Quantum Statistical Derivation of Rate Equations for Electronic Processes in Polar Crystals with External Electric Field

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Applying the Nakajima-Zwanzig method to the von Neumann equation of a system of interacting electrons and nuclei, etc., and evaluating the Pauli-Master equation according to Rieckers-Stumpf, we obtain a system of reaction equations for electron-phonon-photon processes in a polar crystal. Further elaboration of these reaction equations leads to rate equations for electrons which include impurity center processes as well as conduction band processes in an external electric field. If the conduction band processes run faster than the other processes, the rate equations can be reduced to a Boltzmann equation with drift term for the conduction electrons, coupled to rate equations for impurity center electrons where the number of conduction electrons must not be conserved. Furthermore, the basic problem of electronic state formation in external fields is discussed, the corresponding interaction terms are derived and a functional for the calculation of "bound" states in external fields is given.

Introduction

The electronic reaction kinetics of semiconductors and insulators have been intensively studied both experimentally and theoretically in the past three decades. In spite of this effort there are still basic problems which have not yet been treated satisfactorily. For instance there is no consistent theoretical formalism for the incorporation of electronic impurity center states into the reaction kinetics of charge carriers with and without external fields. This problem will be treated here. In a series of papers Stumpf and coworkers, cf. Stumpf [1], derived rate equations etc. for electronic reactions in semiconductors and insulators, while Stumpf and Rieckers [2] and Rieckers and Stumpf [3] developed a theory of equilibrium and non-equilibrium thermodynamics which is based on the derivation and the use of quantum statistical rate equations resp. reaction equations. In this paper we will combine both approaches for a treatment of the electronic reaction kinetics in a mixed electronic bound state — band state spectrum. For simplicity we specialize to the case of an external static electric field. Then two different problems have to be solved:

i) the treatment of bound states in the external electric field;

ii) the treatment of the reaction kinetics in the mixed discrete-continuous spectrum.

Concerning i), bound states in electric fields have been treated from the beginning of quantum theory by direct solution of simple models. However, the introduction and derivation of rate equations requires a distinction between interactions which lead to reversible effects (state formation) and those which lead to irreversible effects. This problem has not yet been satisfactorily treated in the literature. We will discuss it in Section 2. Concerning ii), in the majority of papers this topic is treated on a phenomenological level. On this level the effect of electron-phonon transitions in the conduction band is described by the mobility of the charge carriers leading to a phenomenological conductivity and diffusion, while the other transitions are described by phenomenological rate equations, i.e. equations whose analytical form with corresponding values of the coefficients are not derived from microscopic quantum statistics. This approach has been widely applied to the calculation of reactions of the classical covalent semiconductors and to the calculation of photoconductivity, thermoluminescence, etc., of polar insulators. It has to be supported and justified by a quantum statistical derivation.

On the microscopic quantum level the band-state-bound-state reaction kinetics was treated by only a few authors. In connection with plasma problems the kinetics of continuous states and bound states was considered by Klimontovich

[4, 5]. Peletminski [6] obtained kinetic equations in the presence of bound states of particles. Tsukanov [7] described the kinetics of electron-impurity systems when bound states of electrons can be formed in impurities. His method is based on a direct evolution for the density operator of the system in a Fockspace representation and is developed so far only at a formal level. So no decision can be made about its practical applicability to semiconductor reaction kinetics. Zehe and Röpke [8] directly calculated the time derivative of average values of characteristic observables of a coupled electron-phonon-photon system in a Fockspace representation by means of linear response theory for radiative recombination from non-equilibrium states in cathodo excited semiconductors. Although in this case direct calculations can be performed, the disadvantage is the absence of kinetic rate equations which are required for the treatment of more complicated models and phenomena and the a priori knowledge required for the definition of the Fock representation which is too simple to cover more complicated models. In our approach we will derive an electron Boltzmann equation coupled to a system of rate equations by ab initio calculations from the original many-particle Hamiltonian of electrons and atomic cores. And it will be demonstrated in following papers that numerical evaluation is possible for instance for the calculation of current-voltage characteristics.

The application of the Boltzmann equation is often critisized in the literature although it is used in the majority of practical calculations. We prefer to work with the Boltzmann equation as in our way of derivation the transition from reversible to irreversible statistics can be clearly seen, the derivation allows the treatment of mixed discrete continuous spectra and the derivation can be generalized to other base systems, higher order transitions, resonance transitions, memory effects, etc., leading to generalized Boltzmann equations. In particular with respect to criticism the latter point is of interest, since most of the criticism is concerned with such extensions which were missed in the original form of the Boltzmann equation. Furthermore it should be noticed that the competing calculation methods so far have been applied only to very idealized models which do not reflect correctly the crystal electron situation whereas our

approach is concerned with the crystal model from the beginning. Concerning the literature an extensive account will be given in the book of Stumpf [9] to appear.

1. State Representations and Interactions in an Electric Field

In ordinary quantum mechanics the influence of an external static electric field on bound states is treated by a time-independent perturbation theory leading to the Stark effect. But this treatment disguises the fact that the action of such a field upon the system causes qualitative changes in the spectrum of the crystal operator. Considering bound states the corresponding potentials have to satisfy boundary conditions which are not fulfilled by static or quasistatic external fields. Therefore, by applying such a field to a system with bound states, the spectrum is changed from a partly discrete one into a completely continuous one, if no artificial boundary conditions are imposed upon the external field. Thus, in order to get an appropriate description, we have to look for another theoretical treatment.

In experiments, the external field is switched on at a definite time. Therefore a time-dependent description is required.

At the time $t = t_0$ all crystal electrons have to be localized in the crystal volume. This means that the wave function $\chi(\mathfrak{r}, \mathfrak{R})$ of these electrons must be normalizable. For a time-dependent evolution of the process we have to represent $\chi(\mathfrak{r}, \mathfrak{R})$ in terms of stationary eigenfunctions belonging to the continuous spectrum. Denoting these eigenfunctions by the set $\{\chi(\mathfrak{r}, \mathfrak{R}, E)\}$, where E is an energy parameter, we get for $t = t_0$

$$\chi(\mathfrak{r}, \mathfrak{R})_{t = t_0} = \int c(E, t_0) \, \chi(\mathfrak{r}, \mathfrak{R}, E) \, \mathrm{d}E. \qquad (1.1)$$

Imposing now the normalization condition

$$\int \chi^*(\mathfrak{r}, \mathfrak{R})_{t = t_0} \chi(\mathfrak{r}, \mathfrak{R})_{t = t_0} \mathrm{d}^3 r = 1 \qquad (1.2)$$

the coefficients $c(E, t_0)$ must be spread over the energy spectrum, as the set $\{\chi(\mathfrak{r}, \mathfrak{R}, E)\}$ cannot be normalized according to (1.2). But then (1.1) cannot be a stationary eigensolution and $\chi(\mathfrak{r}, \mathfrak{R})$ is a non-trivial wave packet. From this it follows that imposing the normalization condition and requiring $\chi(\mathfrak{r}, \mathfrak{R})$ to be an eigensolution of the Hamiltonian with field are incompatible postulates.

Because of the physical reasons mentioned above we decide to impose the normalization condition. Then a general crystal wave function $\Psi(t)$ must be represented in the adiabatic coupling scheme by an expansion

$$\Psi(t) = \sum_{nm} c_{nm}(t)\, \chi_n(\mathfrak{r}, \mathfrak{R})\, \varphi_m^n(\mathfrak{R}) \qquad (1.3)$$

where $\{\chi_n\}$ is a set of orthonormalized wave functions. These functions, however, cannot be eigenfunctions of the adiabatic electron energy operator including the external field, as has been pointed out above. Thus, both in a reversible and in an irreversible evolution of the system with field, non-diagonal elements of the energy will appear. These elements induce transitions between the different configurations $\chi_n \varphi_m^n$, and are for instance responsible for tunnel effects.

In order to use a system of normalizable wave functions which enables us to fulfill the timescale postulate of the irreversible kinetics, it is necessary to look for a normalizable system which optimally approximates stationary states. Such a system can be found by minimizing the corresponding energy expectation values. This leads to the bound state field effects, while the remaining nondiagonal elements lead to tunneling. Thus, under the assumption of normalizable states, one gets a unique description of all types of effects which are usually not reconciled. This program will be performed in detail for polar crystals in the following.

Minimizing the energy expectation values, one has to distinguish between bound states (local impurity center states) and band states (valence band and conduction band states). For bound states the inclusion of the external field leads to Stark levels, while for band states the calculations with simple one-electron Hamiltonians show that in the approximation corresponding to the minimization of the energy expectation values, Wannier levels occur, Callaway [10]. If such improved valence band- and conduction band states are used for the calculation of the transition probabilities in these models, the tunneling rate just exhibits the appropriate field-dependence for electric field ionization, i.e. interband transitions, namely $\exp(-c/|\mathfrak{E}|)$, Callaway [10]. Thus it is desirable to use the improved state functions both for bound states and for band states. On the other hand, it will be shown that the use of simple Bloch

functions instead of the field improved band functions leads to the Boltzmann equation with the ordinary drift term, which is basic for nearly all phenomenological semiconductor calculations. In order to connect our formalism with these phenomenological calculations we use simple Bloch functions instead of the improved band functions[*]. As the Bloch functions do not depend on the special external forces we have only to consider the modifications of the bound states.

To obtain a simple system of rate equations we use a Hartree-Fock-representation for the electronic states. Of course, more complicated representations, such as configuration interaction etc., are not excluded but they lead to a much more complicated reaction kinetics and we will not consider them here.

The H. F.-representation is characterized by an appropriate set of one-electron states which is determined by the minimum principle of the H. F.-representation and by the special crystal model. Here we shall treat the most simple model of a defect crystal in the mosaicblock approximation, Stumpf [1], which is given by a polar semiconductor with F- and F'-centers, acting as donors and traps, respectively. In this model of an n-type semiconductor the crystal contains a number of equally distributed anion vacancies which are occupied by different numbers of electrons. To guarantee the charge neutrality of the total crystal, we assume a monovalent polar crystal which contains in the mosaicblock s anion vacancies which are neutralized by s impurity center electrons. Then a mosaicblock in general contains vacancies, F-, F'-centers, and conduction electrons.

In the field free case, the electron states can be divided into bound states (F-, F'-impurity center states) and into quasifree states[**] (conduction band and valence band states) belonging to the discrete part and to the quasi-continuous part of the spectrum, respectively. Switching on the external field the spectrum is changed into a completely quasicontinuous one. According to our program for an appropriate description of the field effects in the framework of statistical quantum

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[*] In principle the calculation with improved band functions runs on the same pattern but leads to modified kinetic equations.

[**] The expression quasifree is used because of the periodic boundary conditions imposed upon the mosaicblock.

mechanics we have in spite of this drastic change to maintain the field free classification of the states with the only difference that now the normalizable states are calculated by a minimum condition of the H.F.-energy of the total mosaicblock including the external field.

Concerning the explicit calculation of bound states, however, we suppress the interaction between different centers and work with the simpler model of one anion vacancy in a practically infinite crystal volume (microblock model), Stumpf [11]***. For the energy calculation of this microblock model Renn [12] derived a theorem which is based on a general calculation procedure of Stumpf [13]. We give this theorem without proof and refer for the proof to Stumpf [9].

Theorem: If the total electronic wave functions $|\chi_n\rangle$ are represented by H.F.-states, the corresponding static one-electron states Ψ_n for F-centers under the influence of a homogeneous static electric field $\mathfrak{E}$ have to be obtained by minimizing the expression

$$U_n[\Psi, \mathfrak{E}] = U_0 + \frac{1}{8\pi} \int \mathfrak{E}^2 \, d^3r + U_n[\Psi] + e \int \varrho(\mathfrak{v}) \, V(\mathfrak{v}) \, d^3r$$
$$+ (\hat{\varrho} - \mathfrak{E}) \cdot \mathbb{K} \cdot (\hat{\varrho} - \mathfrak{E}) + (\hat{\varrho} - \mathfrak{E}) \cdot [\mathbb{A} \, \mathsf{G} - \mathsf{g} \, \mathbb{C} \, \mathbb{A} \, \mathsf{G}] \cdot \hat{v} - \tfrac{1}{2} \hat{v} \, \mathbb{C} \, \hat{v} \tag{1.4}$$

with the charge tensor $\mathbb{A} = a_\mu \delta_{l\mu k\varrho}$ and with

$$\mathbb{K} := -\tfrac{1}{2} \mathsf{g} - \tfrac{1}{2} \mathbb{A} \, \mathsf{G} \, \mathbb{A} + \mathbb{A} \, \mathsf{G} \, \mathbb{A} \, \mathbb{C} \, \mathsf{g} - \tfrac{1}{2} \mathsf{g} \, \mathbb{C} \, \mathbb{A} \, \mathsf{G} \, \mathbb{A} \, \mathbb{C} \, \mathsf{g},$$

$$\mathsf{G}^{-1} := \left\{ \tau_\mu^{-1} \delta_{l\mu h\nu} + a_\mu C_{l\mu h\nu} a_\nu - \sum_{\substack{k\varrho \\ g\varkappa}} a_\mu C_{l\mu k\varrho} \, g_{k\varrho g\varkappa} \, C_{g\varkappa h\nu} a_\nu + \nabla_{l\mu} \nabla_{h\nu} C^{ex}(l\,\mu\,h\,\nu) \right\},$$

$$\mathsf{g}^{-1} := \alpha_\mu^{-1} \delta_{l\mu kg} + C_{l\mu k\varrho},$$

$$\mathbb{C} := \nabla_{l\mu} \nabla_{k\varrho} C(l\,\mu, k\,\varrho)(1 - \delta_{l\mu k\varrho}); \qquad \hat{\varrho}(\mathfrak{r}) := \varrho(\mathfrak{r}) - a_{00} \delta(\mathfrak{r} - \mathfrak{R}_{00}),$$

$$(\hat{\varrho} - \mathfrak{E}) := \nabla_{l\mu} [\int \hat{\varrho}(\mathfrak{r}) C(\mathfrak{r}, l\,\mu) \, d^3r + V(\mathfrak{R}_{l\mu}^0)]; \qquad \hat{v} := \nabla_{l\mu} V^{ex}(s, l\,\mu),$$

and

$$U_n[\Psi] := -\frac{\hbar^2}{2m} \int \Psi^*(\mathfrak{r}) \Delta \Psi(\mathfrak{r}) \, d^3r + \int \varrho(\mathfrak{r}) \left[\sum_{l\mu} a_\mu C(\mathfrak{r}, l\,\mu) \right] d^3r$$

where $V(\mathfrak{r})$ is the electric field potential defined by $\mathfrak{E} = \nabla V(\mathfrak{r})$, $C(l\mu, k\varrho)$, resp. $C^{ex}(l\mu, k\varrho)$ is the ionic Coulomb, resp. exchange potential, V^{ex} is the exchange energy between the electron and the lattice, and α_μ and τ_μ are material dependent constants *.

Using a definite state representation we define the interactions between the different configurations by the non-diagonal elements of the total energy. Defining the crystal energy operator

$$K := h(\mathfrak{r}, \mathfrak{R}) - \sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \Delta_i$$

where $h(\mathfrak{r}, \mathfrak{R})$ is the adiabatic electron-lattice Hamiltonian and where the second term represents the kinetic energy of the nuclei, we obtain

$$K |\chi_{n'}\rangle |\varphi_{m'}^{n'}\rangle = (E_{m'}^{n'} + K^t + K^s) |\chi_{n'}\rangle |\varphi_{m'}^{n'}\rangle$$

with

$$\langle \chi_n | \langle \varphi_m^n | K^t | \chi_{n'}\rangle | \varphi_{m'}^{n'}\rangle := (1 - \delta_{nn'} \delta_{mm'}) \langle \chi_n | \langle \varphi_m^n | \sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \Delta_i | \chi_{n'}\rangle | \varphi_{m'}^{n'}\rangle \tag{1.5}$$

and

$$\langle \chi_n | \langle \varphi_m^n | K^s | \chi_{n'}\rangle | \varphi_{m'}^{n'}\rangle := (1 - \delta_{nn'} \delta_{mm'}) \langle \chi_n | \langle \varphi_m^n | h(\mathfrak{r}, \mathfrak{R}) | \chi_{n'}\rangle | \varphi_{m'}^{n'}\rangle. \tag{1.6}$$

Evaluating the matrix elements (1.5) and (1.6) with the initial states $|\chi_{n'}\rangle |\varphi_{m'}^{n'}\rangle$ and the final states $|\chi_n\rangle |\varphi_m^n\rangle$ we have to distinguish between bound states and Bloch states as initial states.

*** This is done only for state calculations, not for reaction kinetics.

* For details of the evaluation of the operators etc. cf. Stumpf [9].

As the Bloch states do not depend on variable nucleus positions, the matrix element (1.5) vanishes if the initial state is a Bloch state. We then have only to consider the action of the operator $h(\mathfrak{r}, \mathfrak{R})$ on the state under consideration. To evaluate its matrix elements for one-particle transitions we consider the adiabatic crystal energy which is given by

$$U_n(\mathfrak{R}) = \langle \chi_n | h(\mathfrak{r}, \mathfrak{R}) | \chi_n \rangle_{\text{Min}} \tag{1.7}$$

where the expectation value has to be taken at its minimum achieved by variation of the electron wave functions. As we use a H.F.-representation of the crystal electron wave function $|\chi_n\rangle$ we can write

$$\langle \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_\alpha}^n \ldots \Psi_{\lambda_s}^n | h(\mathfrak{r}, \mathfrak{R}) | \Psi_{\lambda_1}^n \ldots \Psi_{\lambda'_\alpha}^{n'} \ldots \Psi_{\lambda_s}^n \rangle$$
$$= \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) \left\{ \frac{\delta}{\delta \Psi_{\lambda_\alpha}^{n*}} \frac{\delta}{\delta \Psi_{\lambda_\alpha}^n} \langle \chi_n | h(\mathfrak{r}, \mathfrak{R}) | \chi_n \rangle \right\}_{\substack{\text{Min} \\ \text{ionshell}}}$$
$$\cdot \Psi_{\lambda'_\alpha}^{n'}(\mathfrak{r}) \, d^3r \tag{1.8}$$

where the functional derivation is taken by definition only with respect to the s states involved in reaction processes. Therefore we can commute differentiation and the minimization of (1.8) with respect to ion shell functions. If this minimization of the ion shell function is performed we obtain

$$\langle \chi_n | h(\mathfrak{r}, \mathfrak{R}) | \chi_n \rangle_{\substack{\text{Min} \\ \text{ionshell}}} =: U_n[\mathfrak{M}, \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_s}^n].$$

For details of the calculation technique see Stumpf [13]. According to Renn [12] $U_n[\mathfrak{M}, \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_s}^n]$ is given by

$$U_n[\mathfrak{M}, \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_s}^n] := U_s(\mathfrak{M}) + H(s) + \sum_{\{l\mu\}} \left\{ \int \varrho_s(\mathfrak{r}) \, a_{l\mu} \, C(\mathfrak{r}, l\mu) \, d^3r + V^{\text{ex}}(s, \mathfrak{R}_{l\mu}) \right\}$$
$$- \frac{1}{2} \frac{\alpha_e}{1 + \alpha_e} \int \hat{\varrho}_s^*(\mathfrak{r}) \, F(\mathfrak{r}, \mathfrak{r}') \, \hat{\varrho}_s(\mathfrak{r}') \, d^3r \, d^3r'$$
$$+ \frac{1}{1 + \alpha_e} \sum_{\{l\mu\}} \int \hat{\varrho}_s(\mathfrak{r}) \, a_{l\mu} \, \mathfrak{M}_{l\mu} \nabla_{l\mu} C(\mathfrak{r}, l\mu) \, d^3r + \int \hat{\varrho}_s(\mathfrak{r}) \, V(\mathfrak{r}) \, d^3r + U(\mathfrak{E}). \tag{1.9}$$

$\mathfrak{M}_{l\mu}$ are the ionic displacements $\mathfrak{R}_{l\mu}^0 - \mathfrak{R}_{l\mu}$, where $\mathfrak{R}_{l\mu}^0$ is the ideal lattice position. The sum $\sum_{\{l\mu\}}$ runs over all lattice positions except those ones occupied by impurity centers. $H(s)$ is defined by

$$H(s) := -\tfrac{1}{2} \int \Delta \varrho_s(\mathfrak{r}) \, d^3\mathfrak{r} + \tfrac{1}{2} \int e^2 \, C(\mathfrak{r}, \mathfrak{r}') \, [\varrho_s(\mathfrak{r}) \, \varrho_s(\mathfrak{r}') - \varrho_s^2(\mathfrak{r}, \mathfrak{r}')] \, d^3r \, d^3r'$$
$$- \sum_{i=1}^s H_{l_i\mu_i} + \tfrac{1}{2} \sum_{i,j=1}^s V(\mathfrak{R}_{l_i\mu_i}, \mathfrak{R}_{k_j\varrho_j})$$

with the internal impurity center energy $H_{l_i\mu_i}$. $U(\mathfrak{E})$ denotes the field dependent terms which are independent of the impurity electron wave functions $\Psi_{\lambda_i}^n$, $1 \leq i \leq s$, as it is $U_s(\mathfrak{M})$, too. Therefore the derivation of (1.9) with respect to $\Psi_{\lambda_\alpha}^{n*}$ and $\Psi_{\lambda_\alpha}^n$ yields

$$\frac{\delta}{\delta \Psi_{\lambda_\alpha}^{n*}} \frac{\delta}{\delta \Psi_{\lambda_\alpha}^n} U_n[\mathfrak{M}, \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_s}^n] = -\frac{\hbar^2}{2m} \Delta_{\mathfrak{r}} + \sum_{\{l\mu\}} a_{l\mu} C(\mathfrak{r}, l\mu) + (1 + \alpha_e)^{-1} \sum_{\{l\mu\}} a_{l\mu} (\mathfrak{M}_{l\mu} \nabla_{l\mu}) C(\mathfrak{r}, l\mu)$$
$$+ \int e^2 C(\mathfrak{r}, \mathfrak{r}') \, \varrho_s(\mathfrak{r}') \, d^3r' - a_e(1 + \alpha_e)^{-1} \int F(\mathfrak{r}, \mathfrak{r}') \, \hat{\varrho}_s(\mathfrak{r}') \, d^3r' + V(\mathfrak{r}) + \text{exch. terms}. \tag{1.10}$$

The exchange terms are included only formally as they are very complicated in explicit calculations. As by definition the Bloch states are given by the wave functions of an excess electron in the ideal crystal they satisfy the eigenwert equation

$$\left[-\frac{\hbar^2}{2m} \Delta_{\mathfrak{r}} + \sum_{\{l\mu\}} a_{l\mu} C(\mathfrak{r}, l\mu) + \text{exch. terms} \right] \Psi(\mathfrak{r}, k) = E(k) \, \Psi(\mathfrak{r}, k). \tag{1.11}$$

Identifying $\Psi(\mathfrak{r}, k)$ with $\Psi_{\lambda'_\alpha}^{n'}(\mathfrak{r})$ and observing (1.11), the matrix element (1.8) becomes

$$\langle \Psi_{\lambda_1}^n \ldots \Psi_{\lambda_\alpha}^n \ldots \Psi_{\lambda_s}^n | h(\mathfrak{r}, \mathfrak{R}) | \Psi_{\lambda_1}^n \ldots \Psi_{\lambda'_\alpha}^{n'} \ldots \Psi_{\lambda_s}^n \rangle = \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) \, E(k) \, \Psi(\mathfrak{r}, k) \, d^3r$$
$$- \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) \left\{ \sum_{i=1}^s e \, a_{l_i\mu_i} C(\mathfrak{r}, l_i\mu_i) + e^2 \int C(\mathfrak{r}, \mathfrak{r}') \, \varrho_{\lambda_i}^n(\mathfrak{r}') \, d^3r' \right\} \Psi(\mathfrak{r}, k) \, d^3r$$

$$+ (1 + \alpha_e)^{-1} \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) \sum_{\{k\varrho\}} a_{k\varrho} (\mathfrak{M}_{k\varrho} \nabla_{k\varrho}) C(\mathfrak{r}, k\varrho) \Psi(\mathfrak{r}, k) d^3 r$$

$$- \alpha_e (1 + \alpha_e)^{-1} \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) F(\mathfrak{r}, \mathfrak{r}') \hat{\varrho}_s(\mathfrak{r}') d^3 r' \Psi(\mathfrak{r}, \mathfrak{k}) d^3 r + \int \Psi_{\lambda_\alpha}^{n*}(\mathfrak{r}) V(\mathfrak{r}) \Psi(\mathfrak{r}, \mathfrak{k}) d^3 r$$

$$+ \text{exch. terms} = \langle \chi_n | K^s | \chi_{n'} \rangle =: \langle \chi_n | \bar{K}^s + V | \chi_{n'} \rangle. \tag{1.12}$$

Due to the orthonormality which is assumed to hold approximately also in this case, the first term on the right-hand side of (1.12) vanishes. Therefore, the initial state being a Bloch state, only the second to fifth terms are left which are giving the impurity lattice potential and the interaction energy of the electron under consideration with the other active electrons, the interaction with the lattice deformation, the interaction with the selftrapping potential of the lattice, and the interaction with the field potential, respectively.

If the initial state is a bound state, both (1.5) and (1.6) have to be evaluated.

2. Rate Equations with Fields

In phenomenological semiconductor physics the motion of conduction electrons is described by the Boltzmann equation, where the drift term contains the classical part of statistical motion in an external field, while the collision term contains the quantized interactions of electrons with phonons and impurity centers etc. Theoretically, the semiconductor processes and reactions have to be described in the framework of quantum statistical mechanics. To do this we use a formalism based upon the general treatment of quantum statistical mechanics given by Rieckers and Stumpf [3]. For special proofs we refer to this treatment.

Let us consider an ensemble of equivalent systems Σ_μ with the energy operators $H_\mu = H$, $1 \leq \mu \leq m$. The time-dependent density operator $f = f(t)$, which is defined in the Hilbert space $\mathscr{H}$ and which contains the information about the physical state of the system fulfills the reversible von Neumann equation

$$\frac{\partial}{\partial t} f = i [f(t), H]. \tag{2.1}$$

The operator f is positive definit and selfadjoint and $\mathrm{Tr} f(t) = 1$ is valid. Defining the tensor of fourth rank over $\mathscr{H}$

$$\mathscr{L} := \sum_{i,j,k,l} | \varphi_i \rangle \langle \varphi_j | \otimes | \varphi_k \rangle \langle \varphi_l |$$
$$\cdot [H_{il} \delta_{jk} - H_{jk}^+ \delta_{il}] \tag{2.2}$$

where $\{| \varphi_\alpha \rangle\}$ is a set of base vectors spanning the Hilbert space $\mathscr{H}$ and where $\otimes$ means the tensor product, we can rewrite (2.1) as an operator equation

$$\frac{\partial}{\partial t} f = - i \mathscr{L} \cdot f(t). \tag{2.3}$$

This tensor formalism can easily be embedded into a linear metrical space in analogy to linear vector spaces, where the set of second order tensors $\{g, h, f\}$ defined by

$$f = \sum_{i,j} | \varphi_i \rangle f_{ij} \langle \varphi_j | \tag{2.4}$$

replace the vectors. Equation (3.3) then can be written

$$\frac{\partial}{\partial t} | f(t)) = - i \mathscr{L} | f(t)). \tag{2.5}$$

In this space, the so-called Liouville space $\mathfrak{H}$ over $\mathscr{H}$, the operator multiplication just corresponds to the ordinary matrix multiplication in linear vector spaces. The scalar product of two elements f, g is defined by

$$(f | g) = \mathrm{Tr}[f^+ g] = \sum_{i,j,k,l} \langle \varphi_j | \varphi_k \rangle \langle \varphi_l | \varphi_i \rangle f_{ij}^+ g_{kl}$$
$$= \sum_{i,j} f_{ij}^+ g_{ji}. \tag{2.6}$$

Equation (2.5) is still reversible. To derive an irreversible behaviour we have to consider the thermodynamic information losses which occur because of the impossibility to extract the maximum of information provided by quantum theory in a given definite experimental situation.

In the classical case the thermodynamic information loss is defined by dividing the space of events into cells and by giving occupation probabilities for these cells. However, in quantum mechanics this procedure does not lead automatically to an irreversible behaviour of the corresponding reduced distributions, Rieckers and Stumpf [3]. Therefore additional conditions have to be satisfied:

i) the complete set of observables specifying the space of events must not commute with the

total energy H of the system under consideration;

ii) the irreversible behaviour of the dynamics of a system Σ can be achieved only in the thermodynamic limes.

These conditions mean in our case

i) the time-dependent processes in crystals have to be described by a suitable interaction representation;

ii) the crystal under consideration has to be in contact with a heat reservoir and with a radiation field.

To derive an irreversible quantum dynamics we reformulate the von Neumann equation (2.3) by a method introduced by Nakajima [14] and by Zwanzig [15]. In order to do this according to condition i) we assume the set $\{|\varphi^i_h\rangle\}$ to be a complete base set of $\mathcal{H}$ which does not diagonalize the total energy H of Σ. (h denotes the degeneration of the general i.) Representing the density operator with respect to this base set we get

$$f(t) = \sum_{i,j,k,l} |\varphi^i_k\rangle\langle\varphi^l_j| f^{il}_{jk}. \qquad (2.7)$$

We define a set of projectors in $\mathcal{H}$ by

$$\Pi_i = \sum_h |\varphi^i_h\rangle\langle\varphi^i_h|, \quad 1 \leqq i \leqq \infty, \qquad (2.8)$$

and the corresponding set of projectors in $\mathfrak{H}$ by

$$\mathbf{\Pi}_i = |\Pi_i)(\Pi_i| \mu_i^{-1} \qquad (2.9)$$

where $\mu_i = \dim \mathcal{H}(i)$ holds and where $\mathcal{H}(i)$ is the subspace of $\mathcal{H}$ belonging to the degenerate level i. The operator $f(t)$ of (2.7) will have non-diagonal elements as the base set $\{|\varphi^i_h\rangle\}$ is not a set of eigenvectors of H. The operator

$$\mathbf{\Pi} := \sum_i \mathbf{\Pi}_i \qquad (2.10)$$

entailes a diagonalization of $f(t)$

$$\mathbf{\Pi} |f(t)) = \sum_{i,h} |\varphi^i_h\rangle \mu_i^{-1} (\Pi_i f(t)) \langle\varphi^i_h|$$
$$= \sum_i P_i(t) |\Pi_i) \mu_i^{-1} \qquad (2.11)$$

thus yielding formally a reduced distribution. This operator means a projection of f into a genuine subspace of the Liouville space $\mathfrak{H}$. Therefore, defining the complementary operator to $\mathbf{\Pi}$ in $\mathfrak{H}$ by

$$\mathbb{K} := \mathbb{1} - \mathbf{\Pi} \qquad (2.12)$$

and decomposing $f(t)$

$$f(t) = (\mathbf{\Pi} + \mathbb{K}) f(t) =: f_\pi(t) + f_K(t) \qquad (2.13)$$

we obtain from (2.3)

$$\dot{f}_\pi(t) = -i L_{\pi\pi} \cdot f_\pi(t) - i L_{\pi K} f_K(t),$$
$$\dot{f}_K(t) = -i L_{K\pi} f_\pi(t) - i L_{KK} f_K(t) \qquad (2.14)$$

with $L_{\pi\pi} = \mathbf{\Pi}\mathscr{L}\mathbf{\Pi}$ etc. To evaluate these equations we divide H into $H_0 + \lambda H_1$ in such a way that the set $\{|\varphi^i_h\rangle\}$ is a complete set of eigenvectors of H_0 without further degeneracy ($\mu_i = 1$) and H_1 is defined by

$$H_1 := \bar{K}^s + K^t + H^s + H^w + V$$

where $\bar{K}^s + V = K^s$ form the interaction operator defined in (1.6), while H^s and H^w are the interaction energies of the crystal with the radiation field and the heat bath, respectively.

This division leads to a division of $\mathscr{L}$ into $\mathscr{L}_0 + \lambda\mathscr{L}_1$. Introducing this in (2.14) we obtain because of the identity $\mathscr{L}_0 \mathbf{\Pi} f = \mathbf{\Pi}\mathscr{L}_0 f = 0$

$$\dot{f}_\pi(t) = -i L_{1\pi K} f_K(t),$$
$$\dot{f}_K(t) = -i L_{1K\pi} f_\pi(t) - i L_{KK} f_K(t) \qquad (2.15)$$

with $L_{1K\pi} = \lambda \mathbb{K}\mathscr{L}_1\mathbf{\Pi}$ etc.

According to our model of a polar semiconductor with $s - n_c$ impurity center electrons distributed over n_F F-centers, n_{F*} F*-centers (excited F-centers), and $n_{F'}$ F'-centers and with n_c conduction band electrons, which is in contact with a heat bath and a radiation field, we can denote the base set by

$$\{|\varphi^i\rangle\} =: \{|\lambda_1 \ldots \lambda_{n_F}, \mu_1 \ldots \mu_{n_{F*}}, \nu_1 \ldots \nu_{n_{F'}},$$
$$\cdot \mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}, m, \nu, \varrho\rangle\} \qquad (2.16)$$

or shortly by

$$\{|i\rangle\} =: \{|\Lambda_{s-n_c}, k(n_c), \zeta\rangle\}$$

where ζ contains the quantum numbers m, ν, and ϱ of the crystal lattice, the radiation field, and the heat bath and where Λ_{s-n_c} contains the quantum numbers of the impurity centers. This set can be divided into subsets given by the number n_c of conduction band electrons. As for a fixed number n_c the quantum numbers Λ_{s-n_c}, $k(n_c)$, and ζ are still variable, we finally obtain

$$\{|i\rangle\} = \bigcup_{n_c=0}^{s} \bigcup_{\Lambda s-n_c} \bigcup_{k(n_c)} \bigcup_{\zeta} |\Lambda_{s-n}, k(n_c), \zeta\rangle. \qquad (2.17)$$

In this basis the operator $\boldsymbol{\Pi}$ can be written

$$\boldsymbol{\Pi} = \sum_{n_c=0}^{s} \sum_{\Lambda s-n_c} \sum_{k(n_c)} \sum_{\zeta}$$
$$\cdot \, | \sim \rangle \langle \sim | \otimes | \sim \rangle \langle \sim | \qquad (2.18)$$

with $| \sim \rangle := | \Lambda_{s-n_c}, k(n_c), \zeta \rangle$. We now decompose the operator $\mathbb{K}$ into $\mathbb{K}_0 + \tilde{\mathbb{K}}$ where $\mathbb{K}_0$ is defined by

$$\mathbb{K}_0 = \sum_{n_c=0}^{s} \sum_{\Lambda} \sum_{\zeta \zeta'} \sum_{k,k'}{}' \, | \Lambda k \zeta \rangle \langle \Lambda k \zeta |$$
$$\otimes \, | \Lambda k' \zeta' \rangle \langle \Lambda k' \zeta' | \qquad (2.19)$$

where we have used the abbreviations $\Lambda := \Lambda_{s-n_c}$, $k := k(n_c)$, and $k' := k'(n_c)$. This means a further division of the subspace defined by $\mathbb{K}$. $\mathbb{K}_0$ is now projecting into a subspace in which only the conduction band processes take place. We now divide $\mathscr{L}_1$ into $\mathscr{L}_1 = \mathscr{L}_1^0 + \mathscr{L}_1^v$, where $\mathscr{L}_1^v$ depends on the interaction V, and introduce the definitions

$$\tilde{\mathscr{L}} := \mathscr{L}_0 + \tilde{\mathscr{L}}_1; \quad \tilde{\mathscr{L}}_1 := \mathscr{L}_1^0 + \tilde{\mathscr{L}}_1^v,$$
$$\tilde{\mathscr{L}}_1^v := \mathscr{L}_1^v - \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0 - \mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0$$
$$- \mathbb{K}_0 \mathscr{L}_1^v \boldsymbol{\Pi}. \qquad (2.20)$$

Because of the orthonormality relations of the operators $\boldsymbol{\Pi}$ and $\mathbb{K}_0$ the following equation holds:

$$\boldsymbol{\Pi} \tilde{\mathscr{L}}_1^v \mathbb{K} = \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K} - \boldsymbol{\Pi} (\boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0$$
$$- \mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0 - \mathbb{K}_0 \mathscr{L}_1^v \boldsymbol{\Pi}) \, \mathbb{K}$$
$$= \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K} - \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0$$
$$= \boldsymbol{\Pi} \mathscr{L}_1^v \tilde{\mathbb{K}} =: \mathscr{L}_{1\pi\tilde{K}}^v. \qquad (2.21)$$

Remembering the meaning of the operators $\mathbb{K}_0$ and $\tilde{\mathbb{K}}$, we see that the operator $\tilde{\mathscr{L}}_1^v$ just contains the impurity-band transitions which are caused by

the crystal field operator V. The operator $\mathscr{L}_{1\pi K_0}^v$, on the other hand, contains the interband transitions caused by V.

The operator $\tilde{\mathscr{L}}_1$ is then responsible for all one-particle electron transitions except of the interband transitions caused by V as we can write

$$\tilde{\mathscr{L}}_{1\pi K} := \boldsymbol{\Pi} (\mathscr{L}_1^0 + \tilde{\mathscr{L}}_1^v) \, \mathbb{K}$$
$$= \mathscr{L}_{1\pi K}^0 + \mathscr{L}_{1\pi\tilde{K}}^v \qquad (2.22)$$

By means of the definitions (2.20−2.22) we obtain from (2.15)

$$\dot{f}_\pi(t) = - i \, \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0 f_K(t)$$
$$\qquad\qquad - i \, \tilde{\mathscr{L}}_{1\pi K} f_K(t), \qquad (2.23)$$
$$\dot{f}_K(t) = - i \, \mathbb{K}_0 \mathscr{L}_1^v \boldsymbol{\Pi} f_\pi(t)$$
$$\qquad\qquad - i \, \mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0 f_K(t)$$
$$\qquad\qquad - i \, \tilde{\mathscr{L}}_{1K\pi} f_\pi(t) - i \, \tilde{\mathscr{L}}_{KK} f_K(t).$$

By this procedure we have therefore separated the drift terms which are caused by the external electrical field, as in an analogous way to (2.21) we can show

$$\tilde{\mathscr{L}}_{KK} = \mathbb{K} \mathscr{L}_0 \mathbb{K} + \mathbb{K} \mathscr{L}_1^0 \mathbb{K} + \mathbb{K} \mathscr{L}_1^v \mathbb{K}$$
$$\qquad - \mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0$$
$$= \mathbb{K} \mathscr{L}_0 \mathbb{K} + \mathbb{K} \mathscr{L}_1^0 \mathbb{K} + \tilde{\mathbb{K}} \mathscr{L}_1^v \tilde{\mathbb{K}}.$$

To evaluate (2.23) further, we consider the terms containing $\mathscr{L}_1^v$. By direct calculation we obtain

$$\langle \Lambda, k, \zeta | \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0 f_K | \Lambda k \zeta \rangle \qquad (2.24)$$
$$= \sum_{k'} \langle \Lambda k \zeta | V | \Lambda k' \zeta' \rangle f(\Lambda k' \zeta'; \Lambda k \zeta)$$
$$- \sum_{k'} \langle \Lambda k' \zeta' | V | \Lambda k \zeta \rangle f(\Lambda k \zeta, \Lambda k' \zeta').$$

We first consider the pure case. Then the density operator is given by $f_{ij} = c_i c_j$. As V does not depend on lattice coordinates, the phonon part ζ remains unchanged and thus drops out due to normalization. Since V is a sum of one-particle operators we obtain in the H.F.-representation

$$\sum_{k'} \langle \Lambda k' \zeta' | V | \Lambda k \zeta \rangle c^*(\Lambda k \zeta) c(\Lambda k' \zeta) = \left[\sum_{i=1}^{n_c} \int \langle \mathfrak{k}_i' | V | \mathfrak{k}_i \rangle c(\Lambda, \mathfrak{k}_1 \ldots \mathfrak{k}_i' \ldots \mathfrak{k}_{n_c}) \right]$$
$$\cdot \, c^*(\Lambda, \mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) \mathrm{d}^3 k_i'. \qquad (2.25)$$

A similar expression is valid for the second term of (2.24). According to Haug [16] the formula

$$\int \langle \mathfrak{k}_i' | V | \mathfrak{k}_i \rangle c(_1\mathfrak{k} \ldots \mathfrak{k}_i' \ldots \mathfrak{k}_{n_c}) \mathrm{d}^3 k_i' = - i e \, \mathfrak{E} \nabla_{k_i} c(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) + \langle u_\mathfrak{k} | \nabla | u_\mathfrak{k} \rangle c(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) \qquad (2.26)$$

holds. Observing this and (2.25) we obtain for (2.24)

$$- i \langle \Lambda k \zeta | \boldsymbol{\Pi} \mathscr{L}_1^v \mathbb{K}_0 f_K(t) | \Lambda k \zeta \rangle = - 2 e \, \mathfrak{E} \left[\sum_i \nabla_{\mathfrak{k}_i} \right] f(\Lambda k \zeta | \Lambda k \zeta), \qquad (2.27)$$

because of the relation [16]

$$\int_{\Omega_0} [u(\mathfrak{k}) \nabla u^*(\mathfrak{k}) + u^*(\mathfrak{k}) \nabla u(\mathfrak{k})] \, \mathrm{d}^3 r = \int_{\Omega_0} \nabla [u^*(\mathfrak{k}) u(\mathfrak{k})] \, \mathrm{d}^3 r = 0 .$$

To derive the usual form of the Boltzmann equation we therefore have to normalize the Bloch functions of the ideal crystal by a factor $1/2$ whereafter the factor 2 in (2.27) vanishes. Observing this and defining the operator

$$\mathbb{V} := e \, \mathfrak{E} \sum_{n_c=0}^{s} \sum_{\Lambda} \sum_{\zeta} \sum_{k(n_c)} \left(\sum_{i=1}^{n_t} \nabla_{\mathfrak{k}_i} \right) | \Lambda k \zeta \rangle \langle \Lambda k \zeta | \otimes | \Lambda k \zeta \rangle \langle \Lambda k \zeta |$$

we obtain from the first equation of (2.23)

$$\left(\frac{\partial}{\partial t} + \mathbb{V} \right) f_\pi(t) = - i \tilde{L}_{1\pi K} f_K(t) . \qquad (2.28)$$

This is valid for pure states. However, as mixed states are a superposition of pure states and as (2.28) is a linear equation, it holds for mixed states, too. In a similar way we can treat the second equation of (2.23), where the drift terms vanish since for pure states $f_{ij} = f_{ij}^*$ is valid and since all electronic states can be assumed to be real (see Appendix A). We therefore obtain for (2.23)

$$\left(\frac{\partial}{\partial t} + \mathbb{V} \right) f_\pi(t) = - i \tilde{L}_{1\pi K} f_K(t) , \qquad (2.29)$$

$$\frac{\partial}{\partial t} f_K(t) = - i \tilde{L}_{1K\pi} f_\pi(t) - i \tilde{L}_{KK} f_K(t) .$$

So far we have only evaluated the von Neumann equation (2.14) for our special model and with the assumption that the band states are Bloch states. As shown in [3] under the initial condition $f_K(0) = 0$ the system (2.29) is equivalent to the integro-differential equation

$$\left(\frac{\partial}{\partial t} + \mathbb{V} \right) f_\pi(t) = - \int_0^t \tilde{L}_{1\pi K} \qquad (2.30)$$

$$\cdot \exp\{ - i \tilde{L}_{KK} t' \} \, \tilde{L}_{1K\pi} f_\pi(t - t') \, \mathrm{d}t'$$

the so-called Nakajima-Zwanzig equation, which is still reversible. One way to introduce information losses and thus to obtain irreversibility is the transition from the Zwanzig equation to the Pauli-Master equation. In this procedure the information losses are caused by the approximate evaluation of the kernel of (2.30). To justify this approximation we have to impose the so-called timescale postulate. This means, that we assume a base system $\{| \varphi_i \rangle\}$ to be chosen in such a way that the corresponding time-dependence of $f_\pi(t)$ is in

the range of macroscopic observability while all rapidly changing components of f are contained in f_K, Rieckers and Stumpf [3]. Applying this postulate to (2.30) we obtain

$$\int_0^t \tilde{L}_{1\pi K} \exp\{ - i \tilde{L}_{KK} t' \} \, \tilde{L}_{1K\pi} f_\pi(t - t') \, \mathrm{d}t'$$

$$\approx \int_0^t \tilde{L}_{1\pi K} \exp\{ - i \tilde{L}_{KK} t' \}$$

$$\cdot \tilde{L}_{1K\pi} f_\pi(t - t') \, \mathrm{d}t' \qquad (2.31)$$

where τ is a time for which the relation $\tau_0 \ll \tau \ll \tau_\nu$ holds, τ_ν and τ_0 being the characteristic times in which noticeable time variations occur of f_π and f_K, respectively. Observing the relation

$$P(\Lambda_{s-n_c}, k(n_c), m, \nu, \varrho, t) :$$
$$= (\Pi(\Lambda_{s-n_c} k(n_c), m, \nu, \varrho) f_\pi(t)) \qquad (2.32)$$

we obtain from (2.30) with (2.31) by projection with $\Pi(\Lambda, k, \zeta)$ according to [3]

$$\left(\frac{\partial}{\partial t} + e \, \mathfrak{E} \sum_{i=1}^{n_L} \nabla_{k_i} \right) P(\Lambda_{s-n_c} k(n_c), m \, \nu \, \varrho)$$

$$= \sum_{\Lambda' k'(n_c') n_c' m' \nu' \varrho'} W_{\Lambda k(n_c) m \nu \varrho, \Lambda' k'(n_c') m' \nu' \varrho'}$$

$$\cdot [P_{\Lambda' k'(n') m' \nu' \varrho'} - P_{\Lambda k(n_c) m \nu \varrho}] \qquad (2.33)$$

where the transitions probabilities $W_{\Lambda k m \nu \varrho, \Lambda' k' m' \nu' \varrho'}$ $=: W_{ij}$ are defined by [3]

$$W_{ij} := (\Pi_i, W \Pi_j) \qquad (2.34)$$

$$= - \left(\Pi_i, \tilde{L}_{1\pi K} \int_0^\tau \exp(- i \tilde{L}_{KK} t) \, \mathrm{d}t \, \tilde{L}_{1K\pi} \Pi_j \right) .$$

We now introduce the expansion parameter λ by defining $\tilde{\mathscr{L}}_1 = \lambda \tilde{\mathscr{L}}_1'$ and put later on $\lambda = 1$. We evaluate then $\exp(- i L_{KK} t)$ into a series with respect to the parameter λ

$$\exp\left(-i\, \tilde{L}_{KK}\, t\right) = \exp\left(-i\, \tilde{L}_{KK}^0\, t\right) - i\,\lambda \int\limits_0^t dt_1 \exp\left(-i\, \tilde{L}_{KK}^0\, (t-t_1)\right) \tilde{L}_{1K\pi^*} \exp\left(-i\, \tilde{L}_{KK}^0\, t_1\right) + \cdots . \tag{2.35}$$

We assume that the interaction terms $\tilde{\mathscr{L}}_1$ are so small that even for $\lambda = 1$ the series (2.35) converges.

Then we only take into account the first term, as in (2.34) we only want to consider terms up to the order λ^2. Observing $\Pi\, |\varphi_i\rangle\langle\varphi_i| = |\varphi_i\rangle\langle\varphi_i|$ (2.34) goes over into

$$W_{ij} \approx -\lambda^2 \int\limits_0^\tau \langle\varphi_i, \{\tilde{\mathscr{L}}_1'\, \mathbb{K}\, \exp\left(-i\, \tilde{L}_{KK}^0\right) \mathbb{K}\, \tilde{\mathscr{L}}_1'|\, \varphi_j\rangle\langle\varphi_j|\}, \varphi_i\rangle\, dt \tag{2.36}$$

which is evaluated in Appendix B.

To evaluate (2.33) we formally separate the in-band transitions from those transitions where impurity centers are involved, and obtain from (2.33)

$$\left(\frac{\partial}{\partial t} + e\,\mathfrak{E} \sum_{i=1}^{n_c} \nabla_{\mathfrak{k}_i}\right) P_{\Lambda_{s-n_c},\, k(n_c)m\nu\varrho}(t) = \sum_{\Lambda' k'(n'_c) n'_c m'\nu'\varrho'} W_{\Lambda km\nu\varrho,\, \Lambda' k'm'\nu'\varrho'}\, [P_{\Lambda' k'(n') m'\nu'\varrho'} - P_{\Lambda k(n) m\nu\varrho}]$$

$$+ \sum_{\Lambda k''(n_c) n'_c m'\nu'\varrho'} W_{\Lambda km\nu\varrho,\, \Lambda k'' m'\nu'\varrho'}\, [P_{\Lambda k''(n_c) m'\nu'\varrho'} - P_{\Lambda k(n_c) m\nu\varrho}] \tag{2.37}$$

where we have to observe that in the first term of the right-hand side of (2.37) the electron quantum numbers may not differ only in the conduction electron quantum numbers.

From (2.37) we can now derive both rate equations for the mean occupation numbers of the electrons and the Boltzmann equation.

By definition the heat bath is in thermal equilibrium. Additionally we assume the phonon relaxation to be so fast that the phonon system is in thermal equilibrium with respect to the initial states of electronic reactions. Furthermore, we neglect the direct correlation of electrons and photons. We then can write

$$P_{\Lambda_{s-n_c} k(n_c) m\nu\varrho} = P_{\Lambda_{s-n_c} k(n_c)}\, P_\nu \cdot f_m(\beta)\, f_\varrho(\beta) \tag{2.38}$$

where P_ν is the reduced occupation probability of the radiation field and $f_m(\beta)$ and $f_\varrho(\beta)$ are the thermal equilibrium distribution functions $(\beta = 1/kT)$. Finally, as the in-band transitions are running much faster than those where impurity centers are involved we separate them by the ansatz

$$P_{\Lambda_{s-n_c} k(n_c)} =: P_{\Lambda_{s-n_c}}(t)\, f(\mathfrak{k}_1 \ldots \mathfrak{k}_n, t). \tag{2.39}$$

Inserting (2.39) and (2.38) into (2.37) and summing over m, ν, ϱ and over Λ_{s-n_c} and $f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c})$ respectively, we obtain by means of the normalization conditions of the subsystems

$$\sum_\varrho f_\varrho(\beta) = \sum_m f_m(\beta) = \sum_\nu P_\nu = \sum_{\Lambda_{s-n_c}} P_{\Lambda_{s-n_c}} = \sum_{\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}} f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) = 1$$

the equations

$$\frac{\partial}{\partial t} P_{\Lambda s-n_c} = \sum_{\Lambda'_{s-n_c}\, n'_c} [W^K_{\Lambda_{s-n_c},\, \Lambda'_{s-n_c}}(f')\, P_{\Lambda'_{s-n_c}} - W^K_{\Lambda'_{s-n_c},\, \Lambda_{s-n_c}}(f)\, P_{\Lambda_{s-n_c}}]$$

$$+ \sum_{\Lambda'_{s-n_c}\, n'_c} [W^s_{\Lambda_{s-n_c},\, \Lambda'_{s-n_c}}(f')\, P_{\Lambda'_{s-n_c}} - W^s_{\Lambda'_{s-n_c},\, \Lambda_{s-n.}}(f)\, P_{\Lambda_{s-n_c}}] \tag{2.40}$$

and

$$\left(\frac{\partial}{\partial t} + e\,\mathfrak{E} \sum_{i=1}^{n_i} \nabla_{\mathfrak{k}_i}\right) f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) = \sum_{\mathfrak{k}'_1 \ldots \mathfrak{k}'_{n'_c}} [W^K_{k(n_c),\, k'(n_c)}\, f(\mathfrak{k}'_1 \ldots \mathfrak{k}'_{n_c}) - W^K_{k(n_c),\, k(n_c)}\, f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c})$$

$$+ W^s_{k(n),\, k'(n)}\, f(\mathfrak{k}'_1 \ldots \mathfrak{k}'_{n_c}) - W^s_{k'(n_c),\, k(n_c)}\, f(\mathfrak{k}'_1 \ldots \mathfrak{k}'_{n_c})], \tag{2.41}$$

if we observe that in the first order calculation $W = W^K + W^S$ holds. The definition of the various transition probabilities is given in the Appendix B.

As we have restricted ourselves to one-particle transitions we can write

$$f(\mathfrak{k}_1' \ldots \mathfrak{k}_{n_c}') = f(\mathfrak{k}_1 \ldots \mathfrak{k}_i' \ldots \mathfrak{k}_{n_c}), \qquad 1 \leqq i \leqq n_c$$

and therefore obtain from (2.41)

$$\left(\frac{\partial}{\partial t} + e\,\mathfrak{E}\sum_{i=1}^{n_c}\right) f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) = \sum_{\mathfrak{k}_i' \neq \mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}} \left[\sum_{i=1}^{n_L} W_{k(n_c),k'(n_c)} f(\mathfrak{k}_1 \ldots \mathfrak{k}_i' \ldots \mathfrak{k}_{n_c}) - W_{k'(n_c),k(n_c)} f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c})\right]. \quad (2.42)$$

Introducing now the occupation number representation of all possible conduction electron states $\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}$ we have

$$f(\mathfrak{k}_1 \ldots \mathfrak{k}_{n_c}) = f[n(\mathfrak{k}_1) \ldots n(\mathfrak{k}_N)] =: f(n_1 \ldots n_N)$$

where $n(\mathfrak{k}_i) = n_i = 1$; $i \in M = \{1 \ldots n_c\}$ and $n(\mathfrak{k}_j) = n_j = 0$, $j \in N - M$, $N = \{1, \ldots, n_N\}$ is valid. The first term on the right-hand side of (2.42) describes a transition from state $|\mathfrak{k}_k'\rangle =: j$ to state $|\mathfrak{k}_i\rangle = i$. Therefore, it is $n_i = 1$, $n_j = 0$ in the final state, the occupation numbers of the other states remaining unchanged. A similar argument holds for the second term. Introducing the occupation number representation on the left-hand side of (2.42) it has to be observed that the derivation has to be done only with respect to those states k_i with $n_i = 1$. We therefore obtain

$$\left(\frac{\partial}{\partial t} + e\,\mathfrak{E}\sum_{i=1}^{N} n_i \nabla_{\mathfrak{k}_i}\right) f(n_1 \ldots n_N) = \sum_{n'_1 \ldots n'_N} W_{n_1 \ldots n_N, n'_1 \ldots n'_N}\, f(n_1 \ldots n_i' \ldots n_j' \ldots n_N)$$
$$- \sum_{n'_1 \ldots n'_N} W_{n'_1 \ldots n'_N, n_1 \ldots n_N}\, f(n_1 \ldots n_N) \qquad (2.43)$$

with the definitions

$$W_{n_1 \ldots n_N, n'_1 \ldots n'_N} := \sum_{i,j=1}^{N} W_{ij}\, n_i(1 - n_j)\, \delta_{n_1 n'_1} \ldots \delta_{n_i-1, n'_i} \ldots \delta_{n_j+1, n'_j} \ldots \delta_{n_N, n'_N},$$
$$W_{n'_1 \ldots n'_N, n_1 \ldots n_N} := \sum_{k,i=1}^{N} W_{Ki}\, n_K(1 - n_i)\, \delta_{n_1 n'_1} \ldots \delta_{n_k-1, n'_k} \ldots \delta_{n_i+1, n'_i} \ldots \delta_{n_N, n'_N}. \qquad (2.44)$$

Because of the Pauli principle the occupation numbers are restricted to the values 0, 1.

Introducing now the mean value of the occupation number $\bar{n}_l$ by

$$\sum_{n_1 \ldots n_N} n_l f(n_1 \ldots n_N) =: \bar{n}_l =: f(\mathfrak{k}_l, t) \qquad (2.45)$$

we obtain from (2.43) by multiplication with n_l and summation over all possible occupation numbers

$$\dot{\bar{n}}_l + \sum_{n_1 \ldots n_N} \left(e\,\mathfrak{E}\sum_{i=1}^{N} n_i \nabla_{\mathfrak{k}_i}\right) n_l f(n_1 \ldots n_N)$$
$$= \sum_{n_1 \ldots n_N} \sum_{n'_1 \ldots n'_N} n_l [W_{n_1 \ldots n_N, n'_1 \ldots n'_N} f(n'_1 \ldots n'_N) - W_{n'_1 \ldots n'_N, n_1 \ldots n_N} f(n_1 \ldots n_N)]. \qquad (2.46)$$

If we change n into n' in the first term of the right-hand side of (2.46), then by inserting the definition (2.44), equation (2.46) goes over into

$$\dot{\bar{n}}_l + \sum_{n_1 \ldots n_N} \left(e\,\mathfrak{E}\sum_{i=1}^{N} n_i \nabla k_i\right) n_l f(n_1 \ldots n_N)$$
$$= \sum_{n_1 \ldots n_N} \left[\sum_j W_{lj}\, n_l(1 - n_j)\, \delta_{n_l-1, n_l} \delta_{n_j+1, n_j} - \sum_k W_{k,l}\, n_K(1 - n_l)\, \delta_{n_k-1, n_k} \delta_{n_l+1, n_L}\right] f(n_1 \ldots n_N) \qquad (2.47)$$

Decomposing the sum in the drift term into $n_l \nabla_{\mathfrak{k}_l} + \sum_{i \neq l} n_i \nabla_{\mathfrak{k}_i}$ and observing $n_l^2 = n_l$ due to $n_l = 0, 1$, then by means of the mean value approximation $\bar{a}\bar{b} = \overline{ab}$ and (2.45) we finally obtain with (2.45) the Boltzmann equation

$$\left(\frac{\partial}{\partial t} + e\,\mathfrak{E}\nabla_{\mathfrak{k}}\right) f(\mathfrak{k}, t) = \sum_{\mathfrak{k}'} [W_{\mathfrak{k}, \mathfrak{k}'} f(\mathfrak{k}')(1 - f(\mathfrak{k})) - W_{\mathfrak{k}, \mathfrak{k}'} f(\mathfrak{k})(1 - f(\mathfrak{k}'))] \qquad (2.48)$$

where the subscripts i, j, k of $\mathfrak{k}$ have been suppressed.

Using the method introduced by Stumpf [1] and improved by Schöll [17] we can derive the rate equations of the mean occupation numbers of the impurity center electrons and the conduction band electrons from (2.40). With the definition

$$W(n, n') := W^K(n, n') + W^s(n, n') \qquad (2.49)$$

for the one-particle transition probabilities from state n' to state n we obtain for our model

$$\dot{\bar{n}}_F = W(F, F^*)\,\bar{n}_{F*} - W(F^*, F)\,\bar{n}_F$$
$$- W(F', c)\,\bar{n}_{F'} + W(c, F')\,\bar{n}_{F'}\,,$$
$$\dot{\bar{n}}_{F*} = - W(F, F^*)\,\bar{n}_{F*} + W(F^*, F)\,\bar{n}_F$$
$$- W(c, F^*)\,\bar{n}_{F*} + W(F^*, c)\,(\bar{n}_{F*} + \bar{n}_c)\,,$$
$$\dot{\bar{n}}_{F'} = W(F', c)\,\bar{n}_{F'} - W(c, F')\,\bar{n}_{F'}\,,$$
$$\dot{\bar{n}}_l = - W(F, c)\,\bar{n}_F + W(c, F')\,\bar{n}_F$$
$$+ W(c, F^*)\,\bar{n}_{F*}$$
$$- W(F^*, c)\,(\bar{n}_{F*} + \bar{n}_c)\,. \qquad (2.50)$$

As recombination and ionization of the impurity centers are assumed to occur radiationless, the transition proabilities of these effects are given by

$$W(c, i) = \sum_{\mathfrak{k}} W^K(\mathfrak{k}, i)\,, \quad i = F^*, F' \qquad (2.51)$$

for the ionization, and

$$W(i, c) = \sum_{\mathfrak{k}} W^K(i, \mathfrak{k})\,f(\mathfrak{k})\,, \quad i = F^*, F' \qquad (2.52)$$

for the recombination, if the Pauli principle is neglected for the conduction band electrons.

3. Steady State Solutions

The distribution function $f(k)$ of the conduction band electrons has to be determined by means of the Boltzmann equation. If no external static or quasistatic fields are present, the Fermi-Dirac distribution

$$f_{\mathfrak{k}}(\beta, \bar{n}_c) = \left[\exp\{(2\,m^*)^{-1} \beta \hbar^2 \mathfrak{k}^2\} \left(\frac{n_0}{\bar{n}_c} - \frac{1}{4} \right) + 1 \right]^{-1} \qquad (3.1)$$

is a solution of the Boltzmann equation. Here m^* denotes the effective electron mass and n_0 is a dimensionless degeneration parameter

$$n_0 := \frac{1}{4} \left(\frac{2\,m^* k\,T}{\pi \hbar^2} \right)^{3/2} . \qquad (3.2)$$

In the case of complete non-degeneracy for which $n \ll n_0$ holds, the Fermi-Dirac distribution can be

approximated by the classical Boltzmann distribution

$$f_{\mathfrak{k}}(\beta, \bar{n}_c) \approx \frac{\bar{n}_c}{n_0} \exp\left(- \frac{\beta^2 \hbar^2 \mathfrak{k}^2}{2\,m^*} \right). \qquad (3.3)$$

If an external field is present, the Boltzmann equation (2.41) has to be solved. This can be done approximately by a phenomenological expression. The electric field causes a drift motion of the conduction electrons which can be taken into account by a momentum shift of the conduction band electrons in the Boltzmann equation

$$f_{\mathfrak{k}}(\beta, \bar{n}) \approx \frac{\bar{n}_c}{n_0'} \qquad (3.4)$$
$$\cdot \exp\left(- \beta(\hbar\,\mathfrak{k} - m^* \mathfrak{v}_D)^2/2\,m^* \right) = \bar{n}_c\,f'(\mathfrak{k})$$

with the drift velocity $\mathfrak{v}_D$ and the degeneration parameter

$$n_0' = n_0 \sqrt{\frac{\pi}{2\,\beta\,m^*}} \cdot \frac{1}{V_D} \Phi\left(\sqrt{\frac{m}{2}\,\beta}\,V_D \right)$$

where $\Phi(x)$ denotes the error integral

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,\mathrm{d}t\,.$$

With (3.2) we obtain

$$W(i, c) = \bar{n}_c \sum_{\mathfrak{k}} W^K(i, \mathfrak{k})\,f'(\mathfrak{k}) = \bar{n}_c\,W(i, L)\,.$$

Then the rate equations (2.50) achieve their final form

$$\dot{\bar{n}}_F = W(F, F^*)\,\bar{n}_{F*} - W(F^*, F)\,\bar{n}_F$$
$$- W(F', L)\,\bar{n}_{F'}\,\bar{n}_c + W(L, F')\,\bar{n}_{F'}\,,$$
$$\dot{\bar{n}}_{F*} = - W(F, F^*)\,\bar{n}_{F*} + W(F^*, F)\,\bar{n}_F$$
$$- W(L, F^*)\,\bar{n}_{F*}$$
$$+ W(F^*, L)\,\bar{n}_c(\bar{n}_{F*} + \bar{n}_c)\,,$$
$$\dot{\bar{n}}_{F'} = W(F', L)\,\bar{n}_F\,\bar{n}_c - W(L, F')\,\bar{n}_{F'}\,,$$
$$\dot{\bar{n}}_c = - W(F', L)\,\bar{n}_F\,\bar{n}_c + W(L, F')\,\bar{n}_{F'}$$
$$+ W(L, F^*)\,\bar{n}_{F*}$$
$$- W(F^*, L)\,\bar{n}_c(\bar{n}_{F*} + \bar{n}_c)\,. \qquad (3.5)$$

Of course, the approximation of the electron distribution function $f(k)$ by (3.4) is not necessary and has been introduced only to maintain the simple form of the rate equations of the field free case.

From (3.5) we can now determine the steady state concentration of the conduction electron

number $\bar{n}_L$, which is a function of the temperature T, the radiation field and the external field, and then obtain a current-voltage characteristic with T and the radiation field as parameters.

By calculating the transition probabilities $W_{k,k'}$ in (2.40) and solving this Boltzmann equation it is therefore possible to obtain numerical results from first principles which can be compared with experimental ones.

Appendix A

Here the drift terms $\mathbb{K}_0 \mathscr{L}_1^v \mathbf{\Pi} f_\pi$ and $\mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0 f_K$ of equation (3.23) will be evaluated. Because of

$$\mathbf{\Pi} f_\pi = \sum_i |\varphi_i\rangle\langle\varphi_i|\langle\varphi_i, f \varphi_i\rangle = f_\pi$$

we have

$$\begin{aligned}
\mathscr{L}_1^v f_\pi &= \sum_{\alpha,\beta,\gamma,\delta,i} |\varphi_\alpha\rangle\langle\varphi_\beta| \otimes \langle\varphi_i|\varphi_\gamma\rangle\langle\varphi_\delta|\varphi_i\rangle \{V_{\alpha\delta}\delta_{\beta\gamma} - V_{\beta\gamma}\delta_{\alpha\delta}\} \\
&= \sum_{\alpha,\beta,i} |\varphi_\alpha\rangle\langle\varphi_\beta| \{V_{\alpha i}\delta_{\beta i} - V_{\beta i}^+\delta_{\alpha i}\} f_{ii}
\end{aligned} \tag{A.1}$$

where we have used the definition $V_{\alpha\beta} = \langle\varphi_\alpha|V|\varphi_\beta\rangle$. Applying $\mathbb{K}_0$ to (A.1) we obtain

$$\begin{aligned}
\mathbb{K}_0 \mathscr{L}_1^v f_\pi = &\sum_{l,m}\sum_{\alpha,\beta,i} |l\rangle\langle l| \otimes \langle m|\varphi_\alpha\rangle\langle\varphi_\beta|m\rangle \{V_{\alpha i}\delta_{\beta i} - V_{\beta i}^+\delta_{\alpha i}\} f_{ii} \\
&- \sum_l\sum_{\alpha,\beta,i} |l\rangle\langle l| \otimes \langle l|\varphi_\alpha\rangle\langle\varphi_\beta|l\rangle \{V_{\alpha i}\delta_{\beta i} - V_{\beta i}^+\delta_{\alpha i}\} f_{ii} .
\end{aligned}$$

Evaluating the Kronecker symbols we obtain

$$\begin{aligned}
\mathbb{K}_0 \mathscr{L}_1^v f_\pi &= \sum_{l,m,i} |l\rangle\langle l| \{V_{mi}\delta_{mi} - V_{mi}^+\delta_{mi}\} f_{ii} - \sum_{l,i} |l\rangle\langle l| \{V_{li}\delta_{li} - V_{li}^+\delta_{li}\} f_{ii} \\
&= \sum_{l,m} |l\rangle\langle l| \{V_{mm} - V_{mm}^+\} f_{mm} - \sum_l |l\rangle\langle l| \{V_{ll} - V_{ll}^+\} f_{ll} = 0 . \quad \text{q.e.d.}
\end{aligned}$$

In a similar way we can treat the second term. By

$$\mathbb{K}_0 f = \sum_{i,j} |i\rangle\langle i, f j\rangle\langle j| - \sum_i |i\rangle\langle i, f i\rangle\langle i|$$

we obtain

$$\begin{aligned}
\mathscr{L}_1^v \mathbb{K}_0 f &= \sum_{l,m,n,o,i,j} |l\rangle\langle m| \otimes \langle j|n\rangle\langle o|i\rangle [V_{lo}\delta_{mn} - V_{mn}^+\delta_{lo}]\langle i, f j\rangle \\
&\quad - \sum_{l,m,n,o,i} |l\rangle\langle m| \otimes \langle i|n\rangle\langle o|i\rangle [V_{lo}\delta_{mn} - V_{mn}^+\delta_{lo}]\langle i, f i\rangle \\
&= \sum_{l,m,i,j} |l\rangle\langle m| [V_{li}\delta_{mj} - V_{mj}^+\delta_{li}]\langle i, f j\rangle \\
&\quad - \sum_{l,m,i} |l\rangle\langle m| [V_{li}\delta_{mi} - V_{mi}^+\delta_{li}]\langle i, f i\rangle
\end{aligned}$$

and finally

$$\begin{aligned}
\mathbb{K}_0 \mathscr{L}_1^v \mathbb{K}_0 f &= \sum_{a,b}\sum_{l,m,i,j} |a\rangle\langle a| \otimes \langle b|l\rangle\langle m|b\rangle [V_{li}\delta_{mj} - V_{mj}^+\delta_{li}]\langle i, f j\rangle \\
&\quad - \sum_{a,b}\sum_{l,m,i} |a\rangle\langle a| \otimes \langle b|l\rangle\langle m|b\rangle [V_{li}\delta_{mi} - V_{mi}^+\delta_{li}]\langle i, f i\rangle \\
&= \sum_{a,b,i,j} |a\rangle\langle a| [V_{bi}\delta_{bj} - V_{bj}^+\delta_{bi}]\langle i, f j\rangle \\
&\quad - \sum_{a,b,i} |a\rangle\langle a| [V_{bi}\delta_{bi} - V_{bi}^+\delta_{bi}]\langle i, f i\rangle .
\end{aligned}$$

The second term is equal to zero. The first term can be transformed into

$$\sum_{a,b,i} |a\rangle\langle a| V_{bi}\langle i, f b\rangle - \sum_{a,b,j} V_{bj}^+\langle b, f j\rangle .$$

As the summations over i and j are independent from each other we obtain

$$\sum_{a,b,i} |a\rangle\langle a| V_{bi}\langle i, fb\rangle - \sum_{a,b,i} V_{bi}^+ \langle b, fi\rangle = 0$$

because of $f_{ij} = f_{ij}^+$, q.e.d.

Appendix B

The definitions of the transition probabilities of the reaction equations (2.40) are given by

$$W_{A_{s-n_c}, A'_{s-n'_c}}^K (f') := \sum_{k(n_c)} \sum_{k'(n'_c)} \left[\sum_{m,m'} W_{nmv\varrho, n'm'v'\varrho'}^K f_{m'}(\beta) \right] f(\mathfrak{k}'_1 \dots \mathfrak{k}'_{n_c})$$

$$W_{A_{s-n_c}, A'_{s-n'_c}}^s (f') := \sum_{k(n_c)} \sum_{k'(n'_c)} \left\{ \sum_{\nu,\nu'} \left[\sum_{m,m'} W_{nmv\varrho, n'm'v'\varrho'}^s f_{m'}(\beta) \right] P_\nu \right\} f(\mathfrak{k}'_1 \dots \mathfrak{k}'_{n_c}) \tag{B.1}$$

with

$$W_{nmv\varrho, n'm'v'\varrho'}^s := \frac{2\pi}{\hbar} |\langle nm\nu| H^s |n'm'\nu'\rangle|^2 \delta_{\varrho\varrho'} \delta_\gamma (E_m^n - E_{m'}^{n'} + E_\nu^s - E_{\nu'}^s) * \tag{B.2}$$

while the corresponding transition probabilities of the reaction equations (2.41) are given by

$$W_{k(n_c), k'(n_c)} := \sum_{A_{s-n_c}n_c} \sum_{A'_{s-n_c}n_c} \left[\sum_{m,m'} W_{nmv\varrho, n'm'v'\varrho'}^K f_{m'}(\beta) \right] P_{A'_{s-n_c}}$$

where for pure conduction band processes $P_{A'_{s-n_c}}$ drops out.

We now show that by our choice of the set of base states $\{|nm\rangle\}$ the transition probabilities W^K for transitions occurring within the conduction band, respectively, for all other transitions are given by

$$W_{nmv\varrho, n'm'v'\varrho'}^K = \frac{2\pi}{\hbar} |\langle nm| \bar{K}^s |n'm'\rangle|^2 \delta_{\nu\nu'} \delta_{\varrho\varrho'} \delta_\gamma (E_m^n - E_{m'}^{n'}) \tag{B.3}$$

and

$$W_{nmv\varrho, n'm'v'\varrho'}^K = \frac{2\pi}{\hbar} |\langle nm| \bar{K}^s + K^t + V |n'm'\rangle|^2 \delta_{\nu\nu'} \delta_{\varrho\varrho'} \delta_\gamma (E_m^n - E_{m'}^{n'}) \tag{B.4}$$

respectively.

We start with rewriting Eq. (3.34) taking into account the first term of the evaluation (3.35) only.

$$W_{ij}^K = - \langle \varphi_i | \left\{ \tilde{\mathscr{L}}_{1\pi K} \int_0^\tau \exp(-i \tilde{\mathscr{L}}_{KK}^0 t) \, dt \, \tilde{\mathscr{L}}_{1K\pi} | \varphi_j\rangle\langle\varphi_j| \right\} | \varphi_i\rangle . \tag{B.5}$$

With the relations (3.22)

$$\tilde{\mathscr{L}}_{1\pi K} = \mathscr{L}_{1\pi K}^0 + \tilde{\mathscr{L}}_{1\pi K}^v = \mathscr{L}_{1\pi K}^0 + \mathscr{L}_{1\pi K}^v - \mathscr{L}_{1\pi K_0}^v = \mathscr{L}_{1\pi K}^0 - \mathscr{L}_{1\pi \tilde{K}}^v \tag{B.6}$$

or equivalently

$$\tilde{\mathscr{L}}_{1\pi K} = \mathscr{L}_{1\pi K}^0 + \tilde{\mathscr{L}}_{1\pi K}^v = \mathscr{L}_{1\pi K}^0 + \mathscr{L}_{1\pi K}^v - \mathscr{L}_{1\pi K_0}^v = \mathscr{L}_{1\pi K} - \mathscr{L}_{1\pi K_0}^v \tag{B.7}$$

we obtain from (B.5) with (B.6) and

$$W_{ij}^K = - \langle \varphi_i | \left\{ \mathscr{L}_1^0 \mathbb{K} \int_0^\tau \exp(-i \tilde{\mathscr{L}}_{KK}^0 t) \, dt \, (\mathbb{K} \mathscr{L}_1^0 - \tilde{\mathbb{K}} \mathscr{L}_1^v) | \varphi_j\rangle\langle\varphi_j| \right\} | \varphi_i\rangle$$

$$+ \langle \varphi_i | \left\{ \mathscr{L}_1^v \tilde{\mathbb{K}} \int_0^\tau \exp(-i \tilde{\mathscr{L}}_{KK}^0 t) \, dt \, (\mathbb{K} \mathscr{L}_1^0 - \tilde{\mathbb{K}} \mathscr{L}_1^v) | \varphi_j\rangle\langle\varphi_j| \right\} | \varphi_i\rangle \tag{B.8}$$

* $\delta_\gamma (E - E') = \frac{1}{2\pi} \gamma \left[(E - E')^2 + \frac{1}{4} \gamma^2 \right]^{-1}$.

and with (B.7)

$$
\begin{aligned}
W_{ij}^K = &- \langle \varphi_i | \left\{ \mathscr{L}_1 \, \mathbb{K} \int_0^\tau \exp(-i\,\tilde{\mathscr{L}}_{KK}^0 t)\, dt\, (\mathbb{K}\mathscr{L}_1 - \mathbb{K}_0\,\mathscr{L}_1^v)\,|\varphi_j\rangle \langle \varphi_j| \right\} |\varphi_i\rangle \\
&+ \langle \varphi_i | \left\{ \mathscr{L}_1^v\, \mathbb{K}_0 \int_0^\tau \exp(-i\,\tilde{\mathscr{L}}_{KK}^0 t)\, dt\, (\mathbb{K}\mathscr{L}_1 - \mathbb{K}_0\,\mathscr{L}_1^v)\,|\varphi_j\rangle \langle \varphi_j| \right\} |\varphi_i\rangle .
\end{aligned}
\tag{B.9}
$$

We now assume that the states $|\varphi_i\rangle$, $|\varphi_j\rangle$ in (B.8) differ only in quantum numbers of the conduction band electrons, while for (B.9) this is not the case. Then, by the properties of the operators $\tilde{\mathbb{K}}$ and $\mathbb{K}_0$, the terms in (B.8) containing $\tilde{\mathbb{K}}$ and the terms in (B.9) containing $\mathbb{K}_0$ cancel. We then have

$$
W_{ij}^K = - \langle \varphi_i | \left\{ \mathscr{L}_1^0 \, \mathbb{K} \int_0^\tau \exp(-i\,\tilde{\mathscr{L}}_{KK}^0 t)\, dt\, \mathbb{K}\,\mathscr{L}_1^0\,|\varphi_j\rangle \langle \varphi_j| \right\} |\varphi_i\rangle
\tag{B.10}
$$

for transitions within the conduction band and

$$
W_{ij}^K = - \langle \varphi_i | \left\{ \mathscr{L}_1 \, \mathbb{K} \int_0^\tau \exp(-i\,\tilde{\mathscr{L}}_{KK}^0 t)\, dt\, \mathbb{K}\,\mathscr{L}_1\,|\varphi_j\rangle \langle \varphi_j| \right\} |\varphi_i\rangle
\tag{B.11}
$$

for transitions where impurity center states are involved. Equations (B.10) and (B.11) can now be treated to get the form

$$
W_{nm v\varrho,\,n'm'v'\varrho'}^K = \frac{2\pi}{\hbar}\,|\langle nm|\hat{O}|n'm'\rangle|^2\,\delta_{vv'}\,\delta_{\varrho\varrho'}\,\delta_\gamma(E_m^n - E_{m'}^{n'})
$$

where $\hat{O}$ is the interaction operator corresponding to $\mathscr{L}_1^0$ and $\mathscr{L}_1$ respectively. Taking into account the definitions of $\mathscr{L}_1^0$ and $\mathscr{L}_1$ we get equation (B.4) for transitions, where impurity center states are involved and

$$
\bar{W}_{nm v\varrho,\,n'm'v'\varrho'}^K = \frac{2\pi}{\hbar}\,|\langle nm|\bar{K}^s + K^t|n'm'\rangle|^2\,\delta_{vv'}\,\delta_{\varrho\varrho'}\,\delta_\gamma(E_m^n - E_{m'}^{n'}).
\tag{B.12}
$$

However, as the operator K^t in (B.12) is always operating on Bloch states of the ideal lattice, which are independent of the ion coordinates, its contribution vanishes and we finally arrive at equation (B.3) for transitions within the conduction band, q.e.d.

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