$\frac{16\omega_{fi}^2}{\alpha^2 v_0^2} \operatorname{cosech}^2\left(\frac{\pi\omega_{fi}}{\alpha v_0}\right)$$

so that we can write the relation

$$p_{i,f} = \frac{4\omega_{fi}^2 \mu^2}{\alpha^2 \hbar^2} \left(\frac{M_A}{M_A + M_B}\right)^2 \operatorname{cosech}^2\left(\frac{\pi\omega_{fi}}{\alpha v_0}\right) |Y_{if}|^2$$

where  $|Y_{if}|^2$  is the square of the matrix element inducing the harmonic oscillator transitions.

The  $|Y_{if}|^2$  are well known and have the following properties:

$$|Y_{n,n+1}|^2 = \left(\frac{n+1}{2\beta}\right)$$

$$|Y_{n,n-1}|^2 = \frac{n}{2\beta}$$

where  $\beta = \frac{2\pi\mu\omega_{if}}{\hbar}$ .

$$|Y_{if}|^2 = 0 \text{ if } \Delta n \neq \pm 1$$

The above equations define our transition probability per collision for a given  $\epsilon_k = 1/2(\mu v_0^2)$ .

The observed probability will be that integrated over a Maxwell-Boltzmann distribution of energies. Since we solved the mechanics in one dimension we should use the one dimensional distribution for consistency. This will be given by

$$dn = n \left( \frac{\mu}{2\pi kT} \right)^{1/2} e^{-\frac{\mu v_0^2}{2kT}} dv_0.$$

In our result for transition probability we also used the term  $v_0$ , but this should actually be called  $v_a$ , which is the velocity corresponding to the average of the kinetic energies of approach and recession. This introduces collisional symmetrization into the trajectory calculation which was previously ignored. The velocities  $v_0$  and  $v_a$  are related by the equations

$$\mu v_0^2 = \mu v_a^2 - h\omega \quad \text{for deactivation}$$

and 
$$\mu v_0^2 = \mu v_a^2 + h\omega \quad \text{for activation.}$$

We will also make the further simplification that since  $\pi\omega \gg \alpha v_a$  for an adiabatic collision we can make the simplification

$$\text{cosech}(x) \approx 2\exp(-x).$$

The velocity distribution is integrated from 0 to  $\infty$  since we are interested only in those velocities moving toward our target. If we define

$$A = \frac{16\omega^2 \mu^2}{\alpha^2 n^2} \left( \frac{M_A}{M_A + M_B} \right)^2 |Y_{if}|^2 \left( \frac{\mu}{2\pi kT} \right)^{1/2},$$

then the averaged transition probability is given by

$$\bar{p}_{if} = A \int_0^\infty e^{-\frac{2\pi\omega}{\alpha v_a} e^{-\frac{\mu v_0^2}{2kT}}} dv_0$$

By using our relations between  $v_a$  and  $v_0$  we can rewrite this as

$$\bar{p}_{if} = Ae^{\frac{\pm \hbar \omega}{2kT}} \int_0^{\infty} \exp\left[-\frac{2\pi\omega}{\alpha v_a} - \frac{\mu v_a^2}{2kT}\right] dv_a$$

where the + sign refers to deactivation and the - sign to activation. The integrand is a sharply peaked function of  $v_a$  and will give a significant contribution to the transition probability only in the region of some critical velocity  $v_a^*$ . This velocity  $v_a^*$  can be found by differentiating the integrand and setting it equal to zero, giving

$$v_a^* = \left(\frac{2\pi\omega kT}{\alpha\mu}\right)^{1/3}.$$

If we expand the term in the exponent about  $v_a^*$  we can make the approximation,

$$-\left(\frac{2\pi\omega}{\alpha v_a}\right) - \left(\frac{\mu v_a^2}{2kT}\right) \approx -3\left\{\frac{\pi^2 \omega^2}{2\alpha^2 kT}\right\}^{1/3} - \frac{3}{2} \frac{\mu}{kT} (v_a - v_a^*)^2.$$

By making the definition

$$B = Ae^{\frac{\pm \hbar \omega}{2kT}} \exp\left\{-3\left\{\frac{\pi^2 \omega^2}{2\alpha^2 kT}\right\}^{1/3}\right\}$$

we can write

$$\bar{p}_{if} = B \int_0^{\infty} \exp\left\{-\frac{3}{2} \frac{\mu}{kT} (v_a - v_a^*)^2\right\} dv_a$$

which can be readily evaluated to give the result

$$\bar{p}_{if} = \frac{B}{\alpha} \left(\frac{2\pi kT}{3\mu}\right)^{1/2}.$$

Suppose we note initial and final states by the vibrational quantum number  $n$  and restrict ourselves to transitions such that  $\Delta n = \pm 1$ . The relations can fall out immediately that

$$\bar{p}_{n,n-1} = \bar{p}_{n-1,n} e^{\frac{\pm \hbar \omega}{kT}}$$

and that

$$\bar{p}_{n,n-1} = n p_{1,0}$$

#### Modifications to Treatment

There are several modifications that can be made to this treatment that will give some interesting results.

If one does want to look at multiquantum transitions this can be done readily by keeping higher order terms in the expansion of

$$e^{CY} = 1 + CY + \frac{(CY)^2}{2!} + \dots$$

In looking at the first term the orthogonal vibrational wavefunctions vanish. The second term gives a non-vanishing matrix element for wavefunctions whose vibrational quantum number differs by 1, the third term for those with  $\Delta n = \pm 2$ , etc. The probabilities drop off rapidly with increasing  $\Delta n$  as expected. Another alternative is to use anharmonic wavefunctions and compute the matrix element for the Y term, this can give non-vanishing probabilities for  $\Delta n = \pm 2$  and greater depending on how far one carries the anharmonicity.

If one wishes to deal with complex vibrational energy transfer as illustrated below,



then we can look at this as a simultaneous deactivation of mode 1 and activation of mode 2. Since the probability of two events occurring simultaneously may be approximated as the product of probabilities for the individual events we can express this as

$$\bar{p}_{n,n-1}^{k,k+1} = \bar{p}_{n,n-1} \cdot \bar{p}_{k,k+1}$$

which will be proportional to the term

$$e^{-\frac{\hbar}{2kT}(\omega_1 - \omega_2)}$$

An identical result is obtained when we look at  $V \rightarrow V$  transfer as illustrated by

$$AB(v_1 = n) + CD(v_2 = k) \rightarrow AB(v_1 = n-1) + CD(v_2 = k+1).$$

Complex  $V \rightarrow T$  transfer as well as  $V \rightarrow V$  transfer can be expressed in terms of the probabilities of individual simple  $V \rightarrow T$  transfers.

If there is an attractive force with a potential well of depth  $\epsilon_a$  then  $e^{\epsilon_a/kT}$  is added to the velocity distribution function. This is a constant and integrates out. Such a term merely multiplies the probability given earlier. If we want to take into account collisional symmetry (that is C colliding with B instead of A, as we assumed in the trajectory calculation) we replace the ratio  $M_A/M_B$  by  $\frac{1}{2}(M_A/M_B + M_B/M_A)$  wherever it appears in the previous expressions.