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A CLASSICAL/SEMICLASSICAL THEORY FOR THE INTERACTION OF
INFRARED RADIATION WITH MOLECULAR SYSTEMS*

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Abstract

A classical model for the interaction of molecular systems with infrared radiation is presented. It differs from the usual "semiclassical theory of radiation and matter" in that the molecular system is treated by classical rather than quantum mechanics, and the radiation field is described as classical (mechanical) harmonic oscillators rather than as a classical field (i.e., via Maxwell's equations). The classical Hamiltonian for the composite system--molecules, radiation, and their interaction--is thus that of a completely mechanical system, and its classical dynamics is determined by computing the classical trajectories of the system. Quantum mechanical interference and tunneling effects can be built into the description within the framework of classical S-matrix theory. Even within the strictly classical limit of the model it is shown that all dynamical effects in the interaction of radiation and matter are obtained; in the perturbative limit, for example, it is shown that absorption and induced emission, and even spontaneous emission, which is often difficult to obtain in other classical or semiclassical models, appear in a completely straight-forward manner.

I. Introduction

The advent of high power infrared lasers has stimulated the need for non-perturbative theoretical methods of describing the interaction between infrared radiation and molecular systems. There is interest in the response of isolated molecules to high power infrared lasers (e.g., "multiphoton" dissociation¹ of small polyatomic molecules) and also in the influence of such radiation on the dynamics of molecular collision processes.²

The standard "semiclassical theory of radiation and matter"³ takes the radiation as a classical time-dependent electromagnetic field, described by Maxwell's equations, and describes the "matter", i.e., molecules, quantum mechanically. The time dependent Schrödinger equation is used to determine the influence of the external time-dependent field on the quantum mechanical molecular system.

This approach has several shortcomings, perhaps the most severe being that an accurate quantum mechanical description of any molecular system other than a diatomic molecule is not generally possible. Classical and semiclassical methods are often a good description of molecular dynamics, however, so one can expect to overcome this shortcoming by treating the molecular system by classical, rather than quantum mechanics. Assuming that no electronic transitions are involved, the theoretical model then consists of classical trajectories moving on a potential energy surface with an external time-dependent force from the classical electromagnetic field.

The above classical approach has already been applied^{4,5} to several

examples of "multiphoton" dissociation by high power infrared lasers, and one expects it to be a realistic model of this phenomenon. It is not completely satisfactory, however. Apart from being strictly classical and thus missing any quantum effects that might be significant, this model also has the drawback that the classical Hamiltonian is time-dependent (because of the external time-dependent field) so that the energy of the system is not conserved. (This is correct, of course, since the molecule gains or loses energy from the external electromagnetic field.) This means that energy conservation cannot be used as a check on the accuracy of the classical trajectories as it commonly is for ordinary trajectory calculations without external fields.

This paper presents a new theoretical model which also treats both the radiation field and the molecular system classically. Rather than treating the radiation as a classical field, i.e., via Maxwell's equations, however, the equivalence of the radiation field to a set of harmonic oscillators⁶ is invoked, and the harmonic oscillators representing the field are treated as classical oscillators, i.e., as following classical trajectories. (This, of course, was Planck's model for the radiation field by which he explained black body radiation. This "new" model is thus actually very old!) The Hamiltonian for the complete system--radiation field, molecules, and their interaction--is introduced, and it conserves the total energy of the complete system, molecules plus radiation field. It is also possible to combine this classical treatment of the dynamics with the quantum mechanical principle of superposition via "classical S-matrix" theory,⁷ and thus build quantum effects into the description.

Even at the classical level, i.e., neglecting effects of the superposition principle, this model describes all the dynamical effects in the interaction of molecules with radiation: absorption and emission of energy by the molecular system, and even spontaneous emission of the molecular system. That spontaneous emission is obtained at the completely classical level is interesting since it is often considered to be an inherently quantum mechanical effect.^{6,8,9}

The interaction of radiation and matter is a well-worn topic in general, and in particular there are several other kinds of "semiclassical" approaches^{8,9} that are capable of describing supposedly quantum-like features such as spontaneous emission. The "neoclassical" theory of Jaynes⁸ is the approach most akin to the present work. The primary difference between the two is that the "neoclassical" approach retains a quantum mechanical description of the particles while using a classical treatment of the radiation field. Because of this mixed description the analysis is much more cumbersome than the present and it is also necessary to introduce various dynamical approximations into the treatment; this is typically the case when some degrees of freedom are described quantum mechanical and others are described classical.⁷ Since the present approach treats both particles and radiation field on an equal dynamical footing, i.e., classically, a rather elementary calculation is possible without invoking any dynamical approximations (other than the use of classical mechanics). As mentioned above, the system can be "quantized" via classical S-matrix theory if this is deemed desirable or necessary. The primary advantage of the present formulation is that non-perturbative calculations are possible, and even quite straightforward, since one can numerically compute the classical trajectories of

the complete (particles plus field) system.

Section II develops the general classical/semiclassical model. It is shown in Section III how the field variables can, without approximation, be eliminated from the equations of motion. The resulting equations of motion for the molecular system involve the instantaneous force from the unperturbed electromagnetic field and a "memory force" that involves the history of the molecular motion. Absorption and emission are discussed in some detail in Section IV, and it is seen that the classical expressions for the rate of absorption and induced emission, and even spontaneous emission, are the precise analogs of the quantum mechanical expressions.

II. Theory

a. Classical Model

It is useful to begin with the quantum mechanical Hamiltonian for the molecular system and a single mode radiation field. Generalization to include an arbitrary number of modes is straightforward. The interaction between the field and the molecular system is described within the dipole approximation; again, high order terms in the interaction can be included if they are needed.

The Hamiltonian operator is^{6,10}

$$\begin{aligned}
 H &= H_m + H_{\text{rad}} + H_{\text{int}} \\
 &= H_m(\underline{p}, \underline{x}) + \hbar\omega a^\dagger a + i\sqrt{\frac{2\pi\hbar\omega}{V}} (a^\dagger - a) \underline{\mu}(\underline{x})
 \end{aligned}
 \tag{2.1a}$$

where

$$\underline{\mu}(\underline{x}) = \hat{\epsilon} \cdot \vec{\underline{\mu}}(\underline{x})
 \tag{2.1b}$$

\underline{p} and \underline{x} are the momentum and coordinate operators for the molecular system, and $H_m(\underline{p}, \underline{x})$ is the Hamiltonian for the isolated molecular system; if \underline{p} and \underline{x} are cartesian variables, then it is of the form

$$H_m(\underline{p}, \underline{x}) = \frac{\underline{p}^2}{2m} + V(\underline{x})
 \tag{2.2}$$

a^\dagger and a are creation and annihilation operators of the photon field whose frequency is ω and polarization $\hat{\epsilon}$, and V is the volume of the radiation cavity. $\vec{\underline{\mu}}(\underline{x})$ is the dipole moment of the molecular system as a function

of the molecular coordinates.

To make the classical limit more intuitive it is useful to replace a and a^\dagger by the operators P and X ,

$$P = \sqrt{\frac{\hbar\omega}{2}} (a + a^\dagger) \quad (2.3a)$$

$$X = \sqrt{\frac{\hbar}{2\omega}} i(a - a^\dagger) \quad (2.3b)$$

so that the Hamiltonian becomes

$$H(\underline{p}, \underline{x}, P, X) = H_m(\underline{p}, \underline{x}) + \frac{1}{2} P^2 + \frac{1}{2} \omega^2 X^2 - \sqrt{\frac{4\pi\omega^2}{V}} \mu(\underline{x}) X \quad (2.4)$$

P and X are the abstract cartesian momentum and coordinate of the radiation field, in terms of which the field is seen to appear as a mechanical harmonic oscillator of unit mass.

The classical limit is now taken. The operators \underline{p} , \underline{x} , P , and X become classical variables, and $H(\underline{p}, \underline{x}, P, X)$ of Eq. (2.4) becomes the classical Hamiltonian function. Hamiltons equations,

$$\dot{\underline{x}} = \frac{\partial H}{\partial \underline{p}} = \underline{p}/m \quad (2.5a)$$

$$\dot{\underline{p}} = -\frac{\partial H}{\partial \underline{x}} = -\frac{\partial V}{\partial \underline{x}} + \sqrt{\frac{4\pi\omega^2}{V}} X \frac{\partial \mu(\underline{x})}{\partial \underline{x}} \quad (2.5b)$$

$$\dot{X} = \frac{\partial H}{\partial P} = P \quad (2.5c)$$

$$\dot{P} = -\frac{\partial H}{\partial X} = -\omega^2 X + \sqrt{\frac{4\pi\omega^2}{V}} \mu(\underline{x}) \quad (2.5d)$$

determine the time evolution of the classical coordinates and momenta. This classical dynamical system may be thought of as the original molecular system with one extra vibrational degree of freedom; the potential surface $V(\underline{x}, X)$ for the composite system is

$$V(\underline{x}, X) = V(\underline{x}) + \frac{1}{2} \omega^2 X^2 - \sqrt{\frac{4\pi\omega^2}{V}} \mu(\underline{x}) X$$

Since ordinary classical trajectory calculations for a triatomic molecule, or an A + BC collision process, involve 6 degrees of freedom in its center of mass, it is little increase in effort to compute the trajectories with one additional vibrational degree of freedom. The total energy of the complete system is conserved, of course, since the classical Hamiltonian of Eq. (2.4) is not an explicit function of time.

The time dependence of the field variables is simpler if P and X are replaced by the action-angle variables¹¹ N and Q:

$$X = \sqrt{\frac{2\hbar N}{\omega}} \sin Q \quad (2.6a)$$

$$P = \sqrt{2\hbar N \omega} \cos Q \quad (2.6b)$$

In terms of these variables the classical Hamiltonian of Eq. (2.4) becomes

$$H(\underline{p}, \underline{x}, N, Q) = H_m(\underline{p}, \underline{x}) + \hbar\omega N - \sqrt{\frac{8\pi\hbar\omega N}{V}} \mu(\underline{x}) \sin Q \quad (2.7)$$

Since the unperturbed time-dependence of N and Q is

$$N(t) = \text{constant}$$

$$Q(t) = \omega t + \text{constant} \quad ,$$

their time dependence in the coupled system is expected to be simple also.

b. Semiclassical Model

It is also clear how one can incorporate quantum effects into the picture within the framework of "classical S-matrix" theory.⁷ Suppose, for example, the molecular system is a collinear A + BC collision process. There are two molecular degrees of freedom, translation and vibration, characterized by variables (P,R) and (n,q), respectively; n and q are the action-angle variables for the B-C vibrational motion. The complete system thus has a translational, or scattering degree of freedom and two vibrational degrees of freedom, B-C motion with action-angle variables (n,q), and the field with action-angle variables (N,Q). n has the interpretation of the vibrational quantum number for the diatomic molecule, and N is the number of photons in the field. For a total energy E the scattering parameters of interest are the S-matrix elements,

$$S_{n_2 N_2, n_1 N_1}(E), \quad (2.8)$$

which are the probability amplitudes for the $n_1 N_1 \rightarrow n_2 N_2$ transition. This S-matrix element describes a collision in which the vibrational state of BC changes from n_1 to n_2 with the absorption (or emission) of $(N_2 - N_1)$ photons from the field.

The S-matrix elements of Eq. (2.8) are determined semiclassically by the classical S-matrix formalism.⁷ One requires classical trajectories of the system for which n and N are initially the integers n_1 and N_1 , while the initial values of the conjugate angle variables, q_1 and Q_1 , must be chosen so that n and N are the integers n_2 and N_2 at the end of the

trajectory. The expression for the classical S-matrix is of standard form and need not be given here, other than to note that the phase ϕ of the S-matrix element is given by

$$\phi = - \int_{t_1}^{t_2} dt [R(t)\dot{P}(t) + q(t)\dot{n}(t) + Q(t)\dot{N}(t)] \quad (2.9)$$

This semiclassical picture also shows unambiguously how the strictly classical version of the calculations should be carried out. Following the usual "quasi-classical" Monte Carlo procedure,¹² the initial action variables n_1 and N_1 are taken to be integers, and the conjugate angle variables are chosen by Monte Carlo,

$$q_1 = 2\pi\xi_1$$

$$Q_1 = 2\pi\xi_2 \quad ,$$

where ξ_1 and ξ_2 are random numbers between 0 and 1. The classical trajectory is computed, and the final values of n and N , not necessarily integral, are assigned to the appropriate n_2 - and N_2 -quantum number "boxes". The number of trajectories assigned to a particular (n_2, N_2) box, divided by the total number of trajectories run, is the classical transition probability $P_{n_2 N_2, n_1 N_1}$. If one is uninterested in how many photons are absorbed or emitted and only in what happens to the molecular system, then one simply ignores the final value of N and assigns the final value of n to n_2 -boxes. Averaging over the initial phase of the classical field, Q_1 , thus corresponds to summing over all the number of photons

that are absorbed or emitted. Definite photon processes--i.e., a one-photon process, or a two-photon process, etc.,--on the otherhand, correspond to specific values of the initial phase.

III. Elimination of Field Variables

Eq. (2.5c) and (2.5d) can be combined to eliminate P, giving the following equation for X(t):

$$\ddot{X}(t) + \omega^2 X(t) = \sqrt{\frac{4\pi\omega^2}{V}} \mu(\underline{x}(t)) \quad (3.1)$$

This is a linear inhomogeneous equation for X(t) which is easily solved,

$$X(t) = X_0(t) + \sqrt{\frac{4\pi\omega^2}{V}} \int_{t_1}^t dt' \frac{\sin[\omega(t-t')]}{\omega} \mu(\underline{x}(t')), \quad (3.2)$$

where $X_0(t)$ is the "unperturbed" solution, i.e., the solution to the homogeneous equation:

$$X_0(t) = \sqrt{\frac{2N_1 \hbar}{\omega}} \sin[\omega(t-t_1) + Q_1] \quad (3.3)$$

where (N_1, Q_1) are the values of the action-angle variables at the initial time t_1 .

Eq. (3.2) for X(t) can now be combined with Eq. (2.5a) and (2.5b) to obtain a closed set of equations for the molecular variables ($\underline{p}, \underline{x}$):

$$\dot{\underline{x}}(t) = \underline{p}/m \quad (3.4a)$$

$$\begin{aligned} \dot{\underline{p}}(t) = & - \frac{\partial V(\underline{x})}{\partial \underline{x}} + \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \frac{\partial \mu(\underline{x})}{\partial \underline{x}} \sin[\omega(t-t_1) + Q_1] \\ & + \frac{4\pi\omega^2}{V} \frac{\partial \mu(\underline{x})}{\partial \underline{x}} \int_{t_1}^t dt' \frac{\sin[\omega(t-t')]}{\omega} \mu(\underline{x}(t')) \quad (3.4b) \end{aligned}$$

The three terms in Eq. (3.4b) may be interpreted, respectively, as the instantaneous intramolecular force, the instantaneous force due to the unperturbed radiation field, and a "memory" force that depends on the trajectory at all previous times. This elimination of the field variables $X(t)$ and $P(t)$ from the equations of motion for the molecular variables is analogous to the way a similar elimination occurs in quantum electrodynamics.¹³ It is also the same trick used by Zwanzig,¹⁴ and amplified by Adelman and Doll,¹⁵ to eliminate the degrees of freedom of the harmonic substrate in describing collisions of a gas atom with a solid surface.

It should be noted that the equations of motion Eq. (3.4) for the molecular variables do involve the initial values of the field variables, (N_1, Q_1) . In carrying out a classical Monte Carlo calculation, for example, it is thus still necessary to choose an initial integer value for N_1 and to choose Q_1 randomly in the interval $(0, 2\pi)$.

From $X(t)$ as given by Eq. (3.2) it is possible to determine the final value of the photon quantum number N from the expression

$$\hbar\omega N(t_2) = \frac{1}{2} \dot{X}(t_2)^2 + \frac{1}{2} \omega^2 X(t_2)^2 \quad (3.5)$$

A rather straight-forward calculation gives $N_2 \equiv N(t_2)$ as

$$N_2 \hbar\omega = N_1 \hbar\omega + \sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt \mu(\underline{x}(t)) \cos[\omega(t-t_1) + Q_1] + \frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(\underline{x}(t)) \right|^2 \quad (3.6)$$

where the molecular trajectory $\underline{x}(t)$ is determined by Eq. (3.4).

IV. Absorption and Emission in the Perturbative Limit

Although the classical/semiclassical model described in Sections II and III is expected to be of most use for high power radiation fields when a non-perturbative treatment is necessary, it is interesting in making contact with other approaches to see how this model describes absorption, induced emission, and spontaneous emission of radiation in the perturbative limit. Since spontaneous emission is often thought of as an intrinsically quantum mechanical phenomenon, it is particularly interesting to see here that it comes about in a completely straight-forward way in a totally classical theory.

Consider specifically the change in the energy of the molecular system during the time interval (t_1, t_2) :

$$\begin{aligned} \Delta E_m &= \int_{t_1}^{t_2} dt \frac{d}{dt} H_m(\tilde{p}, \tilde{x}) \\ &= \int_{t_1}^{t_2} dt \frac{d}{dt} \left[\frac{\tilde{p}^2}{2m} + V(\tilde{x}) \right] \\ &= \int_{t_1}^{t_2} dt \left[\frac{\tilde{p}}{m} \dot{\tilde{p}} + \frac{\partial V}{\partial \tilde{x}} \dot{\tilde{x}} \right] \quad ; \end{aligned} \quad (4.1)$$

with the equations of motion of the molecular variables [Eq. (2.5a) and (2.5b)] this becomes

$$\Delta E_m = \int_{t_1}^{t_2} dt \sqrt{\frac{4\pi\omega^2}{V}} \frac{\partial \mu(\tilde{x})}{\partial \tilde{x}} \dot{\tilde{x}} X \quad ,$$

and integration by parts gives

$$\Delta E_m = - \int_{t_1}^{t_2} dt \sqrt{\frac{4\pi\omega^2}{V}} \mu(\underline{x}(t)) \dot{\underline{x}}(t) \quad (4.2)$$

From Eq. (3.2) one finds

$$\begin{aligned} \dot{\underline{x}}(t) &= \sqrt{2N_1 \hbar \omega} \cos[\omega(t-t_1) + Q_1] \\ &+ \sqrt{\frac{4\pi\omega^2}{V}} \int_{t_1}^t dt' \mu(\underline{x}(t')) \cos[\omega(t-t')] \quad , \quad (4.3) \end{aligned}$$

and substituting this into Eq. (4.2) gives

$$\begin{aligned} \Delta E_m &= -\sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt \mu(\underline{x}(t)) \cos[\omega(t-t_1) + Q_1] \\ &- \frac{4\pi\omega^2}{V} \int_{t_1}^{t_2} dt \int_{t_1}^t dt' \mu(\underline{x}(t)) \mu(\underline{x}(t')) \cos[\omega(t-t')] \quad . \quad (4.4) \end{aligned}$$

In the second term of the RHS of Eq. (4.4) the integrand is symmetric with respect to exchange of t and t' , so that

$$\int_{t_1}^{t_2} dt \int_{t_1}^t dt' = \frac{1}{2} \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt' \quad , \quad (4.5)$$

so that the second term can be written as

$$\begin{aligned}
 & -\frac{2\pi\omega^2}{V} \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt' \mu(\underline{x}(t)) \mu(\underline{x}(t')) \cos(\omega t - \omega t') \\
 & = -\frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(\underline{x}(t)) \right|^2 .
 \end{aligned} \tag{4.6}$$

With Eq. (4.6) the expression for the change in energy of the molecular system thus becomes

$$\begin{aligned}
 \Delta E_m & = -\sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt \mu(\underline{x}(t)) \cos[\omega(t-t_1) + Q_1] \\
 & = -\frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(\underline{x}(t)) \right|^2 .
 \end{aligned} \tag{4.7}$$

One notes that the same expression is obtained by considering the energy change in the radiation field, $\hbar\omega(N_2 - N_1) \equiv \hbar\omega\Delta N$; i.e., from Eqs. (3.6) and (4.7) one sees that

$$\hbar\omega\Delta N = -\Delta E_m . \tag{4.8}$$

The energy gained or lost by the molecular system thus shows up in the energy of the radiation field.

Eq. (4.7) is the exact classical expression; now the perturbative limit

is taken. The natural perturbation parameter is $V^{-1/2}$, and one needs to evaluate ΔE_m to second order in it (i.e., to order V^{-1}) and also to average over the initial phase of the field Q_1 . Since the first term in Eq. (4.7) has a factor $V^{-1/2}$, it is necessary to calculate the molecular trajectory $\tilde{x}(t)$ through first order in $V^{-1/2}$. From the equation of motion for $\tilde{x}(t)$, Eq. (3.4), one sees that to first order in $V^{-1/2}$ $\tilde{x}(t)$ is given by

$$\tilde{x}(t) = \tilde{x}_0(t) + \Delta\tilde{x}(t) + O(V^{-1}) \quad , \quad (4.9)$$

where the equations of motion for the zeroth order term $\tilde{x}_0(t)$ and first order correction $\Delta\tilde{x}(t)$ are

$$m \ddot{\tilde{x}}_0(t) + \frac{\partial V(\tilde{x}_0)}{\partial \tilde{x}_0} = 0 \quad (4.10a)$$

$$\left[m \frac{d^2}{dt^2} + \frac{\partial^2 V(\tilde{x}_0)}{\partial \tilde{x}_0^2} \right] \cdot \Delta\tilde{x}(t) = \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \frac{\partial \mu(\tilde{x}_0(t))}{\partial \tilde{x}_0} \sin[\omega(t-t_1) + Q_1] \quad (4.10b)$$

$\tilde{x}_0(t)$ is thus the field-free molecular trajectory. The initial conditions for $\tilde{x}_0(t)$ and $\Delta\tilde{x}(t)$ are

$$\tilde{x}_0(t_1) = \tilde{x}_1 \quad , \quad \dot{\tilde{x}}_0(t_1) = \dot{p}_1/m \quad (4.11a)$$

$$\Delta\tilde{x}(t_1) = \dot{\Delta\tilde{x}}(t_1) = 0 \quad (4.11b)$$

Through order V^{-1} ΔE_m of Eq. (4.7) is thus given by

$$\begin{aligned}
 \Delta E_m &= -\sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt \mu(x_0(t)) \cos[\omega(t-t_1) + Q_1] \\
 &\quad -\sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt \frac{\partial\mu(x_0(t))}{\partial x_0} \cdot \Delta x(t) \cos[\omega(t-t_1) + Q_1] \\
 &\quad - \frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(x_0(t)) \right|^2, \quad (4.12)
 \end{aligned}$$

It is shown in the Appendix that the solution of Eq. (4.10b) for $\Delta x(t)$ is

$$\Delta x(t) = \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \left(\frac{\partial x_0(t)}{\partial p_1} \cdot \frac{\partial}{\partial x_1} - \frac{\partial x_0(t)}{\partial x_1} \cdot \frac{\partial}{\partial p_1} \right) \int_{t_1}^t dt' \mu(x_0(t')) \sin[\omega(t'-t_1) + Q_1], \quad (4.13)$$

where $x_0(t) \equiv x_0(t; x_1, p_1)$ is the field-free molecular trajectory as a function of its initial conditions. Using this result for $\Delta x(t)$ in Eq. (4.12) and averaging over Q_1 gives

$$\begin{aligned}
 \Delta E_m &= -\frac{4\pi\hbar\omega^2 N_1}{V} \int_{t_1}^{t_2} dt \int_{t_1}^t dt' \left[\frac{\partial\mu(x_0(t))}{\partial p_1} \cdot \frac{\partial\mu(x_0(t'))}{\partial x_1} \right. \\
 &\quad \left. - \frac{\partial\mu(x_0(t))}{\partial x_1} \cdot \frac{\partial\mu(x_0(t'))}{\partial p_1} \right] \sin(\omega t' - \omega t) \\
 &\quad - \frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(x_0(t)) \right|^2. \quad (4.14)
 \end{aligned}$$

Eq. (4.5) can also be applied to the first term on the RHS of Eq. (4.14) and the result written equivalently as

$$\Delta E_m = -\frac{4\pi\hbar\omega^2 N_1}{V} \operatorname{Im} \left[\int_{t_1}^{t_2} dt e^{-i\omega t} \frac{\partial \mu(\underline{x}_0(t))}{\partial p_1} \right] \left[\int_{t_1}^{t_2} dt e^{i\omega t} \frac{\partial \mu(\underline{x}_0(t))}{\partial x_1} \right]$$

$$= -\frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt e^{-i\omega t} \mu(\underline{x}_0(t)) \right|^2 \quad (4.15)$$

The first term in Eq. (4.15) is the induced term (i.e., absorption and induced emission) since it is proportional to the number of photons in the field. The second term, which is present even if $N_1 = 0$, describes spontaneous emission; note that it is negative, i.e., as a result of spontaneous emission the molecular system loses energy.

The rate that the molecular energy changes can be found from Eq. (4.15) by setting $t_1 = -T/2$, $t_2 = +T/2$, dividing by T , and taking the limit $T \rightarrow \infty$. By making use of the spectral density theorem,¹⁶ i.e.,

$$\lim_{T \rightarrow \infty} \frac{1}{T} \left[\int_{-T/2}^{T/2} dt e^{-i\omega t} f(t) \right] \left[\int_{-T/2}^{T/2} dt e^{i\omega t} g(t) \right] = \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t) \quad (4.16a)$$

where $C(t)$ is the following time correlation function

$$C(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} dt' f(t') g(t' + t) \quad (4.16b)$$

one obtains

$$\begin{aligned} \dot{\Delta E}_m &\equiv \lim_{T \rightarrow \infty} \left(\frac{\Delta E_m}{T} \right) \\ &= - \frac{4\pi\omega^2 N_1}{V} \operatorname{Im} \int_{-\infty}^{\infty} dt e^{-i\omega t} C_i(t) \quad , \\ &\quad - \frac{2\pi\omega^2}{V} \int_{-\infty}^{\infty} dt e^{-i\omega t} C_r(t) \quad , \end{aligned} \quad (4.17)$$

where

$$C_r(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} dt' \mu(\underline{x}_0(t')) \mu(\underline{x}_0(t'+t)) \quad (4.18a)$$

$$C_i(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} dt' \hbar \frac{\partial \mu(\underline{x}_0(t'))}{\partial p_1} \cdot \frac{\partial \mu(\underline{x}_0(t'+t))}{\partial x_1} \quad (4.18b)$$

Since $\dot{\Delta E}_m$, C_r , and C_i are real quantities, Eq. (4.17) can be simplified to

$$\begin{aligned} \dot{\Delta E}_m &= \frac{4\pi\omega^2 N_1}{V} \int_{-\infty}^{\infty} dt \sin(\omega t) C_i(t) \\ &\quad - \frac{2\pi\omega^2}{V} \int_{-\infty}^{\infty} dt \cos(\omega t) C_r(t) \quad . \end{aligned} \quad (4.19)$$

Eq. (4.19), with the correlation functions defined by Eq. (4.18), is the final classical expression for the rate the molecular system gains (or loses) energy from the field.

One now wishes to compare this classical result to the appropriate quantum mechanical expression. For a single mode radiation field of frequency ω and polarization $\hat{\epsilon}$ the rate of transitions from molecular state n_1 to n_2 is given in first order perturbation theory by¹⁷

$$\Gamma_{n_2 \leftarrow n_1} = \frac{4\pi^2 \omega}{V} |\langle n_2 | \mu | n_1 \rangle|^2 [N_1 \delta(\epsilon_{n_2} - \epsilon_{n_1} - \hbar\omega) + (N_1 + 1) \delta(\epsilon_{n_2} - \epsilon_{n_1} + \hbar\omega)] \quad (4.20)$$

where

$$\mu = \vec{\mu} \cdot \hat{\epsilon}$$

The net rate of change of the molecular energy for the initial state n_1 is thus

$$\begin{aligned} \Delta \dot{E}_{n_1} &\equiv \sum_{n_2} (\epsilon_{n_2} - \epsilon_{n_1}) \Gamma_{n_2 \leftarrow n_1} \\ &= \frac{4\pi^2 \omega^2 \hbar}{V} \sum_{n_2} |\langle n_2 | \mu | n_1 \rangle|^2 [N_1 \delta(\epsilon_{n_2} - \epsilon_{n_1} - \hbar\omega) - (N_1 + 1) \delta(\epsilon_{n_2} - \epsilon_{n_1} + \hbar\omega)] \quad (4.21) \end{aligned}$$

Since the delta function can be represented as

$$\delta(\epsilon_{n_2} - \epsilon_{n_1} \pm \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{\pm i\omega t} e^{i\epsilon_{n_2} t/\hbar} e^{-i\epsilon_{n_1} t/\hbar} \quad (4.22)$$

Eq. (4.21) can be written as

$$\begin{aligned} \dot{\Delta E}_{n_1} &= \frac{2\pi\omega^2 N_1}{V} \left[\int_{-\infty}^{\infty} dt e^{-i\omega t} C_Q(t) - \int_{-\infty}^{\infty} dt e^{i\omega t} C_Q(t) \right] \\ &\quad - \frac{2\pi\omega^2}{V} \int_{-\infty}^{\infty} dt e^{i\omega t} C_Q(t) \quad , \end{aligned} \quad (4.23)$$

where $C_Q(t)$ is the quantum mechanical dipole correlation function:¹⁸

$$\begin{aligned} C_Q(t) &= \sum_{n_2} e^{i\epsilon_{n_2} t/\hbar} e^{-i\epsilon_{n_1} t/\hbar} |\langle n_2 | \mu | n_1 \rangle|^2 \\ &= \sum_{n_2} \langle n_1 | \mu | n_2 \rangle \langle n_2 | e^{iH_m t/\hbar} \mu e^{-iH_m t/\hbar} | n_1 \rangle \\ &= \langle n_1 | \mu e^{iH_m t/\hbar} \mu e^{-iH_m t/\hbar} | n_1 \rangle \quad , \end{aligned} \quad (4.24)$$

where H_m is the molecular Hamiltonian operator. Since the real and imaginary parts of $C_Q(t)$ are even and odd functions¹⁸ of t , respectively,

Eq. (4.23) becomes

$$\begin{aligned} \dot{\Delta E}_{n_1} &= \frac{4\pi\omega^2 N_1}{V} \int_{-\infty}^{\infty} dt \sin(\omega t) \text{Im } C_Q(t) \\ &\quad - \frac{2\pi\omega^2}{V} \int_{-\infty}^{\infty} dt [\cos(\omega t) \text{Re } C_Q(t) - \sin(\omega t) \text{Im } C_Q(t)] \quad , \end{aligned}$$

or

$$\begin{aligned} \Delta \dot{E}_{n_1} &= \frac{4\pi\omega^2}{V} (N_1 + \frac{1}{2}) \int_{-\infty}^{\infty} dt \sin(\omega t) \text{Im } C_Q(t) \\ &- \frac{2\pi\omega^2}{V} \int_{-\infty}^{\infty} dt [\cos(\omega t) \text{Re } C_Q(t)] \end{aligned} \quad (4.25)$$

This is the final quantum mechanical expression.

Comparing the classical [Eq. (4.19)] and quantum [Eq. (4.25)] expressions, one sees that in terms of their respective correlation functions the expressions are identical if one (1) identifies the classical dipole correlation function of Eq. (4.18a) with the real part of the quantum mechanical dipole correlation function

$$C_r(t) \leftrightarrow \text{Re } C_Q(t) \quad , \quad (4.26a)$$

(2) identifies the correlation function $C_i(t)$ of Eq. (4.18b) as the imaginary part of the quantum mechanical dipole correlation function,

$$C_i(t) \leftrightarrow \text{Im } C_Q(t) \quad , \quad (4.26b)$$

and (3) replaces the photon quantum number N_1 in the classical expression, Eq. (4.19), by $(N_1 + \frac{1}{2})$.

Eq. (4.26a) is an obvious and well-known¹⁸ correspondence, but Eq. (4.26b) is not. The latter provides a general way of using classical mechanics to determine an approximation to the imaginary part of the quantum mechanical dipole correlation function. (Note that $C_i(t)$ is proportional to \hbar , so that it vanishes in the completely classical limit $\hbar = 0$; i.e., in this limit absorption and induced emission exactly cancel

each other.) If one averages $C_i(t)$ in Eq. (4.18b) over a Boltzmann distribution of initial conditions, then one can show that it can be written as

$$\bar{C}_i(t) = -\frac{\hbar}{2kT} \frac{d}{dt} \bar{C}_r(t) + O(\hbar^2) \quad , \quad (4.27)$$

where \bar{C}_r and \bar{C}_i are the Boltzmann averages of C_r and C_i ; this is a known relation.¹⁸

It is also interesting to see that the proper identification requires one to add " $\frac{1}{2}$ " to the photon quantum number N_1 in the classical expression, Eq. (4.19). Since the present classical model treats the field as a classical mechanical harmonic oscillator, it is perhaps not surprising to see the quantum number for the field, N_1 , appear with the familiar " $\frac{1}{2}$ " added to it.

Finally, a simple example which illustrates the above formulae is the case that the molecular system is a single harmonic oscillator of frequency ω_0 . If $\mu(x) = x$, it is easy to show from Eq. (4.24) that the quantum mechanical dipole correlation function is

$$\begin{aligned} C_Q(t) &= \sum_{n_2} |\langle n_2 | x | n_1 \rangle|^2 e^{i(n_2 - n_1)\omega_0 t} \\ &= \frac{\hbar}{2m\omega_0} [(n_1 + 1) e^{i\omega_0 t} + n_1 e^{-i\omega_0 t}] \\ &= \frac{(n_1 + \frac{1}{2})\hbar}{m\omega_0} \cos(\omega_0 t) + \frac{i\hbar}{2m\omega_0} \sin(\omega_0 t) \quad , \end{aligned}$$

so that

$$\text{Re } C_Q(t) = \frac{(n_1 + \frac{1}{2})\hbar}{m\omega_0} \cos(\omega_0 t) \quad (4.28a)$$

$$\text{Im } C_Q(t) = \frac{\hbar}{2m\omega_0} \sin(\omega_0 t) \quad (4.28b)$$

Classically, the field-free molecular trajectory $x_0(t)$ is

$$x_0(t) = x_1 \cos[\omega_0(t-t_1)] + \frac{p_1}{m\omega_0} \sin[\omega_0(t-t_1)] \quad (4.29)$$

From Eq. (4.18) one then easily finds that

$$C_r(t) = \frac{(n_1 + \frac{1}{2})\hbar}{m\omega_0} \cos(\omega_0 t) \quad (4.30a)$$

$$C_i(t) = \frac{\hbar}{2m\omega_0} \sin(\omega_0 t) \quad (4.30b)$$

where n_1 is the vibrational quantum number corresponding to the initial conditions (x_1, p_1) ,

$$n_1 + \frac{1}{2} = \left(\frac{p_1^2}{2m} + \frac{1}{2} m\omega_0^2 x_1^2 \right) / (\hbar\omega_0)$$

Comparing Eqs. (4.28) and (4.30), one sees that this classical theory gives the correct result for both the real and imaginary parts of the quantum mechanical dipole correlation function.

V. Concluding Remarks

The classical/semiclassical model that has been presented here differs from the standard semiclassical theory of radiation and matter in two essential ways: the molecular system is treated by classical, rather than quantum mechanics, and the radiation field is described as classical (mechanical) harmonic oscillators rather than as a classical field. The degrees of freedom of the molecular system and the degrees of freedom of the radiation field thus appear on an equal footing. The classical dynamics of the system corresponds to the coordinates and momenta of the molecule and of the field evolving in time according to Hamilton's equations, i.e., following classical trajectories. Quantum effects (i.e., interference and tunneling) can be built into the model via classical S-matrix theory. It is thus possible to describe complete state-selected processes, i.e., specific quantum transitions of the molecular system that correspond to a specific number of photons being absorbed or emitted.

Even within the completely classical version of the model it is seen that all the dynamical features of the interaction of radiation with matter appear. Spontaneous emission, for example, which is often difficult to describe within other classical or semiclassical models, is seen to appear in the model in a completely straightforward manner.

One would in general expect this model to be most reliable when the quantum numbers of the molecular system and of the field are large. Since the intramolecular potential surface is a smooth function, however, and the field a harmonic oscillator linearly coupled to the molecular

system, it is not surprising that the model can also be accurate even for small quantum numbers. In Section IV it was thus shown that absorption and emission, which are single photon processes in first order perturbation theory, are described correctly. For weak fields, as well as for high power lasers, one therefore expects this model to be a useful description of the interaction of molecular systems with infrared radiation fields. One expects it to be particularly useful when non-perturbative treatments are necessary.

Appendix

The purpose of this appendix is to show that the solution of Eq. (4.10b), with the initial conditions of Eq. (4.11b), is given by Eq. (4.13). For simplicity, vector notation is not used here, but the multidimensional version of the calculation is essentially identical to that given here.

Since Eq. (4.10b) is a linear second-order inhomogeneous equation, its general solution can be expressed in terms of any two linearly independent solutions of the homogeneous equation. Thus let $f(t)$ and $g(t)$ be two such solutions:

$$\left[m \frac{d^2}{dt^2} + \frac{\partial^2 V(x_0(t))}{\partial x_0^2} \right] \begin{Bmatrix} f(t) \\ g(t) \end{Bmatrix} = 0 \quad . \quad (A.1)$$

Then the most general solution of Eq. (4.10b) is

$$\Delta x(t) = c_1 f(t) + c_2 g(t) + (mW)^{-1} \int_{t_1}^t dt' [f(t) g(t') - f(t') g(t)] I(t') \quad , \quad (A.2)$$

where c_1 and c_2 are arbitrary constants (to be determined by the boundary conditions), W is the Wronskian

$$W = \dot{f}(t) g(t) - f(t) \dot{g}(t) \quad (A.3)$$

≠ function of t ,

and $I(t)$ is the inhomogeneity, the RHS of Eq. (4.10b). The initial conditions, Eq. (4.11b), require that

$$c_1 = c_2 = 0 \quad , \quad (A.4)$$

so that

$$\Delta x(t) = (mW)^{-1} \left[f(t) \int_{t_1}^t dt' g(t') I(t') - g(t) \int_{t_1}^t dt' f(t') I(t') \right] . \quad (A.5)$$

The two solutions $f(t)$ and $g(t)$ can be obtained as follows. The field-free trajectory $x_0(t; x_1, p_1)$ satisfies the classical equation of motion

$$m \frac{d^2}{dt^2} x_0(t; x_1, p_1) + \frac{\partial V(x_0(t; x_1, p_1))}{\partial x_0} = 0 \quad . \quad (A.6)$$

Differentiating this equation with respect to the initial condition x_1 gives

$$m \frac{d^2}{dt^2} \frac{\partial x(t; x_1, p_1)}{\partial x_1} + \frac{\partial^2 V(x_0(t; x_1, p_1))}{\partial x_0^2} \frac{\partial x_0(t; x_1, p_1)}{\partial x_1} = 0 \quad , \quad (A.7a)$$

and similarly differentiating with respect to p_1 :

$$m \frac{d^2}{dt^2} \frac{\partial x(t; x_1, p_1)}{\partial p_1} + \frac{\partial^2 V(x_0(t; x_1, p_1))}{\partial x_0^2} \frac{\partial x_0(t; x_1, p_1)}{\partial p_1} = 0 \quad , \quad (A.7b)$$

Since Eq. (A.7) is the homogeneous equation, one can choose

$$f(t) = \frac{\partial x_0(t; x_1, p_1)}{\partial p_1} \quad (A.8a)$$

$$g(t) = \frac{\partial x_0(t; x_1, p_1)}{\partial x_1} \quad (A.8b)$$

Since for short times one has

$$x_0(t; x_1, p_1) \approx x_1 + \frac{p_1}{m} (t-t_1) \quad , \quad (\text{A.9})$$

and thus for short times

$$f(t) \approx (t-t_1)/m \quad (\text{A.10a})$$

$$g(t) \approx 1 \quad , \quad (\text{A.10b})$$

the Wronskian, which can be evaluated at t_1 , is

$$\begin{aligned} W &= \dot{f}(t_1)g(t_1) - f(t_1)\dot{g}(t_1) \\ &= 1/m \quad . \end{aligned} \quad (\text{A.11})$$

With Eqs. (A.8), (A.11), and putting in the specific form $I(t)$ from Eq. (4.10b), the solution in Eq. (A.5) becomes

$$\begin{aligned} \Delta x(t) &= \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \left\{ \frac{\partial x_0(t)}{\partial p_1} \int_{t_1}^t dt' \frac{\partial \mu(x_0(t'))}{\partial x_0} \frac{\partial x_0(t')}{\partial x_1} \sin[\omega(t'-t_1) + Q_1] \right. \\ &\quad \left. - \frac{\partial x_0(t)}{\partial x_1} \int_{t_1}^t dt' \frac{\partial \mu(x_0(t'))}{\partial x_0} \frac{\partial x_0(t')}{\partial p_1} \sin[\omega(t'-t_1) + Q_1] \right\} \\ &= \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \left\{ \frac{\partial x_0(t)}{\partial p_1} \int_{t_1}^t dt' \frac{\partial \mu(x_0(t'))}{\partial x_1} \sin[\omega(t'-t_1) + Q_1] \right. \\ &\quad \left. - \frac{\partial x_0(t)}{\partial x_1} \int_{t_1}^t dt' \frac{\partial \mu(x_0(t'))}{\partial p_1} \sin[\omega(t'-t_1) + Q_1] \right\} \\ &= \sqrt{\frac{8\pi\hbar\omega N_1}{V}} \left[\frac{\partial x_0(t)}{\partial p_1} \frac{\partial}{\partial x_1} - \frac{\partial x_0(t)}{\partial x_1} \frac{\partial}{\partial p_1} \right] \int_{t_1}^t dt' \mu(x_0(t')) \sin[\omega(t'-t_1) + Q_1], \end{aligned} \quad (\text{A.12})$$

where $x_0(t) \equiv x_0(t; x_1, p_1)$. This is the desired result.

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