The Sudden Approximation Applied to Molecular Problems.

I. Non-reactive Collisions.*

by

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ABSTRACT

The sudden approximation for transition probabilities is derived using an evolution operator formalism. The assumptions required are explicitly stated and their validity and applicability are discussed in relation to energy transfer during collisions between molecules and atoms. It is shown that sufficient conditions ensuring the validity of the sudden approximation are (1) that a classical description be adequate to describe the relative motion of the molecules or atoms, and (2) that the energy levels of the states mainly involved in the process be such that the product of their energy difference and the collision time be small compared to $\hbar$.

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I. INTRODUCTION

Several papers have recently been published[1-4], in which use is made of the sudden approximation to calculate transition probabilities for energy exchange in inelastic collisions between atoms or molecules. Since the method seems to promise advantages in computational ease and may therefore gain in popularity it seems worthwhile to appraise its applicability to molecular problems in contrast to the nuclear problems for which it was originally developed[5]. In this article the assumptions underlying the sudden approximation are explicitly stated, and their validity is assessed in relation to non-reactive atomic and molecular collisions. A subsequent paper will contain an extension to reactive scattering.

In order to establish the notation, an expression is derived, using the evolution operator formalism, for the transition probability for a system (composed of two composite particles) initially in state i going to a final state f. The evolution operator[6] $U(t,t')$ connects the state vector $\Psi(t)$ describing the system at time t with that at time t' by the relation

$$\Psi(t) = U(t,t')\Psi(t') \tag{1}$$

Combining this with the Schrödinger equation

$$i\hbar \frac{d\Psi(t)}{dt} = H\Psi(t) \tag{2}$$

yields

$$i\hbar \frac{dU(t,t')}{dt} = H\,U(t,t') \tag{3}$$

$$U(t,t') = 1 \quad . \tag{3a}$$

If H depends explicitly on time then Eq. (3) has the solution

$$U(t,t') = 1 + \int_{t'}^{t} H(\tau)U(\tau,t')\,d\tau = P\exp\left[\frac{1}{i\hbar}\int_{t'}^{t} H(\tau)\,d\tau\right] \tag{4}$$

in which P is the Dyson time ordering operator[7]. If H is not explicitly time-dependent then P reduces to unity and

$$U(t,t') = \exp\left[(t-t')H/i\hbar\right] . \tag{5}$$

For convenience some properties of U(t,t') which are used throughout the paper are set down here; they can easily be derived[6].

$$U(t,t'')\,U(t'',t') = U(t,t') . \tag{6}$$

If H is Hermitian

$$U(t,t')\,U^{+}(t,t') = U^{+}(t,t')\,U(t,t') = 1 , \tag{7}$$

$$U^{+}(t,t') = U(t',t) . \tag{8}$$

We shall have occasion to define evolution operators corresponding to different Hamiltonians. For each pair (U_i , H_i) equations analogous to Eqs. (1)-(8) are valid. Those Hamiltonians which are explicitly time dependent are denoted by greek subscripts.

At a time t_0, long before the collision, the system is supposed to be in an eigenstate $|i, t_0\rangle$ of some Hamiltonian H_0 . The probability that at a time t_1, long after the collision, the system will be in some other eigenstate $|f, t_1\rangle$ of H_0 is

$$|c_{Fi}(t_1,t_0)|^2 = |\langle t_1, F|\Psi(t_1)\rangle|^2 = |\langle t_1, F|U(t_1,t_0)|i,t_0\rangle|^2 . \quad (9)$$

We introduce the evolution operator $U_0(t,t_0)$ corresponding to H_0 and define the phase of the vectors $|n,t\rangle$ such that

$$|n,t_0\rangle = |n\rangle \ . \quad (10)$$

The functions $|n\rangle$ are time-independent eigenfunctions of H_0 ; therefore

$$(H_0 - E_n)|n\rangle = 0 \ . \quad (11)$$

Equation (9) then becomes

$$|c_{Fi}(t_1,t_0)|^2 = |\langle F|U_0^\dagger(t_1,t_0)U(t_1,t_0)|i\rangle|^2 = |\langle F|U_\gamma(t_1,t_0)|i\rangle|^2 \quad (12)$$

The second equality defines U_γ , the evolution operator in the interaction representation, to which corresponds the Hamiltonian H_γ ,

$$H_\gamma(t) = U_0^\dagger(t,t_0)\left[H - H_0\right]U_0(t,t_0) = e^{\frac{i}{\hbar}(t-t_0)H_0} V e^{\frac{-i}{\hbar}(t-t_0)H_0} . \quad (13)$$

The transition probability for collision is obtained by taking the limit of Eq. (12) as $t_1 \to +\infty$, $t_0 \to -\infty$. There are in the general case severe restrictions on $V \equiv H - H_0$ required so that these limiting processes converge[8]. Apart from such possible difficulties, the explicit time dependence of H_γ makes the rigorous evaluation of the matrix elements in Eq. (12) (via Eq. (6)) well-nigh impossible. To overcome this difficulty, one approach is to expand U_γ in a power series of V . (This yields essentially the Born series). This kind of expansion does not usually converge in chemical problems because of the strength and range of the potentials involved. The other possibility is to use the semiclassical approximation. This is an essential prerequisite to the sudden approximation as it is applied to molecular problems and is described in detail in the next section. It is worth noting here that in the semiclassical approximation the difficulties associated with the limiting process mentioned earlier usually vanish.

II. The Semiclassical Approximation.

Although we are here concerned with two body collisions, it is assumed that these may involve composite particles made up of N elementary (structureless) particles. Equation (11) therefore involves $3N-3$ independent space coordinates (in the barycentric system)[9]. Suppose that the coordinates can be collected into two sets *a* and *b*, such that Eq. (11) becomes separable. The choice of the sets a and b will depend on the particular problem. The coordinates in set a are eventually treated classically throughout, and will generally include the coordinates of relative motion of the two bodies, but may also include some internal coordinates. The set b is treated quantally at all times. We write, instead of Eq. (11),

$$(H_a - E_n^{(a)})\,|a,n\rangle = 0 \quad , \tag{14a}$$

$$(H_b - E_m^{(b)})\,|b,m\rangle = 0 \quad , \tag{14b}$$

the connection with Eq. (11) being

$$H_0 = H_a + H_b \quad , \tag{15a}$$

$$E_i = E_i^{(a)} + E_j^{(b)} \quad ; \quad E_f = E_f^{(a)} + E_g^{(b)} \quad , \tag{15b}$$

$$|i\rangle = |a,i\,;\,bj\rangle \quad , \quad |f\rangle = |a,f\,;\,b,g\rangle \; . \tag{15c}$$

Since H_a and H_b operate on functions of different coordinates, they always commute. However $V \equiv H - H_a - H_b$ in general depends explicitly on coordinates from both sets a and b, so that in general

$$[H_a, V] \neq 0 \qquad , \quad [H_b, V] \neq 0 \, . \tag{16}$$

As will become clear presently, it is convenient to rewrite H as

$$H_a + \bar{V}_m(\underline{a}) + H_b + V(\underline{a}, \underline{b}) - \bar{V}_m(\underline{a}) = H_a^m + H_b + V(\underline{a}, \underline{b}) - \bar{V}_m(\underline{a})$$

where

$$\bar{V}_m(a) = \langle b,m \,|\, V(\underline{a}, \underline{b}) \,|\, b,m \rangle \tag{17}$$

is the potential V averaged over all coordinates b in the state $|\, b,m \rangle$.

In the semiclassical approximation the potential $V(\underline{a}, \underline{b}) - \bar{V}_m(a)$ is replaced during a specified time interval by another potential, $V_\beta(\underline{b}, t)$ which depends explicitly on the time and on the coordinates in set b. The time dependence of V_β (other than a possible original explicit time dependence of V) is obtained by replacing the coordinates in set a by some suitably chosen function a(t), wherever they occur in $(V - \bar{V})$ [10]. The function a(t) describes classically the evolution in time of the coordinates in set a. For the moment we assume it to be a known function; its evaluation is discussed in detail below. Since H_a^m is independent of time, we have at all times,

$$[H_a^m, V_\beta] = 0 \quad . \tag{18}$$

We introduce the evolution operators U_a^m and U_β corresponding to the Hamiltonians H_a^m and $(H_b + V_\beta)$ respectively. Obviously U_a^m operates only on functions of a and U_β only on those of b. It follows from the general properties, Eqs. (1)-(8), and from Eq. (18) that if $(V - \bar{V})$ is replaced by V_β in the time interval $t \leq \tau \leq t'$ then

$$U(t',t) = U_a^m(t',t)\,U_\beta(t',t) = U_\beta(t',t)\,U_a^m(t',t). \tag{19}$$

To make use of this result we rewrite Eq. (9) with the help of Eqs. (6), (14) and (15),

$$\left|C_{fg,ij}(t_1,t_0)\right|^2 = \left|\langle t_1 a f; t_1 b g|U(t_1,t')U(t',t'')U(t'',t_0)|a i t_0; b j t_0\rangle\right|^2. \tag{20}$$

Equation (18) is now assumed to be valid in the time intervals $\underline{t}_0 \leq \tau \leq \underline{t}''$ ("before" the collision) and $\underline{t}' \leq \tau \leq \underline{t}_1$, ("after" the collision), i.e. $V - \bar{V}$ is replaced by V_β during these periods. Eq. (19) can now be written

$$|C_{fg,ij}(t_1,t_0)|^2 = |<t_1 bg; t_1 af| U_a^g(t_1,t') U_\beta(t_1,t') U(t',t'') U_\beta(t'',t_0) U_a^j(t'',t_0) |ait_0; bjt_0>|^2 . \tag{21}$$

To obtain a semiclassical description of the system at all times, the limit of Eq. (21) must be taken as $\underline{t}' \rightarrow \underline{t}''$. There are some subtle points involved. The first concerns the evaluation of the function $\underline{a}(t)$. This is obtained as a solution to the classical equations of motion, with the coordinates in set $\underline{b}$ averaged over all possible values consistent with the quantal state $|b,m>$, appropriate to the time period considered. The appropriate Hamiltonian is therefore the classical analog of H_a^m. Thus before the collision ($\underline{t}_0 \leq \tau \leq \underline{t}''$), $\underline{a}(t)$ is given by $\underline{a}_{ij}(t)$, say, which is the solution to

$$T(\underline{a}) + \bar{V}_j(\underline{a}) = E - E_j^{(b)} = E_i^{(a)} . \tag{22}$$

Here $T(\underline{a})$ is the kinetic energy associated with the coordinates in set $\underline{a}$, $\bar{V}_j(\underline{a})$ is the potential $V(\underline{a},\underline{b})$ averaged over all values of b in the state $|b,j\rangle$ whose energy is $E_j^{(b)}$ (Eq.(14b) and (17)). Since Eq.(22) is a first order differential equation there will appear one constant of integration for each coordinate in set a. In the time interval after the collision, $\underline{t}' \leq \tau \leq \underline{t}$, $\underline{a}(t) = \underline{a}_{ij}(t)$, which is the solution to

$$T(\underline{a}) + \overline{V}_g(\underline{a}) - E_f^{(a)} = 0 \quad , \tag{23}$$

wherein the terms are defined analogously to those in Eq. (22). Again there appears one constant of integration for each coordinate in a. In the limit $\underline{t}' \to \underline{t}''$, we require that the coordinates in a be single-valued at the time $\underline{t} = \underline{t}' = \underline{t}''$, which implies[11]

$$\lim_{t' \to t''} \underline{a}_{fg}(t') = \underline{a}_{ij}(t'') \ . \tag{24}$$

This condition fixes the constants of integration in $\underline{a}_{fg}(t)$ in terms of $\underline{t}''$ and the constants in $\underline{a}_{ij}(t)$. The time $\underline{t}''$ is the time at which the energy is redistributed among the sets a and b, and at which the quantal system b jumps from the state $|b,j\rangle$ to the state $|b,g\rangle$[12]. The remaining set of constants of integration is determined by the initial conditions at the time $\underline{t_o}$.

The quantum mechanical analogs of $\underline{a}_{ij}(t)$ and $\underline{a}_{fg}(t)$ must obey an equation equivalent to Eq. (24), namely

$$\lim_{t'\to t''} U_a^{g\dagger}(t_1,t')|aft_1\rangle = U_a^{j}(t'',t_0)|ait_0\rangle. \tag{25}$$

Using this equation and the definition of the phase for $|b,mt\rangle$ analogous to Eq. (10), the limiting process $\underline{t}'\to\underline{t}''$ transforms Eq. (21), for given $\underline{t}''$ into

$$|C_{fg,ij}(t_1,t_0)|^2_{t''} = |\langle bg|U_{\beta\gamma}(t_1,t_0)|bj\rangle|^2_{t''} \tag{26}$$

Here $U_{\beta\gamma}$ is the evolution operator in the interaction representation,

$$U_{\beta\gamma}(t_1,t_0) = U_b^{\dagger}(t_1,t_0)\,U_\beta(t_1,t_0) = P\exp\left[\frac{1}{i\hbar}\int_{t_0}^{t_1} H_{\beta\gamma}(\tau)\,d\tau\right]. \tag{27}$$

$H_{\beta\gamma}$ is defined analogously to H_γ in Eq. (13),

$$H_{\beta\gamma}(\tau) = e^{\frac{i}{\hbar}(\tau-t_0)H_b}\,V_\beta(\underline{b},\tau)\,e^{-\frac{i}{\hbar}(\tau-t_0)H_b} \tag{28}$$

where

$$V_\beta(\underline{b},\tau) = \begin{cases} V(\underline{a}_{ij}(\tau),\underline{b}) - \overline{V}_j(\underline{a}_{ij}(\tau)), & t_0 \le \tau \le t'' \\ V(\underline{a}_{fg}(\tau),\underline{b}) - \overline{V}_g(\underline{a}_{fg}(\tau)), & t'' \le \tau \le t_1 \end{cases} \tag{29}$$

Since it is in general impossible to define the time at which the energy redistribution takes place, a complete semiclassical description must include an averaging over all possible values of $\underline{t}''$. Equation (26) becomes

$$\left|C_{Fg,ij}(t_1,t_0)\right|^2 = (t_1-t_0)^{-1}\int_{t_0}^{t_1} \left|\langle bg|U_{\beta\gamma}(t_1,t_0)|b,j\rangle\right|^2_{t''} dt'' \qquad (30)$$

To obtain the transition probability, the limits are taken as $\underline{t_1} \rightarrow \infty$, $\underline{t_0} \rightarrow -\infty$ as before.

For small fractional energy change $\Delta E/E \equiv |E_i^{(a)} - E_f^{(a)}|/E$, the functions $\underline{a}_{ij}(t)$ and $\underline{a}_{Fg}(t)$ are very similar and consequently the value of the matrix element of $U_{\beta\gamma}$ is only weakly dependent on $\underline{t}''$. (In the limit that $\Delta E \rightarrow 0$, $\underline{a}_{ij} \rightarrow \underline{a}_{Fg}$ and the potent~~ial~~ V_β and hence $U_{\beta\gamma}$ becomes independent of t''). Therefore, when $\Delta E \ll E$ it will generally be permissible to omit the laborious averaging over $\underline{t}''$. For example, if the set $\underline{a}$ contains the coordinates of relative motion of the two bodies, one might choose as a representative trajectory the one for which the energy redistribution takes place at the distance of closest approach. An alternative choice, equally valid when $\Delta E \rightarrow 0$, and perhaps more easily calculated, is to choose the trajectory for which $\underline{t}'' \rightarrow \infty$ (i.e. $\underline{a}_{ij}(t)$ is used at all times). In order to preserve symmetry and satisfy the principle of microscopic reversibility, it would be necessary to calculate the average of the matrix elements with $\underline{t}'' \to \infty$ and $\underline{t}'' \to -\infty$ in which the functions $\underline{a}_{ij}(t)$ and $\underline{a}_{fg}(t)$ respectively are used at all times. In a closely related approximation which also obeys the principle of microscopic reversibility one calculates an approximate function using the geometric mean of $E_i^{(a)}$ and $E_f^{(a)}$ at all times. This procedure violates the principle of the conservation of energy but when $\Delta E \ll E$ this is not serious. For another discussion of the evaluation of $\underline{a}(t)$ reference is made too the work of Takayanagi[13].

When the averaging over $\underline{t}''$ is included, the limiting process $\underline{t}' \to \underline{t}''$ merely extends the semiclassical description to all times, and does not imply any instantaneous interaction or energy redistribution. When the averaging over $\underline{t}''$ is not included, then there appears a discontinuity in the slope of the potential V_β at the time $\underline{t}''$, corresponding to an impulsive force and instantaneous energy redistribution. Even in this case, however, from the point of view of the quantal system b, the interaction represented by the potential V_β is extended over a period of time and cannot be considered impulsive. There are therefore subtle differences between these approximations and, for example, an impulse approximation[16].

For a discussion of the validity of the semiclassical approximation see refs. 10, 11, 14, and 15.

III The Sudden Approximation

The matrix elements in Eq. (26) are no easier to calculate than those in Eq. (12). The essential difference however is that the potential V_β appearing in Eq. (28) is explicitly time dependent, whereas V of Eq. (13) is, for molecular problems, generally not an explicit function of time. Use is made of this fact in what follows.

For simplicity all reference to $\underline{t}''$ is omitted. In principle (if not in practice!) the averaging procedure over $\underline{t}''$ proceeds as in the semiclassical approximation.

In order to obtain a useful expression for the operator we expand the right hand side of Eq. (27),

$$U_{\beta\gamma}(t_1,t_0) = \exp\left[\frac{1}{i\hbar}\int_{t_0}^{t_1} V_\beta\, dt\right]\left\{1 + \frac{1}{i\hbar}\int_{t_0}^{t_1}(H_{\beta\gamma}-V_\beta)\,dt + \frac{1}{2!}\left[\frac{1}{i\hbar}\int_{t_0}^{t_1}(H_{\beta\gamma}-V_\beta)\,dt\right]^2 + \ldots\right\}$$

$$- \frac{1}{2!}(i\hbar)^{-2}\int_{t_0}^{t_1} dt' \int_{t'}^{t_1} dt\,\left[H_{\beta\gamma}(t'), H_{\beta\gamma}(t)\right] + \ldots \qquad (31)$$

+ other terms involving higher order commutators.

We introduce the notation

$$F_{mn}(b,t_1,t_0) = \langle bm|\exp\left[\frac{1}{i\hbar}\int_{t_0}^{t_1} V_\beta\, dt\right]|bn\rangle \qquad (32)$$

$$G_{k\ell}(b,t_1,t_0)=\frac{1}{i\hbar}\langle bk|\int_{t_0}^{t_1}(H_{\beta\gamma}-V_\beta)\,dt\,|b\ell\rangle=\frac{1}{i\hbar}\int_{t_0}^{t_1}\left[e^{i\omega_{k\ell}^{(b)}(t-t_0)}-1\right]V_{\beta,k\ell}(t)\,dt, \tag{33}$$

where

$$\omega_{k\ell}^{(b)}=(E_k^{(b)}-E_\ell^{(b)})\hbar^{-1}=\Delta E\,\hbar^{-1}, \tag{34a}$$

and

$$V_{\beta,k\ell}(t)=\langle bk|V_\beta(t)|b\ell\rangle . \tag{34b}$$

The matrix elements of $U_{\beta\gamma}$ can be written in terms of these integrals by using Eqs. (31)-(33) (the cumbersome qualifying parentheses on F and G are dropped)

$$\langle bg|U_{\beta\gamma}(t_1,t_0)|bj\rangle=F_{gj}+\mathop{S}_k F_{gk}G_{kj}+\frac{1}{2!}\mathop{S}_k\mathop{S}_\ell F_{gk}G_{k\ell}G_{\ell j}+\ldots \tag{35}$$

+ matrix elements of the cummutator terms,

[illegible],

In the sudden approximation only the first term on the right hand side of Eq. (35) is retained. Eq. (35) therefore becomes

$$|c_{f_g,i_j}(t_1,t_0)|^2=|F_{gj}(t_1,t_0)|^2 \tag{36}$$

From Eq. (31) it is seen that for Eq. (36) to converge in the limits $t_1 \rightarrow \infty$, $t_0 \rightarrow -\infty$ it is necessary that $|t| V_\beta \rightarrow 0$ as $|t| \rightarrow \infty$. This is why the sudden approximation cannot be applied to Eq. (12) directly in the usual case that V is not explicitly time dependent.

The integrals G_{kl} given by Eq. (32) also converge as $t_1, |t_0| \rightarrow \infty$ when $|t| V_\beta \rightarrow 0$ as $|t| \rightarrow \infty$.

The neglect of all but the first term in Eq. (35) is tantamount to the assumption that for all times $t_0 \leq t \leq t_1$

$$[H_b, V_\beta] = 0 , \tag{37}$$

and

$$[V_\beta(t), V_\beta(t')] = 0 , \tag{38}$$

Since if these equations are valid all the G_{kj} and commutator terms become identically zero. Equation (37) is equivalent to the assumption that all the eigenvalues of H_b are degenerate (i.e. $\omega^{(b)}_{m,n} = 0$ for all m,n).[17] Eq. (38) is generally satisfied in molecular problems since the potential V_β usually involves only the position coordinates in the set b and not the momenta. In most cases the neglected terms in Eq. (35) are expected to be small even when Eq. (37) is strongly violated (e.g. when H_b has a continuous spectrum of eigenvalues). Takayanagi[11] considered as an approximation for $U_{\beta\gamma}$ the expression

$$U_{\beta\gamma}(t_1,t_0) = \exp\left[\frac{1}{i\hbar}\int_{t_0}^{t_1} H_{\beta\gamma}(t)\,dt\right], \qquad (39)$$

which is equivalent to neglecting all the commutator terms in Eq. (30). For the rotational excitation of molecules he showed that provided the higher order terms in the expansion of the exponential factor in Eq. (39) are taken into account, it is a very good approximation. This indicates that the commutator terms were negligible in his case and we expect them to be negligible in most cases, although we have been unable to show this in general. (see however Ref. 17 for an estimate of the error for nuclear excitations).

As can be seen from Eqs. (31) and (35), the sudden approximation is obtained from Eq. (39) by neglecting all the terms involving G integrals. This procedure will be valid provided $|\sum_k F_{gk}G_{kj}| \ll |F_{gj}|$. To obtain an estimate of the relative magnitude of these terms, we write

$$\hbar^{-1}\langle k|\int_{-\infty}^{+\infty} V_\beta\,dt|j\rangle = \hbar^{-1}\,\overline{V}_{kj}\,\Delta T$$

where $\overline{V}_{kj}$ is the mean interaction energy between the states k and j during the time ΔT, and it is assumed that $V_{\beta,kj}$ is negligible at all other times (ΔT is therefore the effective interaction or collision time). Hence Eq. (33) shows that

$$G_{kj} \approx \omega_{kj} \overline{V}_{kj} \Delta T^2 / 2\hbar \, . \tag{40}$$

Similarly, from Eq. (32),

$$F_{gj} \approx \overline{V}_{gj} \Delta T (i\hbar)^{-1} - \Delta T^2 (2\hbar^2)^{-1} \mathop{S}_{k} \overline{V}_{gk} \overline{V}_{kj} + \cdots \tag{41}$$

and

$$\left| \mathop{S}_{k} F_{gk} G_{kj} \right| \approx \left| \Delta T^2 (2\hbar^2)^{-1} \mathop{S}_{k} \overline{V}_{gk} \overline{V}_{kj} (\Delta E_{kj} \Delta T / i\hbar) + \cdots \right| \tag{42}$$

A sufficient condition that the latter quantity be negligible compared to $|F_{gj}|$ is therefore seen to be that

$$\Delta E_{kj} \Delta T << \hbar \tag{43}$$

for all the states k which make a significant contribution to the sum. Since, generally speaking, states which are widely separated in energy are weakly coupled (small $\overline{V}_{kj}$), this condition is likely to be met whenever ΔT is sufficiently small. If H_b has a finite spectrum then the inequality (43) can be written as

$$\Delta T \overline{\Delta E} \ll \hbar \qquad (44)$$

in which $\overline{\Delta E}$ represents an average of ΔE_{kj} over all important transitions. Condition (44) was proposed by Takayanagi[13]. From Eqs. (41) and (44) it can also be concluded that if $\left| \int_{-\infty}^{+\infty} V_\beta dt \right| \ll \hbar$, the sudden approximation will be valid, but in that case only the first term in the expansion of the exponential factor in Eq. (32) need be retained, which is equivalent (apart from the replacement of V by V_β) to the first Born approximation.

It is a characteristic of perturbation expansions that the unitarity of the sum of the calculated transition probabilities is not maintained. Indeed, for strong coupling the perturbation methods usually diverge in the higher orders. Takayanagi[1] showed that the use of Eq. (39) leads to both convergence and unitarity when applied to rotational transitions provided the higher order terms in the exponential are kept. The sudden approximation has the advantage over Eq. (39) that no infinite expansion of the exponential is required. Provided that condition (43) is met therefore, one may consider the sudden approximation to be equivalent to a special infinite order perturbation expansion with the advantages of convergence and unitarity over a wide range of coupling strength. For possible corrections to the sudden approximation see references 5, 17 and 18.

IV. Applications.

Takayanagi's work on rotational excitation of a molecule (BC) by the scattering of an atom (A) has already been referred to[1]. Kramer and Bernstein[2] used the sudden approximation, Eq. (36), tocalculate the transition probabilities between rotational states. We here describe in some detail the derivation of their first equation, in order to show some further properties of the sudden approximation. The total Hamiltonian (with self-evident notation) is

$$H = -\frac{\hbar^2}{2\mu_{A,BC}} \nabla^2_{\underset{\sim}{r}_{A,BC}} - \frac{\hbar^2}{2\mu_{BC}} \nabla^2_{\underset{\sim}{r}_{BC}} + V_{ABC}(\underset{\sim}{r}_{A,BC}, \underset{\sim}{r}_{BC}) .$$

Kramer and Bernstein treat classically the internuclear distance r_{BC} and the vecotr of relative position of A and BC, $\underset{\sim}{r}_{A,BC}$. These four coordinates are therefore placed in set a, leaving Θ_{BC} and ϕ_{BC} for set b. To obtain the function a(t) the classical analog of H is taken, averaging the coordinates in set b over all their possible values. Thus

$$H_{cl} = P^2_{A,BC}(2\mu_{A,BC})^{-1} + P^2_{r_{BC}}(2\mu_{BC})^{-1} + \overline{V}_{ABC}(\underset{\sim}{r}_{A,BC}, r_{BC}) = E - E_{rot} \quad (45)$$

where E is the total energy of the system and E_{rot} is the energy associated with the angular coordinates Θ_{BC} and ϕ_{BC} .

(In fact they assumed r_{BC} to be a constant, and the trajectory of A relative to BC to be nearly a straight line, which is equivalent to putting $\bar{V} \approx 0$ and $p_{r_{BC}} = 0$ in Eq. (45). Also they used the geometric mean of the initial and final rotational energies, as described above. As was shown, such approximations while sufficient for their purpose, are not essential[19]).
Using $H_{c\ell}$ the classical equations of motion are solved and $\underline{a}(t)$ obtained. H_a^m is the quantum mechanical analog of $H_{c\ell}$.

$$H_a^m = \frac{-\hbar^2}{2\mu_{A,BC}} \nabla^2_{\underset{\sim}{r}_{A,BC}} - \frac{\hbar^2}{2\mu_{BC}} \nabla^2_{r_{BC}} + \bar{V}_{ABC}(\underset{\sim}{r}_{A,BC}, r_{BC}) \tag{46}$$

while for H_b it is convenient to choose the Hamiltonian operator of a rigid rotor, whose eigenfunctions are the spherical harmonics $Y_{\ell m}(\Theta, \phi)$.
The potential V is therefore

$$V = H - H_a - H_b = V_{ABC}(\underset{\sim}{r}_{A,BC}, \underset{\sim}{r}_{BC}) - \bar{V}_{ABC}(\underset{\sim}{r}_{A,BC}, r_{BC}) \tag{47}$$

and V_β is obtained according to the prescription, described previously,

$$V_\beta = V_{ABC}(\underline{a}(t), \Theta, \phi) - \bar{V}_{ABC}(\underline{a}(t)) \tag{48}$$

When this expression is substituted into Eq. (36) it will be seen that the last term $\overline{V}$ contributes only a phase factor to the integral and can therefore be ignored when calculating transition probabilities. This useful result is quite general for the case of non-reactive scattering in the sudden approximation. The remaining term of Eq. (48) yields precisely their expression for the transition probability,

$$W_{\ell' m', \ell m} = \left| < \ell' m' \left| \exp\left[\frac{1}{i\hbar} \int_{-\infty}^{+\infty} V_{ABC}(\Theta_{BC}, \phi_{BC}, t)\,dt \right] \right| \ell m > \right|^2 \qquad (49)$$

Rapp and coworkers[3], have applied the semiclassical approximation both to the vibrational excitation of a diatomic molecule by collision with an atom, and to resonant or near-resonant exchange of vibrational energy between two diatomic molecules. They used the first significant term of the expansion of the exponential function in Eq. (39).

Byron and Foley[4] have recently used a similar formalism to study pressure broadening of certain atomic spectral lines.

V Conclusions

As a result of this derivation of the sudden approximation, it is seen that the following approximations are essentially involved.

1. Some coordinates (usually those of relative motion) are treated classically, as if under the influence of a potential averaged over the remaining coordinates. Rapp[3c] has pointed

out that in some cases this average may not be a sufficiently accurate representation of the potential. The semiclassical approximation then breaks down. There are also difficulties in the proper evaluation of the classical function $\underline{a}(t)$ arising from the averaging over $\underline{t}''$, but these become unimportant when the fractional energy change is small.

2. The inequality (43) is assumed to be valid. This will most likely be the case when the spacing between the energy levels of the quantally treated system $\underline{b}$ is small, and when only a few of these states are important in the transitions. The faster the collision, the more likely also will it be that ΔT is small and (43) valid.

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