Theory of Radiative and Nonradiative Electronic Processes in Ionic Crystals with Point Imperfections

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After an outline of the quantum theory of decaying states on the basis of the resolvent method, a Hamiltonian is considered describing an ionic micro-crystal containing one electronic impurity center. The complete Hamiltonian of the coupled system micro-crystal plus radiation field can be decomposed into a diagonalized part and a "perturbation", so that the perturbation leads to terms associated with nonradiative electronic transitions, anharmonic lattice transitions, radiative electronic transitions, and radiative lattice transitions. The state of the system micro-crystal plus radiation field is supposed to be given by a density operator in the representation where the unperturbed Hamiltonian is diagonal. By means of the assumption of initial random phases the quantum theory of decaying states yields an approximatively valid differential equation for the diagonal elements of the density operator describing the time-dependent radiative and nonradiative electronic processes in the micro-crystal. Under certain additional conditions the differential equation has the form of the Pauli-Master-Equation.

1. Introduction

Real crystals are always imperfect in some respect. Any deviation from a perfect space lattice is an imperfection. A point imperfection is localized near a point of the perfect lattice, in contrast to a line or plane imperfection. Much work has already been carried out with particular reference to point imperfections in alkali and silver halides, and therefore the nature of many point imperfections in those ionic crystals is fairly well understood. Electronic processes associated explicitly with the presence of point imperfections modify many important properties of the host crystal, which may act only as a vehicle or solvent for the imperfections. So absorption and emission spectra, luminescence, electronic conductivity, and photochemical phenomena are usually controlled by electrons localized near a point imperfection. Such point imperfections we shall call electronic impurity centers. There are recent monographs and articles e.g. of MARKHAM[1], STASIW[2], PICK[3], and LÜTY[4] treating in particular the experimental research in the field of electronic impurity centers in ionic crystals. Experimental details are therefore not discussed here.

The theory of the absorption or emission of light by an impurity center in a crystal with an accompanying electronic transition in the center has developed out of the work of HUANG and RHYS[5], LAX[6], PEKAR[7], and KRIVOGLAZ and PEKAR[8]. Subsequent theoretical work was done by many authors; it is referred to the papers of MCCUMBER[9]. On the other hand, as far as the author knows, a complete theoretical treatment of nonradiative electronic processes in impurity centers has not yet been given. An approach on the basis of the adiabatic approximation and the time-dependent pertubation theory has been made e.g. by KUBO[10], MEYER[11], VASILEFF[12], STUMPF[13], and LAX[14]. Only STUMPF and LAX were able to evaluate their formulas numerically. A simple treatment of both radiative and nonradiative electronic processes in impurity centers in ionic crystals has been given by STUMPF[15]. However STUMPF has justified his formulas for nonradiative transition probabilities per unit time by heuristic considerations rather than byderivations.

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[1] J. J. MARKHAM, Solid State Phys., Suppl. 8, [1966].

[2] O. STASIW, Elektronen- und Ionenprozesse in Ionenkristallen, Springer-Verlag, Berlin 1959.

[3] H. PICK, Springer Tracts in Modern Physics **38**, 1 [1965].

[4] F. LÜTY, Halbleiterprobleme VI, Vieweg & Sohn, Braunschweig 1961, (p. 238).

[5] K. HUANG and A. RHYS, Proc. Roy. Soc. London A **204**, 406 [1950].

[6] M. LAX, J. Chem. Phys. **20**, 1752 [1952].

[7] S. I. PEKAR, Usp. Fiz. Nauk. **50**, 197 [1953].

[8] M. A. KRIVOGLAZ and S. I. PEKAR, Tr. Inst. Fiz. Akad. Nauk. Ukr. SSR **4**, 37 [1953].

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[10] R. KUBO, Phys. Rev. **86**, 929 [1952].

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[12] H. D. VASILEFF, Phys. Rev. **96**, 603 [1954 and **97**, 891 [1955].

[13] H. STUMPF, Z. Naturforschg. **10a**, 971 [1955]; **13a**, 171 [1958]; **13a**, 621 [1958], and **14a**, 659 [1959].

[14] M. LAX, Phys. Rev. **119**, 1502 [1960].

[15] H. STUMPF, Quantentheorie der Ionenrealkristalle, Springer-Verlag, Berlin 1961.

In this paper using the resolvent method the author proposes a uniform derivation of differential equations describing the kinetics of both radiative and nonradiative electronic processes associated with point imperfections in ionic crystals.

We imagine an arbitrary ionic crystal consisting of micro-crystals, each of which contains one electronic impurity center as the only imperfection. We assume the micro-crystal to be large enough to neglect the interaction of impurity centers with each other and with the boundary surfaces of the micro-crystals. Then the macro-crystal appears as an ensemble of micro-crystals. Hence it is sufficient to treat a micro-crystal quantum mechanically.

We know from measurements of the relative quantum efficiency that irreversible transitions of excited localized electrons into lower levels are often nonradiative. The decay of any bound state has to be explained by the theorem of FOCK and KRYLOW[16]. This theorem says, that an excited bound state decays, i.e. makes irreversible transitions into lower states, if and only if the bound state is coupled with continuous states so that the spectrum of the Hamiltonian describing the coupled system becomes continuous. Hence it is easy to explain the decay of excited states of localized electrons on account of their coupling with the radiation field or with continuous lattice oscillations. However there are localized electrons coupled with good approximation only with localized lattice modes and the radiation field. Provided that radiative decay is forbidden, the nonradiative decay is rendered possible because of the finite lifetime of localized lattice modes. The finite lifetime is connected with cubic and higher anharmonic terms in the potential energy for the lattice ions.[17]

We first shall give an outline of the quantum theory of decaying states on the basis of the resolvent method[18]. After this rather abstract introductory part a Hamiltonian will be considered which describes in particular nonradiative processes in an electronic impurity center[18]. Of course there is no clear way to find such a Hamiltonian. We shall assume the adiabatic coupling of the motion of the electrons of the micro-crystal as relative particles with the motion of the mass centers of the lattice ions. The electronic equation is supposed to be diagonalized. Its eigenvalues are functions of the ionic mass center positions and are supposed to be potential energies of the ionic motion. The equation of the ionic motion is assumed to be solved in the harmonic approximation. We then imagine the complete Hamiltonian H of the micro-crystal system to be decomposed into an diagonalized "unperturbed" part ${}^0H$ and a "perturbation" ${}^1H$. The unperturbed Hamiltonian describes the crystal system in the adiabatic and the harmonic approximation and the free radiation field. The perturbation ${}^1H$ consists of terms describing nonradiative electronic transitions, anharmonic lattice transitions, radiative electronic transitions, and radiative ionic transitions. The state of the micro-crystal system will be characterized by the matrix elements of a certain density operator relative to the eigenstates of ${}^0H$ which is assumed to be diagonal at $t=0$. The quantum theory of decaying states will lead to differential equations describing in particular the kinetics of all radiative and nonradiative electronic processes in the impurity center of a micro-crystal. It will be shown that an approximative equation having the form of the Pauli-Master-Equation[19] often governs the time dependence of the electronic processes. The derived transition probabilities per unit time, in particular for nonradiative electronic processes, are generalizations of those used by STUMPF[15].

The principal aim of this paper has been to provide a simple description of all time-dependent electronic processes in ionic crystals with impurity centers, rather than a detailed evaluation of specific models. In a paper now in preparation the author will present an application of the theory to particular impurity center models.

2. Quantum Theory of Decaying States

In this section we shall give a brief and rather abstract review of the quantum theory of decaying states using resolvent operator techniques comprehensively described by GOLDBERGER and WATSON[20]

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[16] A. S. DAVYDOW, Quantum Mechanics, Pergamon Press, Oxford 1965.

[17] W. LUDWIG, Springer Tracts in Modern Physics, **43** [1967].

[18] H. RAMPACHER, Thesis, University of Munich, 1967.

[19] R. ZWANZIG, Lectures in Theoretical Physics, Boulder, Vol. III, Interscience Publishers, Inc. New York, 1961.

[20] M. L. GOLDBERGER and K. M. WATSON, Collision Theory, John Wiley & Sons, New York 1964.

and MESSIAH[21]. In the following sections we shall apply the theory to our physical problems.

We consider a system with the Hamiltonian H and imagine this to be decomposed into an "unperturbed" part T and a "perturbation" V. It is assumed that T has been diagonalized and that its eigenstates form a complete set of states for the system. Thus

$$H = T + V, \tag{2.1}$$

$$T P_a = P_a T = E_a P_a \tag{2.2}$$

where E_a is the eigenvalue of T for the state described by the projector P_a. For simplicity we shall assume that the possible states of the system are quantized in a large box of volume N. This is consistent with the following considerations of decay if, and only if, we pass to the limit $N \to \infty$ before evaluating sums over virtual states.

The observable T does not commute with H, hence its eigenstates have a time-dependent distribution. We assume that at $t=0$ the matrix elements of the density operator[22] $\varrho(t)$ relative to the set of states of the observable T are known. Then the probability $p_{\mathrm{D}}^{T}(t)$ to measure at time t one of the eigenvalues E_a of T belonging to a certain domain D of the spectrum of T is

$$p_{\mathrm{D}}^{T}(t) = \frac{\operatorname{Tr} \varrho(t)\, P_{\mathrm{D}}^{T}}{\operatorname{Tr} \varrho(0)} = \frac{\operatorname{Tr} \{U(t)\, \varrho(0)\, U^{\dagger}(t)\, P_{\mathrm{D}}^{T}\}}{\operatorname{Tr} \varrho(0)}, \tag{2.3}$$

where the projector P_{D}^{T} projects upon the subspace of states with eigenvalues E_a located in D. The unitary evolution operator $U(t)$ is the solution of

$$i \frac{\partial}{\partial t} U(t) = H U(t), \quad U(0) = \mathbf{1}, \tag{2.4}$$

where $\mathbf{1}$ is the identity operator. We are able to evaluate (2.3) provided that we know the matrix elements of the evolution operator $U(t)$ relative to the set of states of the observable T.

Instead of the operator $U(t)$ we investigate the resolvent $G(z)$ defined by

$$G(z) := \frac{\mathbf{1}}{\mathbf{1} z - H}\,. \tag{2.5}$$

(For simplicity we subsequently shall suppress the identity operator in all formulas.) It can be shown that the resolvent exists and is bounded for non real z. The following simple relation between $G(z)$ and $U(t)$ can be proven[23]

$$U(t) = \frac{1}{2 \pi i} \oint e^{-izt}\, G(z)\, \mathrm{d}z. \tag{2.6}$$

In (2.6) the path of integration is a contour C around the real axis of the complex z plane running from $\infty + i\varepsilon$ to $-\infty + i\varepsilon$ and from $-\infty - i\varepsilon$ to $\infty - i\varepsilon$.

We first look for an expression for the diagonal element of $G(z)$ giving us, because of (2.6), the law of motion of the state P_a. We introduce

$$Q_a := 1 - P_a\,, \tag{2.7}$$

$$H^a := T + Q_a V Q_a\,, \tag{2.8}$$

$$H^{a\prime} := P_a V P_a + P_a V Q_a + Q_a V P_a\,, \tag{2.9}$$

$$H = H^a + H^{a\prime}. \tag{2.10}$$

Note that

$$[Q_a, H^a] = 0\,, \quad H^a P_a = P_a H^a = E_a P_a\,. \tag{2.11}$$

From the operator identity

$$(A - B)^{-1} \equiv A^{-1} + A^{-1} B (A - B)^{-1}$$

we obtain on account of (2.10)

$$G(z) = \frac{1}{z - H^a} + \frac{1}{z - H^a} H^{a\prime} G(z)\,. \tag{2.12}$$

With regard to (2.7) to (2.11) we find in particular

$$Q_a G(z)\, P_a = \frac{1}{z - H^a}\, Q_a V P_a G(z)\, P_a\,. \tag{2.13}$$

From the definition of $G(z)$ it follows

$$(z - T)\, G(z) = 1 + V G(z)\,. \tag{2.14}$$

Thus using (2.7) and (2.13)

$$(z - E_a)\, P_a G(z)\, P_a = P_a + P_a R^a(z)\, P_a G(z)\, P_a \tag{2.15}$$

with the definition

$$R^a(z) := V + V Q_a \frac{1}{z - H^a}\, Q_a V\,. \tag{2.16}$$

Equation (2.15) gives

$$P_a G(z)\, P_a = \frac{P_a}{z - E_a - P_a R^a(z)\, P_a}\,. \tag{2.17}$$

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[21] A. MESSIAH, Quantum Mechanics, Vol. II, North-Holland Publishing Company, Amsterdam 1962.

[22] U. FANO, Rev. Mod. Phys. **29**, 74 [1957].

[23] P. ROMAN, Advanced Quantum Theory, Addison-Wesley, Reading/Mass. 1965.

To obtain the nondiagonal elements of $G(z)$ we find from (2.13) in particular

$$P_b G(z)\, P_a = P_b (z - H^a)^{-1} Q_a V P_a G(z)\, P_a\,, \quad b \neq a\,. \tag{2.18}$$

Introducing

$$Q_{(a)b} := 1 - P_a - P_b = Q_a - P_b \tag{2.19}$$

we can rewrite (2.18)

$$P_b G(z)\, P_a = P_b \{(z - H^a)^{-1} P_b + P_b (z - H^a)^{-1} Q_{(a)b} V\}\, P_a G(z)\, P_a\,. \tag{2.20}$$

Let us replace $P_b(z - H^a)^{-1} Q_{(a)b}$ using the identity $(A-B)^{-1} \equiv (A-B)^{-1} B A^{-1} + A^{-1}$ and the definitions

$$H^{(a)b} := T + Q_{(a)b} V Q_{(a)b}\,, \tag{2.21}$$

$$H^{(a)b\prime} := P_b V P_b + P_b V Q_{(a)b} + Q_{(a)b} V P_b \tag{2.22}$$

by

$$P_b (z - H^a)^{-1} Q_{(a)b} = P_b (z - H^a)^{-1} P_b V Q_{(a)b} (z - H^{(a)b})^{-1} Q_{(a)b}\,. \tag{2.23}$$

Defining

$$G^a(z) := 1/(z - H^a) \tag{2.24}$$

and analogous to (2.16)

$$R^{(a)b}(z) := V + V Q_{(a)b} (z - H^{(a)b})^{-1} Q_{(a)b} V \tag{2.25}$$

we obtain from (2.20) and (2.23)

$$P_b G(z)\, P_a = P_b G^a(z)\, P_b R^{(a)b}(z)\, P_a G(z)\, P_a\,. \tag{2.26}$$

Analogous to (2.17) we have

$$P_b G^a(z)\, P_b = \frac{P_b}{z - E_b - P_b R^{(a)b}(z)\, P_b}\,. \tag{2.27}$$

From (2.6), (2.17), (2.26), (2.27) result the following exact relations

$$P_a U(t)\, P_a = \frac{1}{2\pi i} \oint \mathrm{d}z \frac{P_a e^{-izt}}{z - E_a - P_a R^a(z)\, P_a} \tag{2.28}$$

and

$$P_b U(t)\, P_a = \frac{1}{2\pi i} \oint \mathrm{d}z\, e^{-izt} \frac{P_b}{z - E_b - P_b R^{(a)b}(z)\, P_b} R^{(a)b}(z) \frac{P_a}{z - E_a - P_a R^a(z)\, P_a}\,. \tag{2.29}$$

In particular — assuming for simplicity nondegenerated eigenvalues E_a and E_b — (2.28) implies

$$U_{aa}(t) = \frac{1}{2\pi i} \oint \mathrm{d}z\, e^{-izt} \frac{1}{z - E_a - R^a_{aa}(z)} \tag{2.28a}$$

and (2.29) leads to

$$U_{ba}(t) = \frac{1}{2\pi i} \oint \mathrm{d}z\, e^{-izt} \frac{1}{z - E_b - R^{(a)b}_{bb}(z)} R^{(a)b}_{ba}(z) \frac{1}{z - E_a - R^a_{aa}(z)}\,. \tag{2.29a}$$

Here $A_{ba} := \langle b|A|a\rangle$, where $|a\rangle$, $|b\rangle, \ldots$ are the eigenstates of T.

Let us find out the conditions which must be fullfilled for an eigenstate $|a\rangle$ of T being able to decay. It follows from (2.3) in particular

$$p_a^{\mathrm{T}}(t) = \mathrm{Tr}\, U(t)\, P_a U^\dagger(t)\, P_a = |U_{aa}(t)|^2\,, \tag{2.30}$$

provided our system is in the pure state P_a at $t=0$. Because of (2.30) and (2.28a) respectively (2.6) we must investigate the diagonal element $G_{aa}(z)$ of $G(z)$. For this purpose we shall introduce the true propagators G^+ and G^- as limits of the resolvent. We define

$$x^\pm := x \pm i\varepsilon\,, \quad \varepsilon > 0\,. \tag{2.31}$$

Because of

$$\lim_{\varepsilon \to 0} \frac{1}{x^\pm - A} = PP \frac{1}{x - A} \mp i\pi\delta(x - A)\,, \tag{2.32}$$

where PP means the Cauchy principal value, we particularly find from (2.16)

$$R^{a\pm}_{aa}(x) := \lim_{\varepsilon \to 0} R^a_{aa}(x^\pm) = D^a_{aa}(x) \mp \frac{i}{2} \Gamma^a_{aa}(x) \tag{2.33}$$

with
$$D^a_{aa}(x) := \langle a | V Q_a PP (x - H^a)^{-1} Q_a V | a \rangle , \tag{2.34}$$
and
$$\Gamma^a_{aa}(x) := 2\pi \langle a | V Q_a \delta (x - H^a) Q_a V | a \rangle . \tag{2.35}$$

On account of (2.33) it follows from (2.17)

$$G^{\pm}_{aa}(x) = \frac{1}{x - E_a - D^a_{aa}(x) \pm \frac{i}{2} \Gamma^a_{aa}(x)} . \tag{2.36}$$

The diagonal element $G^{\pm}_{aa}(x)$ of the true propagator is defined for all real x if, and only if, $\Gamma^a_{aa}(x)$ has a finite value $\neq 0$ for all real x. Due to the δ-function in (2.35) this is possible only in case the spectrum of H^a, which essentially equals the spectrum of H, is continuous for nonfinite normalization volume N. The analogous must hold for the imaginary part of $R^{(a)b\pm}_{bb}(x)$ if the state $|b\rangle$ is not the ground state.

Subsequently we always take for granted the spectrum of H to be entirely continuous for $N \to \infty$, running from a point E_M on the real axis to $+\infty$. Thus $G(z)$ is no analytical function for $x > E_M$. On the other hand $G^{\pm}(x)$ as defined by (2.36) exists for $x > E_M$ provided that $\Gamma^a_{aa}(x) \neq 0$ and the absolute value of $R^{a\pm}_{aa}(x)$ is finite for $N \to \infty$. Hence $G^{\pm}(x)$ is an analytical continuation of $G(z)$. We subsequently shall assume that $R^{a+}(x)$ and $R^{(a)b+}(x)$ always exist for $N \to \infty$ and particularly that the respective imaginary parts are different from zero for all x.

It can be shown[20] that (2.34) and (2.35) can be replaced by

$$D^a_{aa}(x) = V_{aa} - \frac{1}{2\pi i} PP \int\limits_{-\infty}^{+\infty} \frac{\Gamma^a_{aa}(x')}{x' - x} \mathrm{d}x' , \tag{2.34a}$$

and
$$\Gamma^a_{aa}(x) = 2\pi \langle a / R^{a-}(x)\, Q_a\, \delta (x - T)\, Q_a\, R^{a+}(x) | a \rangle . \tag{2.35a}$$

If we lower the contour C to the real axis it follows from (2.28a) and (2.29a) in particular for $t > 0$

$$\underset{t>0}{U_{aa}(t)} = - \frac{1}{2\pi i} \int\limits_{-\infty}^{+\infty} e^{-ixt} \frac{\mathrm{d}x}{x - E_a - R^{a+}_{aa}(x)} , \tag{2.37}$$

and
$$\underset{t>0}{U_{ba}(t)} = - \frac{1}{2\pi i} \int\limits_{-\infty}^{+\infty} e^{-ixt} \frac{1}{x - E_b - R^{(a)b+}_{bb}(x)} R^{(a)b+}_{ba}(x) \frac{1}{x - E_a - R^{a+}_{aa}(x)} \mathrm{d}x . \tag{2.38}$$

Both relations (2.37) and (2.38) are exact.

In this paper we suppose that it is always possible to prepare the eigenstate $|a\rangle$ of T or at least a subset of states $|a'\rangle$ of T with $E_{a'}$ located in a small domain D of the spectrum of T. Otherwise the eigenstates of T will not ordinarily provide a useful representation for the system being observed. Thus $R^{a+}_{aa}(x)$ is small compared with E_a and $R^{(a)b+}_{bb}(x)$ is small compared with E_b for all x. Consequently we shall restrict our evaluation of the integrals (2.37) and (2.38) to this situation.

Due to the smallness of $D^a_{aa}(x)$ and $\Gamma^a_{aa}(x)$ compared with E_a the integral (2.37) has a sharp maximum at about the point $x = E_a$. Hence we have in good approximation

$$D^a_{aa}(x) \approx D^a_{aa}(E_a) := \delta_a , \quad \Gamma^a_{aa}(x) \approx \Gamma^a_{aa}(E_a) := \gamma_a . \tag{2.39}$$

We find
$$\underset{t>0}{U_{aa}(t)} = e^{-i(E_a + \delta_a)t - \frac{1}{2}\gamma_a t} , \tag{2.40}$$

and with regard to (2.30)
$$p^T_a(t) = e^{-\gamma_a t} . \tag{2.41}$$

For integral (2.38) we obtain using the calculus of residues and an iterative process for evaluating the poles and the approximations

$$R^{a+}_{aa}(E_b) \approx R^{a+}_{aa}(E_a) = \delta_a - \tfrac{i}{2}\gamma_a, \quad R^{(a)b+}_{bb}(E_a) \approx R^{(a)b+}_{bb}(E_b) = \delta_b - \tfrac{i}{2}\gamma_b, \quad R^{(a)b+}_{ba}(E_a) \approx R^{(a)b+}_{ba}(E_b), \tag{2.42}$$

$$U_{ba}(t) = \frac{R^{(a)b+}(E_b)}{{}^*E_b - {}^*E_a + \frac{i}{2}(\gamma_a - \gamma_b)} \left(e^{-i({}^*E_b - (i/2)\gamma_b)t} - e^{-i({}^*E_a - (i/2)\gamma_a)t}\right) , \qquad t > 0 \tag{2.43}$$

where
$$*E_a := E_a + \delta_a\,, \qquad *E_b := E_b + \delta_b\,. \tag{2.44}$$

According to (2.40) the modification of the law of motion of the state $|a\rangle$ due to the "perturbation" V consists essentially of adding to the "unperturbed" energy E_a the complex energy $\delta_a - \frac{1}{2} i \gamma_a$. The real part δ_a is the level shift due to V. The imaginary part γ_a is different from zero if, and only if, the spectrum of the "perturbed" Hamiltonian H is continuous. Thus we have proved the Fock-Krylow-Theorem. γ_a is the part responsible for the existence of the exponential falling-off, and $\gamma_a{}^{-1}$ is the lifetime of the decaying state.

Knowing the $U_{aa}(t)$ and $U_{ba}(t)$ from (2.40) and (2.43) we can evaluate (2.3) for any given density operator $\varrho(0)$. Moreover by straightforward calculation we can deduce a differential equation from (2.3) using (2.40) and (2.43). We assume the density operator to be diagonal at $t=0$ (assumption of initial random phases) and obtain with $\operatorname{Tr} \varrho(0) = 1$

$$\dot{\varrho} \sum_{E_b \in \mathrm{D}} bb(t) = -\gamma_b \sum_{E_b \in \mathrm{D}} \varrho_{bb}(t) + \sum_{E_b \in \mathrm{D}} \sum_{a \neq b} \frac{|R_{ba}^{[a]b+}(E_b)|^2 e^{-\gamma_a t}}{(*E_b - *E_a)^2 + \frac{1}{4}(\gamma_b - \gamma_a)^2} \times \{\gamma_b - \gamma_a + e^{-(\frac{1}{2})(\gamma_b - \gamma_a)}$$
$$[2(*E_b - *E_a)\sin(*E_b - *E_a)t - (\gamma_b - \gamma_a)\cos(*E_b - *E_a)t]\}\, \varrho_{aa}(0)\,. \tag{2.45}$$

In section 5 we shall apply (2.45) to the problem of radiative and nonradiative electronic decay processes in impurity centers. Then we shall simplify equation (2.45) considerably. However we first must find a Hamiltonian describing a micro-crystal with an electronic impurity center. We shall briefly treat this question in the following two sections.

3. The Hamiltonian of the System Micro-Crystal/Radiation Field

We shall consider a micro-crystal described by the Hamiltonian K containing just a single electronic impurity center. We assume the micro-crystal to be large enough to neglect the effect of the boundary conditions on the processes in the point imperfection. S may be the Hamiltonian of the free radiation field and I the operator of the interaction between crystal and radiation field. Thus the complete Hamiltonian can be written

$$H = K + S + I\,. \tag{3.1}$$

We imagine K to be decomposed into an "unperturbed" part ${}^0K$ and a "perturbation" ${}^1K$. ${}^0K$ should include the essential part of all the interactions between the electrons and the nuclei of the crystal, and the perturbation ${}^1K$ should produce nonradiative electronic transitions. That is why the eigenstates of ${}^0K$ must be labelled by certain electronic quantum numbers n_r.

There is no clear way for decomposing K adequately. To be definite we use a decomposition seeming suitable for ionic crystals. In those nonmetals we may consider the ions to be stable subsystems of the crystal, provided that a certain prepared irradiation does not destroy the tight binding between the electrons and the nucleus of an ion. This will be presupposed henceforth. Impurity center electrons not attached to a certain nucleus we shall describe by $\boldsymbol{r}_s$ and momentum $\boldsymbol{p}_s$, and all the other electrons and the nuclei by "relative particle" quantities $\boldsymbol{x}_i(j)$ and $\boldsymbol{p}_i(j)$ and ionic or center of mass quantities $\boldsymbol{X}_j$ and $\boldsymbol{P}_j$. We obtain for K[24]

$$K = \sum_s \frac{1}{2m} \boldsymbol{p}_s^2 + \sum_j \left\{ \sum_i \frac{1}{2m} \boldsymbol{p}_i^2(j) + \frac{1}{2M_j} \boldsymbol{P}_j^2 + \frac{1}{m_j} \sum_{i,i'} \boldsymbol{p}_i(j)\, \boldsymbol{p}_{i'}(j) \right\} + V \tag{3.2}$$

with mass m_j of the nuclei and ionic mass $\quad M_j := m_j + z_j m\,,$ (3.3)

where z_j is the number of electrons of the j-th ion and m the electronic mass. V includes in principle all the other nonrelativistic interactions in the crystal.

Consider the "electronic Hamiltonian" K^{e} defined by

$$K^{\mathrm{e}} = \sum_s \frac{1}{2m} \boldsymbol{p}_s^2 + \sum_j \left\{ \sum_i \frac{1}{2m} \boldsymbol{p}_i^2(j) + \frac{1}{m_j} \sum_{i,i'} \boldsymbol{p}_i(j)\, \boldsymbol{p}_{i'}(j) \right\} + V\,. \tag{3.4}$$

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[24] H. A. BETHE and E. E. SALPETER, Quantum Mechanics of One- and Two-Electron Atoms, Springer-Verlag, Berlin 1957

Since $\boldsymbol{X}_j$ and K^{e} are commuting observables they possess common eigenstates. To each set $\boldsymbol{X} := \{\boldsymbol{X}_j\}$ of ionic positions there corresponds a set of eigenstates $|n\,\boldsymbol{X}'\rangle$ and a set of eigenvalues $U^n(\boldsymbol{X})$ labelled by the index set $n := \{n_r\}$ of electronic quantum numbers. Thus the eigenvalue problem for K^{e} takes the form

$$K^{\mathrm{e}}\,|n\,\boldsymbol{X}'\rangle = U^n(\boldsymbol{X}')\,|n\,\boldsymbol{X}'\rangle\,. \tag{3.5}$$

Since $\boldsymbol{X}_j$ and the crystal Hamiltonian K does not commute, the eigenstates of K^{e} are not eigenstates of K. However the set of

$$|\Psi_n[\tilde{\varphi}^n]\rangle := \int |n\,\boldsymbol{X}'\rangle\,\tilde{\varphi}^n(\boldsymbol{X}')\,\mathrm{d}\boldsymbol{X}' \tag{3.6}$$

labelled by n is a complete system of states for the crystal described by K, where the functions $\tilde{\varphi}^n(\boldsymbol{X}')$ still have to be determined. Now the state (3.6) will be difficult to observe unless it is as stable as possible with respect to the crystal Hamiltonian K. Hence the precise form of (3.6) is given by a variational method with trial function (3.6): $\delta\langle\Psi_n|K|\Psi_n\rangle = 0$. It can be shown[21] that $\tilde{\varphi}^n(\boldsymbol{X})$ must then be an eigenfunction of the operator

$$K^n := \sum_j \frac{1}{2\,M_j}\,\boldsymbol{P}_j^2 + G^n(\boldsymbol{X})\,, \tag{3.7}$$

where

$$G^n(\boldsymbol{X}) := U^n(\boldsymbol{X}) + \sum_j \frac{1}{2\,M_j}\,\langle n\,\boldsymbol{X}'\,|\,\boldsymbol{P}_j^2|\,n\,\boldsymbol{X}'\rangle\,. \tag{3.8}$$

To derive (3.7) one must assume the states $|n\,\boldsymbol{X}'\rangle$ to be real. This is possible under rather mild conditions[21]. In the $\{\boldsymbol{r}, \boldsymbol{x}, \boldsymbol{X}\}$ representation we have to replace (3.6) by

$$\tilde{\Psi}_n(\boldsymbol{r}, \boldsymbol{x}, \boldsymbol{X}) = \psi_n(\boldsymbol{r}, \boldsymbol{x}, \boldsymbol{X})\,\tilde{\varphi}^n(\boldsymbol{X})\,, \tag{3.9}$$

where ψ_n is an eigenfunction of the electronic Hamiltonian (3.4). (3.9) brings about the so-called adiabatic coupling[25]. Ordinarily, by the adiabatic coupling, the motion of electrons is coupled with the motion of nuclei rather than the motion of electronic "relative particles" with the motion of the ionic centers of mass.

The potential energy in the ionic Hamiltonian K^n depends on the electronic state n. We define for each state n the crystal is still existing

$${}^1G_j^n := \nabla(\boldsymbol{X}_j)\,G^n(\boldsymbol{X})\,\big|_{X^n} = 0\,, \qquad \boldsymbol{X}^n := \{\boldsymbol{X}_j^n\}\,. \tag{3.10}$$

Expanding $G^n(\boldsymbol{X})$ into a power series in $(\boldsymbol{X}_j - \boldsymbol{X}_j^n)$ we find

$$\begin{aligned} G^n(\boldsymbol{X}) = {}^0G^n &+ \tfrac{1}{2}\sum_{j,j'} {}^2G_{jj'}^n(\boldsymbol{X}_j - \boldsymbol{X}_j^n)(\boldsymbol{X}_{j'} - \boldsymbol{X}_{j'}^n) + \\ &+ \tfrac{1}{6}\sum_{j,j',j''} {}^3G_{jj'j''}^n\,(\boldsymbol{X}_j - \boldsymbol{X}_j^n)(\boldsymbol{X}_{j'} - \boldsymbol{X}_{j'}^n)(\boldsymbol{X}_{j''} - \boldsymbol{X}_{j''}^n) + \cdots\,. \end{aligned} \tag{3.11}$$

Let us introduce

$${}^0K^n := \sum_j \frac{1}{2\,M_j}\,\boldsymbol{P}_j^2 + {}^0G^n + \tfrac{1}{2}\sum_{j,j'} {}^2G_{jj'}^n(\boldsymbol{X}_j - \boldsymbol{X}_j^n)(\boldsymbol{X}_{j'} - \boldsymbol{X}_j^n)\,. \tag{3.12}$$

We imagine (3.12) to be the Hamiltonian describing the motion of the lattice ions. The cubic and higher terms are supposed to be perturbations. These assumptions seem to be reasonable for sufficient low lattice temperatures. The eigenvalue problem of (3.12) becomes

$${}^0K^n\,\varphi_m^n(\boldsymbol{X} - \boldsymbol{X}^n) = E_m^n\,\varphi_m^n(\boldsymbol{X} - \boldsymbol{X}^n)\,. \tag{3.13}$$

In (3.13) m is an index set of ionic quantum numbers $m := \{m_r\}$. Because of the harmonicity of (3.12) we have

$$\langle\varphi_m^n\,|\boldsymbol{X}_j - \boldsymbol{X}_j^n|\,\varphi_m^n\rangle = 0; \tag{3.14}$$

in the "harmonic approximation" the $\boldsymbol{X}_j^n$ coincide with the average positions of the ions.

We replace (3.9) by

$$\Psi_{nm}(\boldsymbol{r}, \boldsymbol{x}, \boldsymbol{X}) = \psi_n(\boldsymbol{r}, \boldsymbol{x}, \boldsymbol{X})\,\varphi_m^n(\boldsymbol{X} - \boldsymbol{X}^n) \tag{3.15}$$

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[25] A. Haug, Theoretische Festkörperphysik, Franz Deuticke, Wien 1964.

presuming Ψ_{nm} to be real and for all $\boldsymbol{X}$

$$\langle \Psi_{nm} | \Psi_{n'm'} \rangle = \langle \psi_n | \psi_{n'} \rangle \langle \varphi^n_m | \varphi^{n'}_{m'} \rangle = \delta_{nn'} \delta_{mm'} . \tag{3.16}$$

With respect to the definition of the system (3.15) we obtain from (3.2) with

$${}^{t}K_{n',m'\ nm} = (1-\delta_{n'n}) \sum_j \frac{1}{2M_j} \langle \varphi^{n'}_{m'} | \langle \psi_{n'} | \boldsymbol{P}_j^2 | \psi_n \rangle + 2\boldsymbol{P}_j | \psi_n \rangle \boldsymbol{P}_j | \varphi^n_m \rangle \tag{3.17}$$

$${}^{a}K_{n'm'\ nm} = \delta_{n'n} \langle \varphi^n_{m'} | (K^n - {}^{0}K^n) | \varphi^n_m \rangle , \tag{3.18}$$

and

$$K_{n'm',nm} = \delta_{n'n} \delta_{m'm} E^n_m + {}^{t}K_{n'm'\ nm} + {}^{a}K_{n'm',nm} . \tag{3.19}$$

Equation (3.19) is that representation of

$$K := {}^{0}K + {}^{1}K, \quad {}^{1}K := {}^{t}K + {}^{a}K , \tag{3.20}$$

in which ${}^{0}K$ is diagonal. The matrix elements (3.17) produce nonradiative electronic transitions attended with transitions in the subsystem of the lattice ions with respect to the strong coupling between the electronic and the ionic motion. The matrix elements (3.18) of the anharmonic lattice interactions bring about nonradiative transitions in the system of the lattice ions.

Excited electronic states may decay because of their coupling with the radiation field emitting photons; the same holds for excited lattice states. Hence the radiation field and its interactions with electrons ${}^{e}I$ and with ions ${}^{i}I$ must necessarily be taken into account.

Photons quantized in a large box with momentum $\boldsymbol{k}$ and polarization $\boldsymbol{e}$ have the energy

$$E(\nu_{\boldsymbol{k},\boldsymbol{e}}) = \sum_{\boldsymbol{k},\boldsymbol{e}} c\, |\boldsymbol{k}|\, \nu_{\boldsymbol{k},\boldsymbol{e}} , \quad \nu_{\boldsymbol{k},\boldsymbol{e}} = 0, 1, 2, \ldots , \tag{3.21}$$

thus

$${}^{0}H\, |n m ; \nu\rangle = E^n_m(\nu)\, |n m ; \nu\rangle , \quad \nu := \{\nu_{\boldsymbol{k},\boldsymbol{e}}\} \tag{3.22}$$

with

$${}^{0}H := {}^{0}K + S , \quad E^n_m(\nu) := E^n_m + E(\nu) , \quad |n m ; \nu\rangle = |n m\rangle \times |\nu\rangle . \tag{3.23}$$

$|\nu\rangle$ is an eigenstate of S.

To describe our complete system micro-crystal/radiation field we now have to replace (2.1) by

$$H := {}^{0}H + {}^{1}H , \tag{3.24}$$

where

$${}^{1}H := {}^{t}K + {}^{a}K + {}^{e}I + {}^{i}I . \tag{3.25}$$

Since the Hamiltonian H according to (3.24) does not commute with ${}^{0}H$ the eigenstates of ${}^{0}H$ are metastable, provided that the perturbation (3.25) is sufficiently small. Otherwise the eigenstates of ${}^{0}H$ will not ordinarily provide a useful representation for the system being studied.

After having considered briefly the spectrum of ${}^{0}K^n$ in the next section we shall discuss in section 5 some aspects of the transitions brought about by ${}^{1}H$.

4. The Spectrum of the Ionic Hamiltonian

It is often convenient in lattice dynamics to use the so-called dynamical matrix

$$D^n(j, j') := M_j^{-(1/2)}\, {}^{2}G^n_{jj'}\, M_j^{-(1/2)} \tag{4.1}$$

and the reduced displacements

$$\boldsymbol{Y}^n(j) := M_j^{1/2} (\boldsymbol{X}_j - \boldsymbol{X}^n_j) . \tag{4.2}$$

Substituting (4.1) and (4.2) in (3.12) we obtain

$${}^{0}K^n = - \sum_j \frac{\partial^2}{\partial \boldsymbol{Y}^n(j)^2} + {}^{0}G^n + \tfrac{1}{2} \sum_{j,j'} D^n(j, j')\, \boldsymbol{Y}^n(j)\, \boldsymbol{Y}^n(j') . \tag{4.3}$$

The Hamiltonian (4.3) can be diagonalized provided that the eigenvalue problem of the dynamical matrix is solved. In components we get for the eigenvalue problem of D^n

$$\sum_{j'} \sum_{\alpha'} D^n_{\alpha\alpha'}(j,j')\, \xi^n_{\alpha'}(j') - (\omega^n)^2\, \xi^n_\alpha(j) = 0\,, \tag{4.4}$$

where there exist in a micro-crystal with N ions for every state n $3N$ eigenvalues $(\omega^n_t)^2$. The respective eigenvectors $\xi^n_\alpha(j\,|\,t)$ can always be chosen so that

$$\sum_j \sum_a \xi^n_\alpha(j\,|\,t)\, \xi^n_\alpha(j\,|\,t') = \delta_{tt'}\,, \qquad \sum_t \xi^n_\alpha(j\,t)\, \xi^n_{\alpha'}(j'\,|\,t) = \delta_{\alpha\alpha'}\, \delta_{jj'}\,. \tag{4.5}$$

If there is degeneracy, certain arbitrariness in the choice of $\xi^n_\alpha(j\,|\,t)$ still remains. By means of a set of $\xi^n_\alpha(j\,|\,t)$ we can introduce normal coordinates Q^n_t and the respective conjugate momenta P^n_t

$$Q^n_t = \sum_j \sum_\alpha \xi^n_\alpha(j\,|\,t)\, Y^n_\alpha(j)\,, \qquad P^n_t = -\,i \sum_j \sum_\alpha \xi^n_\alpha(j\,|\,t) \frac{\partial}{\partial Y_\alpha{}^n(j)}\,. \tag{4.6}$$

By means of the normal coordinates, the Hamiltonian (4.3) will be transformed into

$$^0K^n = \tfrac{1}{2} \sum_t [(P^n_t)^2 + (\omega^n_t)^2\, (Q^n_t)^2] + {}^0G^n\,. \tag{4.7}$$

It is often convenient to introduce annihilation and creation operators

$$b^n_t = (2\,\omega^n_t)^{-1/2}\, (\omega^n_t\, Q^n_t + i\, P^n_t)\,, \qquad (b^n_t)^+ = (2\,\omega^n_t)^{-1/2}\, (\omega^n_t\, Q^n_t - i\, P^n_t)\,. \tag{4.8}$$

Then $^0K^n$ becomes

$$^0K^n = \sum_t \omega^n_t \{(b^n_t)^+\, b^n_t + \tfrac{1}{2}\}\,. \tag{4.9}$$

Provided that the eigenvalues and eigenvectors of (4.4) are known we can obtain immediately the solutions of (4.7) or (4.9) describing a set of uncoupled oscillators. Hence the main task is to solve (4.4).

Here it is not necessary to discuss in detail the methods for solving (4.4) with respect to micro-crystals containing point defects, as there are excellent review articles by MARADUDIN[26] and LUDWIG[17] concerning this problem. But note: The solution of (4.4) generally leads to both discrete and quasi-continuous labelled eigenvectors. The discrete eigenvectors are attached to localized modes; these states have decreasing amplitudes with increasing distance from the point imperfection. The quasi-continuous eigenvectors are belonging to scattering solutions which for long wavelengths approximately coincide with the acoustical and the optical branches of the ideal lattice waves.

We now can state that the Hamiltonian (4.9) can be decomposed at least in two operators, namely an operator $^0K^n_l$ being attached to the localized states and an operator $^0K^n_q$ describing the quasi-continuous states. Hence we may introduce

$$^0K^n_l\, |\,\varphi^n_m\rangle = E^n_m\, |\,\varphi^n_m\rangle \tag{4.10}$$

with

$$|\,\varphi^n_m\rangle := \prod_t \frac{((b^n_t)^+)^{m_t}}{(m_t!)^{1/2}}\, |\,\varphi^n_l\rangle\,, \qquad m := \{m_t\}\,, \tag{4.11}$$

and

$$^0K^n_q\, |\,\varphi^n_\mu\rangle = E^n_\mu\, |\,\varphi^n_\mu\rangle \tag{4.12}$$

with

$$|\,\varphi^n_\mu\rangle := \prod_\tau \frac{((b^n_\tau)^+)^{\mu_\tau}}{(\mu_\tau!)^{1/2}}\, |\,\varphi^n_q\rangle\,, \qquad \mu := \{\mu_\tau\}\,. \tag{4.13}$$

$|\,\varphi^n_l\rangle$ is the ground state of the localized modes, $|\,\varphi^n_q\rangle$ is the ground state of the quasi-continuous modes. The m_t and μ_τ are phonon occupation numbers. Furthermore we can write

$$^0K^n\, |\,\varphi^n_{m\mu}\rangle = E^n_{m\mu}\, |\,\varphi^n_{m\mu}\rangle \tag{4.14}$$

with

$$E^n_{m\mu} := E^n_m + E^n_\mu\,, \qquad |\,\varphi^n_{m\mu}\rangle := |\,\varphi^n_m\rangle \times |\,\varphi^n_\mu\rangle\,. \tag{4.15}$$

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[26] A. MARADUDIN, Solid State Phys. **18**, 274 [1966] and **19**, 1 [1966].

5. Radiative and Nonradiative Electronic Decay Processes

Now we are prepared to describe all time-dependent processes in our microcrystal using the quantum theory of decaying states. Nevertheless in this paper we shall confine ourselves to a brief discussion of some important aspects of radiative and nonradiative electronic decay processes in the weak-coupling approximation.

Let us consider equation (2.45). In our system micro-crystal/radiation field we have to identify the operator T with ${}^0H$ and the operator V with ${}^1H$. The eigenvalues of ${}^0H$ are

$$E^n_{m\mu}(\nu) := E^n_{m\mu} + E(\nu)\,, \tag{5.1}$$

and the eigenstates of ${}^0H$ can be written

$$|n\,m\,\mu\,;\nu\rangle := |\nu\rangle \times \int |n\,Q^n_l\,Q^n_q\rangle\,\varphi^n_m(Q^n_l, Q^n_q)\,\mathrm{d}Q^n_l\,\mathrm{d}Q^n_q\,, \tag{5.2}$$

where Q^n_l and Q^n_q mean the set of the normal coordinates of the localized states and the continuous states of the lattice oscillations respectively. To evaluate (2.45) we must know the matrix elements of the operators $R^{a+}(x)$ and $R^{(a)b+}(x)$ in the representation, where ${}^0H$ is diagonal.

To determine first $R^{nm\mu\nu}(z)$ we go back to the definition (2.16). With respect to (2.8) we obtain

$$\begin{aligned} R^a(z) &= V + V\,Q_a(z - H^a)^{-1}\,Q_a\,V = V + V\,Q_a(z - T)^{-1}\,Q_a\,V \\ &\quad + V\,Q_a(z - T)^{-1}\,Q_a\,V\,Q_a(z - H^a)^{-1}\,Q_a\,V = V + V\,Q_a(z - T)^{-1}\,R^a(z)\,. \end{aligned} \tag{5.3}$$

The analogous formula for $R^{(a)b}(z)$ has the form

$$R^{(a)b}(z) = V + V\,Q_{(a)b}(z - T)^{-1}\,R^{(a)b}(z)\,. \tag{5.4}$$

The equations (5.3) and (5.4) provide integral equations for $R^a(z)$ and $R^{(a)b}(z)$ respectively. If we iterate these equations by successive substitution into the right-hand sides, expansions are obtained for the R in powers of the "perturbation" V. The lowest approximation for both $R^a(z)$ and $R^{(a)b}(z)$ is obviously V. In this approximation we particularly have

$$R^{nm\mu\nu}_{n'm'\mu'\nu',\,nm\mu\nu}(z) = \langle n'\,m'\,\mu'\,;\nu'\,|\,{}^1H\,|n\,m\,\mu\,;\nu\rangle\,. \tag{5.5}$$

We can write for the right-hand side of (5.5) with respect to the definitions (3.17), (3.18), and (3.25)

$$\begin{aligned} \langle n\,m\,\mu\,;\nu\,|\,{}^1H|\,n'\,m'\,\mu'\,;\nu'\rangle &= \delta_{\nu\nu'}\langle n\,m\,\mu\,|\,{}^{\mathrm{t}}K|\,n'\,m'\,\mu'\rangle + \delta_{nn'}\,\delta_{\nu\nu'}\langle m\,\mu\,|\,{}^{\mathrm{a}}K|\,m'\,\mu'\rangle \\ &\quad + \langle n\,m\,\mu\,;\nu\,|\,{}^{\mathrm{e}}I|\,n'\,m'\,\mu'\,;\nu'\rangle + \delta_{nn'}\langle m\,\mu\,;\nu\,|\,{}^{\mathrm{i}}I|\,m'\,\mu'\,;\nu'\rangle\,. \end{aligned} \tag{5.6}$$

From (5.6) it follows that for a certain transition only one of the matrixelements on the right-hand side is different from zero, hence (5.5) is decomposed into terms attached to respectively nonradiative electronic transitions, nonradiative lattice transitions, radiative electronic transitions, radiative lattice transitions. $({}^{\mathrm{t}}\varkappa)$ my measure the strength of the perturbation ${}^{\mathrm{t}}K$, $({}^{\mathrm{a}}\varkappa)$ the strength of ${}^{\mathrm{a}}K$, and $({}^{\mathrm{e}}\iota)$ the strength of ${}^{\mathrm{e}}I$. Hence the order of magnitude of the right-hand side of (6.6) is $0\,({}^{\mathrm{t}}\varkappa) + 0\,({}^{\mathrm{a}}\varkappa) + 0\,({}^{\mathrm{e}}\iota)$.

Relative to equation (2.45) we have to distinguish two important cases due to the structure of the impurity center. Firstly there may be infinitely many continuous eigenvalues of ${}^0H$ in D for normalization volume→∞. Secondly there may be only one discrete eigenvalue of ${}^0H$ belonging to the domain D. In both cases (2.45) can considerably be simplified. We shall discuss this briefly, and to be definite we assume the existence of impurity centers with the following characteristics: The motion of the impurity center electrons is coupled only with the localized lattice modes (This may happen if the point defect as a whole is electrical neutral). Hence in particular the matrix-elements of ${}^{\mathrm{t}}K$ and ${}^{\mathrm{e}}I$ are

$${}^{\mathrm{t}}K_{n'm'\mu'\nu'\,;\,nm\mu\nu} = \delta_{\nu'\nu}\,\delta_{\mu'\mu}\langle n'\,m'\,|\,{}^{\mathrm{t}}K|\,n\,m\rangle\,, \tag{5.7}$$

$${}^{\mathrm{e}}I_{n'm'\mu'\nu'\,;\,nm\mu\nu} = \delta_{\mu'\mu}\,{}^{\mathrm{e}}I_{n'm'\nu'\,;\,nm\nu} = -\,\delta_{\mu'\mu}\langle n'\,m'|\,\sum_i \frac{\boldsymbol{p}_i\cdot\boldsymbol{e}}{mc}\,|n\,m\rangle\,e\left(\frac{2\,\pi\,\hbar^2\,c}{V\,k}\right)^{1/2} \times \sqrt{\nu_{\boldsymbol{k},\,\boldsymbol{e}} + 1}\,, \tag{5.8}$$

where $\nu_{\boldsymbol{k},\boldsymbol{e}}$ represents the number of photons already in the state $(\boldsymbol{k}, \boldsymbol{e})$ with momentum $\boldsymbol{k}$ and polarization $\boldsymbol{e}$ before the transition has occurred, $\boldsymbol{p}_i$ is the momentum of an impurity center electron, and V here is the normalization volume. In (5.8) we confined ourselves to electrical dipol emission. Provided that the lattice temperature T is so low that phonons attached to the continuous lattice modes cannot create phonons belonging to the localized modet on energetical grounds, we may assume the subsystem of the continuous lattice modes to be in its ground state. Omitting henceforth the index $\mu = 0$ the density operator becomes at $t = 0$

$$\varrho(0) = \sum_{nm} |n\,m\,;\nu\rangle\, p_{nm}(0)\, \langle n\,m\,;\nu| \,. \tag{5.9}$$

The subsystem of the photons in (5.9) is supposed to be in the pure state $|\nu\rangle\,\langle\nu|$.

Let us now consider equation (2.45). Using (5.1), (5.2), and (5.5) we obtain setting $E(\nu) := E_\nu$

$$\begin{aligned} \sum_{E_\nu \in \mathrm{D}} \langle n'\,m'\,;\nu'\,|\,\dot{\varrho}(t)|\,n'\,m'\,;\nu'\rangle = &- \gamma^{n'}_{m'\nu'} \sum_{E_\nu \in \mathrm{D}} \langle n'\,m'\,;\nu'\,|\,\varrho(t)|\,n'\,m'\,;\nu'\rangle \\ &+ \sum_{E_\nu \in \mathrm{D}} \sum_{nm \neq n'm'} \frac{|\langle n'\,m'\,;\nu'\,|\,{}^1H\,|\,n\,m;\,\nu\rangle|^2 \exp\{-\gamma^n_{m\nu} t\}}{({}^*E^{n'}_{m'\nu'} - {}^*E^n_{m\nu})^2 + \frac{1}{4}(\gamma^{n'}_{m'\nu} - \gamma^n_{m\nu})^2} \\ \times \{\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu} + e^{-\frac{1}{2}(\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu})t}\,&[2({}^*E^{n'}_{m'\nu'} - {}^*E^n_{m\nu}) \sin({}^*E^{n'}_{m'\nu'} - {}^*E^n_{m\nu})\, t \\ &- (\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu}) \cos({}^*E^{n'}_{m'\nu'} - {}^*E^n_{m\nu})\, t]\}\, p_{nm}(0) \,. \end{aligned} \tag{5.10}$$

With respect to (5.6) for $n \neq n'$ we can replace ${}^1H$ by ${}^tK$ for nonradiative electronic transitions and by ${}^eI$ for radiative electronic transitions. There are infinitely many continuous eigenvalues $E_{\nu'}$ of ${}^0H$ in D for infinite normalization volume. This means that we should replace the sum over $E_{\nu'}$ by an integral using

$$\sum_{E_{\nu'} \in \mathrm{D}} = \int\!\!\int_{E_{\nu'} \in \mathrm{D}} \mathrm{d}\sigma_s(E_{\nu'} - E_\nu)\, \mathrm{d}E_{\nu'} \,, \qquad \int\!\!\int \mathrm{d}\sigma_s(E_{\nu'} - E_\nu)\, \mathrm{d}E_{\nu'} = 1 \,, \tag{5.11}$$

where $\mathrm{d}\sigma_s(E_{\nu'} - E_\nu)$ is the number of states of the emitted photon per unit energy. Generally σ_s depends on the energy and on certain additional variables such as the solid angle, hence we write $\mathrm{d}\sigma_s(E_{\nu'} - E_\nu)$. We define

$$p_{n'm'}(t) := \int\!\!\int_{E_{\nu'} \in \mathrm{D}} \langle n'\,m'\,;\nu'\,|\,\varrho(t)|\,n'\,m'\,;\nu'\rangle\, \mathrm{d}\sigma_s(E_{\nu'} - E_\nu)\, \mathrm{d}E_\nu \,. \tag{5.12}$$

Henceforth we shall neglect the small corrections $\delta^{n'}_{m'\nu'}$ and[27] $\delta^{n'}_{m\nu}$. Let us integrate over $E_{\nu'}$ using the equations (5.6), (5.7), and (5.8). We obtain for $n \neq n'$ replacing ${}^1H$ by ${}^tK$ or ${}^eI$ respectively

$$\begin{aligned} \dot{p}_{n'm'}(t) = &- \gamma^{n'}_{m'\nu'} p_{n'm'}(t) + \sum_{nm \neq n'm'} p_{nm}(0) \exp\{-\gamma^n_{m\nu} t\} \\ &\times \{2\pi \int \mathrm{d}\sigma\,(E^n_m - E^{n'}_{m'})\, |\langle n'\,m'\,;\nu'|\,{}^eI\,n\,m\,;\nu\rangle|^2 \qquad c\,k = E^n_m - E^{n'}_{m'} \\ &+ \frac{\delta_{\nu'\nu}\,|\langle n'\,m'\,|\,{}^tK\,|\,nm\rangle|^2}{(E^n_m - E^{n'}_{m'})^2 + \frac{1}{4}(\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu})^2}\, [\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu} \\ + \exp\{-\tfrac{1}{2}(\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu})\, t\}\, &[2(E^n_m - E^{n'}_{m'}) \sin(E^n_m - E^{n'}_{m'})\, t - (\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu}) \cos(E^n_m - E^{n'}_{m'})\, t]]\} \,. \end{aligned} \tag{5.13}$$

The radiative electronic transition terms on the right-hand side of (5.13) are examples of those simplifications which arise by integration over a domain of continuous levels. Sometimes the transition terms for nonradiative electronic transitions between discrete levels can be considerably simplified also. Provided that the oscillation frequencies $|\,E^n_m - E^{n'}_{m\nu}\,| \neq 0$ are so large that the measuring device cannot record the very fast oscillations described on the right-hand side of (5.13) because of its inertness, equation (5.13) becomes

$$\begin{aligned} \dot{p}_{n'm'}(t) = &- \gamma^{n'}_{m'}\, p_{n'm'}(t) + \sum_{nm \neq n'm'} p_{nm}(0) \exp\{-\gamma^n_{m\nu} t\} \\ \times \{2\pi \int \mathrm{d}\sigma_s(E^n_m - E^{n'}_{m'})\, &|\langle n'\,m'\,;\nu'\,|{}^eI|\,n\,m\,;\nu\rangle|^2 + \frac{\delta_{\nu'\nu}(\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu})\,|\langle n'\,m'\,|{}^tK\,|\,n\,m\rangle|^2}{(E^n_m - E^{n'}_{m'})^2 + \frac{1}{4}(\gamma^{n'}_{m'\nu'} - \gamma^n_{m\nu})^2} \,,\, c\,k = E^n_m - E^{n'}_{m'} \,. \end{aligned} \tag{5.14}$$

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[27] With respect to radiative processes the level shifts $\delta^n_{m\nu}$ are linear divergent, but the renormalized level shifts are small.

Equation (5.14) to be valid $(\gamma^{n'}_{m'\nu'} - \gamma^{n}_{m'}) > 0$ must hold. This means irreversibility: For nonradiative electronic decay $n \rightarrow n'$ $({}^{0}G^{n} > {}^{0}G^{n'})$ the lattice state nm must always be lower excited than the lattice state $n'm'$ into which the transition occurs. Hence the lifetime of the lattice states must be smaller than the average time necessary for a nonradiative electronic transition to happen. $t \gg (\gamma^{n}_{m\nu})^{-1}$ has to be valid, since otherwise electronic return processes should be possible.

Equations (5.13) and (5.14) can be further transfermed. In the weak-coupling approximation we have,

$$p_{nm}(0) \exp(-\gamma^{n}_{m\nu})\, t = p_{nm}(t) - \sum_{\substack{nm \\ n \neq n''}} \Big(\sum_{\nu''} |<nm;\nu\,|\,U(t)\,|\,n''m'';\nu''>|^{2}\Big)\, p_{n',m'}(0)$$

$$= p_{nm}(t) - 0\,({}^{t}\varkappa)^{2} - ({}^{e}\iota)^{2}\,.$$

Replacing $p_{nm}(0) \exp(-\gamma^{n}_{m\nu})\, t$ in (5.13) or (5.14) by $p_{nm}(t)$ means neglecting terms of the order of magnitude $0\,({}^{t}\varkappa)^{2}$ $0\,({}^{e}\iota)^{2}$, $0\,({}^{t}\varkappa)^{4}$, and $0\,({}^{e}\iota)^{4}$ which is consistent with the assumption of weak-coupling in (5.10), (5.13), and (5.14). Provided that $\gg (\gamma^{n}_{m\nu})^{-1}$ is of the order of magnitude $({}^{t}\varkappa)^{-2}$ respectively $({}^{e}\iota)^{-2}$ (possibility of the weak-coupling approximation), then the simple equation holds

$$\dot{p}_{n'm'}(t) = -\gamma^{n'}_{m'\nu'}\, p_{n'm'}(t) + \sum_{nm \neq n'm'} w_{n'm'\;nm}\, p_{nm}(t)\,, \tag{5.15}$$

where

$$w_{n'm'\;nm} := 2\pi \int d\sigma_{s}(E^{n}_{m} - E^{n'}_{m'})\, |\langle n'm';\nu'|\,{}^{e}I\, nm;\nu\rangle|^{2}\,. \qquad ck = E^{n}_{m} - E^{n'}_{m'}$$

$$+ \frac{(\gamma^{n'}_{m'\nu'} - \gamma^{n}_{m\nu})\,\delta_{\nu'\nu}|\langle n'm'|{}^{t}K\,|\,nm\rangle|^{2}}{(E^{n}_{m} - E^{n'}_{m'})^{2} + \frac{1}{4}(\gamma^{n'}_{m'\nu'} - \gamma^{n}_{m\nu})^{2}}\,. \tag{5.16}$$

Equation (5.15) has the form of the Pauli-Master-Equation[19]. $w_{n'm',nm}$ is the constant transition probability per unit time. The first term on the right-hand side of (5.16) is the transition probability per unit time for radiative electronic transitions, and the second term is the transition probability per unit time for nonradiative electronic transitions.

It is practicable to evaluate, at least for simple models of the microcrystal, formula (5.16) for the transition probability per unit time. Further details can be found in two papers which are now in preparation.

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