

Vibronically coupled two-level systems: Radiationless transitions in the slow regime

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We present expressions for rates of radiationless transitions in two-level systems with arbitrary coupling to a set of damped vibrational modes; calculations are limited to transitions slower than vibrational relaxation. Explicit results are discussed within the harmonic approximation and Condon approximation; systematic methods are introduced for treating non-Condon and anharmonic effects. Results relevant to experiment are (1) significant deviations from the energy-gap law when a small number of vibrational modes is coupled to the transition, (2) dependence of transition rate on homogeneous and inhomogeneous vibrational linewidths, (3) nonexponential decay for transitions with vibrational frequency shifts, and (4) persistence of electronic coherence for long times either at low temperature or when frequency shifts are small. Our approach differs from previous work in the partitioning of the Hamiltonian and in the methods of evaluating operator averages; these differences are discussed in relation to the adiabatic approximation and the irreversibility of the transition.

I. INTRODUCTION

The theory of phonon-assisted, or “vibronically coupled,” radiationless transitions has been used to treat a wide variety of phenomena, ranging from internal conversion and intersystem crossing to energy and charge transfer; recent articles^{1,2} have reviewed applications of radiationless transition theory to condensed matter physics. A distinguishing feature of these phenomena, in contrast to other phonon-assisted processes, is that the electron-phonon coupling may be large and is therefore treated nonperturbatively.

Calculations of radiationless transition rates in vibronically coupled systems have proceeded by averaging the vibrational-state to vibrational-state transition probability over an appropriate ensemble. Various methods have been introduced to evaluate this average,^{3–5} but explicit calculations for more realistic Hamiltonians are often difficult.^{2,6} An alternative approach, developed by Soules and Duke,⁷ is to write the transition rate as the spectral density of a specific unitary operator. The spectral-density method was used by Haken and Strobl⁸ for a phenomenological model in which the spectral functions take a simple form. The Haken-Strobl model has the advantage of exact solvability, but, as Wertheimer and Silbey⁹ pointed out, it fails to satisfy detailed balance. Silbey and co-workers^{10–12} applied the spectral-density method in the context of a

reduced density-matrix formalism, which does obey detailed balance. All of these methods require external postulates, not contained in the Hamiltonian, to guarantee irreversibility of the transition and convergence of the integrals which define the transition probability. For example, Kenkre, Knox, and co-workers^{13,14} use a coarse-graining procedure, while Silbey and co-workers restrict their calculations to systems where the vibrational modes form a continuum. The coarse-graining procedure has the disadvantage that the transition rate may depend upon the coarse-grain scale, as is evident in the calculations of Jortner.¹⁵

We present a generalization of the canonical-transformation and spectral-density method for two-level systems, a method subject only to two approximations: perturbation theory in the *electronic* matrix element and assumed slowness of the transition relative to vibrational relaxation. This approach is based on a division of phonon modes into a “quantum system” and a heat bath, thus guaranteeing irreversibility and relating radiationless transition rates to experimentally observable vibrational linewidths. Our approach also provides a tractable calculational method for a wide range of model Hamiltonians. We provide an explicit solution for a two-level system in the harmonic and Condon approximations, and an effective procedure for the inclusion of anharmonic and non-Condon corrections. Using these methods, we draw general conclusions

regarding the dynamics of radiationless transitions in the slow regime.

In the statistical limit of a large number of vibrational modes with incommensurate frequencies, we find that the transition rate is a Gaussian function of the electronic energy gap; this "energy-gap law" has been demonstrated by other workers under more restrictive assumptions. The single-mode case, however, exhibits potentially narrow resonances; non-Condon effects may also provide corrections to the Gaussian form. These results may be significant in the interpretation of observed deviations from the energy-gap law.

We treat cases in which vibrational relaxation is much faster than transition rates, so that the vibrations remain in thermal equilibrium during a reaction. Vibrational operators in the Hamiltonian therefore become stochastic, time-dependent functions, whose properties are determined from the equilibrium phonon Green's functions. In turn, a Hamiltonian with stochastic coefficients can be solved with perturbation theory in analogy to the theory of relaxation in magnetic resonance. Relaxation theory establishes that the expectation values of the operators describing the two-level system follow the Bloch equations and allows time constants— T_1 and T_2 —to be written as Fourier transforms of correlation functions derived from the stochastic coefficients. The distinction between adiabatic and nonadiabatic regimes is not relevant in this method, and therefore our results are valid in both cases.

We discuss relaxation theory in Sec. II and develop a model Hamiltonian in Sec. III. In Sec. IV, we develop a unitary transformation of the entire Hamiltonian that casts it into the form used in Sec. II. We then calculate reaction rates for several special cases in Sec. V and conclude with a general discussion of the consequences of this method.

II. RELAXATION

The theory of relaxation in two-level systems^{16,17} is based on a Hamiltonian of the form

$$H = \frac{1}{2}\epsilon'\sigma_z + H_x(t)\sigma_x + H_y(t)\sigma_y + H_z(t)\sigma_z, \quad (1)$$

where Pauli matrices are used to describe the two-level system. We assume the measurement operator to be σ_z ; thus, an experiment consists of measuring the time dependence of $\langle\sigma_z\rangle$. ϵ' is an energy splitting between the eigenstates of σ_z in the absence of relaxation. The $H_i(t)$ are stochastic functions of time, or more rigorously, coordinates of some "loss mechanism" for the two-level system for which $\langle H_i(t)\rangle = 0$.

If the loss mechanism remains in equilibrium throughout the change of electronic state, and if

measurements are on a time scale long relative to the correlation times of the $H_i(t)$, the expectation values of the σ operators obey the Bloch equations

$$\langle\dot{\sigma}_x\rangle = -\frac{\langle\sigma_x\rangle}{T_2} + \epsilon'\langle\sigma_y\rangle, \quad (2a)$$

$$\langle\dot{\sigma}_y\rangle = -\frac{\langle\sigma_y\rangle}{T_2} - \epsilon'\langle\sigma_x\rangle, \quad (2b)$$

$$\langle\dot{\sigma}_z\rangle = -\frac{\langle\sigma_z\rangle - \sigma_z(\infty)}{T_1}. \quad (2c)$$

To lowest order in perturbation theory, T_1 and T_2 are given by

$$\frac{1}{T_1} = \frac{2}{\hbar^2} [k_{xx}(\epsilon') + k_{yy}(\epsilon')], \quad (3)$$

$$\frac{1}{T_2} = \frac{1}{\hbar^2} [2k_{zz}(0) + k_{xx}(\epsilon') + k_{yy}(\epsilon')], \quad (4)$$

$$k_{ii}(\epsilon') = \int_{-\infty}^{\infty} d\tau \langle H_i(t)H_i(t+\tau) \rangle \times \exp\left[-i\frac{\epsilon'}{\hbar}\tau\right]. \quad (5)$$

Note that T_1 and T_2 depend only on the autocorrelations of the $H_i(t)$, even if the cross correlations are nonzero, and even if the $H_i(t)$ do not commute. In Sec. IV we transform our model Hamiltonian into a form analogous to Eq. (1) and then provide a method for calculating the correlation functions appearing in Eq. (5).

III. MODEL HAMILTONIAN

The measurement operator will not encompass all system degrees of freedom, so that a general Hamiltonian can be written as

$$H = \begin{pmatrix} H_{11}(\vec{p}, \vec{x}) & \tilde{V}(\vec{p}, \vec{x}) \\ \tilde{V}(\vec{p}, \vec{x}) & H_{22}(\vec{p}, \vec{x}) \end{pmatrix}, \quad (6)$$

where \vec{x} and \vec{p} are the coordinates and momenta of the remaining degrees of freedom. The operator \tilde{V} can be made Hermitian by a choice of wave-function phase. We refer to the two-level system as the electronic coordinate, to \vec{x} as the nuclear coordinates, and to the part of the "first-order" Hamiltonian, Eq. (6), that commutes with the measurement operator as the "zeroth-order" Hamiltonian H_0 .

Nuclear vibrations—when measured by infrared absorption or Raman spectroscopy—display finite linewidths, and therefore appear damped. We include damping explicitly by separating the nuclear coordinates into two groups: a small group that will be treated quantum mechanically, and will continue

to be designated by \vec{x} and \vec{p} , and a large group that will be treated as a heat bath. Only the temperature of the heat bath and its coupling to the quantum vibrations need be specified.

Following Senitzky,¹⁸ the Hamiltonian can be written as

$$H = \frac{1}{2}\epsilon\sigma_z + \tilde{V}(\vec{p}, \vec{x})\sigma_x + \frac{1}{2}(1+\sigma_z)H_+(\vec{p}, \vec{x}) + \frac{1}{2}(1-\sigma_z)H_-(\vec{p}, \vec{x}) + \vec{p}\cdot\vec{\Gamma} + H_{hb}, \quad (7)$$

where $\sigma_{\pm} = \frac{1}{2}(\sigma_x \pm i\sigma_y)$; $\vec{p}\cdot\vec{\Gamma}$ describes the coupling between the heat-bath Hamiltonian H_{hb} and the quantum vibrations; and $\frac{1}{2}\epsilon\sigma_z$ allows for an overall energy difference between electronic states. H_+ (H_-) is the effective vibrational Hamiltonian when the electronic subsystem is in the $+$ ($-$) state. It is the difference between H_+ and H_- that provides for coupling between the reaction (transition between electronic states) and the nuclear vibrations. The following four approximations will be made:

(1) the slow approximation, in which the quantum vibrational modes are assumed to remain in thermal equilibrium with the heat bath as the reaction progresses.

(2) a first-order perturbative approximation in \tilde{V}_2 whose validity depends upon the relative values of \tilde{V} and ϵ .

(3) the Condon approximation, in which $\tilde{V}(\vec{x}, \vec{p})$ is assumed to be independent of \vec{x} and \vec{p} .

(4) the harmonic approximation, in which H_+ and H_- describe simple harmonic oscillators with different frequencies or equilibrium positions or both.

IV. TRANSFORMATION OF THE HAMILTONIAN

A transformation U that casts the model Hamiltonian into a form that can be used in relaxation theory can be developed as follows. The part of the zeroth-order Hamiltonian that contains vibrational operators is

$$H_{\text{vib}} = \frac{1}{2}(1+\sigma_z)H_+ + \frac{1}{2}(1-\sigma_z)H_- + \vec{p}\cdot\vec{\Gamma} + H_{hb}, \quad (8)$$

in which H_+ and H_- are expressible in terms of \tilde{a}_j^\dagger and \tilde{a}_j , defined by

$$\tilde{a}_j = \sum_k \left[A_{jk}(\sigma_z)(X_k + \Delta_k\sigma_z) \left[\frac{(\omega_j + \rho_j\sigma_z)}{2\hbar} \right]^{1/2} + iA_{kj}^{-1}(\sigma_z)P_k \left[\frac{1}{2\hbar(\omega_j + \rho_j\sigma_z)} \right]^{1/2} \right]. \quad (9)$$

X_k , P_k , and Δ_k are the position, momentum, and position shift of the k th atom, ω_j is the average frequency of the j th mode, ρ_j is the difference in the j th vibrational frequency between the two electronic states, and A_{jk} expresses the normal mode structure (i.e., combinations of coordinates that define the normal modes).

In the slow approximation, the vibrational coordinates move in obedience to H_{ph} , obtained from Eq. (8) by replacing σ_z with $\langle\sigma_z\rangle$. Correspondingly, we define operators a_j and a_j^\dagger by replacing σ_z with $\langle\sigma_z\rangle$ in Eq. (9) and define U such that $U\tilde{a}_jU^\dagger = a_j$. U commutes with σ_z , but not with σ_+ or σ_- . Thus the transformed Hamiltonian may be written

$$UHU^\dagger = \sigma_z[\epsilon/2 + D(a^\dagger, a)] + VF\sigma_+ + VF^\dagger\sigma_- + H_{\text{ph}} - \langle\sigma_z\rangle D(a^\dagger, a), \quad (10)$$

where

$$(\sigma_z - \langle\sigma_z\rangle)D(a^\dagger, a) = UH_{\text{vib}}U^\dagger - H_{\text{ph}}.$$

$V = U\tilde{V}U^\dagger$ and $F\sigma_+ = U\sigma_+U^\dagger$, so that V has the same form as \tilde{V} but with \tilde{a} replaced by a , and $F = U(\sigma_z \rightarrow +1)U^\dagger(\sigma_z \rightarrow -1)$. Note that in the Condon approximation V is a c number.

It is useful to construct F in its normally ordered form, denoted $:F:$; similar considerations apply to U or to V as would be necessary for explicit treatment of non-Condon models. This is done by first evaluating the commutator of F with a_j , and then solving the equations¹⁹

$$[:F:, a_j] = -\frac{\partial:F:}{\partial a_j^\dagger} \quad \text{and} \quad [:F:, a_j^\dagger] = \frac{\partial:F:}{\partial a_j}. \quad (11)$$

We obtain

$$:F: = K \cdot \exp \left\{ \sum_{ij} \left[a_i^\dagger (R_{ij}^{-1} - \delta_{ij}) a_j + \frac{1}{2} a_i \left[\sum_k T_{ik} R_{kj}^{-1} \right] a_j - \frac{1}{2} a_i^\dagger \left[\sum_k R_{ik}^{-1} T_{kj} \right] a_j^\dagger - a_i^\dagger R_{ij}^{-1} \eta_j + a_i \left[\delta_{ij} - \sum_k T_{ik} R_{kj}^{-1} \right] \eta_j \right] \right\}, \quad (12)$$

where R_{ij} , T_{ij} , and η_j are given by

$$R_{ij} = \sum_{k,l,m} A_{ik}(\langle \sigma_z \rangle) A_{kl}^{-1}(\sigma_z \rightarrow +1) A_{lm}(\sigma_z \rightarrow -1) A_{kj}^{-1}(\langle \sigma_z \rangle) \cosh \left[\ln \left[\frac{(\omega_i + \rho_i \langle \sigma_z \rangle)(\omega_l - \rho_l)}{(\omega_j + \rho_j \langle \sigma_z \rangle)(\omega_l + \rho_l)} \right]^{1/2} \right], \quad (13)$$

$$T_{ij} = R_{ij}(\cosh \rightarrow \sinh), \quad (14)$$

$$\eta_j = [(\omega_j + \rho_j \langle \sigma_z \rangle) / 2\hbar]^{1/2} \times \left[\sum_k A_{jk}(\langle \sigma_z \rangle) (\langle \sigma_z \rangle - 1) \Delta_k - \sum_{n,k,l} A_{jn}(\langle \sigma_z \rangle) A_{nl}^{-1}(\sigma_z \rightarrow +1) A_{lk}(\sigma_z \rightarrow -1) \left[\frac{\omega_l - \rho_l}{\omega_l + \rho_l} \right] (\langle \sigma_z \rangle + 1) \Delta_k \right]. \quad (15)$$

The constant K may be determined from the condition of unitarity.

By comparing Eqs. (1) and (10), the stochastic coefficients can be identified. From these identifications we obtain,²⁰ with $\epsilon' = \epsilon + 2\langle D \rangle$,

$$\frac{1}{T_1} = \frac{2}{\hbar^2} \int_{-\infty}^{\infty} d\tau \exp \left[-i \frac{\epsilon'}{\hbar} \tau \right] \langle V(\tau) F(\tau) F^\dagger(0) V^\dagger(0) + F^\dagger(\tau) V^\dagger(\tau) V(0) F(0) \rangle, \quad (16)$$

$$\frac{1}{T_2} = \frac{2}{\hbar^2} \int_{-\infty}^{\infty} d\tau [\langle D(\tau) D(0) \rangle - \langle D \rangle^2] + \frac{1}{2T_1}. \quad (17)$$

To evaluate these formulas we require a method of computing correlation functions, such as $\langle F^\dagger(\tau) V^\dagger(\tau) V(0) F(0) \rangle$, which in the Condon approximation reduces to $V^2 \langle F^\dagger(\tau) F(0) \rangle$. The expectation value of a single normally ordered operator, such as $\langle :F(a^\dagger, a): \rangle$, can be computed by c -number integrations,^{19,21} provided the generating function $\langle e^{-i\xi' a^\dagger} e^{-i\xi a} \rangle$ is known,

$$\langle :F(a^\dagger, a): \rangle = \int d^2\alpha d^2\xi e^{-i\vec{\xi}' \cdot \vec{\alpha}} \langle e^{-i\xi' a^\dagger} e^{-i\xi a} \rangle :F(\alpha', \alpha):. \quad (18)$$

Note that $\vec{\alpha} = (\alpha', \alpha)$ and $\vec{\xi} = (\xi', \xi)$ are real numbers, not operators, and $:F(\alpha', \alpha):$ has the same functional form as $:F(a^\dagger, a):$, with a^\dagger and a replaced by α' and α , respectively.

This technique can be extended to products of normally ordered operators,

$$\langle :F_1(a_1^\dagger, a_1): :F_2(a_2^\dagger, a_2): \rangle = \int d^4\alpha d^4\xi e^{-i\vec{\xi}' \cdot \vec{\alpha}} \langle e^{-i\xi_1' a_1^\dagger} e^{-i\xi_1 a_1} e^{-i\xi_2' a_2^\dagger} e^{-i\xi_2 a_2} \rangle :F_1(\alpha_1', \alpha_1): :F_2(\alpha_2', \alpha_2):, \quad (19)$$

where $a_1 = a(t_1)$, etc. The two-time generating function may be evaluated by a cumulant expansion; in the harmonic case, this has only two terms because the operators are Gaussian variables. The terms in the cumulant expansion are the irreducible Green's functions^{18,19,22} for the operators a^\dagger and a . If $\tau = t_2 - t_1$ and $\omega' = \omega + \rho \langle \sigma_z \rangle$, these are

$$\langle a_1 a_2 \rangle = \langle a_1^\dagger a_2^\dagger \rangle = 0, \quad (20)$$

$$\langle a_1 a_2^\dagger \rangle = (\bar{\nu} + 1) \exp(i\omega' \tau - \gamma |\tau|), \quad (21)$$

$$\langle a_1^\dagger a_2 \rangle = \bar{\nu} \exp(-i\omega' \tau - \gamma |\tau|), \quad (22)$$

where

$$\bar{\nu} = (e^{\hbar\omega'/k_B T} - 1)^{-1}. \quad (23)$$

From these expressions it may be shown that

$$\langle e^{-i\xi_1' a_1^\dagger} e^{-i\xi_1 a_1} e^{-i\xi_2' a_2^\dagger} e^{-i\xi_2 a_2} \rangle = \exp[-\bar{\nu}(\xi_1 \xi_1' + \xi_2 \xi_2') - (\bar{\nu} + 1)\xi_1 \xi_2' e^{i\omega' \tau - \gamma |\tau|} - \bar{\nu} \xi_1' \xi_2 e^{-i\omega' \tau - \gamma |\tau|}]. \quad (24)$$

For the harmonic and Condon approximations, the above method is sufficient to cast the calculation of relevant correlation functions into two c -number Gaussian integrals over N four-dimensional variables, where N is the number of vibrational modes. Non-Condon effects can be easily incorporated by writing $V(a^\dagger, a)$ in normally ordered form and using a new generating function $\langle e^{-i\xi_1^\dagger a_1^\dagger} \dots e^{-i\xi_4 a_2} \rangle$. This results in two c -number integrals over eight-dimensional variables. At least one integral is Gaussian, and by power series expanding V the other may always be written as a sum of moments of Gaussian integrals.

The Gaussian character of the above generating functions stems from the harmonic approximation. If anharmonic effects are to be incorporated, higher-order Green's functions contribute higher cumulants to the generating functions. It should be stressed, however, that the *only* modification needed in the above method is in the generating function. In particular, the calculation of F need not be changed, although it may be convenient to do so.

V. SPECIAL CASES

A. Single vibrational mode

When a system contains only a single vibrational mode and the frequency shift ρ/ω' is small, then in the harmonic and Condon approximations, we find

$$\frac{1}{T_1} = \frac{2V^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau \exp\{-i[\epsilon/\hbar + (\bar{\nu} + \frac{1}{2})\rho]\tau + \eta^2(x + y - 2\bar{\nu} - 1)\} \times \left[1 + \frac{\rho}{\omega'}(x + y - 2\bar{\nu} - 1) \right], \quad (25)$$

$$\frac{1}{T_2} = \frac{2\rho^2}{\gamma} \bar{\nu}(\bar{\nu} + 1) + \frac{1}{2T_1}, \quad (26)$$

$$\beta = \frac{1}{2} \ln \left[\frac{\omega - \rho}{\omega + \rho} \right], \quad (27)$$

$$\eta = \Delta(m\omega'/2\hbar)^{1/2} [\langle \sigma_z \rangle (1 - e^\beta) - (1 + e^\beta)], \quad (28)$$

$$x = (\bar{\nu} + 1) \exp(i\omega'\tau - \gamma|\tau|), \quad (29)$$

$$y = \bar{\nu} \exp(-i\omega'\tau - \gamma|\tau|). \quad (30)$$

We calculate the integral in Eq. (25) by power series expanding in x and y , and directly integrating the resulting exponentials in τ to obtain a sum of Lorentzians. If the effective energy gap $\epsilon' = \epsilon + (\bar{\nu} + \frac{1}{2})\rho\hbar$ is an integer multiple of $\hbar\omega'$, we can use a Bessel function identity to sum the dominant terms,

$$\frac{1}{T_1} = \frac{4V^2 e^{-S(2\bar{\nu}+1)}}{\hbar^2 \gamma} \left[\frac{\bar{\nu}+1}{\bar{\nu}} \right]^{\epsilon'/2\hbar\omega'} \left[\left[1 - \frac{\rho}{\omega'}(2\bar{\nu}+1) \right] \int_0^1 dz z^{-1} I_{\epsilon'/\hbar\omega'} \{2Sz[\bar{\nu}(\bar{\nu}+1)]^{1/2}\} + \frac{\rho}{\omega'} [\bar{\nu}(\bar{\nu}+1)]^{1/2} \int_0^1 dz z^{-2} I_{\epsilon'/\hbar\omega'-1} \{2Sz[\bar{\nu}(\bar{\nu}+1)]^{1/2}\} + \frac{\rho}{\omega'} [\bar{\nu}(\bar{\nu}+1)]^{-1/2} \int_0^1 dz I_{\epsilon'/\hbar\omega'+1} \{2Sz[\bar{\nu}(\bar{\nu}+1)]^{1/2}\} \right], \quad (31)$$

where $S = \eta^2$, I is a modified Bessel function, and z is a dummy variable.²³

To obtain the rate constant when the vibrational line is inhomogeneously broadened on a time scale faster than T_1 , Eq. (25) must be convolved with the vibrational line shape; if this is Gaussian, the following result obtains, neglecting terms in ρ/ω' ,

$$\frac{1}{T_1'} = \frac{4V^2 e^{-S(2\bar{\nu}+1)}}{\hbar^2 \gamma'} \frac{\hbar\omega'}{\epsilon'} \left[\frac{\pi}{2} \right]^{1/2} \left[\frac{\bar{\nu}+1}{\bar{\nu}} \right]^{\epsilon'/2\hbar\omega'} I_{\epsilon'/\hbar\omega'} \{2S[\bar{\nu}(\bar{\nu}+1)]^{1/2}\}, \quad (32)$$

where $\gamma' \gg \gamma$ is the inhomogeneous linewidth.

These results cannot be extended analytically to nonintegral values of $\epsilon'/\hbar\omega'$, because $\int_{-\infty}^{\infty} d\epsilon' T_1^{-1}(\epsilon')$ calculated from Eq. (31) would differ from the same quantity correctly calculated from Eq. (16). This limitation can be overcome by the following stratagem. Viewed as a function of ϵ' , T_1^{-1} is a sum of Lorentzians, whose peak positions are integral multiples of $\hbar\omega'$, and whose widths depend on γ . We approximate the sum of all

Lorentzians with fixed peak position as a Gaussian whose variance will be determined such that $\int T_1^{-1} d\epsilon' = 4\pi V^2/\hbar$, as can be directly calculated from Eq. (16) in the Condon approximation. For example, in the inhomogeneous case (neglecting terms in ρ/ω'),

$$\frac{1}{T_1} = \sum_{n=-\infty}^{\infty} \frac{4V^2 e^{-S(2\bar{\nu}+1)}}{\gamma' \hbar^2} \left[\frac{\bar{\nu}+1}{\bar{\nu}} \right]^{n/2} \frac{\hbar\omega'}{\epsilon'} \left[\frac{\pi}{2} \right]^{1/2} I_n \{ 2S[\bar{\nu}(\bar{\nu}+1)]^{1/2} \} \exp \left[-\frac{(\epsilon'/\hbar - n\omega')^2}{2\sigma^2} \right], \quad (33)$$

where σ is the standard deviation of the Gaussian. We find

$$\sigma = 2\gamma'/S. \quad (34)$$

B. Statistical limit

When there exists a large number of independent vibrational modes, the integrand in Eq. (5) factors into a product of correlation functions, one for each mode,

$$\frac{1}{T_1} = 2 \left[\frac{V}{\hbar} \right]^2 \int_{-\infty}^{\infty} d\tau \exp \left[-i \frac{\epsilon'}{\hbar} \tau \right] \prod_j C_j(\tau). \quad (35)$$

If the modes have incommensurate frequencies, T_1 can be evaluated by the central limit theorem.²⁴ The result is Gaussian, with a mean and variance given by the sum of means and sum of variances, respectively, of the Fourier transforms of the individual correlation functions. Thus

$$\frac{1}{T_1} = \frac{4\pi V^2}{\hbar^2 \sqrt{2\pi s}} \exp \left[-\frac{(\epsilon'/\hbar - M)^2}{2s} \right], \quad (36)$$

$$M = -i \sum_j \left. \frac{\partial \ln C_j(\tau)}{\partial \tau} \right|_{\tau=0}$$

and (37)

$$s = - \sum_j \left. \frac{\partial^2 \ln C_j(\tau)}{\partial \tau^2} \right|_{\tau=0}.$$

Within the Condon and harmonic approximations, the central limit theorem can still be applied even if the modes are not independent. From above, the correlation function can be written as an integral over N dummy variables, with N proportional to the number of modes; in the harmonic and Condon approximations this integral is Gaussian. It is always possible to bring an N -dimensional Gaussian integral into a product of N Gaussian integrals by a change of variables, and in these new variables the correlation function factors as in Eq. (35). Thus the above method still applies. The Gaussian dependence of the reaction rate on the energy gap is called the energy-gap law.²⁵ This result may be extended to those non-Condon models in which the matrix element has an exponential or Gaussian dependence

on the phonon creation and annihilation operators, but in the general non-Condon case there will be corrections to the Gaussian form.

VI. DISCUSSION

A. Validity of the slow regime

As a reaction proceeds, energy is transferred from an electronic degree of freedom into quantum vibrations, which, in turn, are relaxed by a heat bath. If ν is the ensemble-averaged phonon population of a quantum mode with frequency ω , and $\bar{\nu}$ its equilibrium value, then from conservation of energy

$$\dot{\nu} = \gamma(\bar{\nu} - \nu) + \frac{\epsilon'}{\hbar\omega} \langle \dot{\sigma}_z \rangle, \quad (38)$$

where γ is the vibrational relaxation rate; the deviation from equilibrium $\Delta\nu = \nu - \bar{\nu}$ is therefore $\Delta\nu \approx (\epsilon'/\hbar\omega)/\gamma T_1$. T_1 depends on ν , so that the condition for a slow transition is

$$1 \gg \frac{\partial T_1}{\partial \nu} \frac{\Delta\nu}{T_1} \approx \frac{1}{\gamma T_1} \frac{\epsilon'}{\hbar\omega} \frac{\partial \ln T_1}{\partial \nu}. \quad (39)$$

For example, at high temperature, $T_1 \propto \exp(E^\ddagger/k_B T)$, and $\nu \approx k_B T/\hbar\omega$, so that a slow reaction implies

$$\gamma T_1 \gg \left[\frac{E^\ddagger}{k_B T} \right] \left[\frac{\epsilon'}{k_B T} \right]. \quad (40)$$

Thus the criteria for treating reactions as "slow" are more stringent than $\gamma T_1 \gg 1$.

B. Heat-bath approximation

The separation of vibrational modes into quantum vibrations and a heat bath should be contrasted with that of other workers,^{6,26} who treat all vibrational modes identically. In the absence of a heat bath, one must retain, in principle, anharmonic interactions between modes to account for the equilibration of the system and to ensure the convergence of the integrals which define the transition rate. In practice, irreversible depletion of the final modes is provided

for by fiat, and convergence of the integrals is achieved by coarse graining. This procedure introduces an arbitrary coarse-graining parameter into the expression for the reaction rate.

In contrast, our approach uses the fact that in condensed matter, there is almost always a portion of the system, such as a lattice or solvent, which may be identified as a heat bath. We then use the experimentally measurable vibrational relaxation rate as the parameter which guarantees convergence and introduce no arbitrary parameters.

It is important to note that the reaction rate is inversely related to the vibrational relaxation rate. Increasing the vibrational relaxation rate lowers the density of accepting states, which, according to Fermi's golden rule, produces a smaller transition rate. It is clearly *not* true that if the vibrational relaxation rate is much faster than the reaction rate, then vibrational relaxation can be neglected.

C. Validity of perturbation theory

The condition that a perturbation series converge is that the ratio of successive terms be much smaller than unity. For the theory presented here, a rough argument is as follows. The first term in the reaction rate expansion is the product of $(V/\hbar)^2$ and a single integral over a two-time correlation function. This results in $(V/\hbar)^2$ times a characteristic correla-

tion time τ_c , and in the limit of first-order perturbation theory, represents the reaction rate T_1^{-1} . The second term is the product of $(V/\hbar)^4$ and a triple integral over a four-time correlation function, resulting approximately in $(V/\hbar)^4 \tau_c^3$. Thus the expansion parameter is $(V/\hbar)\tau_c$, and the validity condition is $1 \gg (V/\hbar)\tau_c$, or $1 \ll T_1 V/\hbar$. Given T_1 , the application of perturbation theory therefore requires V to be *greater* than a minimum value \hbar/T_1 .

D. Adiabatic approximation

The division²⁷ of reactions into adiabatic and nonadiabatic regimes—which are often identified on the basis of large or small V , respectively—is based on the use of an adiabatic (or Born-Oppenheimer) approximation²⁸ to the first-order Hamiltonian; Fig. 1 shows the adiabatic energy surfaces for our first-order Hamiltonian with a single harmonic vibration. In our view, however, reactions are defined by transitions between exact eigenstates of the zeroth-order Hamiltonian, which is determined by the experimental apparatus, and not between adiabatic states of the first-order Hamiltonian. The adiabatic approximation is simply not relevant. The magnitude of V is important in our calculation—it determines the validity of perturbation theory—but the conditions of validity for adiabatic approximations and perturbation theory are different.

E. Coherence

Loss of vibrational coherence (γ) and electronic coherence (T_2) occurs on different time scales, and there is no general rule governing their relation. In the absence of vibrational frequency changes between the two electronic states, $T_2 = 2T_1$, so that electronic coherence persists for the full time course of the radiationless transition. Frequency changes can reduce T_2 considerably, but we always have $T_2 = 2T_1$ in the low-temperature limit [cf. Eq. (26)]. This result, in conjunction with the condition for validity of perturbation theory, shows that $T_2 V/\hbar \gg 1$. Thus at low temperature or when frequency changes are very small, electronic coherence persists for many cycles of the “exchange time” \hbar/V ; this result is independent of other features of the model and is in agreement with experiment.²⁹

F. The energy-gap law

A number of workers^{25,30–32} have found that, in some approximation, the transition probability has a Gaussian dependence on the electronic energy gap ϵ . This is the energy-gap law^{25,33} and is the basis for the interpretation of a large body of data on radiationless transitions.³⁴

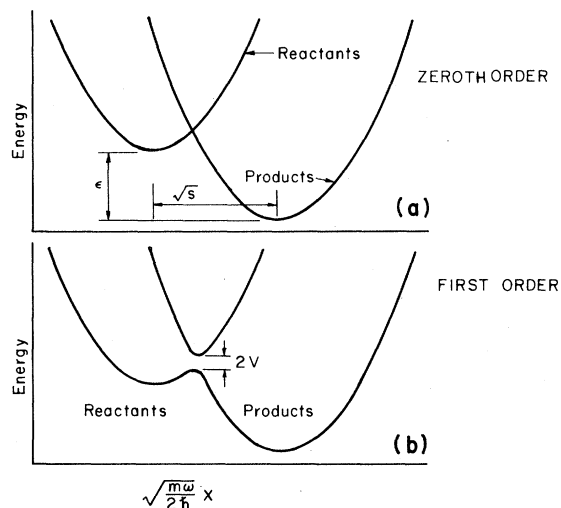


FIG. 1. Energy surfaces for the model Hamiltonian of Eq. (7) in the Condon approximation and for a single harmonic phonon mode. (a) Adiabatic approximation to the zeroth-order surfaces. (b) Adiabatic approximation to the first-order surfaces. “Nonadiabatic” transitions are those which occur between the approximate first-order surfaces, while the radiationless transitions discussed in the text take place between exact zeroth-order surfaces.

In the case of a single vibrational mode, we have shown that the energy-gap dependence of the transition rate has considerable structure and is not well approximated by a Gaussian. This structure arises from resonances between the electronic energy gap and integer multiples of the vibrational frequency and is not an interference effect as may occur with several modes.³⁵ Abram and Silbey¹² have noted the existence of these resonances, but a proper treatment must involve explicit consideration of vibrational relaxation, as given here. Note that the widths of the resonances can be smaller than the width of the relevant vibrational line [Eq. (34)].

In the limit that a large number of vibrational modes are independently coupled to the electronic transition, the energy-gap law is an exact quantum-mechanical result, independent of any semiclassical approximation. We have found that the statistical derivation of the energy-gap law may be extended to an arbitrary transition within the harmonic and Condon approximations and that non-Condon effects may generate polynomial corrections to the Gaussian. For the general case of anharmonic, non-Condon systems, we have not found any simple behavior in the statistical limit; therefore the validity of the energy-gap law remains unclear.

G. Time course of the transition

In the presence of frequency changes, the reaction rate may depend explicitly on $\langle \sigma_z \rangle$, producing a nonexponential decay. The decay rate may either increase or decrease as the reaction progresses, depending on whether the frequencies increase or decrease. This should be distinguished from the nonexponential decay produced by inhomogeneous broadening, which always produces a reaction rate that decreases with reaction progress.

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