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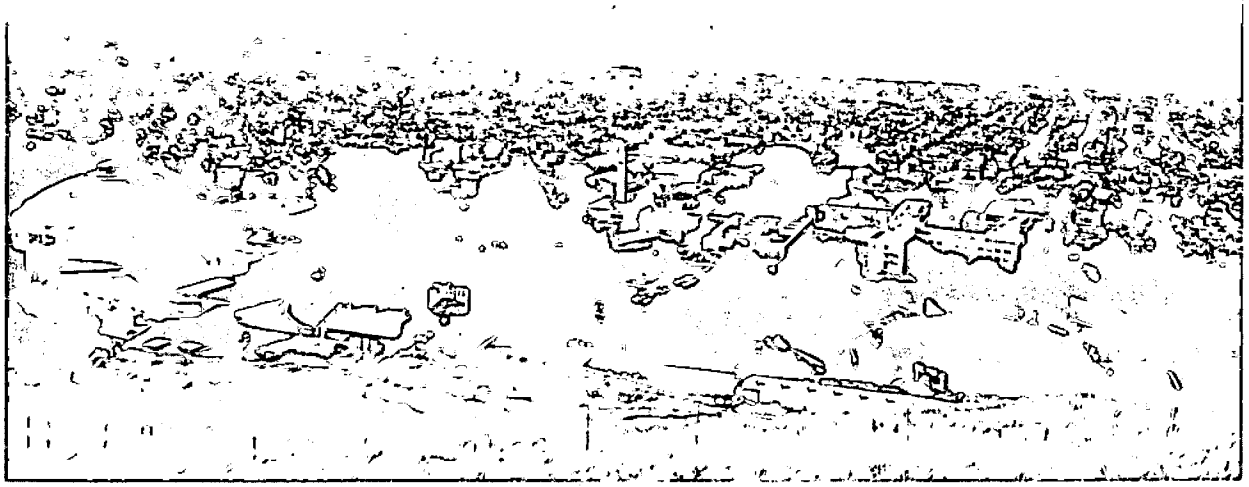

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Abstract

A quantum mechanical theory of collisional recombination (within the Lindemann mechanism, A +B $\leftrightarrow$ AB*, AB* + M $\rightarrow$ AB + M) is presented which provides a proper quantum description of the A + B collision dynamics and treats the M + AB* inelastic scattering within the impact approximation (the quantum analog of a classical master equation treatment). The most rigorous version of the theory is similar in structure to the impact theory of spectral line broadening and involves generalized (4-index) rate constants for describing M + AB* collisions. A simplified version is also presented which involves only the normal (2-index) inelastic rate constants for M + AB* scattering but which also retains a proper quantum description of the A + B dynamics.

I. Introduction

Collisional recombination reactions, i.e.,

$$A + B + M \rightarrow AB + M ,$$

have recently been receiving considerable attention,[1] one reason being their importance in combustion processes (e.g., $H + O_2 \rightarrow HO_2$, $H + CO \rightarrow HCO$, $H + CO_2 \rightarrow HOCO$). The standard Lindemann mechanism for collisional recombination[2],

$$A + B \leftrightarrow AB^* \tag{1.1a}$$

$$AB^* + M \rightarrow AB + M , \tag{1.1b}$$

leads (via the steady-state approximation and with the strong collision approximation (SCA) for the deactivation step, Eq. (1.1b)) to the following well-known expression for the recombination rate constant (units = cm^3/molecule-sec)

$$k_r(T,\omega) = Q_r(T)^{-1} \sum_{\ell} e^{-\beta E_\ell} \omega k_\ell/(\omega+k_\ell) , \tag{1.2}$$

where $\{E_\ell\}$ and $\{k_\ell\}$ are the energies and unimolecular decay rates of the metastable states of AB*, $\beta = (kT)^{-1}$, Q_r is the reactant (A+B) partition function per unit volume, and $\omega \equiv [M]\, k_{deact}$ is the frequency of "strong collisions" (which is proportional to the pressure of the bath gas M), where k_{deact} is the bimolecular rate constant for the M + AB* collisional deactivation step in Eq. (1.1b). Most applications of this theory are within the RRKM framework,[2]

whereby one assumes a classical continuum of metastable AB* states, i.e., $E_\ell \rightarrow E$ and

$$\sum_\ell \rightarrow \int dE\, \rho(E)\,, \tag{1.3a}$$

where $\rho(E)$ is the density of AB* states, and uses microcanonical transition state theory for the unimolecular decay rates,

$$k_i \rightarrow k_{TST}(E)\,. \tag{1.3b}$$

Attempts[1c,1d,3] at a more rigorous, quantum mechanical description of the A + B collision dynamics in Eq. (1.1a) — still with the phenomenological SCA for the relaxation step in Eq. (1.1b) — have focused on identifying the energies $\{E_\ell\}$ and unimolecular decay rates $\{k_\ell\}$ in Eq. (1.2) as the energies and widths ($\Gamma_\ell = \hbar k_\ell$) of *scattering resonances* of the A + B system. In some cases the lifetime (or time delay) matrix introduced by F.T. Smith[4] has been used to describe the quantum dynamics of the A + B system. Though these approaches are appropriate when the A + B collision dynamics is dominated by long-lived resonances, if the separation of the resonant and non-resonant A + B scattering is ambiguous and/or if non-resonant scattering makes a significant contribution, then these approaches are ill-defined and can give unphysical results that are clearly not correct.

A recent paper[5] has presented a more rigorous quantum mechanical description of the A + B collision dynamics which is physically correct whether or not resonances dominate. It is based on flux correlation functions[6] (*vide infra*) and does not require that one separately identify resonant and non-

resonant contributions to the A + B scattering. The initial version of this theory utilized the strong collision approximation (SCA) for the relaxation step, Eq. (1.1b), and it is the purpose of the present paper to go beyond the SCA, i.e., to show how a more general treatment of the M + AB* inelastic scattering can be combined with this rigorous quantum treatment of the A + B collision dynamics.

Section II first summarizes the quantum theory of ref. 5; this provides a rigorous quantum description of the A + B collision dynamics in Eq. (1.1a) but utilizes the SCA for the relaxation step in Eq. (1.1b). Section III next briefly reviews the classical master equation description[7] for going beyond the SCA; this provides a more general treatment of the M + AB* energy transfer process in Eq. (1.1b) but relies on a classical description of the A + B dynamics in Eq. (1.1a). Section IV then presents the new development of the paper, a synthesis of the two previous sections, combining a rigorous quantum description of the A + B collision dynamics with the appropriate quantum qeneralization of the master equation treatment of the M + AB* energy transfer. Finally, an approximation to the general result of Section IV is identified which leads to a much simpler result that also provides a synthesis of Sections II and III; i.e., in the SCA it reverts to the quantum theory of Section II, and in the classical limit it becomes the master equation treatment of Section III.

II. Review of Quantum Theory of Recombination within the SCA

Referring to Fig. 1, the quantum theory of ref. 5 is the quantum analog of a classical trajectory simulation in which one would begin trajectories inward ($\dot{r} < 0$) at time t = 0 from the "dividing surface" r = a (sampled from a

Boltzmann distribution at temperature T) and follow them until the time τ at which they return to the dividing surface, weighting each trajectory by $(1 - e^{-\omega\tau})$, the probability of a "strong" (i.e., stabilizing) collision sometime within the time interval $(0,\tau)$. The quantum mechanical expression for the recombination rate constant corresponding to this classical picture was shown to be

$$k_r Q_r = \int_0^\infty dt\, e^{-\omega t}\, C_f(t)\,, \tag{2.1a}$$

where C_f is the flux autocorrelation function[6]

$$C_f(t) = tr[\hat{F}\, e^{i\hat{H}^* t_c^*/\hbar}\, \hat{F}\, e^{-i\hat{H} t_c/\hbar}]\,, \tag{2.1b}$$

where $t_c = t - i\,\hbar\beta/2$. Here $\hat{F}$ is the usual flux operator,[8] related to the dividing surface in Fig. 1,

$$\hat{F} = \frac{-i}{\hbar}[\hat{H},\hat{h}] = \frac{1}{2}\left[\frac{\hat{p}}{m}\,\delta(\hat{r}-a) + \delta(\hat{r}-a)\,\frac{\hat{p}}{m}\right] \tag{2.2}$$

where $h = h(a-r)$ is the Heaviside function (1 for $r < a$, 0 for $r > a$), and $\hat{H}$ is the Hamiltonian for the A - B system, augmented by the absorbing potential $\varepsilon(\mathbf{q})$ (see Fig. 1),

$$\hat{H} = \hat{H}_{AB} - i\varepsilon(\mathbf{q})\,, \tag{2.3}$$

which enforces outgoing wave boundary conditions[9] for the time evolution operators (and Green's functions).

The correlation function $C_f(t)$ is a property solely of the A + B collision system; the only effect of stabilizing collisions is the factor $e^{-\omega t}$ in Eq. (2.1a). Since the A + B collision system is that of a non-reactive system — i.e., everything that goes in through the dividing surface must come out (if there are no collisions) — one has

$$\int_0^\infty C_f(t) = 0 \,, \tag{2.4}$$

so that Eq. (2.1) gives $k_r \equiv 0$ if $\omega = 0$, an obvious physical requirement. Eq. (2.4) also allows one to write Eq. (2.1a) as

$$k_r Q_r = \int_0^\infty dt(e^{-\omega t} - 1)\, C_f(t) \,, \tag{2.5}$$

which explicitly enforces the limit $k_r \rightarrow 0$ if $\omega \rightarrow 0$ even for an approximate correlation function.

The quantum rate expression can be written more explicitly if one diagonalizes a matrix representation of $\hat{H}$ (a complex symmetric matrix), yielding the complex eigenvalues $\{E_\ell - i\Gamma_\ell/2\}$ and eigenfunctions, $\{|\psi_\ell\rangle\}$. The time evolution operator can then be expressed as follows

$$e^{-i\hat{H}t/\hbar} = \sum_\ell |\psi_\ell\rangle\langle\psi_\ell|\, e^{-i(E_\ell - i\Gamma_\ell/2)t/\hbar} \,, \tag{2.6}$$

where we note that, unless explicitly indicated, the wavefunction is not complex conjugated in the bra state $\langle\psi_\ell|$ in this complex-symmetric algebra.[9] Eq. (2.1b) for the flux correlation function thus becomes

$$C_f(t) = \sum_{\ell,\ell'} e^{-\beta(E_\ell+E_{\ell'})/2} \langle\psi_\ell|F|\psi^*_{\ell'}\rangle\langle\psi^*_{\ell'}|F|\psi_\ell\rangle\, e^{-i(E_\ell-E_{\ell'})t/\hbar}\, e^{-(\Gamma_\ell+\Gamma_{\ell'})t/2\hbar}\,, \tag{2.7a}$$

the time integral of which gives the following expression for the rate

$$k_r Q_r = \sum_{\ell,\ell'} e^{-\beta(E_\ell+E_{\ell'})/2} \frac{\langle\psi_\ell|F|\psi^*_{\ell'}\rangle\langle\psi^*_{\ell'}|F|\psi_\ell\rangle}{\omega + \dfrac{(\Gamma_\ell+\Gamma_{\ell'})}{2\hbar} + i(E_\ell-E_{\ell'})/\hbar}\,. \tag{2.7b}$$

From Eq. (2.7) it is easy to see what approximations are necessary to degrade it to the classical result in Eq. (1.2): one neglects the off-diagonal interference terms, $\ell \neq \ell'$, in Eq. (2.7a) for $t > 0$ and makes the identification

$$\langle\psi^*_\ell|F\psi_\ell\rangle = -\langle\psi_\ell|F|\psi^*_\ell\rangle \equiv \Gamma_\ell/\hbar \equiv k_\ell\,, \tag{2.8}$$

whereby Eq. (2.7a) becomes

$$C_f(t) = -\sum_\ell e^{-\beta E_\ell} k_\ell^2\, e^{-k_\ell t}\,. \tag{2.9}$$

Since this approximation is only valid for $t > 0$, Eq. (2.5) is used[10] to obtain the rate,

$$k_r Q_r = \int_0^\infty dt\,(1-e^{-\omega t}) \sum_\ell e^{-\beta E_\ell} k_\ell^2\, e^{-k_\ell t}\,, \tag{2.10a}$$

$$= \sum_{\ell} e^{-\beta E_\ell} \left(k_\ell - \frac{k_\ell^2}{\omega + k_\ell} \right) , \qquad (2.10b)$$

$$= \sum_{\ell} e^{-\beta E_\ell} \frac{\omega k_\ell}{\omega + k_\ell} , \qquad (2.10c)$$

which is the classical result, Eq. (1.2).

III. Summary of Classical Description of Energy Transfer

Even within the classical RRKM description of the A + B collision dynamics, i.e., Eqs. (1.2) and (1.3), it is common nowadays to go beyond the strong collision approximation in treating the collisional relaxation in Eq. (1.1b). This is typically done[7] via a classical master equation: if $\{c_\ell(t)\}$ denote the populations of the energy levels $\{E_\ell\}$ of AB* at time t, then the master equation is

$$\dot{c}_\ell(t) = - k_\ell c_\ell(t) - \sum_{\ell'} \omega P_{\ell' \leftarrow \ell} c_\ell(t) + \sum_{\ell'} \omega P_{\ell \leftarrow \ell'} c_{\ell'}(t) , \qquad (3.1)$$

where

$$\omega P_{\ell' \leftarrow \ell}(T) \equiv [M] k_{\ell' \leftarrow \ell}(T) , \qquad (3.2a)$$

it being noted that the state-to-state transition probabilities depend on temperature. (Note that the diagonal terms, $\ell' = \ell$, in Eq. (3.1) cancel, but for convenience I leave them in.) The terms on the right hand side of Eq. (3.1) are, respectively, the rate of loss from state ℓ due to unimolecular decay (to A + B), the rate of loss from state ℓ due to collisions that transfer population to other states ℓ', and the rate of gain of population in state ℓ due to transitions from other states. The state-to-state transition probabilities are normalized as

$$\sum_{\ell'} P_{\ell' \leftarrow \ell}(T) = 1 \,, \tag{3.2b}$$

and they satisfy the detailed balance relation

$$P_{\ell' \leftarrow \ell} e^{-\beta E_\ell} = P_{\ell \leftarrow \ell'} e^{-\beta E_{\ell'}} \,. \tag{3.2c}$$

(The normalization condition is essentially a definition of the diagonal element $P_{\ell,\ell} \equiv 1 - \sum_{\ell' \neq \ell} P_{\ell' \leftarrow \ell}$.) It is also useful[7] to introduce the symmetric matrix $\widetilde{P}_{\ell',\ell}$,

$$\widetilde{P}_{\ell',\ell} \equiv e^{\beta(E_\ell + E_{\ell'})/2} P_{\ell' \leftarrow \ell} e^{-\beta E_\ell}$$

$$= e^{\beta E_{\ell'}/2} P_{\ell' \leftarrow \ell} \, e^{-\beta E_\ell/2} \,, \tag{3.3a}$$

or in matrix notation

$$\widetilde{\mathbf{P}} = e^{\beta \mathbf{H}_0/2} \bullet \mathbf{P} \bullet e^{-\beta \mathbf{H}_0/2} \,, \tag{3.3b}$$

where $\mathbf{H}_0$ is the diagonal matrix of energy levels

$$(\mathbf{H}_0)_{\ell',\ell} = \delta_{\ell',\ell} E_\ell \,. \tag{3.4}$$

Because of the normalization, Eq. (3.2b), the master equation reads

$$\dot{c}_{\ell}(t) = - \sum_{\ell'} \left(\delta_{\ell\ell'} k_{\ell} + \omega\delta_{\ell\ell'} - \omega P_{\ell\ell'}\right) c_{\ell'}(t) \,, \tag{3.5}$$

and its solution is conveniently written in matrix form,

$$\mathbf{c}(t) = e^{-[\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]t} \bullet \mathbf{c}(0) \,, \tag{3.6}$$

where $\mathbf{k}$ is the diagonal matrix of unimolecular decay rates

$$(\mathbf{k})_{\ell',\ell} = \delta_{\ell',\ell} k_{\ell} \,. \tag{3.7}$$

Therefore if ℓ' is the initial state at $t = 0$, i.e., $c_{\ell}(0) = \delta_{\ell',\ell}$, then the populations at time t are

$$c_{\ell}(t) \equiv c_{\ell \leftarrow \ell'}(t) = \{e^{-[\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]t}\}_{\ell,\ell'} \,. \tag{3.8}$$

The classical flux correlation function which corresponds to the generalization of the classical SCA result in Eq. (2.9) (including the collisional factor $e^{-\omega t}$), is thus given by

$$C_f(t) = - \sum_{\ell,\ell'} k_{\ell} c_{\ell \leftarrow \ell'}(t)\, k_{\ell'} e^{-\beta E_{\ell'}}$$

$$= - \sum_{\ell,\ell'} k_{\ell} \{e^{-[\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})t]}\}_{\ell,\ell'}\, k_{\ell'} e^{-\beta E_{\ell'}} \,, \tag{3.9}$$

the time integral of which gives

$$k_r Q_r = - \sum_{\ell,\ell'} k_\ell \, [\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]^{-1}_{\ell,\ell'} \, k_{\ell'} e^{-\beta E_{\ell'}} . \qquad (3.10)$$

As before,[10] this result needs to have its $\omega = 0$ limit subtracted from itself, giving

$$k_r Q_r = \sum_{\ell} k_\ell \, e^{-\beta E_\ell} - \sum_{\ell,\ell'} k_\ell \, [\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]^{-1}_{\ell,\ell'} \, k_{\ell'} e^{-\beta E_{\ell'}} ,$$

$$= \sum_{\ell,\ell'} \left\{ \mathbf{k} \bullet [\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]^{-1} \bullet (\mathbf{1}-\mathbf{P})\omega \right\}_{\ell,\ell'} e^{-\beta E_{\ell'}} . \qquad (3.11)$$

Finally, this can be written in a more symmetrical form by noting that the similarity transformation relating $\mathbf{P}$ and $\widetilde{\mathbf{P}}$ in Eq. (3.3b) is also true for any power of these matrices, i.e.,

$$\mathbf{P}^n = e^{-\beta \mathbf{H}_0/2} \widetilde{\mathbf{P}}^n \, e^{+\beta \mathbf{H}_0/2}, \qquad (3.12)$$

and thus also for any function of the matrices, so that in terms of the symmetrized transition probability matrix $\widetilde{\mathbf{P}}$ Eq. (3.11) becomes

$$k_r Q_r = \sum_{\ell,\ell'} e^{-\beta E_\ell/2} \{ \mathbf{k} \bullet [\mathbf{k}+\omega(\mathbf{1}-\widetilde{\mathbf{P}})]^{-1} \bullet (\mathbf{1}-\widetilde{\mathbf{P}})\omega \}_{\ell,\ell'} \, e^{-\beta E_{\ell'}/2}$$

$$= \mathbf{b}^T \bullet \mathbf{k} \bullet [\mathbf{k}+\omega(\mathbf{1}-\widetilde{\mathbf{P}})]^{-1} \bullet (\mathbf{1}-\widetilde{\mathbf{P}}) \bullet \mathbf{b}\omega , \qquad (3.13a)$$

where $\mathbf{b}$ is the "Boltzmann vector"

$$(\mathbf{b})_\ell = e^{-\beta E_\ell/2} . \qquad (3.13b)$$

Eq. (3.13) (or Eq. (3.11) is thus the desired generalization of the classical SCA result, Eq. (1.2); the SCA result is obtained when $\mathbf{P}$ or $\tilde{\mathbf{P}} \to 0$. ($P_{\mathcal{L}'\leftarrow\mathcal{L}} \to 0$ in the SCA because an infinite number of final states $\mathcal{L}'$ are populated.) Note also that the rate vanishes if the collisions are purely elastic, i.e., $\tilde{\mathbf{P}} \to \mathbf{1}$, for inelastic (i.e., energy loss) collisions are clearly necessary for recombination to take place.

IV. Quantum Theory Beyond the SCA

The recombination rate given by Eq. (2.7b) of Section II contains a rigorous quantum description of the A + B collision dynamics but with the (rather crude) strong collision approximation for energy transfer in M + A-B collisions. Eq. (3.11) or (3.13) of Section III, on the other hand, gives the rate with a more general and realistic (classical master equation) treatment of M + A-B inelastic scattering but neglects quantum effects in the A + B dynamics. Here we wish to combine these two approaches, i.e., to have a rigorous quantum description of the A + B dynamics together with a master equation-like treatment of the M + A-B inelastic scattering. We expect this more general theory to reduce to Eq. (2.7b) if the SCA is made and to Eq. (3.11) if one neglects quantum effects in the A + B dynamics.

The general treatment presented here is based on the impact approximation for M + A-B scattering and follows very closely the collisional line broadening theory of Baranger.[11] (See also Fano,[12] Ben Reuven,[13] and Gordon.[14]) The recombination rate is still given by the time integral of the flux autocorrelation function[15]

$$k_r Q_r = \int_0^\infty dt\ tr[e^{-\beta\hat{H}}\,\hat{F}\,\hat{U}(t)^\dagger\,\hat{F}\,\hat{U}(t)]\ , \qquad (4.1)$$

where the evolution operator $\hat{U}(t)$ includes the effect of collisions by the bath gas M. Within the impact approximation — which assumes that the collisions of A-B with M are isolated, independent, and random events — if there are n collisions, at times $t_1 < t_2 < \ldots < t_n$, then this propagator is

$$\hat{U}^{(n)}(t) = e^{-i\hat{H}(t-t_n)/\hbar} S^{(n)}\, e^{-i\hat{H}(t_n-t_{n-1})/\hbar} S^{(n-1)} \ldots S^{(2)}\, e^{-i\hat{H}(t_2-t_1)/\hbar} S^{(1)}\, e^{-i\hat{H}(t_1-0)/\hbar}\ , \qquad (4.2)$$

where $\hat{H} = \hat{H}_{AB} - i\hat{\varepsilon}$ and $S^{(k)}$ is the S-matrix for an M + A-B collision at time t_k. If the classical path approximation[16] is used to treat the M + A-B collisions, then $S^{(k)}$ is a matrix between states of A-B and is a function of impact parameter and relative velocity for the M + A-B collision, $S_{\ell,\ell'}(b_k,v_k)$; Eq. (4.1) is to be averaged over impact parameters in the usual way and also over a Boltzmann distribution of relative M + A-B velocities. (The superscript index in $S^{(k)}$ indicates that the impact parameter b_k and velocity v_k are independent variables for each collision.)

Eq. (4.1) must also be averaged[17] over the various collision times,

$$(n!/t^n) \int_0^t dt_n \int_0^{t_n} dt_{n-1} \ \ldots \int_0^{t_3} dt_2 \int_0^{t_2} dt_1\ , \qquad (4.3)$$

and finally averaged[17] over the number of collisions n, weighted by the probability of having n collisions if ω is the collision frequency,

$$\sum_{n=0}^{\infty} e^{-\omega t} (\omega t)^n / n! \,. \tag{4.4}$$

Applying all of these operations to Eq. (4.1) gives

$$k_r Q_r = \sum_{n=0} \sum_{\ell'_0,\cdots,\ell'_n} \sum_{\ell_0,\cdots,\ell_n} \langle \psi_{\ell'_n}^* | F | \psi_{\ell_n} \rangle \langle \psi_{\ell_0} | F | \psi_{\ell'_0}^* \rangle \, e^{-\beta(E_{\ell_0}+E_{\ell'_0})/2}$$

$$\times \langle S_{\ell'_n,\ell'_{n-1}}{}^* S_{\ell_n,\ell_{n-1}} \rangle \langle S_{\ell'_{n-1},\ell'_{n-2}}{}^* S_{\ell_{n-1},\ell_{n-2}} \rangle \cdots \langle S_{\ell'_1,\ell'_0}{}^* S_{\ell_1,\ell_0} \rangle$$

$$\times \int_0^\infty dt\, e^{-\omega t}\, \omega^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \times e^{\left(i\omega_{\ell'_n \ell_n} - \frac{\Gamma_{\ell'_n} + \Gamma_{\ell_n}}{2\hbar}\right)(t - t_n)}$$

$$e^{\left(i\omega_{\ell'_{n-1}\ell_{n-1}} - \frac{\Gamma_{\ell'_{n-1}} + \Gamma_{\ell_{n-1}}}{2\hbar}\right)(t_n - t_{n-1})} \cdots e^{\left(i\omega_{\ell'_0 \ell_0} - \frac{\Gamma_{\ell'_0} + \Gamma_{\ell_0}}{2\hbar}\right) t_1} , \tag{4.5a}$$

where

$$\omega_{\ell'\ell} = (E_{\ell'} - E_\ell)/\hbar \,, \tag{4.5b}$$

with

$$\omega \langle S_{\ell'_k,\ell'_{k-1}}{}^* \, S_{\ell_k,\ell_{k-1}} \rangle$$

$$\equiv [M]\, \bar{v}\, \beta \int_0^\infty dE_t\, e^{-\beta E_t} (\beta E_t) \int_0^\infty db 2\pi b \; S^*_{\ell'_k,\ell'_{k-1}}(b,v) S_{\ell_k,\ell_{k-1}}(b,v) \tag{4.6}$$

where $E_t = \frac{1}{2}\mu v^2$ is the relative translational energy for the M + A-B collision

and $\bar{v} = \sqrt{8\pi T/\pi\mu}$ the average thermal velocity. The average over impact parameter b produces a (generalized) cross section, and the average over translational energy a (generalized) rate constant. The integral over t in Eq. (4.5a) is recognized[17] to be the Laplace transform of an n-fold convolution, so the result is the product of the n individual Laplace transforms; Eq. (4.5a) thus becomes

$$k_r Q_r = \sum_{n=0} \sum_{\ell_0,\ldots,\ell_n} \sum_{\ell'_0,\ldots,\ell'_n} e^{-\beta(E_{\ell_0}+E_{\ell'_0})/2} \frac{\langle\psi_{\ell_0}|F|\psi^*_{\ell'_0}\rangle\langle\psi^*_{\ell'_n}|F|\psi_{\ell_n}\rangle}{\omega + \frac{\Gamma_{\ell_0}+\Gamma_{\ell'_0}}{2\hbar} + i\omega_{\ell_0\ell'_0}}$$

$$\prod_{k=1}^{n} \frac{\omega\langle S_{\ell'_k\ell'_{k-1}}{}^* S_{\ell_k\ell_{k-1}}\rangle}{\omega + \frac{\Gamma_{\ell_k}+\Gamma_{\ell'_k}}{2\hbar} + i\omega_{\ell_k\ell'_k}} . \qquad (4.7)$$

Further progress in simplifying the general result is made by using a Liouville (or tetradic) vector space:[11-14] each pair of indices (ℓ_k', ℓ_k) is considered a composite *vector* index. The following vectors are thus defined

$$\mathfrak{F}_{\ell'_n\ell_n} = \langle\psi^*_{\ell'_n}|F|\psi_{\ell_n}\rangle \qquad (4.8a)$$

$$\mathfrak{F}_{\ell'_0\ell_0}(\beta) = e^{-\beta(E_{\ell'_0}+E_{\ell_0})/2}\langle\psi^*_{\ell'_0}|F|\psi_{\ell_0}\rangle , \qquad (4.8b)$$

and the matrices

$$\mathfrak{P}_{\ell'_k\ell_k,\ell'_{k-1}\ell_{k-1}} = \langle S^*_{\ell'_k,\ell'_{k-1}} S_{\ell_k,\ell_{k-1}}\rangle \qquad (4.9a)$$

$$K_{\ell'_k \ell_k, \ell'_{k-1} \ell_{k-1}} = \delta_{\ell'_k, \ell'_{k-1}} \delta_{\ell_k, \ell_{k-1}} \frac{\Gamma_{\ell_k} + \Gamma_{\ell'_k}}{2\hbar} \qquad (4.9b)$$

$$\Omega_{\ell'_k \ell_k, \ell'_{k-1} \ell_{k-1}} = \delta_{\ell'_k, \ell'_{k-1}} \delta_{\ell_k, \ell_{k-1}} \frac{E_{\ell_k} - E_{\ell'_k}}{\hbar}, \qquad (4.9c)$$

the latter two of which are diagonal. In this notation Eq. (4.7) reads

$$k_r Q_r = -\sum_{n=0}^{\infty} \mathfrak{F} \bullet [\omega(\omega + \mathbf{K} + i\Omega)^{-1} \bullet \mathcal{P}]^n \bullet (\omega + \mathbf{K} + i\Omega)^{-1} \bullet \mathfrak{F}(\beta), \qquad (4.10)$$

so that the geometric series over n can be summed to give

$$k_r Q_r = -\mathfrak{F} \bullet [\omega(\mathbf{1} - \mathcal{P}) + \mathbf{K} + i\Omega]^{-1} \bullet \mathfrak{F}(\beta), \qquad (4.11a)$$

which in component reads

$k_r Q_r =$

$$\sum_{\ell_0, \ell'_0} \sum_{\ell, \ell'} \langle \psi^*_{\ell} | F | \psi_{\ell} \rangle [\omega(\mathbf{1} - \mathcal{P}) + \mathbf{K} + i\Omega]^{-1}_{\ell' \ell, \ell'_0 \ell_0} \langle \psi_{\ell_0} | F | \psi^*_{\ell'_0} \rangle e^{-\beta(E_{\ell_0} + E_{\ell'_0})/2} \qquad (4.11b)$$

Eq. (4.11) can also be written in the following time-dependent form,

$$k_r Q_r = -\int_0^{\infty} dt \, \mathfrak{F} \bullet e^{-[\omega(\mathbf{1} - \mathcal{P}) + \mathbf{K} + i\Omega]t} \bullet \mathfrak{F}(\beta). \qquad (4.11c)$$

Eq. (4.11) is the desired result that generalizes Eqs. (2.7b) and (3.11); it treats the A + B dynamics fully quantum mechanically and treats energy transfer

(from collisions with M) more generally (via the impact approximation). In the SCA (i.e., $\mathcal{P} \to 0$), it is easy to see that Eq. (2.7b) is recovered, and if one keeps only the "semi-diagonal" elements $\ell'_k = \ell_k$ for all k in Eqs. (4.7)-(4.10), then Eq. (3.11) is obtained (noting that

$$\mathcal{P}_{\ell_k \ell_k, \ell_{k-1} \ell_{k-1}} = \langle |S_{\ell_k, \ell_{k-1}}|^2 \rangle \equiv P_{\ell_k, \ell_{k-1}} , \tag{4.12}$$

is the transition probability matrix of Section III).

This more general result, Eq. (4.11), has been achieved at a heavy price, however, for it involves the generalized "4-index" transition probability matrix of Eq. (4.9a), a "super matrix" in Liouville space. This involves the phases of the S-matrix, as well as their magnitudes, and thus requires much more information about the inelastic M + A-B scattering than simply the transition probability matrix of Section III. It would thus be very desirable to have a theory, necessarily more approximate, that involves only the transition probability matrix but nevertheless contains both Eqs. (2.7b) and (3.11) in the appropriate limits.

One way to achieve such a result is to make a random phase approximation for the phases of the S-matrix elements in Eq. (4.6); i.e., with all the averaging (over impact parameter and relative velocity) that is involved in Eq. (4.6), one assumes that the most oscillatory terms, those involving the phases of the S-matrix elements, average to zero. This corresponds to the following approximation for the generalized transition probabilities matrix of Eq. (4.9a)

$$\mathcal{P}_{\ell'_k\ell_k,\ell'_{k-1}\ell_{k-1}} \equiv \langle S^*_{\ell'_k,\ell'_{k-1}} S_{\ell_k,\ell_{k-1}} \rangle \rightarrow \delta_{\ell'_k,\ell_k}\delta_{\ell'_{k-1},\ell_{k-1}}\, P_{\ell_k,\ell_{k-1}}\,, \tag{4.13}$$

which is now to be used in Eq. (4.7). Separating off the n = 0 term of Eq. (4.7) — since it does not involve any S-matrix factors — Eq. (4.7) thus becomes

$$k_r Q_r = \sum_{\ell_0,\ell'_0} e^{-\beta(E_{\ell_0}+E_{\ell'_0})/2}\, \frac{\langle\psi_{\ell_0}|F|\psi^*_{\ell'_0}\rangle\langle\psi^*_{\ell'_0}|F|\psi_{\ell_0}\rangle}{\omega + \dfrac{\Gamma_{\ell_0}+\Gamma_{\ell'_0}}{2\hbar} + i\omega_{\ell_0\ell'_0}}$$

$$+ \sum_{n=1}^{\infty} \sum_{\ell_0,\cdots,\ell_n} e^{-\beta E_{\ell_0}}\, \frac{\langle\psi_{\ell_0}|F|\psi^*_{\ell_0}\rangle\langle\psi^*_{\ell_n}|F|\psi_{\ell_n}\rangle}{\omega + \Gamma_{\ell_0}/\hbar} \prod_{k=1}^{n} \frac{\omega\, P_{\ell_k\ell_{k-1}}}{\omega + \Gamma_{\ell_k}/\hbar}\,. \tag{4.14}$$

The first term above is recognized as the quantum SCA result of Section II, i.e., Eq. (2.7b), and with the identifications of Eq. (2.8) and recognition of the sums over $\ell_0,\ldots,\ell_n$ in the second term above as a matrix product, Eq. (4.14) becomes

$$k_r Q_r = k_{QM\,SCA} Q_r - \sum_{\ell,\ell'} k_\ell \sum_{n=1}^{\infty} [(\omega+\mathbf{k})^{-1}\bullet\mathbf{P}\omega]^n_{\ell,\ell'} \frac{k_{\ell'}\, e^{-\beta E_{\ell'}}}{\omega + k_{\ell'}}\,. \tag{4.15}$$

The sum over n can be evaluated,

$$\sum_{n=1} [(\omega+\mathbf{k})^{-1}\bullet\mathbf{P}\omega]^n = -\,\mathbf{I} + [\mathbf{k}+\omega(\mathbf{I}-\mathbf{P})]^{-1}\bullet(\omega+\mathbf{k})\,, \tag{4.16}$$

so that the Eq. (4.15) becomes

$$k_r Q_r = k_{QM\,SCA} Q_r + \sum_{\ell} \frac{k_\ell^2}{\omega + k_\ell} e^{-\beta E_\ell} - \sum_{\ell,\ell'} k_\ell \, [\mathbf{k}+\omega(\mathbf{1}-\mathbf{P})]^{-1}_{\ell,\ell'} \, k_{\ell'} \, e^{-\beta E_{\ell'}} . \tag{4.17}$$

The second term on the right hand side above is recognized (once the $\omega = 0$ limit is subtracted off[10]) as the classical SCA result, Eq. (2.10), and the third term as the classical result of Section III, Eq. (3.11), which includes the description of energy transfer via the classical master equation.

The final result of this random phase approximation may thus be written as

$$k_r = k_{QM\,SCA} - k_{CL\,SCA} + k_{CL} , \tag{4.18}$$

where the first term on the right hand side is the rigorous quantum result within the SCA, Eq. (2.7b), the second term is classical result within the SCA, Eq. (2.10c), and the third term the classical result which describes the energy transfer via the classical master equation, Eq. (3.11) or (3.13). If the SCA is valid, then the latter two terms in Eq. (4.18) cancel each other, and one obtains the quantum SCA result. If quantum effects are negligible, then the first two terms cancel, and one obtains the classical master equation result. Eq. (4.18) thus does successfully combine the results of Sections II and III in the appropriate limits.

In various applications one may wish to write Eq. (4.18) as

$$k_r = k_{CL} + \Delta k_Q , \tag{4.19a}$$

where $\Delta k_Q \equiv k_{QM\ SCA} - k_{CL\ SCA}$ is a "quantum correction" to the classical master equation result, the correction being made within the SCA, or as

$$k_r = k_{QM\ SCA} + \Delta k_{Coll}, \tag{4.19b}$$

where $\Delta k_{Coll} \equiv k_{CL} - k_{CL\ SCA}$ is a "collisional correction" to the SCA, the correction being made classically. In either case one notes the important practical feature that Eq. (4.18) requires one to carry out the quantum calculation only within the SCA, so that the more complicated aspects of the energy transfer step are described via the classical master equation. This latter feature is not true, of course, for the more rigorous result given by Eq. (4.11).

V. Summarizing Remarks

Thus it has been possible to combine a proper quantum mechanical treatment of the A + B collision dynamics, Eq. (1.1a), with a more general description of the energy transfer step of the Lindemann mechanism, Eq. (1.1b). The general result, Eq. (4.11), is essentially an adapted version of Baranger's impact theory of spectral line broadening. Unfortunately, however, this result involves the generalized rate constants of Eq. (4.6) for M + A-B collisions, considerably more detailed quantities than the inelastic rates $\omega P_{\ell \leftarrow \ell'}$ that are commonly used[7] to model the classical master equation description of M + A-B energy transfer. A random phase approximation for the S-matrix elements in Eq. (4.6), though, leads to a very simple result, Eq. (4.18), which incorporates both a quantum description of the A + B dynamics and the master

equation description of M + A-B energy transfer. It will be interesting to see in applications the extent to which these more general theories can be applied and the nature of the corrections to the simpler treatments.

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(d) These references, and others below, more often discuss collisional dissociation, the reverse of the reaction in Eq. (1.1), but the two rates are related by detailed balance.

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8. For future references we note that matrix elements of the flux operator are skew-symmetric, $\langle\chi_2|\hat{F}|\chi_1\rangle = -\langle\chi_1|\hat{F}|\chi_2\rangle$, either for real wave functions χ_1 and χ_2 or if one uses (as we do below) the complex-symmetric convention of **not** complex conjugating functions in the bra state.

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10. One may equivalently make the classical approximation directly to Eq. (2.7b) provided one subtracts from the result so obtained its $\omega = 0$ limit;

i.e., $k_r Q_r = -\sum_{\ell} e^{-\beta E_\ell} \frac{k_\ell^2}{\omega + k_\ell} - (-\sum_{\ell} e^{-\beta E_\ell} k_\ell) = \sum_{\ell} e^{-\beta E_\ell} \omega k_\ell / (\omega + k_\ell)$.
This is also equivalent to adding to Eq. (2.9) the very short time transition state theory contribution, $\delta(t) \sum_{\ell} e^{-\beta E_\ell} k_\ell$; see ref. 5 for more discussion of this point.

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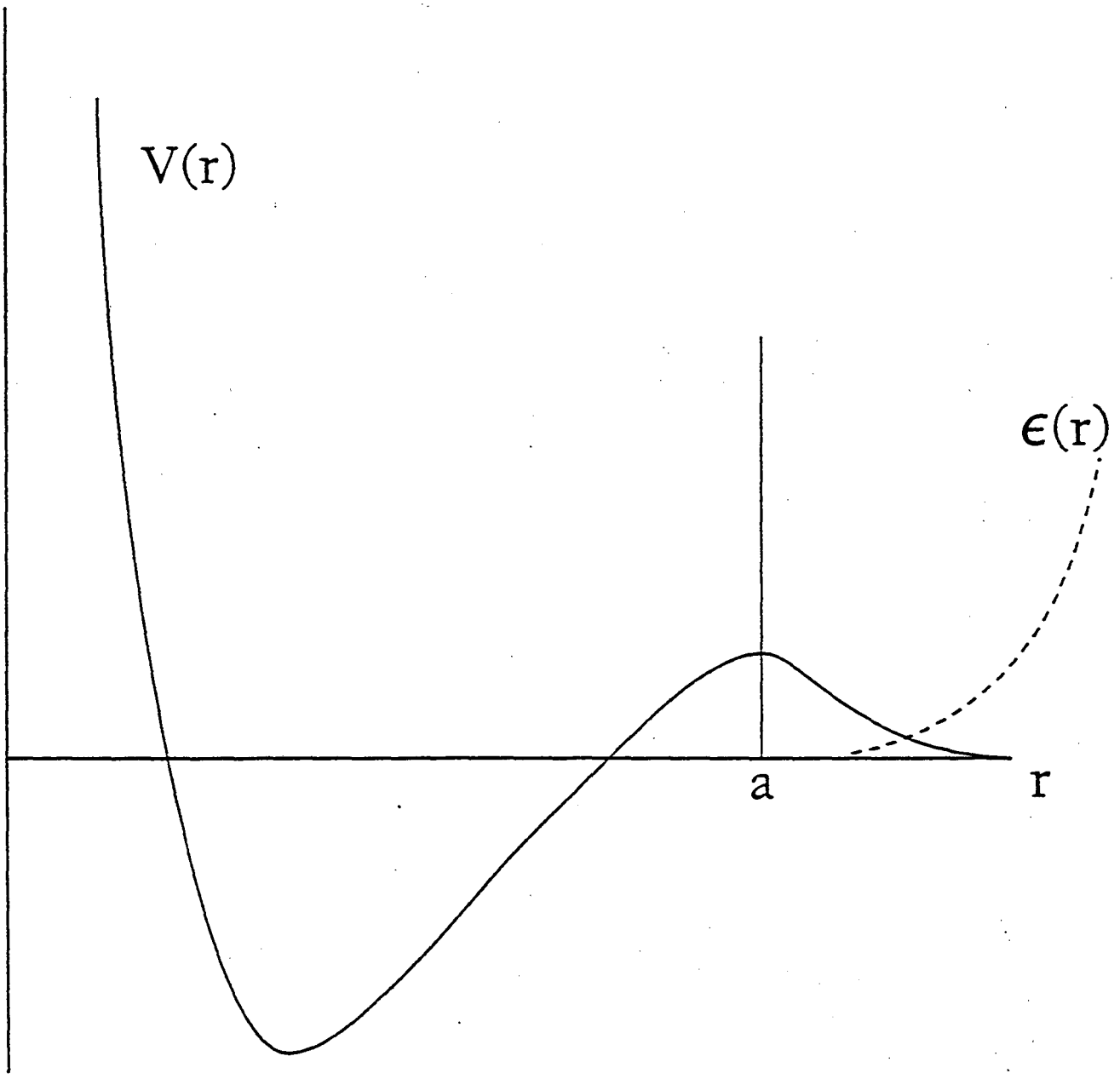
15. This follows from the analysis in ref. 5. The recombination rate is $k_r Q_r = -\text{tr}[e^{-\beta \hat{H}} \hat{F} \hat{P}_r]$, i.e., the Boltzmann flux incident through the dividing surface, where P_r is the recombination probability, which is given by $P_r = \lim_{t \to \infty} \hat{U}^+(t) h \hat{U}(t)$, i.e., the probability that the system is inside the dividing surface as $t \to \infty$; this can also be expressed as $\int_0^\infty dt\, (d/dt)\, \hat{U}^+(t) h \hat{U}(t) = -\int_0^\infty dt\, \hat{U}^+(t) \hat{F} \hat{U}(t)$.

16. It is no problem to relieve this approximation and utilize a fully quantum S-matrix description of M + A-B scattering; see ref. 11.

17. See, for example, D. Chandler, J. Chem. Phys. **60**, 3500 (1974), specifically Appendix A.

Figure Caption

A one-dimensional schematic of the interaction potential for the A + B system, r being the center of mass separation of A and B. $r = a$ is the dividing surface with respect to which the flux operator of Eq. (2.2) is defined, and $\varepsilon(r)$ is the absorbing potential in Eq. (2.3).


V(r)
ϵ(r)
a
r

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