INTERNAL EXCITATION IN MOLECULAR COLLISIONS[*]

by

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ABSTRACT

An analysis of molecular collisions which centers attention on internal excitation during collisions is reviewed.

In the zeroth order description no energy transfer between kinetic energy of relative motion and internal energy is allowed. The evolution of the system is then analyzed as a sequence of corrections to this description. The theory thus centres attention on the migration of energy from kinetic energy of relative motion to internal excitation and back. The collision event can involve participation of states (which are stable to zero order) where the kinetic energy has been transfered into internal energy, so that the resulting motion is a bounded relative motion of internally excited collision partners. These states have only a temporary existence, as eventually energy flows back into the relative motion.

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I. Introduction

The theoretical description of collisions between systems with internal degrees of freedom has recently received considerable attention.[1-3] The primary aim is to obtain a description of the relative motion of the collision partners which takes account of the possibility of internal excitation during the collision process. In other words one seeks an equation of motion for the degree of freedom of relative motion of the collision partners, which takes an implicit, but exact, account of the other degrees of freedom.

When only a small number of internal states should be taken into account, one can obtain a fairly explicit solution of the problem, and this is reviewed in section II. The aim here is to review the basic ideas involved and not to generate approximation schemes.

Section III introduces the same concepts from an explicitly time-dependent point of view. A general discussion of the method, which forms the background for subsequent work in this field is presented in section IV.

II. Internal Excitation

Consider the collision between a structureless particle A and a molecule B-C with one internal degree of freedom, which we describe by coordinate r . We assume that beside the ground state the molecule B-C has several low-lying excited states that are discrete (bound). In other words we assume that for low energies the motion in the r coordinate is quantized.

If h_o is the internal Hamiltonian of the molecule B-C , we can write

$$h_o \phi_n(r) = e_n \phi_n(r) \quad , \tag{1}$$

where $\phi_n(r)$ is a wave function for the n'th internal excited state, and, as usual, wave functions for different excited states are orthogonal,

$$\int \phi_m^*(r)\,\phi_n(r)\,dr = \delta_{n,m} \,. \tag{2}$$

The excited states are labelled in the order of increasing energy

$e_1 < e_2 < e_3 \ldots$.

Before the collision event A and B-C are far apart and non-interacting. The total energy, E, of the collision partners is then the sum of the internal energy of B-C and the kinetic energy of motion. If B-C is unexcited before the collision, and if the energy of the center of mass of the whole system is factored out

$$E = e_1 + \hbar^2 k_1^2/2\mu \,, \tag{3}$$

where μ is the reduced mass of the system A+BC , and $\hbar \underline{k}$ is their relative momentum.

If ρ is the distance from A to the center of mass of B-C , the kinetic energy operator, K, for the relative motion of A and B-C is

$$K = -(\hbar^2/2\mu)\,\nabla_\rho^2 \,. \tag{4}$$

The Hamiltonian, H_o, that governs the evolution of A and B-C prior to the collision is

$$H_0 = K + h_0 \quad . \tag{5}$$

During the collision A interacts with B-C , and the interaction is determined by a potential energy operator $V(r,\rho)$ so that the total Hamiltonian H that describes the collision is

$$H = H_0 + V \quad . \tag{6}$$

The wave function $\psi(r,\rho)$ that describes the course of the collision is the solution of the Schroedinger equation

$$(E - H)\psi(r,\rho) = 0 \tag{7}$$

with the given value of the energy E which is determined by the initial conditions (equation 3). This does not imply, however, that during the collision B-C remain unexcited. Due to the mutual interaction V , energy can be transfered from kinetic energy of relative motion into internal excitation of B-C .

A quantitative characterization of such a phenomena should provide a measure of the internal excitation of B-C during the collision. The simplest way of obtaining such a description is to put

$$\psi(r,\rho) = \sum_n a_n(\rho)\,\phi_n(r) \quad . \tag{8}$$

The significance of the, yet undetermined, coefficients $a_n(\rho)$ is easily seen when we compute, using equation 2.

$$\Delta\rho \int \psi^*(r,\rho)\psi(r,\rho)dr = \sum_n |a_n(\rho)|^2 \Delta\rho, \tag{9}$$

The left hand side is the quantum mechanical probability of observing the colliding systems with a relative separation of ρ to $\rho + \Delta\rho$. We can thus interpret $|a_n(\rho)|^2 \Delta\rho$ as the probability of finding the system with a separation ρ to $\rho + \Delta\rho$ when the internal state n is excited.

We shall thus refer to $a_n(\rho)$,

$$a_n(\rho) = \int \phi_n^*(r)\,\psi(r,\rho)dr \quad , \tag{10}$$

as the amplitude (strictly speaking it is the amplitude density since ρ is continuous) to find the n'th internal state of B-C excited when the relative separation of A and B-C is ρ. It should be remembered (although we have not indicated this explicitly) that $a_n(\rho)$ is a function of E.

Thus, before the collision $|a_1| = 1$ while after the collision $\int |a_n|^2 dS$ is the observed probability that B-C is permanently excited into the n'th state as a result of the collision.

The internal Hamiltonian h_o can also have a continuous spectrum which corresponds to high internal excitation of B-C when the motion in the coordinate r is no longer bounded.

If the index n, in equation 8 takes discrete values only, then the assumed solution for $\psi(r,\rho)$ is at best approximate since it takes no account of the possibility of permanent (or temporary) dissociation of B-C. We shall evaluate this approximation later.

If the total energy E is low so that $E < e_2$ we expect that after the collision $|a_n|^2 = 0$, $n \neq 1$. This need not hold however for finite values of ρ, where the kinetic energy of relative motion can be negative, in the sense that the motion in ρ can be bounded. In other words, during the collision energy in excess of $\hbar^2 k^2/2\mu$ can flow into internal excitation, with the result that A is now bound to B-C, and B-C is internally excited. Eventually energy will be transfered back from internal energy of B-C into energy of relative motion and A and B-C will start to separate from one another.

Even though B-C cannot be permanently excited, it can be temporarily excited during the collision. The resulting unstable system is similar to that normally invoked in theories of unimolecular breakdown,[4] where the delay in fragmentation is due to the time lag necessary to transfer energy from internal excitation to energy of unbounded relative motion. Similar ideas have proved fruitful in the theory of nuclear collisions (i.e. Bohr's compound nucleus). Recently it has become clear that similar phenomena play a role in electron-molecule collisions, when a molecule can temporarily bound an extra electron (which corresponds in our scheme to A) while being internally excited.[5,6]

It is also to be expected that the process of energy transfer from energy of relative motion into internal excitation and then back into energy of relative motion can take place several times in the course of a single collision.[7]

The amplitudes $a_n(\rho)$ satisfy equation 11 below which is obtained by using the assumed form for ψ in the Schroedinger equation, premultiplying by $\phi_n^*(r)$ and integrating over r ,

$$[E-K-H_{nn}(\rho)]\,a_n(\rho)=\sum_m{}'\,H_{nm}(\rho)\,a_m(\rho), \qquad (11)$$

where

$$\begin{aligned} H_{nm}(\rho) &= \int \phi_n^*(r)\,[h_0+V]\,\phi_m(r)\,dr \\ &= e_n\,\delta_{n,m}+V_{n,m}(\rho) \, . \end{aligned} \qquad (12)$$

In matrix notation

$$[(E-K)\underline{I}-\underline{H}]\,\underline{a}=0 \, , \qquad (13)$$

where $\underline{I}$ is the unit matrix $\underline{a}$ is a column vector of components a_n , and $(\underline{H})_{nm} = H_{nm}$.

Equation 13 is best solved using the partitioning technique, as is discussed in section IV. To examine the main features of the solution we shall restrict the discussion to the case when the index n assumes only two values $n = 1,2$, so that

$$[E-K-H_{22}(\rho)]\,a_2(\rho)=H_{21}(\rho)\,a_1(\rho), \qquad (14a)$$

$$[E - K - H_{11}(\rho)]\,a_1(\rho) = H_{12}(\rho)\,a_2(\rho)\;. \qquad (14b)$$

Consider the homogenous forms of these equations. For $E > e_n$, $n=1,2,\ldots$; the Hamiltonian $K + H_{nn}(\rho)$ will have a continuous spectrum which correspond to the unbounded relative motion of A and B-C in its n'th internal state. If the potential $V_{22}(\rho)$ is attractive, the Hamiltonian $K + H_{22}(\rho)$ will also have bound states $g_i(\rho)$, $i=1,2,\ldots$, of energies below e_2. These correspond to a bounded relative motion of A and the molecule B-C in its first excited state. Thus

$$[E_i - K - H_{22}(\rho)]\,g_i(\rho) = 0\,,\quad E_i < e_2 \qquad (15a)$$

and

$$[E - K - H_{nn}(\rho)]\,a_n^{(0)}(\rho) = 0\;,\quad E > e_n\,. \qquad (15b)$$

The formal solution for $a_2(\rho)$, namely[8]

$$a_2 = [E^+ - K - H_{22}(\rho)]^{-1} H_{21}(\rho)\,a_1(\rho)\;, \qquad (16)$$

can be written out explicitly using the complete set of states of $H_{22}(\rho)$ as

$$a_2(\rho) = \sum_i \frac{g_i(\rho)\int g_i^*(\rho')\,H_{21}(\rho')\,a_1(\rho')\,d\rho'}{E - E_i} \qquad (17)$$

+ Contributions from the Continum.

For $E < e_2$ the contribution from the continuum is small compared to the contribution of the bound states. As $\rho \to \infty$ the contribution from the continuum has the form[8]

$$\exp\left[-\rho\sqrt{e_2 - E}\,\right]$$

and each of the bound state wave functions is also exponentially decreasing at infinity. Thus, as expected

$$\underset{\rho \to \infty}{a_2(\rho) \to 0} \quad , E < e_2 \quad .$$

When $E \sim E_i$, the ρ dependence of $a_2(\rho)$ is essentially that of $g_i(\rho)$, so that as the total energy increases $a_2(\rho)$ gradually changes shape, tracing the successive bound states of the potential $V_{22}(\rho)$. Thus $a_2(\rho)$ can assume significant value during (ρ finite) the collision even though no permanent internal excitation can occur.

The formal solution for $a_2(\rho)$ (equation 16) is substituted in equation 14b to give

$$[E - K - H_{11}]\,a_1 = H_{12}\,[E - K - H_{22}]^{-1}\,H_{21}\,a_1 \quad . \tag{18}$$

The homogenous form of this equation has a solution for any possible E, ($E > e_1$), equation 15b. This function corresponds to a collision event subject to the Hamiltonian $K + H_{11}(\rho)$, namely a Hamiltonian that takes no account of internal excitations of B-C.

The actual solution $a_1(\rho)$ takes implicit account of the internal excitation via the added "potential"

$$H_{12}\left[E-K-H_{22}\right]^{-1}H_{21}$$

which can be written explicitly as

$$\sum_i \frac{H_{12}(\rho)\, g_i(\rho)\cdot g_i^*(\rho')\, H_{21}(\rho')}{E-E_i} + \text{continuum contribution.}$$

Since $E < e_2$ the contribution of the continuum is nonpositive definite, so that the first term is an upper bound to the true potential. We have indicated explicitly the fact that due to the presence of internally excited states this potential is, in principle, non-local. In practice it can often be approximated by a local potential.[7]

Equation 18 is now a single variable equation, and can be solved using the usual procedure of scattering theory. Thus[8]

$$a_1 = a_1^{(0)} + \left[E^{+}-K-H_{11}\right]^{-1} H_{12}\left[E-K-H_{22}\right]^{-1}H_{21}a_1 \quad (19)$$

is the integral equation that determines the form of ψ for large ρ. There are clearly two contributions to $a_1(\rho)$, namely $a_1^{(0)}$ which is the amplitude to find the system with relative separation ρ, when B-C is, and always has been, in its ground state. The second term is enhancement of this amplitude due to the possibility that B-C has previously been in an internally excited state.

The course of the collision can be followed by iterating the integral equation 19. A trial value for a_1 is used in the right hand side, a new value is computed and used as a trial value, and so on.

$a_1^{(o)}$ is a solution of a simple Schroedinger equation, with a local potential, and in the present context it is assumed known. Using $a_1^{(o)}$ as a trial value we get the following series, which we write schematically as

$$a_1 = a_1^{(o)} + G_{11} H_{12} G_{22} H_{21} a_1^{(o)} +$$

$$+ G_{11} H_{12} G_{22} H_{21} G_{11} H_{12} G_{22} H_{21} a_1^{(o)} + \cdots \tag{20}$$

where

$$G_{nn} = (E^{+} - K - H_{nn})^{-1}, \quad E^{+} = E + i\epsilon$$

and the limit $\epsilon \to + 0$ is to be taken only after all the implied integrations in equation 20 have been performed.

The above prescription of the limiting operation insures that each term behaves when $\rho \to \infty$ as an outgoing wave as is required by the physical problem. The above specification also insures that the evolution of the system is forward in time. This is explicitly demonstrated in section III, where it is shown that one can read equation 20 as if time moves from right to left, or in other words in a given term in equation 20, events to the left occur later than events which are to the right.

Successive terms of equation 20 differ by the factor $G_{11}H_{12}G_{22}H_{21}$ which corresponds to the event of excitation transfer from relative kinetic into internal energy (H_{21}) , evolution as an internally excited state (G_{22}) and the eventual transfer of excitation back to kinetic energy (H_{12}) . The last event in any term (G_{11}) corresponds to the unbounded relative motion of A and B-C in its ground state.

In the third term in equation 20 we see for the first time the process of healing, in that after the first time that B-C was excited and de-excited the systems although performing an unbounded relative motion (G_{11}) are knocked by a potential (H_{21}) back into an internally excited state, before they had time to separate completely. Higher order terms in this equation exhibit several healing processes.

We therefore expect that if we let A and B-C colide and observe the "fragmentation" of the collision complex, that the process will require some finite time since some systems will separate rapidly, having never undergone any internal excitation, some will be slightly delayed, and some, due to many healing events will be very slow in separating. A quantitative discussion of this point is given in section III.

The above discussion is subject however to a certain reservation, namely that there is no significant delay due to the potential $H_{11}(\rho)$. Such a time delay cannot be due to internal excitation, but can be due to the functional form of $H_{11}(\rho)$ itself.

In particular the centrifugal barrier may cause a delay in the events described by $a_1^{(o)}$ itself. As we shall argue below (equation 31) this feature is in fact explicitly present in our results, but may require special attention in the interpretation of experimental results.

The formal solution for a_2 in terms of $a_1^{(o)}$ can be written as

$$\left[E - K - H_{21} G_{11} H_{12}\right] a_2 = H_{21} a_1^{(o)} \quad , \qquad (21)$$

using equations 14 and 19.

The transitions $\phi_2 \rightarrow \phi_1$ and $\phi_1 \rightarrow \phi_2$ need not, in general occur at the same value of ρ . The relevant operator $H_{21}G_{11}H_{12}$ is thus non-local. It can be written explicitly as

$$\int H_{21}(\rho')\, a_1^{(o)*}(\rho'; E') \frac{dE'}{E^{+} - E'}\, a_1^{(o)}(\rho; E') H_{12}(\rho)$$

where

$$\left[E' - K - H_{11}(\rho)\right] a_1^{(o)}(\rho; E') = 0$$

Due to the continuous spectrum of the Hamiltonian $K + H_{11}$, the Green's operator G_{11} possess an imaginary part. In the present context this implies that not all the systems that undergo the transition $\phi_2 \rightarrow \phi_1$ will undergo the reverse process. The probability of being in an internally excited state is not constant in time, since the system may undergo a permanent transition to the unexcited state in that A and unexcited B-C separate without healing.

The magnitude of the imaginary part of the effective potential for a_2 is determined by the identity

$$\mathrm{Im}\,(E^{+}-K-H_{11})^{-1}=-\pi\,\delta(E-K-H_{11})\,, \qquad (22)$$

so that

$$\mathrm{Im}\,H_{21}G_{11}H_{12}= \qquad (23)$$

$$-\pi\int dE'\,H_{21}(\rho')\,a_1^{(0)*}(\rho';E')\,\delta(E-E')\,a_1^{(0)}(\rho;E')\,H_{12}(\rho)\,.$$

From equations 14 and 21 we obtain a closed solution for a_1

$$a_1=a_1^{(0)}+G_{11}H_{12}\left[E-H_{22}-H_{21}(E^{+}-K-H_{11})^{-1}H_{12}\right]^{-1}H_{21}a_1^{(0)}\,. \qquad (24)$$

In this equation the role of internally excited states is completely accounted for by the Green's operator in the square bracket.

In the neighborhood of E_i we can approximate $a_2(\rho)$, using equation 17, by

$$a_{2i}=\frac{g_i(\rho)}{E-E_i}\int g_i(\rho')\,H_{21}(\rho')\,a_1(\rho')\,d\rho'\,, \qquad (25)$$

so that

$$a_1 = a_1^{(0)} + G_{11} H_{12} \frac{g_i}{E-E_i} \int g_i(\rho') H_{21}(\rho') a_1(\rho') d\rho' \,, \tag{26}$$

which can be solved, by premultiplying by $g_i(\rho) H_{21}(\rho)$ and integrating over ρ to give

$$\int g_i(\rho) H_{21}(\rho) a_1(\rho) d\rho = \frac{(E-E_i) \int g_i(\rho) H_{21}(\rho) a_1^{(0)}(\rho) d\rho}{E-E_i-\Gamma_i(E)} \,, \tag{27}$$

where

$$\Gamma_i(E) = \langle g_i | H_{21} G_{11} H_{12} | g_i \rangle \tag{28}$$

$$= \iint d\rho\, d\rho'\, g_i^*(\rho) H_{21}(\rho) G_{11}(\rho, \rho') H_{12}(\rho') g_i(\rho') \,,$$

will pose an imaginary part. From equation 23

$$\operatorname{Im} \Gamma_i(E) = -\pi \left| \int g^*(\rho) H_{21}(\rho) a_1^{(0)}(\rho) d\rho \right|^2 \omega(E) \,, \tag{29}$$

where $\omega(E)$ is the density of states.

It is of interest to examine the behaviour of $a_1(\rho)$ for s-wave scattering. In this case there is no centrifugal barrier and one expects the phase shifts due to the potential $H_{11}(\rho)$ to be slowly varying as function of the energy. Thus for $\rho \to \infty$

$$\underset{\rho\to\infty}{a_1^{(0)}(\rho)} \to e^{i\delta}\sin(k\rho+\delta) \qquad (30)$$

From equation 26

$$a_1(\rho) = a_1^{(0)}(\rho) + \int G_{11}(\rho,\rho')H_{12}(\rho')g_i(\rho')d\rho' \times \frac{\int g_i(\rho)H_{21}(\rho)a_1^{(0)}(\rho)d\rho}{E-E_i-\Gamma_i(E)}$$

Using equation 23, 26, and 30 we have as $\rho \to \infty$

$$\begin{aligned} a_1(\rho) &= a_1^{(0)}(\rho) - e^{ik\rho}\,\frac{e^{2i\delta}\,|\mathrm{Im}\,\Gamma_i(E)|}{E-E_i-\Gamma_i(E)}\,, \\ &= e^{i(\delta+\Delta)}\sin(k\rho+\delta+\Delta)\,, \end{aligned} \qquad (31)$$

where

$$\Delta = -\mathrm{tn}^{-1}\,\mathrm{Im}\,\Gamma_i(E)/[E-E_i-\mathrm{Re}\,\Gamma_i(E)] \qquad (32)$$

is the phase shift due to the internal states.

The total phase shift is the sum of the phase shift δ, due to the potential H_{11} only plus the phase shift Δ due to the occupation of the internally excited states. Formally Δ is the phase shift due to the effective potential $H_{12}G_{22}H_{21}$ in equation 18.

The resolution of the phase shift into two contributions is just one example of the integral Hellmann-Feynman theorem. (For other applications see ref. 9). The change in the density of states in one dimensional motion due to the potential V_{11} is given by[10]

$$A^{(0)} = \frac{2}{h}\frac{d\delta}{dE} \quad . \tag{33a}$$

The actual change in the density of states is

$$A = \frac{2}{h}\frac{d(\delta+\Delta)}{dE} = A^{(0)} + \frac{2}{h}\frac{d\Delta}{dE} \quad , \tag{33b}$$

Various statistico-mechanical quantities can be defined in terms of the density of states of the system. In the dilute gas phase the lowest corrections to the isolated molecule approximation are those due to binary encounters between molecules. The change in the density of states due to these encounters is given by A(E) (equation 33b). Most statistico-mechanical expressions are linear in A ,

$$B = L\{A\} \quad ,$$

$$L\{A_1 + A_2\} = L\{A_1\} + L\{A_2\} \quad ,$$

so that

$$B = B^{(0)} + \Delta B \quad , \tag{34}$$

where $\Delta B = L\{A - A^{(0)}\}$ is due to internal excitation during the collision. As we shall show in section III equation 33 is also relevant to computing the duration of collisions.

III. The Time Evolution

At a given time the probability to observe A and B-C at a relative separation ρ, can be written as a sum of the probabilities to observe A and B-C in the n'th internal state at a relative separation ρ, (Eqation 9). The different events "B-C is in the n'th internal state" are thus mutually exclusive. In other words the reduced density matrix $\gamma(\rho,\rho')$ that determines the behaviour in the coordinate ρ is diagonal in the index n

$$\gamma(\rho,\rho') = \int \psi^*(r,\rho)\,\psi(r,\rho')\,dr \quad , \qquad (35)$$

$$= \sum_n a_n^*(\rho)\,a_n(\rho') \quad .$$

Let $U(t)$ be the evolution operator

$$U(t) = \exp(-iHt/\hbar) \quad . \qquad (36)$$

The reduced evolution operator that determines the evolution of the relative separation is defined by

$$U(\rho,\rho';t) = \int \psi^*(r,\rho)\,U(t)\,\psi(r',\rho')\,dr\,dr'$$

$$= \sum_{n,m} a_n^*(\rho)\,\langle n|U(t)|m\rangle\,a_m(\rho) \quad , \qquad (37)$$

where

$$\langle n|U(t)|m\rangle = \int \phi_n^*(r)\langle r|U(t)|r'\rangle \phi_m(r')\,dr\,dr' .$$

$U(\rho, \rho'; t)$ is the amplitude that, if the system were observed with relative separation ρ', it will be found at a time t with relative separation ρ. This expression is not diagonal in the index of internal states since for a finite time t transitions between internal states are possible. The matrix elements $\langle n|U(t)|m\rangle$ are, of course, operators on ρ.

The evolution operator that determines the forward evolution in time $U_+(t)$ is defined by

$$U_+(t) = \Theta(t)U(t) \tag{38}$$

where $\Theta(t)$ is the step function that vanishes for negative values of its argument, and is unity otherwise. It then follows that $U_+(t)$ can be written as the Fourier transform of the convolution of the Fourier transforms of $U(t)$ and the step function.[10]

$$U_+(t) = (2\pi i)^{-1} \int \exp(-Et)(E^+-H)^{-1}dE , \quad E^+ = E + i\epsilon \tag{39}$$

where $(E^+-H)^{-1}$ is the convolution of $(E-H)^{-1}$ and $(E^+)^{-1}$. If we denote $G^+ = (E^+-H)^{-1}$ so that

$$(E^+-H)\, G^+ = I \tag{40}$$

we can evaluate the matrix elements $\langle n|G^+|m\rangle$. In the two state approximation we find, by taking the n,m expectation values of both sides of equation 40,

$$[E^{+}-K-H_{11}(\rho)]\langle 1|G^{+}|1\rangle = 1 + H_{12}(\rho)\langle 2|G^{+}|1\rangle \qquad (41a)$$

$$[E^{+}-K-H_{22}(\rho)]\langle 2|G^{+}|2\rangle = 1 + H_{21}(\rho)\langle 1|G^{+}|2\rangle \qquad (41b)$$

$$[E^{+}-K-H_{11}(\rho)]\langle 1|G^{+}|2\rangle = H_{12}(\rho)\langle 2|G^{+}|2\rangle \qquad (41c)$$

so that, for example

$$\langle 2|G^{+}|2\rangle = [E^{+}-K-H_{22}-H_{21}G_{11}H_{12}]^{-1} \quad , \qquad (42)$$

where

$$G_{11} = (E^{+}-K-H_{11})^{-1} \quad .$$

Equation 24 can now be written as

$$a_1 = a_1^{(0)} + G_{11}H_{12}\langle 2|G^{+}|2\rangle H_{21}a_1^{(0)} \quad , \qquad (43)$$

and the iterated form, equation 20 corresponds to the iteration of $\langle 2|G^{+}|2\rangle$ in terms of G_{22}

$$G_{22} = (E^{+}-K-H_{22})^{-1} \quad .$$

The iteration is thus inherently time ordered.

To incorporate explicitly the initial conditions before the collision it is convenient to introduce the Møller wave operator Ω .[11]

Consider the evolution of the intial, pre-collision, state of the system, in the absence of the mutual interaction between A and B-C. Let $\eta(t)$ be the state of this hypothetical system at time t . The actual state of the system $\psi(t)$ is then given by

$$\psi(t) = \Omega\eta(t) \quad . \tag{44}$$

If $\eta(t)$ is not a sharp energy state it can be written as

$$\eta(t) = \int f(E)\exp(-iEt/\hbar)\phi(E)dE \quad , \tag{45}$$

where $\phi(E)$ is an eigenstate of H_o

$$(E-H_o)\phi(E) = 0 \quad , \quad \phi(E) = \exp(ik_1\rho)\phi_1(r)$$

so that it corresponds to an initial state for a collision with a well defined energy. In practice the energy is not well defined but has a spread of values. The density function f(E) is defined so that f(E)dE is the probability of an initial state to have an energy between E and E+dE . The actual initial state in a collision with f(E) as the energy density is

$$\int f(E)\phi(E)dE \quad .$$

The Møller wave operator, Ω , is linear in the sense that[11]

$$\psi(t) = \int f(E) \exp(-iEt/\hbar) \Omega \phi(E) dE \quad . \tag{47}$$

$\Omega\phi(E)$ is thus an eigenstate of H that evolved from the state $\phi(E)$ of the same total energy E .

It can be shown that an operator definition for Ω is given by[11]

$$(E^{+} - H)^{-1} = \Omega (E^{+} - H_0)^{-1} \quad . \tag{48}$$

The matrix elements of the wave operator have been previously determined when we solved for ψ in section II. Thus, from equations 8, 44 and 45

$$\langle 1 | \psi(t) \rangle = \int f(E) \exp(-iEt/\hbar)\, a_1\, dE \quad . \tag{49}$$

There are two sources of energy variation of the integrand. f(E) which is the experimental energy resolution of the initial state (equation 45) and $a_1(\rho)$ (equation 43). $a_1(\rho)$ can be resolved into $a_1^{(c)}(\rho)$ which (at least for an s-wave) is slowly varying and a component due to internal excitation which can, in some energy interval, vary rapidly, as function of E .

In the same fashion

$$\langle 2 | \psi(t) \rangle = \int f(E) \exp(-iEt/\hbar)\, a_2\, dE \quad . \tag{50}$$

As $\rho \rightarrow \infty$ the second amplitude decreases exponentially ($E < \epsilon_2$), and the amplitude observe the system with a relative separation ρ ($\rho \rightarrow \infty$), at time t is given by $\langle 1|\Psi(t)\rangle$.

For an s-wave, when only one vibrational state $g_i(\rho)$ is internally excited, we have using equations 31 and 49

$$\langle 1|\Psi(t)\rangle = \int f(E)\exp(-iEt/\hbar)\, e^{i\delta(E)} \sin[k\rho+\delta(E)]\,dE$$

$$-\int f(E)\exp[i(k\rho-Et/\hbar)]\, e^{2i\delta(E)} \sin\Delta(E)\,dE. \quad (51)$$

The first integral, $I_1(t)$, is the contribution from the collisions that did not involve internal excitation. If F(t) is the Fourier transform of f(E) and $b_1(t)$ is the value of the integral when $f(E) = 1$, we have that

$$I_1(t) = \int b_1(t-\tau)F(\tau)\,d\tau .$$

If f(E) is a slowly varying function of E

$$I_1(t) \simeq b_1(t)F(0) .$$

The second integral, being the contribution due to internal excitation is given, when $\Delta(E)$ is rapidly varying, as

$$I_2(t) \simeq b_2(t)\int dE\, f(E)\exp[2i\delta(E)] ,$$

where

$$b_2(t) = \int \exp(-iEt/\hbar)\sin[\Delta(E)]\exp(ik\rho)\,dE .$$

The exact result for $I_2(t)$ is, of course, the convolution of F(t) , $b_2(t)$ and the Fourier transform of exp $[i(k\rho+2\delta)]$

Using equation 32, and neglecting the variation of $\Gamma_i(E)$ with E ,

$$|b_2(t)| \simeq \exp[-(\mathrm{Im}\,\Gamma_i)(t-\rho/\bar{v})/\hbar] \quad , \tag{52}$$

where $k\rho = 2E\rho/\hbar v$ and $\bar{v}$ is the average relative velocity of the initial collision partners.

An alternative way to evaluate the integrals is by a stationary phase argument. We want to compute the delay Δt , in the time required for a signal to reach the detector at position ρ due to the interaction. In the absence of interaction the intensity is given by $\langle 1|\eta(t)\rangle$ with, for an s-wave,

$$\phi(E) = \sin(k\rho)\phi_1(r) \, .$$

Due to the interaction the intensity is $\langle 1|\psi(t)\rangle$ with $a_1(\rho)$ given by equation 31. For a given value of ρ the significant values of the integrals occur for values of t that differ by the delay time Δt . Since the significant values of each integral occur for those values of t that the integrands are stationary, we have from equation 31

$$\Delta t = \frac{2}{\hbar}\,\frac{d(\delta+\Delta)}{dE} \quad . \tag{53}$$

(cf. equation 33b. For an alternative derivation see for example references 10 and 11).

In the same fashion we can use the iterated expression for $a_1(\rho)$ (equation 20), in equation 49. For an s-wave when only one vibrational state $g_i(\rho)$ is relevant

$$a_1(\rho) \xrightarrow[\rho \to \infty]{} e^{i\delta} \sin(k\rho + \delta) + \\ + e^{i(k\rho+2\delta)} \frac{\mathrm{Im}\,\Gamma_i}{E - E_i} \left[\sum_{n=0} \left(\frac{\Gamma_i}{E - E_i} \right)^n \right] . \quad (54)$$

As is evident, higher values of n, which correspond to several transitions in and out of the state $g_i(\rho)$ contribute to higher values of t in $I_2(t)$. Thus successive orders of the iteration correspond to events of increasing duration.

IV. Discussion

In general there are several internal states of B-C that should be taken into account even when only $H_{22}(\rho)$ is in the energy region of interest. To consider this case it is convenient to partition the matrix equation 13 as

$$[E - K - H_{11}]\, a_1 = \underline{V}\, \underline{a}^1$$

$$[(E-K)\underline{I} - \underline{H}^{11}]\, \underline{a}^1 = \underline{V}^{\dagger} a_1 \quad , \quad (55)$$

where

$$\underline{a} = \begin{pmatrix} a_1 \\ \underline{a}^1 \end{pmatrix} , \quad \underline{H} = \begin{pmatrix} H_{11} & \underline{V} \\ \underline{V}^{+} & \underline{H}^{11} \end{pmatrix} .$$

These equations reduce to equations 14 when $\underline{a}^1 = a_2$. The one component equation that corresponds to equation 18 can now be written as

$$\left\{E - K - H_{11} - \underline{V}\left[(E-K)\underline{I} - \underline{H}^{11}\right]^{-1}\underline{V}^{+}\right\} a_1 = 0 \quad . \quad (56)$$

The effective potential can be written explicitly in terms of the eigenfunctions of the Hamiltonian

$$K\underline{I} + \underline{H}^{11} \quad .$$

Due to the coupling terms $V_{nm}(\rho)$ $(n,m \neq 1)$ these eigenfunctions cannot be identified with a potential generated by a particular excited state of B-C .

Consider a "step-ladder" model where only near-neighbours are coupled. (In the sense that $H_{n,m} = H_{n,m}\delta_{n,m} + H_{n,m}\delta_{n,m\pm1}$). For the simple case of only three internal states equation 55 can be written

$$(E - K - H_{11})\, a_1 = H_{12}\, a_2 \quad ,$$

$$(E - K - H_{22})\, a_2 - H_{23}\, a_3 = H_{21}\, a_1 \quad ,$$

$$(E - K - H_{33})\, a_3 - H_{32}\, a_2 = 0 \quad ,$$

so that

$$a_3 = (E - K - H_{33})^{-1} H_{32} a_2$$

and

$$[E - K - H_{22} - H_{23} (E - K - H_{33})^{-1} H_{32}] a_2 = H_{21} a_1 \, .$$

Even if $H_{22}(\rho)$ is not binding, the last term in the square bracket may modify $H_{22}(\rho)$ sufficiently to cause binding. In particular when E is below the lowest eigenvalue of $K + H_{33}$, this term is non-negative definite.

Consider a division of the internal state of B-C into two classes. Equation 55 is now written

$$\begin{aligned} [(E - K)\underline{I}_1 - \underline{H}_{11}] \underline{a}_1 &= \underline{U} \underline{a}_2 \\ [(E - K)\underline{I}_2 - \underline{H}_{22}] \underline{a}_2 &= \underline{U}^{\dagger} \underline{a}_1 \end{aligned} \qquad (57)$$

so that

$$\{(E - K)\underline{I}_1 - \underline{H}_{11} - \underline{U}[(E - K)\underline{I}_2 - \underline{H}_{22}]^{-1} \underline{U}^{\dagger}\} \underline{a}_1 = 0 \qquad (58)$$

is the effective Schroedinger equation for the first group only. If

$$\underline{a}_1 = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} ,$$

we replace equations 14 by

$$(E - K - \mathcal{V}_{11})\, a_1 = \mathcal{V}_{12}\, a_2$$

$$(E - K - \mathcal{V}_{22})\, a_2 = \mathcal{V}_{21}\, a_1 \quad , \qquad (58)$$

where

$$\mathcal{V}_{n,m} = V_{n,m} + \sum_{p,q>2} V_{n,p} \left([(E-K)\underline{I}_2 - \underline{H}_{22}]^{-1} \right)_{p,q} V_{q,m} . \qquad (59)$$

Equations 58 bear formal resemblance only to equations 14 since $\mathcal{V}$ is in principle a non-local potential. It should be borne in mind however, that under suitable conditions it can often be approximated by a local potential. One of the possible criteria for the original division of the states of B-C is the generation of a potential $\mathcal{V}$ which can be approximated by a local potential. In this way the distortion of the ρ motion due to the high excited internal states can be taken into account within the formal machinery of a few-state approximation.

As is known it is possible to carry out a partitioning of a wave function using a projection operator formalism.[7,12] The discussion in section II corresponds to introducing a projection operator P ,

$$P = |\phi_1\rangle\langle\phi_1| \quad , \quad P^2 = |\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1| = P , \qquad (60)$$

so that

$$P\psi = |\phi_1\rangle \int \phi_1^*(r)\psi(r,\rho)\,dr$$

$$= \phi_1(r)a_1(\rho) \ . \qquad (61)$$

The approximation of considering only two internal states corresponds to restricting the complement of P , I-P , to

$$I - P = |\phi_2\rangle\langle\phi_2| \ .$$

The corrections to this approximation are introduced by putting

$$I - P = |\phi_2\rangle\langle\phi_2| + Q \ , \qquad Q|\phi_2\rangle = 0 \ ,$$

and eliminating $Q\psi$, which leads to equation 58.

Other choices for P are clearly possible, in that $P\psi$ is only defined so that as $\rho \to \infty$, it includes no internally excited states. One can, for example, define $P\psi$ by

$$P\psi = a_1(\rho)\tilde{\phi}_1(r|\rho) \ ,$$

where $\tilde{\phi}_1(r|\rho)$ is the adiabatic electronic wave functions that tends to $\phi_1(r)$ as $\rho \to \infty$. These aspects of the problem will be discussed in a separate report.

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