$\mathscr{L}_n^{(k)}(x)$ means Laguerre's polynomial

$$\mathscr{L}_n^{(k)}(x) := \sum_{\nu=0}^{n} \binom{n+k}{n-\nu} \frac{(-1)^\nu}{\nu!} x^\nu =: \sum_{\nu=0}^{n} c_\nu x^\nu . \quad \text{(C.4)}$$

For numerical evaluation one must pay attention on the fact, that the known recurrence formulae give rather inexact results, since one uses differences of great numbers of equal order. Hence we calculate the $\mathscr{L}_n^{(k)}$ directly observing the recurrence formula for the coefficients c_ν.

$$c_{\nu+1} = - c_\nu \frac{(n-\nu)}{(\nu+1)(\nu+k+1)} \quad \text{(C.5)}$$

with the normalization

$$c_0 = \binom{n+k}{n} .$$

Using a symbolic notion we obtain the following ALGOL procedure.

```
IF n > m THEN BEGIN h :=m; m := n;
n := h; a := − a; END; s := c : (a/√2) * (m − n)
* exp(− a*a/4) * sqrt(n!/m!) * (m!/((m − n)! * n!));
l := m − n;
x := a * a/2;
FOR i := 0 STEP 1 UNTIL n − 1 DO
BEGIN
    c := − c * a ** (n − i)/((i + 1) * (i + l + 1));
    s := s + c;
END.
```

Non Radiative Electronic Transitions in Ionic Crystals II *

Reaction Formalism and Results

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(Z. Naturforsch. **24 a**, 530—539 [1969]; received 18 December 1968)

A general formalism to describe radiationless electronic decay (RED) is developed. Two conditions are derived that must be fulfilled to make RED possible. Using the data derived in part I of this paper the general formulae are applied to a F-center in KCl and MgO. In KCl the conditions for RED are not fulfilled while in MgO RED proves to be more probable than radiative decay. This is in complete agreement with experimental knowledge.

Introduction

To describe a quantum process it is necessary to calculate wave functions, energy eigenvalues and matrix elements in advance. This has been done in part I of this paper[1]. We did show that the dynamical coupling of the electronic state with the lattice vibrations could be expressed approximately by one normal mode with frequency ω_l. Recently RAMPACHER[2] did prove electronic decay processes to be possible if and only if the states are coupled with a system having a continuous energy spectrum. Since by the non adiabatic interactions of the electron with the lattice the discrete electronic levels are coupled with the discrete energy levels of a localized mode, decay seems impossible in contrast to experimental knowledge. The solution of the problem is given with regard to the fact, that anharmonic terms couple the discrete mode ω_l with the continuous acoustical frequencies.

We calculate transition probabilities by means of the resolvent method of RAMPACHER[2], which is slightly modified to get expressions that could be treated easier numerically. The general formulae then are discussed for two examples: The anion vacancy in MgO is shown to induce radiationless electronic decay (RED), whereas the same imperfection prefers optical transitions in KCl. These results are in best agreement with experimental knowledge: A F-center emission band in MgO until now has not been detected whereas in KCl the F-center emission band about 1.1 eV is well known. It is shown that the probability for RED at an anion vacancy depends on temperature, too. No attempt is made to derive the reaction formulae known from the phenomenological theories, what is kept for future work.

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[1] A. LÖFFLER, Z. Naturforsch. (to be published) quoted hence forth by I.

[2] H. RAMPACHER, Z. Naturforsch. **23 a**, 401 [1968].

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Decay of Excited States

Let H^0 be the Hamiltonian of the system to be considered, and $|\lambda\rangle$ denote the eigenstates, being normalized on the finite volume Ω. We assume at time $t_0 = 0$ an interaction V being switched on that induces transitions between the stationary states of H_0. The dynamical behaviour is then determined by the time dependent probability amplitudes, which can be calculated, if one knows the time translation operator U:

$$|\lambda, t\rangle = U(t - t_0)\,|\lambda, t_0\rangle\,. \tag{1.1}$$

We wish to know the probability of finding the system at time t in the state $|\mu, t_0\rangle$ when it was in the state $|\lambda, t_0\rangle$ at t_0

$$|\langle\mu, t_0|\lambda, t\rangle|^2 = |\langle\mu, t_0|\,U(t - t_0)\,|\lambda, t_0\rangle|^2\,. \tag{1.2}$$

As known from elementary quantum mechanics U must satisfy (1.3):

$$i\,\frac{\partial}{\partial t}\,U(t - t_0) = H\,U(t - t_0) \tag{1.3}$$

and

$$U(t_0 - t_0) = U(0) = \mathbf{1}\,. \tag{1.4}$$

Formally a solution of (1.3) and (1.4) is given by [3]:

$$U(t - t_0) = \frac{1}{2\pi i}\oint\limits_C G(z)\,e^{-izt}\,\mathrm{d}z\,, \tag{1.5}$$

$$G(z) = (z - H)^{-1} = (z - H_0 - V)^{-1} \tag{1.6}$$

where the path of integration C in (1.5) runs from $-\infty - i\varepsilon$ to $+\infty - i\varepsilon$ and from $+\infty + i\varepsilon$ to $-\infty + i\varepsilon$ with all poles of $G(z)$ inside this path, which are because of the hermiticity of H on the real axis. The proof of this statement is given e.g. by ROMAN[3].

By means of (1.5) the calculation of the matrix-elements (1.2) is transferred to that of $G(z)$. RAMPACHER[2] gives some operator equations, which permit us to calculate the matrix elements of G approximately (Appendix A).

He gets the following results: Let P_λ be the projection operator on the states with eigenvalue E_λ, specially for non degenerated states

$$P_\lambda = |\lambda\rangle\langle\lambda| \tag{1.7}$$

and

$$Q_\lambda = \mathbf{1} - P_\lambda \tag{1.8}$$

then for non degenerated states the diagonal matrix elements of $G(z)$ are:

$$\langle\lambda|\,G(z)\,|\lambda\rangle = (z - E_\lambda - \langle\lambda|\,R(z)\,|\lambda\rangle)^{-1} \tag{1.9}$$

where $R(z)$ is defined by the operator equation

$$R(z) = V + V\cdot Q_\lambda(z - H^0)^{-1}Q_\lambda R(z)\,. \tag{1.10}$$

For off-diagonal elements of $G(z)$ one finds

$$\langle\mu\,|G(z)|\,\lambda\rangle = (z - E_\mu)^{-1}\langle\mu\,|\,R(z)|\,\lambda\rangle\,\langle\lambda\,|G(z)|\,\lambda\rangle\,. \tag{1.11}$$

If the Hamiltonian H^0 of the unperturbed system was properly chosen, we expect $R(z)$ to give a weak perturbation of the unperturbed E_λ. Because of (1.5) the matrixelements of $U(t - t_0)$ are

$$\langle\lambda\,|\,U(t - t_0)|\,\lambda\rangle = \frac{1}{2\pi i}\oint\limits_C \frac{e^{-iz(t - t_0)}}{(z - E_\lambda - \langle\lambda|\,R(z)\,|\lambda\rangle)}\,\mathrm{d}z\,, \tag{1.12}$$

$$\langle\mu\,|\,U(t-)|t_0)|\,\lambda\rangle = \frac{1}{2\pi i}\oint \frac{\langle\mu|\,R(z)\,|\lambda\rangle\,e^{-iz(t - t_0)}}{(z - E_\mu)\,(z - E_\lambda - \langle\lambda|\,R(z)\,|\lambda\rangle)}\,\mathrm{d}z\,. \tag{1.13}$$

The residues of (1.12) are given by the zeros z_λ of

$$z_\lambda - E_\lambda - \langle\lambda|\,R(z)\,|\lambda\rangle = 0 \tag{1.14}$$

which can be assumed for weak perturbations V to be approximately

$$z_\lambda \approx E_\lambda + \langle\lambda|\,R(E_\lambda)\,|\lambda\rangle \tag{1.15}$$

and therefore the probability amplitude is

$$\langle\lambda|\,U(t - t_0)\,|\lambda\rangle = \exp[-\,i\,(E_\lambda + R_\lambda(E_\lambda))\,(t - t_0)]\,. \tag{1.16}$$

A decay is characterized by a vanishing occupation probability of the initial state for $t \to \infty$

$$\begin{aligned}\lim_{t\to\infty}&|\langle\lambda, t_0|\,\lambda, t_0\rangle|^2\\ &= \lim_{t\to\infty}|\langle\lambda, t_0|\,U(t - t_0)\,|\lambda, t_0\rangle|^2\\ &= \lim_{t\to\infty}\exp[-\,2\,\mathrm{Im}\,R_\lambda(E_\lambda)\,(t - t_0)] = 0\end{aligned} \tag{1.17}$$

which can be satisfied if and only if

$$\mathrm{Im}\,R_\lambda(E_\lambda) > 0\,. \tag{1.18}$$

To study the decay processes one has to investigate

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[3] P. ROMAN, Advanced Quantum Theory, Addison-Wesley, Reading 1965.

$R(z)$ in the neighbourhood of the real axis. To do this, we use the definitions

$$R^{\pm}(x) := \lim_{y \to +0} R(x \pm i\,y) \qquad (1.19)$$

and

$$\Gamma_\lambda(x) := 2\,\mathrm{Im}\langle\lambda\,|\,R^{+}(x)\,|\,\lambda\rangle = \frac{1}{i}\langle\lambda\,|\,R^{+}(x) - R^{-}(x)\,|\,\lambda\rangle\,. \qquad (1.20)$$

By means of (1.19) we find for (1.20)

$$\Gamma_\lambda(x) = \lim_{y \to 0}\left\langle\lambda\,|\,R(x - i\,y)\,Q_\lambda\,\frac{2\,y}{(x - H^0)^2 + y^2}\,Q_\lambda\,R(x + i\,y)\,|\,\lambda\right\rangle = \langle\lambda\,|\,R^{-}(x)\,Q_\lambda\,\delta(x - H^0)\,Q_\lambda\,R^{+}(x)\,|\,\lambda\rangle \qquad (1.21)$$

which can be further simplified using a representation of Q_λ by the eigenstates of H^0

$$\Gamma_\lambda(x) = \int\!\!\!\!\!\!\sum_{\mu(\neq\lambda)} \mathrm{d}E_\mu\,\delta(x - E_\mu)\,|\langle\mu\,|\,R^{+}(x)\,|\,\lambda\rangle|^2\,. \qquad (1.22)$$

[In (1.22) we have to sum over the discrete and to integrate over the continous energy levels.]

Decay Processes with Two Interactions

We did mention above that by the special nature of the non adiabatic interactions RED is only possible if there exist anharmonic interactions in addition to the nonadiabatic terms. These two interactions are very different in structure and magnitude, hence the calculations of the decay process become very difficult and non-transparent, if one treats them simultaneously.

Let the Hamiltonian of the system H^0 be disturbed by the interactions V and W, where V is much stronger than W

$$H = H^0 + V + W\,. \qquad (1.23)$$

We can build up the resolvent of H in two steps, first calculating

$$G^*(z) := (z - H^*)^{-1} := (z - H^0 - V)^{-1} \qquad (1.24)$$

and then we find for $G(z)$ from (1.6)

$$G(z) = G^*(z) + G^*(z)\,W\,G(z)\,. \qquad (1.25)$$

Provided W is a weak perturbation, we can solve (1.25) by iteration. The term which contains in lowest order both interactions V and W is then given by $G^*(z)\,W\;G^*(z)$. Treating the radiationless electronic transitions, one therefore has at least to take this term into account.

Kinetic Model for RED

To describe RED, we first characterize the crystal states that participate in the process.

1. Before any electronic process has taken place the microblock is in its groundstate (with zero conductivity), it contains an anion vacancy free of electrons. We assume the lattice to be in thermal equilibrium, i.e. the average excitation of the normal modes ω_i is

$$\bar{n}_i = (\exp\{\omega_i/k\,T\} - 1)^{-1}\,. \qquad (2.1)$$

2. Irradiating the crystal with light in the ultraviolet region, it is possible to produce exciton or conduction band states. We wish to follow the development of such a state $|\,\mathrm{I}\rangle$, characterized by the conduction electron c and the oscillator quantum numbers $(\bar{n}_1, \ldots, \bar{n}_{3M})$ $(= \bar{n}_l, \bar{n}(q))$

$$|\,\mathrm{I}\rangle = |\,c, \bar{n}_l, \bar{n}(q)\rangle\,. \qquad (2.2)$$

3. This state $|\,\mathrm{I}\rangle$ can be changed by a great number of different radiative and nonradiative processes, of which we are solely interested in the radiationless trapping of the electron at an impurity center and subsequent radiationless transition to the valence band. (The trapped electron will be denoted by s.) The lattice, immediately after the electron being trapped at the impurity center, finds itself in a highly excited oscillatory state with $m_1 > \bar{n}_1$

$$|\,\mathrm{II}\rangle = |\,s, m_1, \bar{n}_2, \ldots, \bar{n}_{3M}\rangle\,. \qquad (2.3)$$

Without emitting radiation this state can be changed by the anharmonic terms and a second electronic transition to the valence band state

$$|\,\mathrm{III}\rangle = |\,v, l_1, l_2, \ldots, l_{3M}\rangle \qquad (2.4)$$

which differs from the ground state in the oscillator quanta. By the general theory we have seen, that the decay of state $|\,\mathrm{I}\rangle$ is equivalent to the vanishing of the matrixelements of $U(t - t_0)$, a condition which is satisfied if and only if the state is coupled at a group of states with continuous energy spectra.

Within the crystal model outlined in I, we did see, that by K^{t} only states with equal quantum numbers in the continuous spectrum were coupled at one another. K^{a} on the other hand does not contain electronic interactions but couples the discrete optical quanta at the continuous acoustical branch.

Hence only both interactions together can cause RED and we can apply the methods developed above for two interactions. First we calculate the resolvent $G^*(z)$ of the hamiltonian K^*

$$K^* := K^0 + K^{\mathrm{a}}, \tag{2.5}$$

$$G^*(z) := (z - K^*)^{-1}. \tag{2.6}$$

With (2.6) we find from (1.25) for the resolvent $G(z)$ of

$$K := K^* + K^{\mathrm{t}} \tag{2.7}$$

up to first order in K^t:

$$\begin{aligned} G(z) &= (z - K^* - K^{\mathrm{t}})^{-1} \\ &\approx G^*(z) + G^*(z)\, K^{\mathrm{t}}\, G^*(z). \end{aligned} \tag{2.8}$$

[An alternative treatment will be given by Rampacher[4] who investigates the influence of K^{a} and K^{t} on the operator $R(z)$.]

Approximative Calculation of $G^*(z)$

The diagonal matrix elements of G^* are given by (1.7). For the states

$$|a, m_1, \ldots, m_{3M}\rangle = |a, m, m(q)\rangle; \qquad a = \mathrm{c, s, v}$$

we have

$$\langle a, m, m(q) |\, G^*(z)\, | a, m, m(q)\rangle = (z - E^{\mathrm{a}}_{m,m(q)} - R^{*\mathrm{a}}_{m,m(q)}(z))^{-1}. \tag{2.9}$$

$R^{*\mathrm{a}}_{m,m(q)}(z)$ can be calculated from (1.8):

$$\begin{aligned} R^{*\mathrm{a}}_{m,m(q)}(z) &:= \Delta^{\mathrm{a}}_{m,m(q)}(z) - \frac{i}{2}\, \Gamma^{\mathrm{a}}_{m,m(q)}(z) := \langle a, m, m(q) |\, R^*(z)\, | a, m, m(q)\rangle \\ &= \langle a, m, m(q) |\, K^{\mathrm{a}} + K^{\mathrm{a}} Q_{a,m,m(q)} (z - E^{\mathrm{a}}_{m,m(q)})^{-1} R(z)\, | a, m, m(q)\rangle. \end{aligned} \tag{2.10}$$

The integral Eq. (2.10) has not been treated completely until now. An approximative solution is given by Märtl[5], he assumes K^{a} to be a weak perturbation and tries to solve (2.10) by a Neumann series. With some additional assumptions he gets numerical values for $\Gamma^{\mathrm{a}}_{m,m(q)}(z)$ $(z = E^{\mathrm{a}}_{m,m(q)})$ which determines the decay of the state $|a, m, m(q)\rangle$ by means of the anharmonic forces.

In principle the real part of $R^{\mathrm{a}}_{m,m(q)}(z)$ can be calculated from $\Gamma^{\mathrm{a}}_{m,m(q)}(z)$ because of the analytic properties[3,6] of $R^{\mathrm{a}}_{m,m(q)}(z)$. But since we assumed K^{a} to be a weak perturbation, it is consistent with this assumption to neglect the level-shift $\Delta^{\mathrm{a}}_{m,m(q)}$ compared with $E^{\mathrm{a}}_{m,m(q)}$. Then (2.9) becomes

$$G^{*\mathrm{a}}_{m,m(q)}(z) := \langle a, m, m(q) |\, G^*(z)\, | a, m, m(q)\rangle \cong \left(z - E^{\mathrm{a}}_{m,m(q)} + \frac{i}{2}\, \Gamma^{\mathrm{a}}_{m,m(q)}(z)\right)^{-1}. \tag{2.11}$$

The zeros of the denominator are approximately at

$$z \approx E^{\mathrm{a}}_{m,m(q)} - \frac{i}{2}\, \Gamma^{\mathrm{a}}_{m,m(q)}(E^{\mathrm{a}}_{m,m(q)}). \tag{2.12}$$

The relation between diagonal and off-diagonal matrix elements of G^* is obtained from (1.11)

$$\langle a, m, m(q) |\, G^*\, | b, n, n(q)\rangle = \delta_{\mathrm{a,b}} (z - E^{\mathrm{a}}_{m,m(q)})^{-1} R^*_{a,m,m(q);\,a,n,n(q)}(z)\, G^{*\mathrm{a}}_{m,m(q)}(z). \tag{2.13}$$

The matrix elements of G^* vanish unless $a = b$ because K^{a} does not contain any electronic interactions. Since the potential energy of the ionic motion in the adiabatic approximation is determined by the electrons' state, the symmetry of some normal modes depends on the electrons, too. But our assumptions on the vibrational spectrum induce complete independence on the electrons' state for G^*.

Rampacher[4] now eliminates the acoustical quanta, which we are interested in only as far as they are determined by the temperature, using the statistical operator $\varrho(t)$. To avoid large complications and to

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[4] H. Rampacher, Electronic Decay Processes in a Simplified Dynamical Crystal Model [to be published in Z. Naturforsch.].

[5] H. G. Märtl, Diplomarbeit, Institut für Theoretische Physik der Universität München 1967.

get some first numerical results before having treated G^* explicitly, we do not follow his strict way here, but use some physical arguments to find $G^*(z)$ approximately. Integrating over some domain of the continous spectrum of the acoustical quanta we build upwavepackets

$$|a, m, w\rangle := \int \varrho_w(q)\, |a, m, m(q)\rangle\, \mathrm{d}q\,. \tag{2.14}$$

These packets are not any longer eigenstates of H^0 and the formulae of the paragraph ahead can not be applied. Since from collision theory it is known, that the scattering amplitude, which is very closely related to $G^*(z)$, is a continous function of energy[3], we replace the action of G^* on a wave packet approximately by its action on the center of the packet. For the diagonal terms of $G(z)$ this says:

$$\langle a, m, w\,|G^*(z)|\,a, m, w\rangle \cong \left(z - E^{\mathrm{a}}_m - \varepsilon(w) + \frac{i}{2}\,\Gamma^{\mathrm{a}}_m(w)\right)^{-1}, \tag{2.15}$$

where $\Gamma^{\mathrm{a}}_m(w)$ is the average line width and $E^{\mathrm{a}}_m + \varepsilon(w)$ the average energy.

Construction of the Complete Resolvent

By means of the operator identity

$$(A - B)^{-1} = A^{-1} + A^{-1} B (A - B)^{-1} \tag{2.16}$$

we get from $G(z) = (z - K^* - K^{\mathrm{t}})^{-1}$ the relation

$$G(z) = G^*(z) + G^*(z)\, K^{\mathrm{t}}\, G(z) \approx G^*(z) + G^*(z)\, K^{\mathrm{t}}\, G^*(z)\,. \tag{2.17}$$

For different electronic states the off-diagonal matrix elements of $G^*(z)$ vanish, hence we get in first order of K^{t}:

$$\begin{aligned}\langle \mathrm{I}\,|G(z)|\,\mathrm{II}\rangle &= \sum_{m',n'} \sum_{\substack{m'(q)\\ m''(q)}} \langle a, m, m(q)\,|G^*(z)|\,a, m', m'(q)\rangle \langle a, m', m'(q)\,|K^{\mathrm{t}}|\,b, n', m''(q)\rangle \langle b, n', m''(q)\,|G^*|\,b, n, n(q)\rangle\,.\end{aligned} \tag{2.18}$$

(2.18) can be simplified because of the properties of K^{t} and K^{a} to

$$\langle \mathrm{I}\,|G(z)|\,\mathrm{II}\rangle = \sum_{m',n'} [\langle a, m'\,|K^{\mathrm{t}}|\,b, n'\rangle \sum_{m'(q)} \langle a, m, m(q)\,|G^*(z)|\,a, m', m'(q)\rangle \langle b, n', m'(q)\,|G^*(z)|\,b, n, n(q)\rangle]\,. \tag{2.19}$$

Now we use the wavepackets as physically correct intermediate states and get:

$$\begin{aligned}&\langle a, m, w\,|G(z)|\,a', m', w\rangle \\ &\quad = \sum_{n',n''} \langle a, w'\,|K^{\mathrm{t}}|\,a', n''\rangle \sum_{w'} \langle a, m, w\,|G^*(z)|\,a, n', w'\rangle \langle a', n'', w'\,|G^*(z)|\,a', m', w\rangle\,.\end{aligned} \tag{2.20}$$

Inserting (2.20) into (1.5) one obtains the transition amplitude between two crystal states characterized by two different electronic states a, a' and different excitation of the localized mode m, m' but the same wavepackets in the continous phonon spectrum.

$$\begin{aligned}&\langle a, m, w\,|U|\,a', m', w\rangle \\ &\quad = \frac{1}{2\pi i}\, K^{\mathrm{t}}_{a,m;a',m'} \int \mathrm{d}z \left[e^{-izt} \left(z - E^{\mathrm{a}}_m - \varepsilon(w) + \frac{i}{2}\,\Gamma^{\mathrm{a}}_m(w)\right)^{-1} \left(z - E^{\mathrm{a}'}_{m'} - \varepsilon'(w) + \frac{i}{2}\,\Gamma^{\mathrm{a}'}_{m'}(w)\right)^{-1}\right] \\ &\qquad + \sum_{n,n'} K^{\mathrm{t}}_{a,n;a',n'} \int \mathrm{d}z\, [e^{-izt} \langle a, m, w\,|G^*(z)|\,a, n, w'\rangle \langle a', n', w'\,|G^*(z)|\,a', m', w\rangle]\,.\end{aligned} \tag{2.21}$$

Calculating the integrals in (2.21) one observes them to have upper bounds of the form $[(\bar{E}^{\mathrm{a}}_n - \bar{E}^{\mathrm{a}'}_{n'})^2 + \alpha^2]^{-1}$ where α is a small number and the $\bar{E}^{\mathrm{a}}_n$ and $\bar{E}^{\mathrm{a}'}_{w'}$ are any of the wave packets' average energies. Therefore the most important contribution to (2.21) comes from those terms where the average energies of initial, final and intermediate states follow the condition $(E^{\mathrm{a}}_n - E^{\mathrm{a}'}_{n'})^2 \lesssim \alpha^2$. This says that approximately all states should lie on the energy shell. Therefore (2.21) gives in this approximation:

$$\begin{aligned}&\langle a, m, w\,|U|\,a', m', w'\rangle \\ &\quad = K^{\mathrm{t}}_{a,m;a',m'} \frac{1}{(\bar{E}^{\mathrm{a}}_m - \bar{E}^{\mathrm{a}'}_{m'}) - \frac{i}{2}(\Gamma^{\mathrm{a}}_m - \Gamma^{\mathrm{a}'}_{m'})} \exp\left\{-i\left(\bar{E}^{\mathrm{a}}_m - \frac{i}{2}\,\Gamma^{\mathrm{a}}_m\right)t\right\} - \exp\left\{-i\left(\bar{E}^{\mathrm{a}'}_{m'} - \frac{i}{2}\,\Gamma^{\mathrm{a}'}_{m'}\right)t\right\}.\end{aligned} \tag{2.22}$$

Calculation of Transition Probabilities

Taking the absolute square of (2.22) we obtain approximative transition probabilities depending on the average energies of the initial and final wave packets:

$$|\langle a, m, w \,|\, U \,|\, a', m', w \rangle|^2 = \tag{2.23}$$

$$\frac{|\, K^{\mathrm{t}}_{a,m;\,a',m'}|^2}{(\bar{E}^{\mathrm{a}}_m - \bar{E}^{\mathrm{a}'}_{m'})^2 + \frac{1}{4}(\Gamma^{\mathrm{a}}_m - \Gamma^{\mathrm{a}'}_{m'})^2} \cdot [\exp\{-\Gamma^{\mathrm{a}}_m t\} + \exp\{-\Gamma^{\mathrm{a}'}_{m'} t\} - 2\cos[(\bar{E}^{\mathrm{a}}_m - \bar{E}^{\mathrm{a}'}_{m'})\,t] \cdot \exp\{-\tfrac{1}{2}(\Gamma^{\mathrm{a}}_m + \Gamma^{\mathrm{a}'}_{m'})\,t\}].$$

To become free of the arbitrary taking one special average energy, we take the average over all possible initial and final energies contained in the wavepacket.

$$\bar{W}_{a,m;\,a',m'}(t) := \frac{1}{\hbar\,\omega_l} \int\limits_{-\frac{1}{2}\hbar\,\omega_1}^{+\frac{1}{2}\hbar\,\omega_1} \frac{|\, K^{\mathrm{t}}_{a,m;\,a',m'}|^2}{(E^{\mathrm{a}}_m - E^{\mathrm{a}'}_{m'} + \varepsilon)^2 + \frac{1}{4}(\Gamma^{\mathrm{a}}_m - \Gamma^{\mathrm{a}'}_{m'})^2} \tag{2.24}$$

$$\cdot\, [\exp\{-\Gamma^{\mathrm{a}}_m t\} + \exp\{-\Gamma^{\mathrm{a}'}_{m'} t\} - 2\cos([E^{\mathrm{a}}_m - E^{\mathrm{a}'}_{m'} + \varepsilon]\,t)\exp\{-\tfrac{1}{2}(\Gamma^{\mathrm{a}}_m + \Gamma^{\mathrm{a}'}_{m'})\,t\}]\,.$$

Since Γ^{a}_m is of order 10^{-16} erg, the denominator of (2.24) has its minimum for $(E^{\mathrm{a}}_m - E^{\mathrm{a}'}_{m'} + \varepsilon) = 0$, and only those ε for which $|\, E^{\mathrm{a}}_m - E^{\mathrm{a}'}_{m'} + \varepsilon| \lesssim 10^{-16}$ erg will contribute essentially to the integral. Keeping this in mind and using the following approximative values for the integrals

$$\int\limits_{-\varepsilon}^{+\varepsilon} \mathrm{d}x\, \frac{1}{x^2 + \eta^2} \approx \frac{2\,\pi}{\eta}\;; \qquad \int\limits_{-\varepsilon}^{+\varepsilon} \mathrm{d}x\, \frac{\cos(x\,t)}{(x^2 + \eta^2)} = \frac{2\,\pi}{\eta}\, e^{-\frac{1}{2}\eta t}$$

we find for (2.24)

$$\bar{W}_{a,m;\,a',m'}(t) = \frac{2\pi}{\hbar\,\omega_l}\,|\, K^{\mathrm{t}}_{a,m;\,a',m'}|^2\, \frac{\exp\{-\Gamma^{\mathrm{a}}_{u} t\} - \exp\{-\Gamma^{\mathrm{a}'}_{m'} t\}}{\hbar(\Gamma^{m'}_{\mathrm{a}'} - \Gamma^{\mathrm{a}}_{m})}\, \delta_{\hbar\omega_1}(E^{\mathrm{a}}_m - E^{\mathrm{a}'}_{m'})\,. \tag{2.25}$$

In (2.25) $\delta_{\hbar\omega_1}(E^{\mathrm{a}}_m - E)^{\mathrm{a}'}_{m'}$ indicates that for one given initial state E^{a}_m the transition probabilities to only two final states with energies $E^{\mathrm{a}'}_{m'}$ defined by (2.26) will be essentially non zero

$$E^{\mathrm{a}}_m - \hbar\,\omega_l \leqq E^{\mathrm{a}'}_{m'} \leqq E^{\mathrm{a}}_m \leqq E^{\mathrm{a}'}_{m'+1} \leqq E^{\mathrm{a}}_m + \hbar\,\omega_l\,. \tag{2.26}$$

But we have a second restriction resulting from the functional behaviour of the matrixelements $K^{\mathrm{t}}_{a,m;\,a',m'}$. This influence will be discussed in detail in the next section.

Differential Transition Probabilities

If the initial state c, n has been occupied with probability one, (2.26) gives the probability of finding the system at time t in the state s, m. Hence the probabilities (2.26) are conditional probabilities, which are rather clumsy to be treated. We therefore consider the differential transition probabilities known from phenomenological theories.

By the frequency interpretation of probability, we have for an ensemble of z independent microblocks, each finding itself with probability $P_{\mathrm{c},\,n}$ in the state $|\,c, n\rangle$, $z \cdot P_{\mathrm{c},\,n}$ microblocks which are certainly in the state $|\,c, n\rangle$. For a small time interval δt the number of blocks changing their state from $|\,c, n\rangle$ to $|\,s, m\rangle$ is therefore

$$z \cdot P_{\mathrm{c},n}(\bar{W}_{\mathrm{c},n;\,\mathrm{s},m}(\delta t) - \bar{W}_{\mathrm{c},n;\,\mathrm{s},m}(0))\,. \tag{2.27}$$

The change per unit time then is

$$z \cdot \frac{W_{\mathrm{c},n;\,\mathrm{s},m}(\delta t) - W_{\mathrm{c},n;\,\mathrm{s},m}(0)}{\delta t} \cdot P_{\mathrm{c},n}(0)$$

$$\approx z\, \frac{\delta\, W_{\mathrm{c},n;\,\mathrm{s},m}}{\delta t}\, P_{\mathrm{c},n}(0)\,. \tag{2.28}$$

Taking the limit $\delta t \to 0$ we find from (2.26)

$$\frac{\delta(z \cdot P^{\mathrm{s}},_{m})}{\delta t} = \frac{2\,\pi}{\hbar\,\omega}\, \frac{1}{\hbar}\, |\, K^{\mathrm{t}}_{\mathrm{c},n;\,\mathrm{s},m}|^2 (z \cdot P_{\mathrm{c},m})\,. \tag{2.29}$$

Hence we have if c, n and s, m are related by

$$m - n \approx \frac{U^{\mathrm{c}}(R^{0}_{k}) - U^{\mathrm{s}}(R^{\mathrm{s}}_{k})}{\hbar\,\omega_1} \tag{2.30}$$

for the differential transition probability

$$W^{*}{}_{\mathrm{c},n;\,\mathrm{s},m} = \frac{2\,\pi}{\hbar\,\omega_1}\, \frac{1}{\hbar}\, |\, K^{\mathrm{t}}_{\mathrm{c},n;\,\mathrm{s},m}|^2\,. \tag{2.31}$$

Conditions for the Possibility of Radiationless Transitions

As we did see in I, the functional dependence of the transition matrix elements is essentially determined by the displacements A^{cs} (for KCl we found $A^{\mathrm{cs}} \approx 6$). We found ($A^{\mathrm{cs}}$ fixed) the matrix elements to vanish exponentially for the differences of oscillator-quanta $m - n$ becoming greater then a certain $m_{\max}$. Now we replace $\bar{n}$ by its temperature dependent expectation value

$$\bar{n} = [\exp\{\hbar\,\omega_1/k\,T\} - 1]^{-1}$$

and find for all n of interest:

$$m < m_{\max}(A^{\mathrm{cs}}, n) = \frac{(A^{\mathrm{cs}})^2}{2} + \frac{A^{\mathrm{cs}}}{2}\left[\ln\left(1+\frac{1}{n}\right)\right]^{-1} = \frac{(A^{\mathrm{cs}})^2}{2} + \frac{A^{\mathrm{cs}}}{2}\,\frac{k\,T}{\hbar\,\omega_1}. \tag{3.1}$$

On the other hand an energetical condition must be fulfilled in order that the transition probability is of nonnegligible magnitude:

$$U_{\mathrm{c}}(R_k^{\mathrm{c}}) - U_{\mathrm{s}}(R_k^{\mathrm{s}}) \approx \hbar\,\omega_l\,(m - n)\,. \tag{3.2}$$

The physical meaning of these conditions can be best understood by means of the normal coordinate diagram (Fig. 1). (3.1) says something about the adiabatic approximation, since it results from a discussion of the matrix elements. To demonstrate this we derive a condition very similar to (3.1) considering the classical limit (i.e. high quantum numbers):

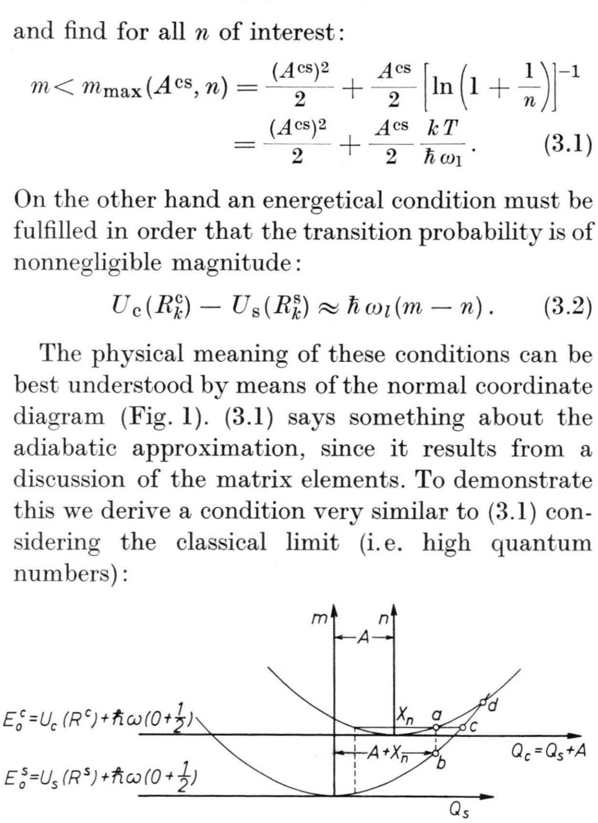

Fig. 1. Part of the normal coordinate diagram as given in I (Fig. 2a, 2b). Energy measured in units $\hbar\,\omega_1 = 1$, normal coordinate such that $\omega^2 = 1$. The possible states can be visualized by points on the parabolas. The point a indicates one possible initial state. b is the corresponding final state with maximum energy which is allowed by the matrix-elements. c gives the final state that is preserving energy. Since from "a" the only allowed transitions are to states with energies lower than the energy of b, no RED is possible. If the temperature is rised up to the point d, RED becomes possible.

In a semiclassical language we characterize the adiabatic approximation in the following way: Since the electronic Hamiltonian depends on the lattice positions only as parameters, we can say that the electron immediatelly follows the motion of the ions, from which results that electronic transitions occur only for fixed lattice positions. In the normal coordinate diagram this means that transitions are possible only along vertical lines.

Secondly we can approximately calculate the amplitude x_n of the oscillator with frequency ω_l if the excitation energy $\hbar\,\omega_l\,(n + \frac{1}{2})$ is known. (For simplicity we use a scale where $\omega_1^2 = 1$ and the energy is given in units $\hbar\,\omega_l = 1$.) In the classical limit we calculate the amplitude x_n from the total energy $(n + \frac{1}{2})$:

$$\tfrac{1}{2}(x_n)^2 \approx n + \tfrac{1}{2}\,; \qquad x_n \approx \sqrt{2\,n + 1}\,. \tag{3.3}$$

This says that the classical motion of the oscillator is restricted to the domain $-\,x_n \leqq Q_{\mathrm{c}} \leqq x_n$.

Now consider an electronic transition: As we did see in I such a transition is accompanied by a change of the equilibrium positions of the lattice; since on the other hand a transition occurs only for fixed lattice position a change A of the equilibrium positions induces a change of the amplitude. As can be seen directly from the figure, we have for the maximum amplitude after such a transition $(x_n + A)$ and for the minimum amplitude the greater of 0 and $(A - x_n)$. Calculating the minimum excitation energies from this amplitudes we find:

$$\bar{m}_{\max} + \tfrac{1}{2} \approx \tfrac{1}{2}(x_n + A)^2\,,$$

$$\bar{m}_{\min} + \tfrac{1}{2} \approx \begin{cases} \tfrac{1}{2} & A < x_n\,, \\ \tfrac{1}{2}(x_n - A)^2 \text{ for } & A > x_n\,. \end{cases} \tag{3.4}$$

Combining (3.3) and (3.4) we have:

$$\bar{m}_{\max} \approx n + \tfrac{1}{2}A^2 + A\sqrt{2\,n+1}\,, \tag{3.5}$$

$$\bar{m}_{\min} \approx \begin{cases} 0 & \\ n + \tfrac{1}{2}A^2 - A\sqrt{2\,n+1} \end{cases} \text{for } \begin{matrix} A < \sqrt{2\,n+1}\,, \\ A > \sqrt{2\,n+1}\,. \end{matrix}$$

The possible final excitation quanta are then restricted to $\bar{m}_{\min} \leqq m \leqq \bar{m}_{\max}$. Comparing $\bar{m}_{\max}$ from (3.5) with $m_{\max}$ as calculated from the Franck-Condon Integrals (Fig. 2) one finds $\bar{m}_{\max}$ slightly greater then $m_{\max}$. In the range of interest for us we use the approximation (3.1). Now we turn our attention to the second condition (3.2). It says that the energy of the initial and the final state must be approximately the same. For the energy diagram (Fig. 1) this says that the final state must have the "classical" amplitude that is given by the crossing of the horizontal energy line and the second lower oscillator. Since the maximum amplitude was

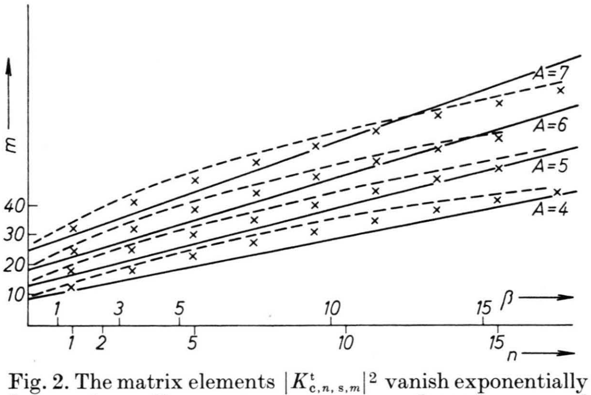

Fig. 2. The matrix elements $|K^{t}_{c,n,s,m}|^2$ vanish exponentially for growing m if m greater m_{MAX}. m_{MAX} depends on n and the displacement of the normal coordinates. We plotted m_{MAX} for $A = 4, 5, 6, 7$ as a function of $[\ln(1 + 1/n]^{-1}$. The straight lines give the approximation (3.1). The marked points are numerically calculated from the matrix elements, and the dashed line results form the "classical" approximation.

determined by (2.1) these two conditions can be fulfilled together if and only if the intersection of the two oscillators lies below the energy of the initial state

$$E_n^{c} - E_0^{s} < \hbar\,\omega_l\,(m_{\max}) = \hbar\,\omega_l \left\{ \frac{A^2}{2} + \frac{A}{2}\left[\ln\left(1+\frac{1}{n}\right)\right]^{-1} \right\}. \tag{3.6}$$

Since the initial excitation n is determined by the temperature

$$n = \left(\exp\left\{\frac{\hbar\,\omega_l}{k\,T}\right\} - 1\right)^{-1}$$

we find for (3.6) (neglecting $\hbar\,\omega_l(n + \frac{1}{2})$):

$$E_0^{c} - E_0^{s} < \hbar\,\omega_l\left[\frac{A^2}{2} + \frac{A}{2}\,\frac{k\,T}{\hbar\,\omega_l}\right]. \tag{3.7}$$

From Fig. 1 one observes easily

$$E_0^{c} - E_0^{s} = E_{\text{abs}} - \hbar\,\omega_l \cdot \frac{A^2}{2} = E_{\text{e}m} + \hbar\,\omega_l \cdot \frac{A^2}{2}, \tag{3.8}$$

where E_{abs} and E_{em} are the maxima of the F-center absorption and emission band respectively for zero temperature. Inserting (3.8) into (3.7) we have as a necessary condition to make radiationless transitions possible:

$$E_{\text{em}}(T = 0) = E_{\text{abs}}(T = 0) - \omega_l \cdot A^2 < \frac{A}{2}\,k T. \tag{3.9}$$

As is well known[7], the change of the polarization energy during an electronic transition can be calculated from the absorption band alone, then $A^2 = 2S_{\text{HR}}$ can be identified with the Huang-Rhys Factor S_{HR}.

Applying these phenomenological equations one should pay attention to the fact, that from the effective frequencies and Huang-Rhys-factors as calculated from the temperature dependence of the absorption band, the correct polarization energies don'tever result[7]. This lack of the conclusions drawn from experimental data is not understood by us until now, in particular since we got with the procedure given in I approximately the same S_{HR} and in addition correct polarization energies. Therefore if E_{em} is known, it seems to us better to use the inequality $E_{\text{em}}(T = 0) < \frac{1}{2} A\,k\,T$ then $E_{\text{abs}}(T = 0) - \hbar\,\omega_l A^2 < \frac{1}{2} A\,k\,T$. But in general the first of these inequalities is useless if RED is possible, because then E_{em} can not be measured.

The condition (3.9) is now applied to an anion vacancy in KCl and MgO. In KCl we have E_{em} $(T = 0) \approx 1.3$ eV and $2S_{\text{HR}} = 48$ (while MARKHAM[7] obtains 57): then $A \approx 7$

$$1.3 < \frac{7}{2}\,0.8 \cdot 10^{-4}\,T \quad \text{or} \quad \frac{1 \cdot 3}{2 \cdot 8}\,10^{4} < T.$$

This says that only for very high temperatures RED will be possible, where the crystal doesn't exist any longer.

In MgO no F-center emission band is known, therefore we have to use the second condition. Assuming[8] $E_{\text{abs}} \approx 5.0$ eV and $\hbar\,\omega A^2 \approx 4.9$ eV $(A \approx 8)$ this leads to

$$0.1 < \tfrac{6}{2}\,0.8 \cdot 10^{-4}\,T \quad \text{or} \quad 300\,^{\circ}\text{K} < T.$$

This means that RED should be possible in MgO. But one should keep in mind that a change of the absorption energy or the polarization energy of about 0.05 eV would change this condition to $T > 150\,^{\circ}$K or $T > 450\,^{\circ}$K. Therefore we feel that we have to calculate the frequency ω_l of the normal mode and the static energies more accurately.

Estimation of Transition Probabilities

To decide whether a special defect will prefer radiative or radiationless transitions it is not sufficient to know the latter being possible. Since

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[6] H. RAMPACHER, Dissertation, Universität München 1967.

[7] O. MARKHAM, Solid State Physics, Supplement 8, Academic Press 1966.

[8] Y. CHEN et al., J. Phys. Chem. Solids (GB) **29**, 863 [1968].

the transition probability for a radiative decay (2p − 1s) of an excited F-center electron is of order $10^{-6}\,\mathrm{sec}^{-1}$ the radiationless transition probabilities should be greater than $10^{-6}\,\mathrm{sec}^{-1}$ to quench the radiative processes. Hence we should calculate the transition probabilities. From I we take the non-adiabatic matrix elements to be

$$K^{\mathrm{t}}_{\mathrm{c},l;\,\mathrm{s},m} \approx \frac{\hbar\,\omega_1}{2}\,S_0\left(\frac{d^3}{\Omega}\right)^{1/2}\{3\,\alpha\,G_{\mathrm{e,\,m}}(A^{\mathrm{cs}})+\cdots\}\,. \tag{3.10}$$

Then by the general theory the transition probabilities are

$$W^*{}_{\mathrm{c},l;\,\mathrm{s},m} = \frac{\pi}{2}\,\omega_l\,S_0^2\left(\frac{d^3}{\Omega}\right)9\,\alpha^2\,|\,G_{\mathrm{c,\,m}}(A^{\mathrm{cs}})\,|^2\,. \tag{3.11}$$

Assuming 10^{-3} defects per regular lattice point we get for MgO

$$\frac{\pi}{2}\,\omega_l\,S_0^2\,\frac{d^3}{\Omega}\,9\,\alpha^2 \approx 10^{10}\,\mathrm{sec}^{-1}\,.$$

The $|G_{\mathrm{c,\,m}}|^2$ are of order 0.1 and therefore the probability for a radiationless decay is 10^3 times greater than for a radiative process.

The Complete Recombination

We had the intention to describe not only the radiationless capture of a conduction band electron, but the complete radiationless decay by a double Franck-Condon process as proposed by STUMPF[9, 10]. For such a recombination the electron immediately after being trapped at the center should fall down to the valence band. If this does not take place at once, the highly excited oscillatory state will decay because of the anharmonic terms. (The line width of these states has been found by MÄRTL[5] to be of order $10^{11}\,\mathrm{sec}^{-1}$.) And after this radiationless processes will be rather improbable. Though the second transition can be approximately calculated by the same formulae as for the radiative capture, we will not do this, since we do think this could be better done by deriving and solving the reaction kinetic formulae known from phenomenological phosphor physics.

Appendix

Calculation of the Resolvent

The resolvent $G(z)$ of the hamiltonian

$$H = H^0 + V \tag{A.1}$$

is defined by:

$$G(z) = (z - H)^{-1}\,. \tag{A.2}$$

Our task is to find the representation of $G(z)$ by means of the eigenstates $|\,\lambda\rangle$ of the unperturbed hamiltonian H^0:

$$H^0\,|\,\lambda\rangle = E_\lambda\,|\,\lambda\rangle\,. \tag{A.3}$$

We use the following definitions

$$\begin{aligned} Q_\lambda &:= \mathbf{1} - P_\lambda\,,\\ H_\lambda &:= H^0 + Q_\lambda\,V\,Q_\lambda\,,\\ H^* &:= H - H_\lambda = P_\lambda\,V\,P_\lambda + Q_\lambda\,V\,P_\lambda + P_\lambda\,V\,Q_\lambda\,. \end{aligned} \tag{A.4}$$

For non degenerated states the projection operator on the eigenstate with eigenvalue E_λ is

$$P_\lambda := |\,\lambda\rangle\langle\lambda\,|\,. \tag{A.5}$$

By means of the operator identities

$$\begin{aligned} (A-B)^{-1} &= A^{-1} + A^{-1}B(A-B)^{-1}\,,\\ (A-B)^{-1} &= A^{-1} + (A-B)^{-1}B\,A^{-1}\,. \end{aligned} \tag{A.6}$$

we get from (A.2)

$$\begin{aligned} G(z) &= (z-H^0)^{-1} + (z-H^0)^{-1}\,V\,G(z)\,, \qquad \text{(A.7)}\\ G(z) &= (z-H_\lambda)^{-1} + (z-H_\lambda)^{-1}H^*\,G(z)\,. \end{aligned}$$

Using (A.6) another time for $(z - H_\lambda)^{-1}$ we find:

$$\begin{aligned} (z-H_\lambda)^{-1} &= (z-H^0)^{-1}\,Q_\lambda V Q_\lambda (z-H_\lambda)^{-1}\\ &\quad + (z-H^0)^{-1}\,. \end{aligned} \tag{A.8}$$

Multiplying (A.8) with $Q_\lambda\,V$ from the right we find:

$$\begin{aligned} &(z-H_\lambda)^{-1}\,Q_\lambda\,V\\ &= (z-H^0)^{-1}\,Q_\lambda[V + V\,Q_\lambda(z-H_\lambda)^{-1}\,Q_\lambda\,V]\,. \end{aligned} \tag{A.9}$$

For the operator in brackets in (A.9) we use a new symbol $R(z)$

$$R(z) := V + V\,Q_\lambda(z-H_\lambda)^{-1}\,Q_\lambda\,V\,. \tag{A.10}$$

For $R(z)$ we find with (A.6) the operator equation

$$R(z) = V + V\,Q_\lambda(z-H^0)^{-1}\,Q_\lambda\,R(z)\,. \tag{A.11}$$

H^0 having a continuous spectrum (A.11) is an integral equation for $R(z)$. With $R(z)$ we get from (A.9) the relations:

$$\begin{aligned} (z-H_\lambda)^{-1}\,Q_\lambda V &= (z-H_0)^{-1}\,Q_\lambda R(z)\,,\\ V Q_\lambda (z-H_\lambda)^{-1} &= R(z)\,Q_\lambda(z-H_0)^{-1}\,. \end{aligned} \tag{A.12}$$

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

[10] H. STUMPF, Z. Naturforsch. **10 a**, 971 [1955]. — H. STUMPF, Z. Naturforsch. **12 a**, 153 [1957]. — H. STUMPF, Z. Naturforsch. **12 a**, 165 [1957].

Multiplying (A.7) from both sides with P_λ

$$P_\lambda G(z)\, P_\lambda = P_\lambda (z - E_\lambda)^{-1} + (z - E_\lambda)^{-1}\, P_\lambda\, V G(z)\, P_\lambda \tag{A.13}$$

and inserting $\mathbf{1} = P_\lambda + Q_\lambda$ in (A.13) we get a relation between diagonal and off-diagonal matrix elements of $G(z)$

$$P_\lambda G(z)\, P_\lambda = P_\lambda (z - E_\lambda)^{-1} + (z - E_\lambda)^{-1}\, P_\lambda V P_\lambda G(z)\, P_\lambda + (z - E_\lambda)^{-1}\, P_\lambda V Q_\lambda G(z)\, P_\lambda\,. \tag{A.14}$$

By means of (A.7) we get

$$Q_\lambda\, G(z)\, P_\lambda = Q_\lambda (z - H_\lambda)^{-1} H^* G(z)\, P_\lambda = (z - H_\lambda)^{-1} Q_\lambda\, V P_\lambda G(z)\, P_\lambda\,. \tag{A.15}$$

From (A.15) we find with (A.12) a second relation between diagonal and off-diagonal matrix elements

$$Q_\lambda G(z)\, P_\lambda = (z - H^0)^{-1} Q_\lambda\, R(z)\, P_\lambda G(z)\, P_\lambda\,. \tag{A.16}$$

Inserting (A.16) into (A.14) this becomes an equation for the diagonal terms alone

$$\begin{aligned}(z - E_\lambda)\, P_\lambda G(z)\, P_\lambda &= P_\lambda + P_\lambda [V + V Q_\lambda (z - H^0)^{-1} Q_\lambda\, R(z)]\, P_\lambda G(z)\, P_\lambda \\ &= P_\lambda + P_\lambda\, R(z)\, P_\lambda G(z)\, P_\lambda\end{aligned} \tag{A.17}$$

or

$$(z - E_\lambda - P_\lambda\, R(z)\, P_\lambda)\, P_\lambda G(z)\, P_\lambda = P_\lambda\,. \tag{A.18}$$

For non degenerated states (A.18) can be solved easily taking the diagonal matrix elements

$$\langle \lambda \,|\, G(z) \,|\, \lambda \rangle = (z - E_\lambda - \langle \lambda \,|\, R(z) \,|\, \lambda \rangle)^{-1}\,. \tag{A.19}$$

The off-diagonal elements are then calculated from (A.15)

$$\langle \mu \,|\, G(z) \,|\, \lambda \rangle = (z - E_\mu)^{-1} \langle \mu \,|\, R(z) \,|\, \lambda \rangle \langle \lambda \,|\, G(z) \,|\, \lambda \rangle\,. \tag{A.20}$$

Therefore the main task is to solve the integral equation (A.11).

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