effective masses, as we do in this paper, the ENP and EP models are identical, i.e., they result in the same curve when plotting $m^*$ vs magnetic field orientation. In this paper we will refer to the two models collectively as the ENP model.

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# Resonant Energy Transfer between Localized Electronic States in a Crystal*

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We propose a model Hamiltonian to describe resonant energy transfer between discrete electronic states each of which is coupled to the same boson field. In this model, the calculation of the transition probabilities for resonant energy transfer, radiationless intraimpurity electronic transitions, and phonon-broadened electromagnetic transitions among the electronic states of a given impurity are rendered formally equivalent, differing only in the selection of various model parameters. The relation of those parameters to microscopic models is described in detail for the case of resonant energy transfer between localized impurity states. A calculation of the energy-transfer probability is presented which is valid to arbitrary order in the electron-phonon interaction, but is the linear-response-theory treatment of the electronic-transfer term. Explicit comparison between the predictions of our model and those of the Förster-Dexter model are given. We present an analysis of the time-dependent Schrödinger equation which permits us to distinguish between dissipative and multiply periodic solutions to the Schrödinger equation and gives a *precise* definition of weak- and strong-coupling limits. Finally, we indicate the application of our results to describe experimental systems involving radiationless energy transfer and electronic relaxation in rare-earth impurities in crystals.

## I. INTRODUCTION

Recently there has been considerable interest in energy transfer between localized states in a wide variety of connections – including sensitized luminescence, exciton diffusion, molecular electronic relaxation, polaron conduction, and energy transfer in biological systems, to name a few. We discuss the transfer of energy between two impurity ion states which, in addition to being coupled to each other, are coupled to the same quasicontinuous modes of vibration of a crystal lattice.[1] We propose this simplified semiphenomonological Hamiltonian in order to describe the absorption (emission) of radiation, electronic relaxation, and energy transfer in impurity ions in crystals. In fact, all three of these phenomena can be described by the same model Hamiltonian with suitable changes in the definition of certain model parameters. In addition, the Hamiltonian contains all of the essential features needed to describe the dynamics of the energy-transfer process. In particular, the coupling to a quasicontinuous distribution of lattice vibrations provides a means whereby the energy transfer can occur irreversibly.

Our motivation for presenting this discussion is two new results which have emanated from our investigation of the model Hamiltonian and which enhance the understanding of the energy-transfer process. The first is the specification of another mechanism for energy transfer in addition to the usual van der Waals interaction between the two impurity centers.[2,3] This mechanism is a consequence of coupling both ions to the same lattice vibrations. Orbach[4] has discussed this mechanism for energy transfer using first-order perturbation theory.

Our second new result concerns the resonant energy-transfer process. It is well known[5] that in "resonant" processes the usual Born-Oppenheimer (BO) approximation breaks down. We are able to describe the energy transfer in the limits that the phonon coordinates are treated semiclassically and an adiabatic hypothesis is used to describe the nuclear motion. Our analysis of this limit follows similar ones given by Holstein[6] and Levich.[7] Finally, we present a more general formal analysis which permits us to define the regions of irreversible radiationless energy transfer.

The model Hamiltonian is defined by

$$H=H_1+H_2+H_{12}+H_{\mathrm{el\text{-}ph}}+H_{\mathrm{ph}} . \qquad (1.1)$$

The single-ion Hamiltonians $H_1$ and $H_2$ describe the electronic states characteristic of two noninteracting impurities in a host insulator, i.e.,

$$H_i=\sum\nolimits_{\gamma_i} E^{(0)}_{\gamma_i} c^\dagger_{\gamma_i} c_{\gamma_i} . \qquad (1.2)$$

The quantities $E^{(0)}_{\gamma_i}$ are the energies of the localized states, and the $c_{\gamma_i}$ their associated annihilation operators. The physical identification of the states associated with the $c_{\gamma_i}$ depends upon the problem under consideration. For example, in descriptions of phonon-broadened "optical" transitions within a single impurity,[8-12] one identifies $H_1$ with the ground state, $H_2$ with the excited state (of the same impurity), and $H_{12}$ with the electromagnetic field causing transitions between these two states. In the energy-transfer problem we identify $E^{(0)}_{\gamma_1}(c_{\gamma_1})$ with the zeroth-order particle-hole state on the sensitizer impurity and $E^{(0)}_{\gamma_2}(c_{\gamma_2})$ with the final "excited" states on the activator impurity which ultimately decays causing the observed luminescence. In this case $H_{12}$ is taken to describe the energy-transfer interaction

$$H_{12}=\sum_{\gamma_1\gamma_2} U_{\gamma_1\gamma_2} c^\dagger_{\gamma_2} c_{\gamma_1}+\mathrm{H.\ c.} , \qquad (1.3)$$

in which $U=U(\vec{R}_1-\vec{R}_2)$ depends on the distance between the impurities. In our analysis, we consider only a single-hole electron state for the sensitizer and also a single state for the activator. Therefore each of the sums in Eqs. (1.2) and (1.3) reduces to a single term. The associated parameters, $E^{(0)}_1$, $E^{(0)}_2$, and $U_{12}$, are taken to be prescribed (e.g., phenomenological) parameters for a given pair of impurities. Finally, the electron-phonon interaction is taken to describe recoilless linear coupling in all of the impurity states:

$$H_{\mathrm{el\text{-}ph}}=\sum_{i,\gamma_i} c^\dagger_{\gamma_i} c_{\gamma_i} \sum_{\vec{k}\lambda} V^{\gamma_i}_{\vec{k}\lambda} b_{\vec{k}\lambda}+\mathrm{H.\ c.} , \qquad (1.4)$$

$$H_{\mathrm{ph}}=\sum_{\vec{k}\lambda} \hbar\,\omega_\lambda(\vec{k})[b^\dagger_{\vec{k}\lambda} b_{\vec{k}\lambda}+\tfrac{1}{2}] , \qquad (1.5)$$

in which the $b_{\vec{k}\lambda}$ are the annihilation operators of the continuous phonon modes of energy $\hbar\,\omega_\lambda(\vec{k})$. In our two-state two-impurity energy-transfer problem the sum over $\gamma_i$ in Eq. (1.4) reduces to a single term. Therefore we obtain the final form of our model Hamiltonain

$$\begin{aligned} H=&\sum_{i=1}^{2} E^{(0)}_i c^\dagger_i c_i+[U_{12}c^\dagger_1 c_2+\mathrm{H.\ c.}]\\ &+\sum_{\vec{k}\lambda}\hbar\omega_\lambda(\vec{k})\,[b^\dagger_{\vec{k}\lambda} b_{\vec{k}\lambda}+\tfrac{1}{2}]\\ &+\sum_{\vec{k}\lambda}\{b_{\vec{k}\lambda}[\,V^1_{\vec{k}\lambda}c^\dagger_1 c_1+V^2_{\vec{k}\lambda}c^\dagger_2 c_2]+\mathrm{H.\ c.}\} . \end{aligned} \qquad (1.6)$$

The expression for the transition probability between states 1 and 2 obtained by treating $U_{12}$ in the approximation of linear response is well known within the context of the phonon broadening of intra-impurity electromagnetic transitions.[8-12] However, with a single exception,[4] analyses of the energy-transfer probability have used some version of the Förster-Dexter model[2,3] in which one assumes that if one site is coupled to phonons of wave vector $\vec{k}$ the other site is not, i.e., $V^1_{\vec{k}\lambda}\neq 0 \Rightarrow V^2_{\vec{k}\lambda}=0$. In solids, such a "decoupling" is unlikely. In addition, Orbach,[4,13] in his calculation of the energy-transfer probability, utilized a perturbation expansion in the $V^i_{\vec{k}\lambda}$ as well as linear response in the $U_{12}$. The former restriction is lifted in the linear-response analysis presented in Sec. III. Indeed, a major conceptual advantage of our formulation of the energy-transfer problem in terms of the Hamiltonian (1.6) is that this formulation reduces the evaluation of the energy-transfer, radiationless-decay, and phonon-broadened-impurity-spectra transition rates to manifestly equivalent calculations. In linear-response theory they differ only in the forms used for $U_{12}$.

A primary motivation for our definition and analysis of the highly simplified model Hamiltonian, specified by Eq. (1.6), is the desire to define a sufficiently simple model problem that we can describe the effects of both the excitation-transfer term $H_{12}$ and the excitation phonon coupling $H_{el-ph}$, without using perturbation theory on either term. Our interest in avoiding perturbation theory via the construction of highly simplified "model" systems stems from discussion in the literature of three closely related topics: (i) the dependence of the transfer probabilities on the values of $U_{12}$ and $\{V^{\gamma}_{\vec{k}\lambda}\}$ (e.g., the distinction between weak and strong coupling)[14]; (ii) the (presumed) irreversible nature of the energy-transfer process[2,3,15,16]; and (iii) the validity of the use of a linear-response-theory treatment of $U_{12}$ to describe the transfer process.[17,18] The periodic nature of initial-value solutions to the Schrödinger equation obtained from Eq. (1.1) when $H_{el-ph}\equiv 0$ has been described in detail by several authors.[15,17,19] Duke and Soules[1] observed that in certain special cases this result persisted even in the presence of electron-phonon coupling to a continuous phonon field. Despite these facts, the linear response analyses of the effects of $U_{12}$ implicitly assume an irreversible energy transfer (i.e., a dissipative as opposed to periodic solution to the initial-value formulation of the Schrödinger equation). It was the desire to determine criteria for the existence of dissipative solutions to the energy-transfer problem which initially led us to study Eq. (1.6). We proceed by first examining in Sec. II the interpretation of the model Hamiltonian in the case of energy transfer between localized impurities. We conclude Sec. II by presenting a semiclassical analysis of the energy-transfer probability in the electron adiabatic limit. Section III is devoted to a linear-response analysis of the energy-transfer probability. Following a simplification of the Hamiltonian by a canonical transform method, we compare our results to those obtained using the Förster-Dexter model and note some significant distinctions between the two. We then show that linear-response theory for phonons with dispersion leads to dissipative energy-transfer probabilities. There is a close analogy to the small polaron model.[6] However, in order to achieve dissipative motion from our semiclassical (nonperturbative) solutions we implicitly invoke additional physical processes (e.g., anharmonic phonon coupling or "rapid" radiative relaxation of the final state[20]) by way of boundary conditions. As the use of such "boundary-condition" techniques constitutes a widespread method of introducing dissipation in systems with few degrees of freedom,[21] we are not surprised at the necessity to introduce them here. Therefore, even the combined linear-response and semiclassical analysis have not demonstrated the necessary criteria for irreversible energy transfer. Consequently, using an extension of methods applied to the study of radiationless transitions in molecules,[5] we construct a heuristic argument in Sec. IV which indicates that for parameters appropriate to dissipative motion, such motion is a consequence of phase mixing, i.e., the decay of a discrete initial state into a continuum of final states. We also show that in certain limits the phase-mixing-induced irreversible energy-transfer probability is described by our original semiclassical calculation. The paper concludes with a summary of our results and a discussion of their relationship to experimental systems.

## II. MODEL HAMILTONIAN

In this section we relate the parameters of our model Hamiltonian, given by Eq. (1.6), to those characterizing microscopic descriptions of resonant-energy transfer between localized electronic states associated with impurities in insulating hosts. We first consider separately in Sec. II A and II B the electronic states and electron-phonon or orbit-lattice coupling. In Sec. II C we discuss the circumstances in which the electronic and vibrational types of motion can be "separated" by use of an adiabatic hypothesis despite the electron-phonon coupling. Finally, we consistently neglect renormalization of the $U_{12}$ interaction[22] by virtue of our assumption that its value is to be determined empirically.

The defect lattice dynamics has been discussed extensively in the literature. Hence we will not reconsider it here, but refer the reader to the number of articles and books[23-25] which use the harmonic approximation to $H_{ph}$. We adopt a generalized definition of the phonon quantum numbers $\vec{k}\lambda$ to apply to the solutions of the defect lattice equations of motion. As we will see in Sec. II C, coupling to discrete local or pseudolocal modes merely adds a periodic term to the equations of motion. Hence, we usually treat the $V^{i}_{\vec{k}\lambda}$'s as effective coupling parameters to the set of quasicontinuous phonon modes. However, they represent the complete set of electron-lattice coupling constants only in the absence of local or pseudolocal modes.

### A. Defect Electronic States

The electronic Hamiltonian $H_i$ describes the $i$th defect-ion electron states in the absence of the interaction $H_{12}$. We assume that the electronic states are discrete, and in general, nondegenerate. They may be shallow donor and acceptor states[10] or deep impurity states.[11,24] However, we restrict our discussion to the latter in order to relate our model to energy transfer in rare-earth and some transition-metal ion systems. Deep defect states may be characterized by the irreducible representation $\Gamma$ of the point-spin group to which they belong.

It is convenient to define the operator $a_i^\dagger = c_{e_i}^\dagger c_{g_i}$ which when acting on the ground-state wave function creates the $i$th defect ion in its excited state. For the system consisting of two ions and two states on each ion the $a_i^\dagger$ obey the commutation relations

$$[a_i^\dagger, a_i] = 1 \ ,$$

which expresses the fact that if the $i$th ion is not in an excited state it must be in its ground state. Thus we write the noninteracting electronic Hamiltonians in the form

$$H_i = E_i^{(0)} a_i^\dagger a_i = (E_{e_i} - E_{g_i}) a_i^\dagger a_i \ . \tag{2.1}$$

$H_{12}$ is the interaction Hamiltonian connecting the two electronic states. In discussing the vibronic structure of impurity-ion spectra, one identifies $H_{12}$ with the electromagnetic field interaction Hamiltonian.[8-11] In electronic relaxation, $H_{12}$ is usually assumed to be the nonadiabaticity operator.[9] In the energy-transfer problem, it represents the interaction between the hole-electron states. It may be exchange, dipolar, or higher multipolar in nature[2,3]:

$$H_{12} = U_{12} a_1^\dagger a_2 + U_{12}^* a_2^\dagger a_1 \ , \tag{2.2}$$

$$U_{12} = \left( e_1 g_2 \middle| \sum_{i,j} \frac{e^2}{|\vec{r}_i - (\vec{R} - \vec{r}_j)|} \middle| e_2 g_1 \right) , \tag{2.3}$$

in which $e$ and $g$ refer to the excited and ground state on the sensitizer and activator, 1 and 2, the sum is over the electrons involved in the energy transfer, and $\vec{R}$ is the distance between the sensitizer and activator ions.

The treatment of energy transfer first given by Förster[2] for organic systems assumed that $U_{12}$ resulted from the interaction of the electric dipole moments of the sensitizer and activator, respectively. Dexter[3] included higher multipole moments in the decomposition of $U_{12}$ in order to cover cases in which the dipole moments vanished by symmetry. The latter case is relevant when the energy transfer involves an intraconfigurational transition at a center of inversion for either ion. An electric dipole process can occur only by admixing odd harmonics in the crystal field potential and hence the wave function through lattice vibrations. These "phonon forced" processes have been considered in the discussions of the vibronic structure of optical transitions in impurity centers.[12]

### B. Electron-Phonon Interaction

The diagonal linear electron-phonon Hamiltonian which was proposed in the Introduction has been used to describe the optical spectra of a variety of defect centers in solids including molecular centers, shallow donors and acceptors, and deep impurity centers. The coefficients $V_{\vec{k}\lambda}^{\gamma_i}$ are diagonal matrix elements of the gradient of the electron-host-lattice interaction projected on the normal lattice coordinates,

$$V_{\vec{k}\lambda}^{\gamma_i} = (\gamma_i | F(\vec{k}\lambda) | \gamma_i) \ . \tag{2.4a}$$

When we discuss energy transfer, we will have occasion to define

$$V_{\vec{k}\lambda}^{i} \equiv V_{\vec{k}\lambda}^{e_i} - V_{\vec{k}\lambda}^{g_i} \ , \tag{2.4b}$$

which represents the difference in the electron-phonon coupling constants in the ground and excited states on the $i$th ion. For tightly bound electrons

$$\vec{F} = e\vec{E} + \vec{F}_s \ , \tag{2.5}$$

where $\vec{E}$ represents the electrostatic interaction with the host lattice ions and $\vec{F}_s$ represents the short-range covalency and exchange forces.

In a series of papers,[26-31] Bron and Wagner have developed the electrostatic model for electron-lattice coupling and used it to describe the vibronic spectrum of rare-earth ions in alkali halides. However, a complete description of the electron-phonon interaction must also include covalency and exchange forces. Covalency and exchange forces are short range. Hence we assign a coupling constant to each of the irreducible representations, $\Gamma'$, of the point group spanned by displacements of the nearest-neighbor ions. For rigid ion coupling to perfect lattice modes, the matrix element $V_{\vec{k}\lambda}^{i}$ may be written as

$$V_{\vec{k}\lambda}^{i} = \sum_{\Gamma'} f_{\Gamma'}^{i} (N)^{1/2} \epsilon_{\Gamma'}(\vec{k}\lambda) e^{-i\vec{k}\cdot\vec{R}} \left( \frac{\hbar}{2\omega_\lambda(\vec{k})} \right)^{1/2} , \tag{2.6}$$

where $f_{\Gamma'}^{i}$ is an interaction function and $\epsilon_{\Gamma'}$ is the projection of the polarization vector of the phonon on symmetry elements of $\Gamma'$.[13,32]

For the longer-range electrostatic electron-phonon interaction

$$E_i = e \sum_{nt} Z_t \frac{(\vec{r}_i - \vec{R}_{nt})}{|\vec{r}_i - \vec{R}_{nt}|^3} \ . \tag{2.7}$$

An expansion is valid if the electrons are well localized within their nearest-neighbor surroundings. Because the dipolar field which exists in the absence of inversion symmetry couples more strongly to the regions of the crystal which are a long distance from the defect ion, it is a good approximation to assume that such coupling will occur to essentially undisturbed lattice modes even in the presence of local or pseudolocal modes.[32] In either case, we see that the model $V_{\vec{k}\lambda}^{i}$ parameters are well defined. However, their detailed form is not essential to our arguments and in a given case they may be regarded as semiempirical in nature.

### C. Nonadiabaticity and Irreversibility

The eigenfunctions of $H$ can be written in the form

$$\psi_n = \sum_{i=1,2} \sum_{\{n_{\vec{k}\lambda}\}} C_{i\{n_{\vec{k}\lambda}\}} \prod_{\vec{k}} \frac{(b^\dagger_{\vec{k}\lambda})^{n_{\vec{k}\lambda}}}{(n_{\vec{k}\lambda}!)^{1/2}} a_i^\dagger |0\rangle , \qquad (2.8)$$

where the basis states are the usual BO states.[25] A single BO state is a suitable eigenfunction of $H$ only if the off-diagonal matrix elements are much smaller than the separation of the diagonal matrix elements

$$\langle i\{n_{\vec{k}\lambda}\}|\, H\, |\{n'_{\vec{k}\lambda}\}j\rangle \lesssim \langle i\{n_{\vec{k}\lambda}\}|\, H |\, \{n_{\vec{k}\lambda}\}i\rangle - \langle j\{n'_{\vec{k}\lambda}\}|\, H |\, \{n'_{\vec{k}\lambda}\}j\rangle . \qquad (2.9)$$

This is probably never the case in solids where the phonon modes give rise to a quasicontinuous distribution of diagonal matrix elements. As a consequence, extensive configuration mixing will occur between basis states of approximately the same energy even when $H_{12}$ is small. This breakdown in the BO approximation is analogous to that which occurs in the dynamical Jahn-Teller effect although in the case of the latter, the off-diagonal matrix element results from the off-diagonal electron-lattice vibronic coupling.[32]

The energy-transfer rate is determined by the equations of motion of the operators in the Heisenberg representation or alternatively by incorporating the time-dependent factors into the coefficients which determine the wave function in the Schrödinger representation. Adopting a mixed representation in which the electronic states are treated in the Schrödinger representation while the phonon operators are treated as Heisenberg operators, it is easy to obtain the time-dependent equations,

$$-i\hbar\dot{C}_1 = [E_1^{(0)} + \sum_{\vec{k}\lambda} V^1_{\vec{k}\lambda}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda})]C_1 + U_{12}C_2 ,$$

$$-i\hbar\dot{C}_2 = [E_2^{(0)} + \sum_{\vec{k}\lambda} V^2_{\vec{k}\lambda}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda})]C_2 + U_{12}C_1 ,$$

$$-i\hbar\dot{b}_{\vec{k}\lambda} = V^1_{\vec{k}\lambda}\,|C_1|^2 + V^2_{\vec{k}\lambda}|C_2|^2 + \hbar\omega_\lambda(\vec{k})b_{\vec{k}\lambda} . \qquad (2.10)$$

The equations of motion for the coefficients $C_1$ and $C_2$ display periodic behavior as a function of time.

We are interested in investigating the nature of the solutions to Eqs. (2.10). Therefore we make no assumption of ergodicity in the behavior of the lattice ions coupled to the local defect centers even though the motions of the "perfect-solid" lattice mode coordinates are taken to be periodic.

We have noted several times the implicit assumption of irreversibility inherent in the use of linear-response theory, and our objective of clarifying the basis for and validity of this assumption. Almost all of the discussions of this topic in the literature[5,14,15,33] hinge on identifying characteristic time scales for the electronic motion $[\tau_{\text{el}}^{-1} \sim \dot{C}(t)]$ and vibrational motion $[\tau_{\text{vib}}^{-1} \sim \dot{b}(t)]$. In Eqs. (2.10) a major effect of the boson degrees of freedom is the modulation of the spacing between the coupled electronic states which in turn modulates the energy-transfer rate between these states.[15] Some insight into the analytic origin of "irreversibility" in model calculations of energy transfer may be achieved by considering a semiclassical analysis of Eqs. (2.10). In such an analysis, the boson coordinates are, by definition, treated as specified, classical variables. In addition, we confine our attention to the slow-electron-transfer case[15] $\tau_{\text{el}} \gg \tau_{\text{vib}}$.

We begin by making the transformation

$$C_i = C_i' \exp\left\{ \frac{-i}{\hbar} \int^t [E_i^{(0)} + \sum_{\vec{k}\lambda} V^i_{\vec{k}\lambda}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda}) + \tfrac{1}{4}\sum_{\vec{k}\lambda} \hbar\omega_\lambda(\vec{k})(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda})^2 ]\, dt' \right\} , \qquad (2.11a)$$

where

$$q_{\vec{k}\lambda}(t) = [\hbar/2\omega_\lambda(\vec{k})]^{1/2}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda}) . \qquad (2.11b)$$

The time dependence extracted in Eq. (2.11a) is that of a state moving with the instantaneous value of the boson coordinates $q_{\vec{k}\lambda}$. The minimum of the $3N$ parabola occurs at

$$E_i = E_i^{(0)} - \sum_{\vec{k}\lambda} |V^i_{\vec{k}\lambda}|^2/\hbar\omega_\lambda(\vec{k}) . \qquad (2.11c)$$

An equation for $c_2'$ is obtained by inserting Eq. (2.11a) into (2.10) and eliminating $C_1'$ and its derivatives. We find that

$$\ddot{C}_2^1 - \frac{i}{\hbar}[E_1^{(0)} - E_2^{(0)} + \sum_{\vec{k}\lambda} \overline{V}_{\vec{k}\lambda}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda})]\dot{C}_2^1 + |U_{12}/\hbar|^2 C_2^1 = 0 ,$$

$$\overline{V}_{\vec{k}\lambda} = V^1_{\vec{k}\lambda} - V^2_{\vec{k}\lambda} . \qquad (2.12)$$

The linearity in the $q_{\vec{k}\lambda}$ of the expression in brackets in Eq. (2.12) permits us (in the semiclassical limit) to describe the transition process in terms of a single "interaction" coordinate $q_1$ defined such that the reaction velocity is proportional to $q_1$. To accomplish this, we define the coordinates $\{q_i\}$ by

$$\omega q_i = \sum_{\vec{k}\lambda} A(i, \vec{k}_\lambda)\omega_\lambda(\vec{k})q_{\vec{k}\lambda} . \qquad (2.13a)$$

The $q_i$ are normalized according to

$$\sum q_i^2 = \sum_{k\lambda} q_{k\lambda}^2 . \qquad (2.13b)$$

$\vec{A}$ is a unitary matrix so that the value of $\omega$ is determined by Eqs. (2.13a) and (2.13b). $\vec{A}$ is specified by requiring that $q_1$ lies along the direction of the change in the lattice ion equilibrium positions:

$$\overline{V}_1 q_1 = \sum_{\vec{k}\lambda} \overline{V}_{\vec{k}\lambda}(b_{\vec{k}\lambda} + b^\dagger_{-\vec{k}\lambda}) . \qquad (2.13c)$$

The nuclear potential energy is invariant to the unitary transformation

$$\tfrac{1}{2}\sum_{\vec{k}\lambda} \omega_\lambda^2(\vec{k})q_{\vec{k}\lambda} = \tfrac{1}{2}\omega^2\sum_i q_i^2 \ . \qquad (2.13\text{d})$$

The set of coordinates $\{q_i\}$ are not solutions of the nuclear Hamiltonian. However, in the semiclassical analysis, the lattice motion is not quantized and hence the lattice kinetic energy does not enter into the problem explicitly.

Energy transfer occurs principally in the region in which the adiabatic potential energy surfaces nearly cross, namely, $E_1^{(0)} - E_2^{(0)} + \bar{V}_1 q_1 \approx 0$. If we assume that in this region the interaction coordinate is moving uniformly in time, $q_1 = \dot{q}_1 t$, and $|U_{12}|$ is approximately constant, the differential Eq. (2.1) is in the form used by Zener,[34]

$$\ddot{C}_2' - \frac{i}{\hbar}(E_1^{(0)} - E_2^{(0)} + \bar{V}_1\dot{q}_1 t)\dot{C}_2' + \frac{|U_{12}|^2}{\hbar^2}C_2' = 0 \ . \qquad (2.14)$$

The solution of Eq. (2.14) subject to suitable initial boundary conditions gives the probability that the system will undergo a nonadiabatic jump to state 2 if it is initially prepared in state 1. Zener obtained, in the limit that $q_1 \to \infty$,

$$|C_2'(\dot{q}_1)|^2 = 1 - \exp(-2\pi|U_{12}|^2/\hbar\bar{V}_1\dot{q}_1) \ . \qquad (2.15)$$

We next introduce irreversibility into the calculation by imposition of a boundary condition. We argue that as the lattice motion is rapid relative to the energy transfer, the probability of an electronic transition is the product of the transition probability for a fixed value of the $\{q_i, \dot{q}_i\}$, $|C_2(\dot{q}_1)|^2$, and the statistical probability that the phase point $\{q_i, \dot{q}_i\}$ is achieved, i.e.,

$$P_{12}(T) \equiv \frac{\int\cdots\int\prod_i(dq_i d\dot{q}_i)P_{12}(q_i, \dot{q}_i)\prod_i e^{-(\dot{q}_i^2+\omega^2 q_i^2)/2\kappa T}}{\int\cdots\int\prod_i e^{-(\dot{q}_i^2+q_i^2\omega^2)/2\kappa T}dq_i d\dot{q}_i} \qquad (2.16)$$

In practice, this integral will be a double integral over the interaction coordinate and its time derivative because these are the only variables on which $P_{12}$ depends. Equation (2.16) is of the form of a typical reaction-rate calculation in which the irreversibility hypothesis is implicit in the assumption that if the reaction occurs, the phase point is unlikely to return back over the energy barrier into its initial value. This particular aspect of the theory can be corrected in our case by use of an appropriate form for $P_{12}(q_i, \dot{q}_i)$.[6,7] The important point for us here is that the use of Eq. (2.16) rather than actual solutions to Eqs. (2.10) has, by imposition of a boundary condition, imposed irreversible behavior on the energy transfer.

The average transition rate from state 1 to state 2 obtained from Eq. (2.16) is given by

$$P_{12}(T) = \frac{\omega e^{-E^*/\kappa T}}{2\pi\kappa T}\int_0^\infty \exp(-\dot{q}_1^2/e^{2\kappa T}) \times\left[1 - \exp\left(-\frac{2\pi|U_{12}|^2}{\hbar\bar{V}_1\dot{q}_1}\right)\right]\dot{q}_1 d\dot{q}_1 \ . \qquad (2.17)$$

The integral is easily evaluated in analytical form in two limits. In the weak-coupling limit $|U_{12}|^2 \ll \hbar\bar{V}_1\dot{q}_1$,

$$P_{12}(T) = \frac{(2\pi)^{1/2}|U_{12}|^2\omega\exp(-E^*/\kappa T)}{2\hbar\bar{V}_1(\kappa T)^{1/2}} \ , \qquad (2.18\text{a})$$

$$E^* = \tfrac{1}{2}\omega^2/\bar{V}_1^2(E_1 - E_2 - \tfrac{1}{2}\bar{V}_1^2/\omega^2)^2 \ . \qquad (2.18\text{b})$$

This is the limit considered by Robinson and Frosch[15] although they did not obtain an analytical expression for the transition rate. In the strong-coupling limit $|U_{12}|^2 \gg \hbar\bar{V}_1\dot{q}_i$ we obtain

$$P_{12}(T) = (\omega/2\pi)\exp(-E^*/\kappa T) \ . \qquad (2.19)$$

Thus in either limit the energy transfer occurs with the activation energy given in Eq. (2.18b). In the strong-coupling limit it also is independent of the interaction matrix element $|U_{12}|^2$.

If we attempt to extend the above analysis, for instance, by more accurately describing the nuclear motion in the region of crossing, we encounter difficulties inherent in the semiclassical approach. By adopting a single configurational coordinate we have drastically reduced the number of degrees of freedom. We have avoided multiply periodic solutions by adopting suitable boundary conditions, but by so doing we have obscured the question of how the $3N$ degrees of freedom and phonon dispersion enable one to obtain irreversible energy transfer. In Sec. III we present the quantum-mechanical solution in the linear-response limit. Phonon dispersion is seen to be important in establishing criteria for conservation of energy. In Sec. III we present a formal analysis of the exact quantum-mechanical solution and discuss the nature of the time-dependent problem, when all of the degrees of freedom are considered.

## III. LINEAR-RESPONSE THEORY

In this section we present the solution for the energy-transfer rate from the electronic or excitonic state 1 which is assumed to be in thermal equilibrium with the surroundings to the second or final state 2. The result is well known for the case in which $U_{12}$ represents an interaction with the electromagnetic radiation field and the transition rate per frequency interval determines the spectral distribution function.[8-12] We present it here for the case of energy transfer between impurity ions in order to contrast our results with the familiar results of Förster[2] and Dexter.[3,35] These authors made the following assumptions: First, the magnitude of the interaction which is responsible for the radiationless energy transfer $H_{12}$ is small compared to the separation of the eigenvalues of $H_1+H_2+H_{\mathrm{el-ph}}+H_{\mathrm{ph}}$ and is independent of the lattice ion vibrations, i.e., $H_{12}=(U_{12}^{(0)}a_1^\dagger a_2+\text{H. c.})$. As a result energy transfer occurs between BO states for which the initial and final energies are equal. It is further assumed that the electron-phonon Hamiltonian may be separated. $H_{\mathrm{el-ph}}=H_{\mathrm{el-ph}}^{(1)}+H_{\mathrm{el-ph}}^{(2)}$, that is, $V_{\vec{k}\lambda}^1\neq 0 \Rightarrow V_{\vec{k}\lambda}^2=0$. This approximation defines a quasimolecular Hamiltonian which is valid if strong coupling occurs only to localized defect modes or molecular vibrations. It also may be useful if one can neglect the effects of the lattice vibrational kinetic energy. In that case the set of normal coordinates may be transformed to a set of "interaction modes"[11] which describe the motion of lattice ions directly coupled to the defect center. This enables one to separate the electron-phonon Hamiltonian if the two defect centers are coupled to different lattice-ion vibrations. The interaction modes, however, are not normal modes of the defect lattice Hamiltonian. We wish to show that an additional interaction mechanism results if both ions are coupled to the same normal-mode lattice vibrations. In addition, we present a useful canonical transformation for removing the linear coupling to the lattice ion displacements which is valid independent of the use of linear-response theory.

The model Hamiltonian for the energy-transfer problem is obtained from Eq. (1.6) by substituting the hole-electron annihilation operator $a_i$ for the $c_i$'s and using the $E_i^{(0)}$'s and $V_{k\lambda}^i$'s defined by Eqs. (2.1) and (2.4b):

$$H=\sum_{i=1,2}\Big[E_i^{(0)}+\sum_{\vec{k}\lambda}V_{\vec{k}\lambda}^2(b_{\vec{k}\lambda}+b_{-\vec{k}\lambda}^\dagger)\Big]a_i^\dagger a_i+(U_{12}a_1^\dagger a_2+\text{H.c.})$$
$$+\sum_{\vec{k}\lambda}\hbar\omega_\lambda(\vec{k})\,[b_{\vec{k}\lambda}^\dagger b_{\vec{k}\lambda}+\tfrac{1}{2}]\ . \tag{3.1a}$$

We define the canonical transformation[1]

$$\tilde{\mathrm{H}}=e^{iS}He^{-iS}\ , \tag{3.1b}$$

where

$$S=i\sum_{i=1,2}a_i^\dagger a_i\sum_{\vec{k}\lambda}\big[V_{\vec{k}\lambda}^i(b_{\vec{k}\lambda}-b_{-\vec{k}\lambda}^\dagger)/\hbar\omega_\lambda(\vec{k})\big]\ . \tag{3.1c}$$

The effect of this transformation on the phonon coordinates is to shift the equilibrium positions from which ion core displacements are measured. The new equilibrium positions are determined by the occupancy of the electron states,

$$\tilde{b}_{\vec{k}\lambda}=e^{iS}b_{\vec{k}\lambda}e^{-iS}$$
$$=b_{\vec{k}\lambda}-\sum\nolimits_i a_i^\dagger a_i V_{\vec{k}\lambda}^i/\hbar\omega_\lambda(\vec{k})\ . \tag{3.2}$$

A polaron shift is added to some of the electronic matrix elements via the operator identity

$$E_i\tilde{a}_i^\dagger\tilde{a}_i\equiv\Big[E_i^{(0)}-\sum_{\vec{k}\lambda}|V_{\vec{k}\lambda}^i|^2a_i^\dagger a_i/\hbar\omega_\lambda(k)\Big]a_i^\dagger a_i. \tag{3.3}$$

The hole-electron operators are transformed according to

$$\tilde{a}_i=a_ie^{i\alpha_i}\ , \tag{3.4a}$$

$$\alpha_i=\sum_{\vec{k}\lambda}V_{\vec{k}\lambda}^i(b_{\vec{k}\lambda}-b_{-\vec{k}\lambda}^\dagger)/\hbar\omega_\lambda(\vec{k})\ , \tag{3.4b}$$

whence

$$\tilde{a}_i^\dagger\tilde{a}_j=a_i^\dagger a_j\,e^{-i\alpha_i}e^{i\alpha_j}$$
$$=a_i^\dagger a_j\,e^{-i\alpha_{ij}}e^{i\theta_{ij}}\ , \tag{3.5a}$$

where

$$\alpha_{ij}=\alpha_i-\alpha_j\ , \tag{3.5b}$$

$$\theta_{ij}=2\,\mathrm{Im}\sum_{\vec{k}\lambda}V_{\vec{k}\lambda}^iV_{\vec{k}\lambda}^{j*}/\hbar^2\omega_\lambda^2(\vec{k})\ . \tag{3.5c}$$

The transformed Hamiltonian is given by

$$\tilde{H}=\tilde{H}_0+\tilde{H}_{\mathrm{int}}+\tilde{H}_N\ , \tag{3.6}$$

where

$$\tilde{H}_0=\sum_{i=1,2}\tilde{E}_ia_i^\dagger a_i\ , \tag{3.7a}$$

$$\tilde{H}_{\mathrm{int}}=U_{12}e^{-i\alpha_{12}}e^{i\theta_{12}}a_1^\dagger a_2+\text{H. c.}\ , \tag{3.7b}$$

$$\tilde{H}_N=\sum_{\vec{k}\lambda}(b_{\vec{k}\lambda}^\dagger b_{\vec{k}\lambda}+\tfrac{1}{2})\hbar\omega_\lambda(\vec{k})\ . \tag{3.7c}$$

In time-dependent perturbation theory, the probability per unit time for a transition or the transition rate is simply related to the thermodynamic Green's function, $\langle\langle\tilde{H}_{\mathrm{int}}(t)\tilde{H}_{\mathrm{int}}(0)\rangle\rangle_T$, for the interaction Hamiltonian where $\langle\langle\ldots\rangle\rangle$ denotes the thermal average at the absolute temperature $T$[36]:

$$P_{12}(T)=(2\pi/\hbar^2)\mathrm{Im}G_T(0), \tag{3.8a}$$

$$\mathrm{Im}G_T(\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\langle e^{i\tilde{H}_0t}\tilde{H}_{\mathrm{int}}e^{-i\tilde{H}_0t}\tilde{H}_{\mathrm{int}}\rangle\rangle_T\ . \tag{3.8b}$$

In the transformed basis, the Green's function is particularly easy to evaluate. The well-known[10] result is

$$\mathrm{Im}G_T(\omega)=|U_{12}|^2e^{-\phi(T,0)}\int_{-\infty}^{\infty}dt\,e^{-i(\omega-\omega^{(0)})t}e^{\phi(T,t)}\ , \tag{3.9a}$$

$$\phi(T,t)=\sum_{\vec{k}\lambda}|\Delta(\vec{k}\lambda)|^2P_{\vec{k}\lambda}(T,t)\ , \tag{3.9b}$$

$$P_{\vec{k}\lambda}(T,t)=n_{\vec{k}\lambda}e^{i\omega_\lambda(\vec{k})t}+(n_{\vec{k}\lambda}+1)e^{-i\omega_\lambda(\vec{k})t}\ , \tag{3.9c}$$

$$\Delta(\vec{k}\lambda)=(\vec{V}_{\vec{k}\lambda}^1-\vec{V}_{\vec{k}\lambda}^2)/\hbar\omega_\lambda(\vec{k})\ , \tag{3.9d}$$

$$n_{\vec{k}\lambda}=(e^{\hbar\omega_\lambda(\vec{k})/\kappa T}-1)^{-1}\ , \tag{3.9e}$$

$$\hbar\omega^{(0)}\equiv E_1-E_2\ . \tag{3.9f}$$

The perturbation theory result exhibits two important features. First, the factor $\exp[-i\times(\omega-\omega^{(0)})t]$ insures that energy transfer will occur only between states of essentially the same energy. The second important feature is the dependence of the energy-transfer rate on the *difference* in the exciton-phonon coupling constants. Since, in the energy-transfer problem, 1 and 2 refer to the hole-electron states on the sensitizer and activator, respectively, each coupling constant is itself a difference between the ground- and excited-state value. $\Delta(\vec{k}\lambda)$ is a measure of the net change in the coupling to the $\vec{k}\lambda$th mode which occurs in the energy transfer. Even for identical impurities $\Delta(\vec{k}\lambda)$ will not vanish if the impurities are located at different lattice positions.

We wish to sketch the solution of $\mathrm{Im}G(\omega)$ and compare our solutions with that obtained by Förster[2] and Dexter.[3] From Eqs. (3.9b) and (3.9d)

$$\phi(T,t)=\sum_{\vec{k}\lambda}\left[\left(|V^1_{\vec{k}\lambda}|^2+|V^2_{\vec{k}\lambda}|^2-2|V^1_{\vec{k}\lambda}V^2_{\vec{k}\lambda}|\right)/\hbar^2\omega^2_\lambda(\vec{k})\right]$$
$$\times P_{\vec{k}\lambda}(T,t)\;. \qquad (3.10)$$

Although $P_{\vec{k}\lambda}$ is periodic in time, $\phi(T,t)\to 0$ for large $t$. Its asymptotic behavior is determined by peaks and discontinuities in the phonon density of states.[37]

If we assumed that the two defect centers coupled to different lattice modes, the cross terms multiplied $(V^1_{\vec{k}\lambda}V^2_{\vec{k}\lambda})$ would vanish. Neglecting these terms leads to the Förster-Dexter results:

$$\mathrm{Im}G^{FD}_T(0)=|U_{12}|^2e^{-\Phi_1(T,0)}e^{-\Phi_2(T,0)}$$
$$\times\int e^{-i\omega^{(0)}t}e^{\Phi_1(T,t)}e^{\Phi_2(T,t)}\,dt\;, \qquad (3.11a)$$

$$\phi_i(T,t)=\sum_{\vec{k}\lambda}\left[|V^i_{\vec{k}\lambda}|^2/\hbar^2\omega^2_\lambda(\vec{k})\right]P_{\vec{k}\lambda}(T,t)\;. \qquad (3.11b)$$

The Fältung theorem gives

$$\mathrm{Im}G^{FD}_T(0)=\frac{|U_{12}|^2}{2\pi}\int_{-\infty}^{\infty}F_1(\omega-\omega^{(0)})F_2(\omega)\,d\omega\;, \qquad (3.12a)$$

where

$$F_i(\omega)=e^{-\Phi_i(T,0)}\int_{-\infty}^{\infty}e^{i\omega t}e^{\Phi_i(T,t)}\,dt\;. \qquad (3.12b)$$

Equation (3.12) implies that the energy-transfer rate is proportional to the integrated overlap of the emission band of the sensitizer and the absorption band of the activator. This is true only in the absence of the phonon-induced cross terms.

The importance of the cross term in Eq. (3.10) arises by virtue of its adding $\vec{R}$-dependent terms to $\mathrm{Im}G_T(0)$. For instance, in the case of nearest-neighbor coupling to acoustical phonon branches, using a Debye spectrum, $\omega=v_sk$, a crude long-wavelength approximation to the coupling functions in Eq. (2.6), $\bar{V}_{k\lambda}\approx\sum_\Gamma f^i_\Gamma\vec{k}a(\hbar/2\omega)^{1/2}$, where $a$ is an average lattice constant, and converting the sum in Eq. (3.10) to an integral, we have

$$\phi_{12}(T,t)=2\sum_\Gamma f^1_\Gamma f^2_\Gamma\frac{(k_Dv_S)^{-3}}{2\hbar}$$
$$\times a^2\int_0^{k_D}\frac{\sin kR}{kR}P_k(T,t)k\,dk$$
$$=2\sum_\Gamma f^1_\Gamma f^2_\Gamma\frac{(k_Dv_S)^{-3}}{2\hbar R^2}$$
$$\times a^2\int_0^{k_D}\sin(kR)P_k(T,t)\,d(kR)\;. \qquad (3.13)$$

Thus if $P_k(T,t)$ does not depend strongly on $k$, e.g., near $T\to 0$, we expect a $1/R^2$ dependence in the limit $k_DR\gg 1$. Hence this term will decrease in importance relative to the diagonal terms in $|f^1_\Gamma|^2$ and $|f^2_\Gamma|^2$ at distances greater than one unit cell length. The explicit $R^{-2}$ dependence is, of course, a consequence of our primitive assumptions about the nature of the phonon coupling function. However, the fact that a long-range (but anisotropic) interaction results from such cross terms is a general result for both transverse and longitudinal phonons. On the other hand if strong coupling occurs to acoustical or optical phonons near $k\approx 0$, there will be little range dependence of the interference term. In this case, the cross term always will be important because the coupling of the phonon field to the two sites is coherent rather than incoherent. Coupling to lattice phonons near the zone boundaries leads to a rapidly oscillating $R$ dependence. Finally, in the case of coupling to (the same) local mode vibrations, the cross term will be important. Such a case can occur, for instance, when the ions are next nearest neighbors.

The above considerations are relevant in the limit that $t=0$ in which they give the $R$ dependence of the (Debye-Waller) renormalization factor, $e^{-\varphi(T,0)}$. However, the $t$-dependent term $e^{-\varphi(T,t)}$ also modifies the effective impurity coupling. For example, in the weak phonon coupling limit, expanding the exponent and keeping only the first-order term, Eq. (3.10), leads to a schematic $R$ dependence of the cross term of

$$\mathrm{Im}G_T(0)\propto R^{-n}\sin(\omega^{(0)}R/V_S)\;. \qquad (3.14)$$

$n=3$ in our example but, in general, $n\geq 1$ and the interaction is anisotropic.

In the strong-coupling limit $\phi(T,t)\gg 1$ it is important to keep the $\vec{R}$-dependent terms in the exponent. In this case, our simple model predicts a contribution to the shift in the resonance frequency

$$\omega'\propto R^{-3}$$

and a change in the width of the line $\sigma^2$ by an amount

$$\Delta\sigma^2\propto R^{-4}$$

in the semiclassical limit, defined by Eq. (3.16a)

$$\Delta\sigma^2\propto R^{-3}\;.$$

As we have noted, it is instructive to evaluate Eq. (3.9) in two important limits.[11] At high temperatures or for systems involving a large change in the electron-phonon coupling between the initial and final states, $\phi(T, t) \gg 1$ so that the exponential factors in $\phi(T, t)$ can be expanded. The first time-dependent terms will damp the exponent $\exp[\phi(T, t)]$ before the expansion is invalid. The result is

$$\operatorname{Im} G_T(0) = |U_{12}|^2 \int_{-\infty}^{\infty} dt\, e^{i(\omega' - \omega^{(0)})t} e^{-\sigma^2 t^2}$$

$$= |U_{12}|^2 (\sqrt{\pi}/\sigma) \exp[-(\omega' - \omega^{(0)})^2/4\sigma^2] , \tag{3.15}$$

$$\sigma^2 = \tfrac{1}{2} \sum_{\vec{k}\lambda} |\Delta(\vec{k}\lambda)|^2 \omega_\lambda^2(\vec{k}) \coth[\hbar\omega_\lambda(\vec{k})/2\kappa T] ,$$

$$\omega' = \sum_{\vec{k}\lambda} |\Delta(\vec{k}\lambda)|^2 \omega_\lambda(\vec{k}) .$$

In the semiclassical limit

$$\coth(\hbar\omega_\lambda(\vec{k})/2\kappa T) \approx 2\kappa T/\hbar\omega_\lambda(\vec{k}) , \tag{3.16a}$$

$$\sigma^2 \approx \sum_{\vec{k}\lambda} |\vec{V}^1_{\vec{k}\lambda} - \vec{V}^2_{\vec{k}\lambda}|^2 \kappa T/\hbar^3 \omega_\lambda(\vec{k}) . \tag{3.16b}$$

Correspondence with the semiclassical expression Eq. (2.18) is achieved by making the identification

$$\sigma^2 \Rightarrow \tfrac{1}{2} \kappa T\, \overline{V}_1^2/\hbar^2\omega^2 \tag{3.17}$$

and from Eqs. (3.8a) and (3.15)

$$P_{12}(T) = \frac{(2\pi)^{3/2}\omega |U_{12}|^2}{(\overline{V}_1^2 \kappa T)^{1/2}\hbar} \times \exp\left(\frac{-\omega^2}{2\overline{V}_1^2} \frac{[E_1 - E_2 - \frac{1}{2}(\overline{V}_1^2/\omega^2)]^2}{\kappa T}\right) , \tag{3.18}$$

which is identical in form to Eq. (2.18). (It differs by a normalization factor of $4\pi$.)

At low temperatures and weak or moderate electron-phonon interaction, the expansion of the exponents is not valid and one must consider multiphonon processes. These may be obtained by expanding $\exp[\phi(T, t)]$. Assuming $T \sim 0$ and adopting a Gaussian to represent the phonon density of states of a given phonon branch weighted by the electron-phonon coupling, we obtain

$$\phi(0, t) = \sum_\lambda |\Delta_\lambda|^2 \int_{-\infty}^{\infty} \exp \frac{[-(\omega_\lambda - \overline{\omega}_\lambda)^2/4\beta_\lambda^2]}{2\sqrt{\pi}\,\beta_\lambda} e^{i\omega_\lambda t} d\omega_\lambda , \tag{3.19}$$

where $\Delta_\lambda$ is equal to $\Delta(\vec{k}\lambda)$ suitably normalized and evaluated near a peak in the weighted density-of-states distribution for the $\lambda$ phonon branch. $\overline{\omega}_\lambda$ is the frequency corresponding to the peak and $\beta_\lambda^2$ is a measure of the width of the phonon dispersion for the strongly coupled branches. Evaluating Eq. (3.19) gives

$$\phi(0, t) = \sum_\lambda |\Delta_\lambda|^2 e^{+i\overline{\omega}_\lambda t} e^{-\beta_\lambda^2 t^2} . \tag{3.20}$$

Expanding $\exp[\phi(0, t)]$ and treating one branch gives

$$P_{12}(0) = \frac{2\pi}{\hbar} |U_{12}|^2 e^{-\phi(0,0)} \times \sum_N \frac{|\Delta_\lambda|^{2N}}{N!} \int_{-\infty}^{\infty} dt\, e^{-i(\omega^{(0)} - N\omega_\lambda)t} e^{-N\beta_\lambda^2 t^2}$$

$$= \frac{2\pi}{\hbar} |U_{12}|^2 e^{-\phi(0,0)} \sum_N \frac{|\Delta_\lambda|^{2N}}{N!} \times \sqrt{\pi} \exp\left[-\frac{(\omega^{(0)} - N\overline{\omega}_\lambda)^2}{4N\beta^2}\right] \Big/ \sqrt{N}\,\beta_\lambda . \tag{3.21}$$

The energy-transfer rate is seen to depend sensitively on the condition

$$\omega^{(0)} - N\overline{\omega}_\lambda \approx 0 , \tag{3.22}$$

where $N$ corresponds to the number of phonons emitted.

At higher temperatures both absorption and emission processes must be considered. It is easily shown that for a narrow phonon distribution around $\overline{\omega}_\lambda$,

$$P_{12}(T) = \frac{2\pi}{\hbar^2} |U_{12}|^2 e^{-\phi(T,0)} \sum_{N_\lambda} \frac{|\Delta_\lambda|^{2N}}{N!} \times \left[\sqrt{\pi} \exp\left(-\frac{(\omega^{(0)} - N\overline{\omega}_\lambda)^2}{4N\beta^2}\right) \Big/ \sqrt{N}\beta_\lambda\right] K_N(T) ,$$

where

$$K_N(T) = \sum_{s=N}^{\infty} \frac{1}{s!(N-s)!} \frac{\exp(s\hbar\overline{\omega}_\lambda/\kappa T)}{[\exp(\hbar\overline{\omega}_\lambda/\kappa T) - 1]^{2s-N}} . \tag{3.23}$$

$K_N(T)$ is a temperature-dependent factor. $s$ is the number of phonons emitted in the energy-transfer process and $N$ is the number emitted minus the number absorbed. $K_N(T) \to [\coth(\hbar\overline{\omega}_\lambda/\kappa T)]^N$ at high temperatures and $K_N(T) \to 1$ at low temperatures $\kappa T \ll \hbar\overline{\omega}_\lambda$.

The energy-transfer rate based on the model Hamiltonian, Eqs. (1.1) and (3.1a), in the semiclassical and linear-response limit are contained in Eqs. (2.18), (2.19), and (3.8)–(3.10). The use of a coherent as opposed to incoherent superposition of electron-phonon coupling amplitudes in the initial and final states to obtain a net coupling amplitude is the major distinguishing characteristic of this model from the Förster-Dexter model.[2,3,35] This coherent superposition leads, in turn, to an activated nature of semiclassical energy-transfer processes in which the activation energy depends on the polaron-shifted impurity-excitation energies [Eqs. (3.15) and (3.18)].

In the quantum limit of weak electron-phonon coupling, the transfer process depends on the sum of the electron-phonon coupling constants and the shape of the phonon density of states, [Eqs. (3.21) and (3.23)]. It ceases to be thermally activated at very low temperatures although the magnitude of the transfer probability still depends approximately exponentially on the difference in the polaron-shifted energy levels or excitation energies through the energy conservation condition, Eq. (3.22).

## IV. BEYOND LINEAR RESPONSE

Virtually all previous effect directed toward understanding radiative and nonradiative transitions between impurity ion states in inorganic crystals has been restricted to the linear-response limit. This is not true in the literature on radiationless transitions in polyatomic molecules where progress has been made recently toward understanding specifically nonlinear effects, such as interference effects.[5, 33, 38-41] In this section we present formally a solution for the time dependence of the energy transfer which is valid to any order in the electronic interaction in order to establish a criterion for the applicability of the linear-response formulation. We adopt the stationary state approach used in the study of polyatomic molecules in order to describe the preparation of the system in its initial nonstationary state.[5] Having removed $H_{\mathrm{el-ph}}$ by means of a canonical transformation in Sec. III, we can discuss an expansion of $\tilde{H}_{\mathrm{int}}$ and hence the dynamics of the energy transfer to any order. In the limit of a strong electronic interaction a system prepared in the electronic state 1 will oscillate between the two electronic states in a manner characteristic of exciton or band motion. In the limit of weak electronic coupling, the probability that the system remains in state 1 decreases exponentially. It is this latter limit in which the energy transfer occurs irreversibly which is encountered in most experimental energy-transfer systems. However, the existence of this limit is seen to be dependent on the magnitude of the coherent difference in the electron-phonon coupling constants and on the width of the phonon dispersion. In this section analytical expressions for the strong- and weak-coupling limit are given.

### A. Initial Conditions

Let us first consider the problem of radiationless electronic relaxation in order to define a suitable set of initial conditions for discussing energy transfer. At time $t=0$, the system is prepared in a set of excited states by a radiation field. The total transition rate to all the excited states of the system is, assuming that first-order perturbation theory can be used to describe the radiation field,

$$P_{12}(T)=(1/c)\int_0^\infty I(\omega)F(\omega)\,d\omega\ , \qquad (4.1\mathrm{a})$$

where

$$F(\omega)=\frac{2\pi}{\hbar}\sum_E \left|\,\langle G|\vec{\epsilon}\cdot\vec{\mathrm{M}}|E\rangle\right|^2\delta(E-\hbar\omega)\ . \qquad (4.1\mathrm{b})$$

$\vec{\epsilon}$ is the polarization vector and $\vec{\mathrm{M}}$ the radiation field interaction operator. The ground- and excited-state vectors, $|G\rangle$ and $|E\rangle$, respectively, are linear combinations of BO states (see Sec. IV D). $I(\omega)$ is the intensity of the light beam per unit frequency interval.

We assume that the ground state is essentially a BO state $|G\rangle\sim|g\rangle$ and the transition matrix elements connect $|g\rangle$ only to the BO states $|e\rangle$. The BO states $|e\rangle$ need not fall in the frequency range of the incident radiation but may be borrowed from neighboring frequency regions through an admixture into the excited states,

$$F(\omega)=\frac{2\pi}{\hbar}\sum_{E,e}\left|\,\langle g|\vec{\epsilon}\cdot\vec{\mathrm{M}}|e\rangle\right|^2\langle e|E\rangle\langle E|e\rangle\delta(E-\hbar\omega)\ . \qquad (4.2)$$

If the intensity of the exciting beam is fairly constant over the band width $\Delta E$ of the excited states then the system will be prepared in the nonstationary BO states $|e\rangle$. If, on the other hand, the slit width of the incident radiation is much more narrow than the excited-state energy band then the BO states $|e\rangle$ will be only partially excited. This latter situation has been discussed in connection with radiationless transitions in polyatomic molecules.[41] It is well known that in solids a system prepared in a distribution of BO states $|e\rangle$ by an electromagnetic radiation field will internally relax, that is, undergo a Stoke's shift, to a thermal distribution in times on the order of $10^{-12}$ sec as the result of anharmonic terms in the crystal lattice Hamiltonian. If this occurs in times fast relative to energy-transfer transitions between electronic states then the distribution at time $t=0$ given by the transition moment factors $|\langle g|\vec{\epsilon}\cdot\vec{\mathrm{M}}|e\rangle|^2\delta(E-\hbar\omega)$ should be replaced by a thermal distribution. Dexter and Fowler[16] qualitatively discuss an alternative view.

### B. Time-Dependent Relaxation

The time dependence of the BO state $|e\rangle$ is defined by the relaxation function

$$\Phi_{ee}(t)=\langle e\,|\,\exp[-(i/\hbar)Ht]|\,e\rangle\ , \qquad (4.3)$$

which is the probability amplitude that the system is in the state $|e\rangle$ at time $t$ if it is prepared in that state at $t=0$. If we choose the transformed BO basis defined in Sec. III and write the time development operator in the interaction representation, we have aside from a phase factor

$$\Phi_{ee}(t)=\left\langle e\left|\,\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_0^t\tilde{H}_{\mathrm{int}}(t')\,dt'\right)\right|e\right\rangle, \qquad (4.4\mathrm{a})$$

where

$$\tilde{H}_{\mathrm{int}}(t')=e^{(i/\hbar)H_0t'}\tilde{H}_{\mathrm{int}}(0)e^{-(i/\hbar)H_0t'}\ . \qquad (4.4\mathrm{b})$$

$T$ represents the time-ordered expansion of the exponential.

The only nonvanishing matrix elements of the time-ordered expansion connect the BO states $|e\rangle$ to the manifold of states $|g\rangle$. Only the even terms survive in the expansion of Eq. (4.4). The first such term is given by

$$\Phi_{ee}(t) = -\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2\, g_T(t_1 - t_2) + \cdots , \quad (4.5a)$$

where

$$g_T(t_1 - t_2) = \langle\langle \tilde{H}_{\text{int}}(t_1)\tilde{H}_{\text{int}}(t_2)\rangle\rangle_T \quad (4.5b)$$

is the correlation function for the interaction Hamiltonian given in Eq. (3.8). Higher-order terms are simply related to linked integrals of products of the correlation function. However, rather than evaluate terms in the time-ordered expansion, it is more useful to examine the gross features of the time development in two important limiting cases.

In the limit of the *strong* electronic coupling defined by extracting $g_T(t)$ from Eqs. (3.15) and (3.21) in the semiclassical and quantum limits, respectively, as

$$|U_{12}| \gg \sigma\hbar \quad \text{(semiclassical)} , \quad (4.6a)$$

$$|U_{12}| \exp(-\tfrac{1}{2}\phi(T, 0)) \frac{|\Delta_\lambda|^N}{(N!)^{1/2}} \gg \sqrt{N}\beta_\lambda\hbar \quad \text{(quantum)} , \quad (4.6b)$$

the time-dependent part of $g_T(t)$ can be neglected compared to the time-independent part in its effect on the time-ordered expansion. $g_T(t)$ is replaced by $g_T(0)$. Also in this limit, the time-ordered expansion in Eq. (4.4) may be evaluated explicitly giving

$$\Phi_{ee}(t) = 1 - \frac{t^2 g_T(0)}{2!\hbar^2} + \frac{t^4 g_T^2(0)}{4!\hbar^4} - \cdots \quad (4.7a)$$

$$= \cos\{[g_T(0)]^{1/2} t/\hbar\} . \quad (4.7b)$$

The energy oscillates between the two states with the angular frequency $[g(0)]^{1/2}/\hbar$. Nuclear motion adds a small time-dependent modulation of the angular frequency in this limit.

In the *weak*-coupling limit,

$$|U_{12}| \ll \sigma\hbar , \quad (4.8a)$$

$$|U_{12}| \exp(-\tfrac{1}{2}\phi)|\Delta_\lambda|^N/(N!)^{1/2} \ll \sqrt{N}\beta_\lambda\hbar . \quad (4.8b)$$

We use the generalized cumulant theorem of Kubo[42] to obtain

$$\Phi_{ee}(t) = e^{\gamma(t)} , \quad (4.9a)$$

$$\gamma(t) = \sum_{n=1}^{\infty} (i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \times \int_0^{t_{n-1}} dt_n \langle\langle \tilde{H}_{\text{int}}(t_1) \cdots \tilde{H}_{\text{int}}(t_n)\rangle\rangle_T . \quad (4.9b)$$

If we truncate the expansion following the second term,

$$\Phi_{ee}(t) = \exp\left(-\frac{1}{2\hbar^2}\int_0^t dt_1 \int_0^t dt_2\, g(\tau)\right) . \quad (4.9c)$$

The latter approximation is in keeping with the assumption of weak coupling. For times which are long compared to $\sigma^{-1}$ or $(\sqrt{N}\beta_\lambda)^{-1}$

$$\Phi_{ee}(t) = \exp\left(-\frac{t}{2\hbar^2}\int_{-\infty}^{\infty} d\tau\, g_T(\tau)\right) . \quad (4.10)$$

The time development of the amplitude $\Phi_{ee}(t)$ is an exponential decay whose time constant is given by perturbation theory.

Davydov[17] has recently discussed the strong-coupling limit. However, neither Davydov nor Dexter, Förster, and Knox,[18] in a recent critique of Davydov's paper, have delineated the regions in which strong and weak coupling were applicable. Our definitions of strong and weak coupling should be compared with the original definitions of Simpson and Peterson.[14] A good discussion of radiationless energy transfer in cases of strong and weak coupling was given by Robinson and Frosch[15] for molecular energy transfer in a dense medium. Their $\beta$ corresponds to our $U_{12}$ or $U_{12}\exp[-\tfrac{1}{2}\phi(T, 0)]\,|\Delta_\lambda|^N/(N!)^{1/2}$ in the quantum limit. Also their $\alpha$ is an approximate measure of the width of a vibronic sideband.[15] $\alpha$ represents the matrix element of the interaction of the molecular vibronic states with the medium and the interaction of these states with each other. It is assumed to be a constant. Our parameter $\beta_\lambda$ on the other hand is a measure of the width of the phonon dispersion weighted by the electron-phonon coupling. In the semiclassical limit, $\sigma$ measures the total electron-phonon coupling. Neither of these parameters represent matrix elements connecting vibronic states in the untransformed Hamiltonian. Hence $\alpha$ is not an analog of either $\beta_\lambda$ or $\sigma$. Also, $E_0^1 - E_0^2$ does not play any role in our distinction between strong and weak coupling. The reason for this is that we have assumed that energy transfer always occurs in a region where the initial and final states are nearly degenerate, $E^1 - E^2 < U_{12}$. Nonresonant energy transfer $E^1 - E^2 > U_{12}$ occurs with a frequency $\omega_{12}$ which corresponds to the energy difference. Similarly our classification scheme contains only indirect analogs to other models used in the study of radiationless transitions in molecular systems.[5,33,38-41]

## IV. RELATIONSHIP TO EXPERIMENT AND SUMMARY

The definition of weak and strong coupling given in Sec. IV is based on the model Hamiltonian presented in the Introduction. This Hamiltonian was suggested as a model for resonant energy transfer between localized states in a crystal. Two important phenomena which are described by the model Hamiltonian are the transfer of a localized excitation between two impurity ions, and radiationless electronic relaxation between two electronic levels on the same impurity center. In a real system, the preceding results must be generalized if there are more than two interacting electronic or excitonic states. Also "strong" and "weak" interactions exhibit different manifestations.

Strong interactions lead to a rapidly oscillating energy transfer which is not generally observable. Hence they are observed as energy level splittings, such as the Davydov splitting between levels on nearby identical ions. The weak interaction of the radiation field samples a statistical average of the lifetimes of the interacting states.

Energy transfer is observed when it is induced by weak interactions. In this case the back-transfer rate is negligible, so that the probability that the system can be found in its initial state decreases exponentially with time according to a rate constant given by the sum of the rate constants for each of the competing energy transfer processes,

$$\Phi_{ii}(t) = \exp\left[ -\sum_j P_{ij}(T)\, t \right] . \tag{5.1}$$

The $P_{ij}(T)$ are given by Eqs. (3.8) and (3.9) and equations derived from them. They are functions of the electronic interaction matrix elements $U_{ij}$ and the distribution of differences in the phonon-coupling constants for the hole-electron pair $\overline{V}_{\vec{k}\lambda}$. For the case of energy transfer between two impurity ions, it is well known that the parameters $U_{ij}$ are sensitive functions of the distance between the impurity ions. They may be dipolar or higher multipolar in character or may decrease exponentially with distance if the interaction is through an exchange mechanism.[2,3] In Sec. III we pointed out that the distribution of coherent differences in the phonon coupling, $\overline{V}_{\vec{k}\lambda} = V^1_{k\lambda} - V^2_{k\lambda}$, is also a sensitive function of the relative positions of two ions in the lattice. The detailed $\vec{R}$ dependence was shown to be $R^{-2}$ for a simple model system [see Eq. (3.13)]. In general, the $\vec{R}$ dependence of the difference in the electron-phonon coupling is determined by the nature of the electron lattice interaction and the defect lattice dynamics. These are seldom known even for the simplest of cases.

There are two qualitative effects of the cross term appearing in Eq. (3.10) on the energy-transfer rate. First, there may be a large short-range contribution to the renormalization factor, $\exp\{-\phi \times (T, 0)\}$. For instance, for two identical ions coupled to bulk lattice modes,

$$\phi(T, 0) = \sum_{\vec{k}\lambda} 2 \left| \overline{V}_{\vec{k}\lambda} / \hbar\omega_\lambda(\vec{k}) \right|^2 (1 - \cos(\vec{k}\cdot\vec{R})) \times \coth\left[\hbar\omega_\lambda(k)/2kT\right] . \tag{5.2}$$

The interference term approximately vanishes if phonon coupling occurs uniformly throughout the Brillouin zone but significantly reduces $\phi(T, 0)$ if coupling is strong near $k \approx 0$. Coupling to local modes may lead to large, short-range interference effects. This is important whenever energy transfer occurs predominantly between nearest neighbors or next nearest neighbors (for instance, when it occurs by an exchange mechanism).

The second important effect of the phonon-induced cross term is its creation of a long-range temperature-dependent modification to the interaction $U_{ij}$. For instance, in the case of a weak electron-phonon interaction when we can expand $\exp[-\phi(T, 0) + \phi(T, t)]$, the first terms in the expansion give a transition rate of the approximate form

$$P_{ij}(T) \propto |U_{ij}|^2 \left[ 1 + f(R) \coth\left( \frac{\hbar\omega_\lambda(k)}{2kT} \right) + \cdots \right] . \tag{5.3}$$

In our simple model, Eq. (3.13), the second term is proportional to $R^{-2}$ and multiplies $|U_{ij}|^2$ adding, for example, an effective quadrupolar interaction if $|U_{ij}|^2$ was dipolar in character. The additional range-dependent terms have a characteristic temperature dependence and might be isolated by studying the combined effects of both temperature and concentration on the energy-transfer rate. In general, their magnitude and range depend on the nature of the electron-phonon coupling. Multiphonon processes would add higher "multipolar" interactions.

In experimental systems, it is often difficult to estimate the magnitude of parameters appearing in the expressions for energy transfer. Dexter[2] extimated that $U_{ij}$ might correspond to a jump time of $10^{-10}$ or $10^{-11}$ sec for next nearest neighbors interacting through an exchange mechanism in alkali halides. Estimating $|\Delta_\lambda|^2$ for trivalent rare-earth ions from the relative intensity of the appropriate one-phonon sideband to the no-phonon line appearing in a typical absorption spectrum to be around 0.1 and $\beta_\lambda \sim 10^{12}$/sec, we obtain from Eq. (3.23) [taking $s = N$ in (3.21)]:

$$P_{12}(T) \sim 10^{+11} \frac{(0.1)^N}{N!} \frac{e^{N\hbar\overline{\omega}_\lambda/\kappa T}}{(e^{\hbar\overline{\omega}_\lambda/\kappa T} - 1)^N \sqrt{N}} , \tag{5.4a}$$

$$N = (E_1 - E_2)/\hbar\overline{\omega}_\lambda . \tag{5.4b}$$

A value of $N$ corresponding to the emission of around 6 or less phonons gives a transition rate which competes with radiative transition rates of around $\sim 10^3$/sec. This energy-gap law together with the temperature dependence indicated in Eq. (5.4) has been verified in measurements of multiphonon relaxation of excited states of several rare-earth ions in crystals.[43]

The result also suggests that energy transfer between rare-earth ions will always be of the weak irreversible type, Eq. (4.8), except perhaps if the no-phonon lines are degenerate ($N=0$).

In summary, our main result in this paper has been the definition of a schematic model Hamiltonian, Eqs. (1.1)–(1.6) and the analysis of the electronic energy transfer predicted by this model. The model describes a wide variety of phenomena associated with electronic transitions which occur in the presence of electron-phonon or orbit-lattice interactions. The semiclassical calculation of the energy-transfer rate given in Sec. II was adapted from a calculation of electron-transfer rates in solution.[7] The linear-response theory analysis, Sec. III, which avoided perturbation theory in the electron-phonon interaction was adapted from one of phonon-broadened impurity ion spectra.[10] The origin of irreversibility in the energy-transfer process was discussed in Sec. IV. The schematic model and the insight obtained from its analysis is relevant for the description of energy transfer in these and other areas.[5,8–13,16,24–31,43,44] In the case of energy transfer, our schematic model constitutes an alternative to the Förster-Dexter model and reduces to it in a well-defined limit. Using the schematic model, we have succeeded in giving a qualitative distinction between weak and strong coupling, demonstrating explicitly that the weak-coupling limit describes the empirical systematics of non-radiative decay in rare-earth-doped phosphors.

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