Two-band density matrix theory: the effect of external fields on transition and transport processes



1994 J. Phys.: Condens. Matter 6 7445

(http://iopscience.iop.org/0953-8984/6/36/024)

J. Phys.: Condens. Matter 6 (1994) 7445–7460. Printed in the UK

# Two-band density matrix theory: the effect of external fields on transition and transport processes

F M Buflert and J Schlössert‡
Institut für Theoretische Physik B, Rheinisch–Westfälische Technische Hochschule Aachen, D–52056 Aachen, Germany

Received 10 May 1994

**Abstract.** We present a derivation of the two-band density matrix dynamics which considers the effect of external fields on *both* the intraband drift motion in the six-dimensional configuration space *and* the interband transitions. This includes in particular the contribution of the light field to the drift term of the interband density matrix which is, for example, responsible for the 'resonant' Stark effect. A relation between the density matrix and electrodynamic quantities is established where our approach directly accounts for the decomposition into interband and intraband polarization. The consideration of a static magnetic field without invoking the 'Peierls substitution' turns out to yield deviations from the usual formulations in magneto-optics and transport theory. In the regime of quantum transport we obtain a general expression for the quantum correction of the energy density which is valid for non-equilibrium conditions and arbitrary band structure and can be used for the derivation of quantum hydrodynamic equations.

## 1. Introduction

Non-linear optics and transport in modern semiconductor devices are characterized by a continuing diminution of the time and length scales involved. While the duration of pulses in ultrafast optical processes lies in the order of femtoseconds, transport is concerned with semiconductor devices that have reached the deep-submicron regime. This suggests that classical or semiclassical descriptions of experiments in these fields have to be replaced by a quantum mechanical treatment [1]. Appropriate theoretical frameworks for studying those effects are non-equilibrium Green function theory [2–7] and density matrix theory [8–27]. In this paper we adopt the density matrix approach because of its relative simplicity and more direct link with physical observables.

An example in optics, which cannot be addressed semiclassically, is the 'non-resonant' dynamical (optical or AC) Stark effect [28, 29], i.e. the modification of the excitonic absorption caused by an intense laser pump beam below the exciton resonance. This effect can be explained by the semiconductor Bloch equations [8–13] where in addition to the electron and hole distributions (intraband density matrices) the electron–hole pair amplitude (interband density matrix) is an independent dynamic variable which is created due to the light field appearing in the source terms of the equations of motion. However, this approach is not sufficient for all situations in optics since the Hamiltonian, from which these equations are derived, includes neither spatially non-uniform situations nor drift contributions in momentum space. It is therefore not adapted to experiments like the emission of THz radiation from semiconductor heterostructures [30, 31] or the 'resonant' Stark effect [32, 33]

† Present address: Institut für Theoretische Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany.
‡ Present address: BASF, D-67056 Ludwigshafen, Germany.

0953-8984/94/367445+16$19.50  

where a pump beam is resonant between two exciton sublevel states. The former effect is associated with spatial inhomogeneity since it is caused by charge oscillations and thus the polarization is related to the electron and hole distributions [23, 24] and not to the electron–hole pair amplitude describing interband transitions. The 'resonant' Stark effect originates from the contribution of the light field to the drift term of the electron–hole pair amplitude, which was first introduced in terms of the vector potential [16–19] and later replaced 'by hand' with a transverse electric field [19–21]. It has to be stressed that a crucial point in this context is the fact that the relation between the dynamic variables and electrodynamic quantities depends on the gauge chosen and that equivalent gauges can lead to different results when using approximations [34]. Similar problems arise when considering a static magnetic field [22], namely the 'Peierls substitution' which has become the subject of serious criticism [35].

Semiclassical transport in the field of semiconductor device simulation is described by the Boltzmann transport equations [36, 37] where the electron–hole pair amplitude is eliminated as an independent variable. On the other hand, the classical hydrodynamic model consisting of balance equations for charge density, conduction current density and energy density is also used [38–40] since its solution requires much less computation time. In view of the increasing miniaturization of semiconductor devices quantum mechanical extensions of these models are under discussion. In the Boltzmann equations higher derivatives of the scalar potential have been considered [1, 14, 27, 41–43], while in the hydrodynamic model a 'quantum potential' has been introduced for which different expressions are being used [27, 42, 43] and the first applications on the device level have been performed [44, 45]. These approaches assume a parabolic bandstructure and in the hydrodynamic case often refer to special shapes of the distribution functions. However, non-parabolic bandstructures are important in hot-electron transport [39, 40] so that formulations are desirable which relax the restriction to parabolic bands and particular shapes of the distribution functions.

The aim of this work is to present a consistent derivation of the density matrix dynamics that incorporates all the interband and intraband processes induced by external fields in the different situations of optics and transport as described above. This requires a decomposition of the effect of the external fields into drift and transition contributions which can be achieved in a site representation of the second-quantized Hamiltonian by making use of localization properties of the Wannier functions. The other focus is to establish a relation between the dynamic variables and physical quantities of interest which will be based on transforming the equations of motion into a version where the expression for the resulting conduction current density is gauge independent. In the case of a light field this is accomplished via a gauge transformation as long as the magnetic component of the light can be neglected. In the presence of a strong static magnetic field an additional transformation of the variables has to be applied which removes the explicit dependence of the conduction current density on the magnetic field. Interband polarization and magnetization are then identified via the expectation value of the corresponding Hamiltonian. The expectation value also yields directly the general expression for the quantum correction of the energy density and permits us in sufficiently localized systems to rewrite the conduction current density in terms of an intraband polarization.

For simplicity we consider only a two-band system and assume in the main part of this work a parabolic band structure. Only in the section on quantum transport are no approximations imposed on the band structure. The Coulomb interaction is omitted since the subject of this paper is the incorporation of external fields. The paper is organized as follows. In section 2 the Hamiltonian is set up in an appropriate form using a gauge transformation as well as localization properties of the Wannier functions. In section 3 the

equations of motion for the density matrix in the presence of a light field and a longitudinal electric field are derived. In section 4 we relate the dynamic variables to macroscopic quantities of interest and in section 5 a static and uniform magnetic field is incorporated into the density matrix dynamics. Finally, in section 6 the regime of quantum transport is discussed and in section 7 some conclusions are drawn.

## 2. Hamiltonian

The second-quantized Hamiltonian describing a two-band semiconductor under the influence of external fields in the electron–hole picture is

$$H = \sum_{i,j} h_{ci,cj} c_i^\dagger c_j - h_{vi,vj} d_j^\dagger d_i + h_{vi,cj} d_i c_j + h_{vi,cj}^* c_j^\dagger d_i^\dagger \tag{2.1a}$$

$$h_{ni,n'j} = \int_V w_n^*(\boldsymbol{r} - \boldsymbol{R}_i) h w_{n'}(\boldsymbol{r} - \boldsymbol{R}_j)\, \mathrm{d}^3 r \tag{2.1b}$$

$$h = \frac{1}{2m_0}\left(\frac{\hbar}{\mathrm{i}}\nabla + eA'(\boldsymbol{r}, t)\right)^2 - e\Phi'(\boldsymbol{r}, t) + U(\boldsymbol{r}) \tag{2.1c}$$

where $n$ denotes the band index (characterizing the valence band ($n = v$) or the conduction band ($n = c$)), $m_0$ the free electron mass, $e > 0$ the magnitude of the elementary charge, $V$ the volume of the crystal and $U(\boldsymbol{r})$ the periodic potential of the lattice; $w_n(\boldsymbol{r} - \boldsymbol{R}_j)$ stands for the Wannier functions. They are related to the Bloch functions $\psi_{nk}(\boldsymbol{r})$, which are eigenstates of the single-particle Hamiltonian

$$h_0 = -\frac{\hbar^2}{2m_0}\Delta + U(\boldsymbol{r}) \tag{2.2}$$

with eigenvalues $\epsilon_n(\boldsymbol{k})$, through the transformation

$$w_n(\boldsymbol{r} - \boldsymbol{R}_j) = \frac{1}{\sqrt{N}} \sum_{k \in \mathrm{BZ}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j} \psi_{nk}(\boldsymbol{r}). \tag{2.3}$$

Here, $N$ is the number of unit cells in the crystal and the summation over $\boldsymbol{k}$ is confined to the first Brillouin zone BZ. The creation and annihilation operators of electrons (holes) at site $\boldsymbol{R}_j$ are given by $c_j^\dagger(d_j^\dagger)$ and $c_j(d_j)$, respectively.

We suppose that $A'$ and $\Phi'$ are obtained from potentials in the Coulomb gauge ($\nabla \cdot \boldsymbol{A} = 0$) via the gauge transformation (see the appendix)

$$\boldsymbol{A}'(\boldsymbol{r}, t) = \boldsymbol{A}(\boldsymbol{r}, t) + \nabla\chi(\boldsymbol{r}, t) \tag{2.4a}$$

$$\Phi'(\boldsymbol{r}, t) = \Phi(\boldsymbol{r}, t) - \frac{\partial}{\partial t}\chi(\boldsymbol{r}, t) \tag{2.4b}$$

with the gauge function

$$\chi(\boldsymbol{r}, t) = -\int_0^1 \mathrm{d}u\, \boldsymbol{r} \cdot \boldsymbol{A}(u\boldsymbol{r}, t) \tag{2.5}$$

as given by Fiutak [46] and used by other authors [47,48] which goes back to the transformation of Göppert-Mayer [49]. This yields for the new potentials [46,47]

$$\boldsymbol{A}'(\boldsymbol{r}, t) = \int_0^1 \mathrm{d}u\, \boldsymbol{B}(u\boldsymbol{r}, t) \times u\boldsymbol{r} \approx \tfrac{1}{2}\boldsymbol{B}(\boldsymbol{0}, t) \times \boldsymbol{r} \tag{2.6a}$$

$$\Phi'(\boldsymbol{r}, t) = \Phi(\boldsymbol{r}, t) - \int_0^1 \mathrm{d}u\, \boldsymbol{r} \cdot \boldsymbol{E}_\perp(u\boldsymbol{r}, t) \approx \Phi(\boldsymbol{r}, t) - \boldsymbol{r} \cdot \boldsymbol{E}_\perp(\boldsymbol{0}, t) \tag{2.6b}$$

where we have applied the long-wavelength approximation to the magnetic field $\boldsymbol{B}$ and the transverse electric field $\boldsymbol{E}_\perp = -\partial \boldsymbol{A}/\partial t$ by approximating them in the integral with their values at the origin. The consideration of a space-dependent light field would require us to start with its explicit spatial dependence (e.g. a plane wave) and then to perform the integration over $u$ in (2.6).

We now calculate the matrix elements (2.1*b*) of the single-particle Hamiltonian (2.1*c*) involving the electric field. For this we (i) assume that the integration in (2.1*b*) can be restricted to an overlap region due to localization properties of the Wannier functions [50] and (ii) relate the position vector in a dipole matrix element to the centre $\boldsymbol{R}_{ij} = (\boldsymbol{R}_i + \boldsymbol{R}_j)/2$ of the overlap region. The assumption of the overlap region being of the order of a unit cell is supported by the experimental value of $7.88\,e$Å for the dipole matrix element in GaAs [29] to be compared with the corresponding lattice constant of 5.65 Å. For simplicity we concentrate on the limiting case where the integration in (2.1*b*) is only over a single unit cell and terms with Wannier functions centred around different sites vanish. Hence

$$\begin{aligned} h^E_{ni,n'i} &= -e \int_{\Omega_{\mathrm{cell}}(\boldsymbol{R}_i)} w_n^*(\boldsymbol{r}-\boldsymbol{R}_i)\Phi'(\boldsymbol{r},t)w_{n'}(\boldsymbol{r}-\boldsymbol{R}_i)\,\mathrm{d}^3r \\ &= -e \int_{\Omega_{\mathrm{cell}}(\boldsymbol{R}_i)} w_n^*(\boldsymbol{r}-\boldsymbol{R}_i)[\Phi(\boldsymbol{r},t) - \boldsymbol{E}_\perp(0,t)\cdot\boldsymbol{R}_i \\ &\quad - \boldsymbol{E}_\perp(0,t)\cdot(\boldsymbol{r}-\boldsymbol{R}_i)]w_{n'}(\boldsymbol{r}-\boldsymbol{R}_i)\,\mathrm{d}^3r \\ &= -e\,\delta_{n,n'}[\Phi(\boldsymbol{R}_i,t) - \boldsymbol{E}_\perp(0,t)\cdot\boldsymbol{R}_i] + e\,\boldsymbol{r}_{n,n'}\cdot[\boldsymbol{E}_\parallel(\boldsymbol{R}_i,t) + \boldsymbol{E}_\perp(0,t)] \end{aligned} \tag{2.7}$$

expanding in the last step the scalar potential $\Phi$ to first order about $\boldsymbol{R}_i$ and changing the variable of integration to $\boldsymbol{r} - \boldsymbol{R}_i$. Here, we have introduced the longitudinal electric field $\boldsymbol{E}_\parallel = -\nabla\Phi$ and the dipole matrix element

$$-e\boldsymbol{r}_{n,n'} = -e\int_{\Omega_{\mathrm{cell}}} w_n^*(\boldsymbol{r})\boldsymbol{r}w_{n'}(\boldsymbol{r})\,\mathrm{d}^3r \tag{2.8}$$

Overlap regions exceeding a single unit cell can be taken into account for example via a 'smeared-out' dipole $-e\tilde{\boldsymbol{r}}_{n,n'}(\boldsymbol{R}_i - \boldsymbol{R}_j)$ [14]. The matrix element involving the magnetic field is obtained by applying an analogous procedure, i.e. adding and subtracting the overlap centre $\boldsymbol{R}_{ij}$ as well as restricting, if necessary, the integration to the overlap region, and using the definitions

$$v_n(k) = \frac{1}{m_0}\int_V \psi_{nk}^*(\boldsymbol{r})\frac{\hbar}{\mathrm{i}}\nabla\psi_{nk}(\boldsymbol{r})\,\mathrm{d}^3r = \frac{1}{\hbar}\nabla_k\epsilon_n(k) \tag{2.9}$$

$$\boldsymbol{p}_{n,n'} = \int_{\Omega_{\mathrm{cell}}} w_n^*(\boldsymbol{r})\frac{\hbar}{\mathrm{i}}\nabla w_{n'}(\boldsymbol{r})\,\mathrm{d}^3r \tag{2.10}$$

$$\boldsymbol{L}_{n,n'} = \int_{\Omega_{\mathrm{cell}}} w_n^*(\boldsymbol{r})\left(\boldsymbol{r}\times\frac{\hbar}{\mathrm{i}}\nabla\right)w_{n'}(\boldsymbol{r})\,\mathrm{d}^3r \tag{2.11}$$

$$(r^2)_{n,n'} = \int_{\Omega_{\mathrm{cell}}} w_n^*(\boldsymbol{r})(x^2+y^2)w_{n'}(\boldsymbol{r})\,\mathrm{d}^3r \tag{2.12}$$

where the magnetic field is taken along the $z$ axis. Finally, the remaining matrix element of the single-particle Hamiltonian $h_0$ given in (2.2) results from replacing the Wannier functions through the Bloch functions via (2.3). The total matrix element (2.1*b*) is then

$$h_{ni,n'j} = h^0_{ni,n'j} + h^E_{ni,n'j} + h^B_{ni,n'j} \tag{2.13a}$$

$$h^0_{ni,n'j} = \delta_{n,n'}\frac{1}{N}\sum_{k\in\mathrm{BZ}}\epsilon_n(k)\mathrm{e}^{\mathrm{i}k\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)} \tag{2.13b}$$

$$h^{E}_{ni,n'j} = \delta_{n,n'}(-e)[\Phi(\boldsymbol{R}_i,t) - \boldsymbol{E}_{\perp}(\boldsymbol{0},t)\cdot\boldsymbol{R}_i]\delta_{i,j} + (1-\delta_{n,n'})e\boldsymbol{r}_{n,n'}\cdot[\boldsymbol{E}_{\parallel}(\boldsymbol{R}_i,t)+\boldsymbol{E}_{\perp}(\boldsymbol{0},t)]\delta_{i,j} \tag{2.13c}$$

$$h^{B}_{ni,n'j} = \delta_{n,n'}\left[\frac{1}{N}\sum_{k\in BZ}\tfrac{1}{2}e\boldsymbol{B}(0,t)\cdot\boldsymbol{R}_{ij}\times\boldsymbol{v}_n(\boldsymbol{k})e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)} + \left(\frac{e}{2m_0}\boldsymbol{B}(0,t)\cdot\boldsymbol{L}_{n,n}+\frac{e^2}{8m_0}\big(\boldsymbol{B}(\boldsymbol{0},t)\times\boldsymbol{R}_i\big)^2+\frac{e^2}{8m_0}\big(\boldsymbol{B}(\boldsymbol{0},t)\big)^2(r^2)_{n,n}\right)\delta_{i,j}\right] + (1-\delta_{n,n'})\frac{e}{2m_0}\boldsymbol{B}(0,t)\cdot(\boldsymbol{R}_i\times\boldsymbol{p}_{n,n'}+\boldsymbol{L}_{n,n'})\delta_{i,j} \tag{2.13d}$$

assuming $\boldsymbol{r}_{n,n}$ to cancel due to selection rules and neglecting $e\boldsymbol{r}_{n,n'}\times\boldsymbol{B}$ against $\boldsymbol{p}_{n,n'}$ as well as $e\boldsymbol{B}(r^2)_{n,n'}$ against $\boldsymbol{L}_{n,n'}$. Without spin–orbit interaction only $\boldsymbol{L}_{n,n}$ has to be extended to $\boldsymbol{J}_{n,n}=\boldsymbol{L}_{n,n}+\boldsymbol{S}_{n,n}$ when including the spin.

The field-independent matrix element (2.13*b*) allows for hopping between different sites, the first term in (2.13*c*) will lead to the contribution of the electric field to the drift motion in the six-dimensional configuration space, while the other term yields transition processes between valence and conduction band. A similar decomposition as in (2.13*c*) holds for the magnetic contributions.

## 3. Equations of motion

In this section we derive the equations of motion for the expectation values of pairs of creation and annihilation operators which are usually summarized in the density matrix

$$\begin{pmatrix}\langle c_i^{\dagger}c_j\rangle & \langle c_j^{\dagger}d_i^{\dagger}\rangle\\ \langle d_ic_j\rangle & \langle d_i^{\dagger}d_j\rangle\end{pmatrix}. \tag{3.1}$$

Here $C_{ij}=\langle c_i^{\dagger}c_j\rangle$ and $D_{ij}=\langle d_i^{\dagger}d_j\rangle$ denote the electron and hole distributions, respectively, whereas the electron–hole pair amplitude is given by $Y_{ij}=\langle d_ic_j\rangle$. Setting up the Heisenberg equation of motion $i\hbar\mathrm{d}A/\mathrm{d}t=[A,H]$ for an operator $A$ and then taking the expectation value $\langle A\rangle=\mathrm{Tr}(\rho A)$ with the statistical operator $\rho$ yields for the elements of the density matrix (3.1)

$$-i\hbar\frac{\mathrm{d}}{\mathrm{d}t}Y_{ij}+\sum_l h_{cj,cl}Y_{il}-\sum_l h_{vl,vi}Y_{lj}=-h_{cj,vi}+\sum_l h_{cl,vi}C_{lj}-\sum_l h_{cj,vl}D_{li} \tag{3.2a}$$

$$-i\hbar\frac{\mathrm{d}}{\mathrm{d}t}C_{ij}+\sum_l h_{cj,cl}C_{il}-\sum_l h_{cl,ci}C_{lj}=\sum_l h_{vl,ci}Y_{lj}-\sum_l h_{cj,vl}Y^{*}_{li} \tag{3.2b}$$

$$-i\hbar\frac{\mathrm{d}}{\mathrm{d}t}D_{ij}+\sum_l h_{vi,vl}D_{lj}-\sum_l h_{vl,vj}D_{il}=\sum_l h_{vi,cl}Y_{jl}-\sum_l h_{cl,vj}Y^{*}_{il}. \tag{3.2c}$$

The next step is the introduction of densities as proposed by Stahl and Balslev [14] in the spirit of an interpolation scheme:

$$Y(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_{i,j}Y_{ij}\Delta^{*}(\boldsymbol{r}_1-\boldsymbol{R}_i)\Delta(\boldsymbol{r}_2-\boldsymbol{R}_j) \tag{3.3a}$$

$$C(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_{i,j}C_{ij}\Delta^{*}(\boldsymbol{r}_1-\boldsymbol{R}_i)\Delta(\boldsymbol{r}_2-\boldsymbol{R}_j) \tag{3.3b}$$

$$D(\boldsymbol{r}_1,\boldsymbol{r}_2)=\sum_{i,j}D_{ij}\Delta(\boldsymbol{r}_1-\boldsymbol{R}_i)\Delta^{*}(\boldsymbol{r}_2-\boldsymbol{R}_j) \tag{3.3c}$$

which are defined on the spatial continuum with the $\delta$-like sampling function $\Delta$ being

$$\Delta(\boldsymbol{r}-\boldsymbol{R}_j)=\frac{1}{N\sqrt{\Omega_{\mathrm{cell}}}}\sum_{k\in\mathrm{BZ}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R}_j)}. \tag{3.4}$$

The corresponding equations of motion are then transformed by introducing relative $\boldsymbol{x}=\boldsymbol{r}_2-\boldsymbol{r}_1$ and centre $\boldsymbol{R}=(\boldsymbol{r}_2+\boldsymbol{r}_1)/2$ coordinates. As is indicated, for example, by the electron distribution in thermal equilibrium $C^{\mathrm{eq}}(\boldsymbol{x})$, which is a Gaussian with a width given by the thermal wavelength $\lambda_{\mathrm{th}}=\hbar(m_{\mathrm{c}}k_{\mathrm{B}}T)^{-1/2}$ where $k_{\mathrm{B}}$ and $T$ denote the Boltzmann constant and the lattice temperature, respectively ($\lambda_{\mathrm{th}}=64.7\,\text{Å}$ in GaAs for $T=300\,\mathrm{K}$), the density matrices tend to 0 as $x\to\infty$. Hence, one can approximate the scalar potential according to

$$\Phi(\boldsymbol{R}\pm\tfrac{1}{2}\boldsymbol{x},t)\approx\Phi(\boldsymbol{R},t)\pm\tfrac{1}{2}\nabla\Phi(\boldsymbol{R},t)\cdot\boldsymbol{x} \tag{3.5}$$

if the length scale of its spatial variation is sufficiently large (for extensions see section 6). Furthermore, we restrict ourselves in the remaining part of this section to the case of a longitudinal electric field and a light field. It is then possible to neglect the magnetic field since the relation between the amplitudes $B=E_\perp/c$ leads to negligible magnetic contributions to both the drift motion (the Lorentz force is $v/c$ times the electric force) and the transition processes (terms associated with magnetic dipoles are small compared to the electric counterparts). The resulting equations in the effective mass approximation ($\epsilon_{\mathrm{v}}(\boldsymbol{k})\approx-\hbar^2\boldsymbol{k}^2/2m_{\mathrm{v}}$ with $m_{\mathrm{v}}>0$, $\epsilon_{\mathrm{c}}(\boldsymbol{k})\approx E_{\mathrm{g}}+\hbar^2\boldsymbol{k}^2/2m_{\mathrm{c}}$ with $E_{\mathrm{g}}$ denoting the band gap) are

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}+E_{\mathrm{g}}+\Omega_{\mathrm{vc}}\right)Y(\boldsymbol{R},\boldsymbol{x})=-e\boldsymbol{r}_{\mathrm{vc}}^*\cdot[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(0,t)][\delta_{\mathrm{B}}(\boldsymbol{x})-C(\boldsymbol{R},\boldsymbol{x})-D(\boldsymbol{R},-\boldsymbol{x})]+\frac{\mathrm{i}\hbar}{\tau_2}Y(\boldsymbol{R},\boldsymbol{x}) \tag{3.6a}$$

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}+\Omega_{\mathrm{cc}}\right)C(\boldsymbol{R},\boldsymbol{x})=-e[\boldsymbol{r}_{\mathrm{vc}}^*Y^*(\boldsymbol{R},-\boldsymbol{x})-\boldsymbol{r}_{\mathrm{vc}}Y(\boldsymbol{R},\boldsymbol{x})]\cdot[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(\boldsymbol{0},t)]+\frac{\mathrm{i}\hbar}{\tau_1}[C(\boldsymbol{R},\boldsymbol{x})-C^{\mathrm{eq}}(\boldsymbol{x})] \tag{3.6b}$$

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}+\Omega_{\mathrm{vv}}\right)D(\boldsymbol{R},\boldsymbol{x})=-e[\boldsymbol{r}_{\mathrm{vc}}^*Y^*(\boldsymbol{R},\boldsymbol{x})-\boldsymbol{r}_{\mathrm{vc}}Y(\boldsymbol{R},-\boldsymbol{x})]\cdot[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(\boldsymbol{0},t)]+\frac{\mathrm{i}\hbar}{\tau_1}[D(\boldsymbol{R},\boldsymbol{x})-D^{\mathrm{eq}}(\boldsymbol{x})] \tag{3.6c}$$

where the band-limited $\delta$ function is given by $\delta_{\mathrm{B}}(\boldsymbol{x})=V^{-1}\sum_{k\in\mathrm{BZ}}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})$. In view of the constitutive relations to be derived as limiting cases in the next section phenomenological relaxation times have been added to account for irreversible processes. The definitions of the drift operators are

$$\Omega_{\mathrm{vc}}=-\frac{\hbar^2}{8\mu}\Delta_R-\frac{\hbar^2}{2}\left(\frac{1}{m_{\mathrm{c}}}-\frac{1}{m_{\mathrm{v}}}\right)\nabla_R\cdot\nabla_x-\frac{\hbar^2}{2\mu}\Delta_x+e[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(\boldsymbol{0},t)]\cdot\boldsymbol{x} \tag{3.7a}$$

$$\Omega_{\mathrm{cc}}=-\frac{\hbar^2}{m_{\mathrm{c}}}\nabla_R\cdot\nabla_x+e[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(\boldsymbol{0},t)]\cdot\boldsymbol{x} \tag{3.7b}$$

$$\Omega_{\mathrm{vv}}=-\frac{\hbar^2}{m_{\mathrm{v}}}\nabla_R\cdot\nabla_x-e[\boldsymbol{E}_\parallel(\boldsymbol{R},t)+\boldsymbol{E}_\perp(\boldsymbol{0},t)]\cdot\boldsymbol{x} \tag{3.7c}$$

with $\mu^{-1} = m_c^{-1} + m_v^{-1}$ being the reduced mass. Note that there are also cases where it can be advantageous to use in the equation for $Y$ the centre-of-mass instead of the centre-coordinate [14]. In the limiting case where $Y$, $C$ and $D$ do not depend on $R$ and $x$ (effective masses $\to \infty$ and relative coordinate $\to 0$), i.e. when the drift operators can be neglected, these equations represent the optical Bloch equations describing the dynamics of independent two-level atoms [51].

In order to establish the relation to the $k$-space density matrix formulation a Fourier transform with respect to the relative coordinate $x$ has to be applied which has a certain analogy to the Wigner transformation [14, 41]

$$p(R,k) = \int_V Y(R,x)\mathrm{e}^{-\mathrm{i}k\cdot x}\,\mathrm{d}^3x = \sum_{k'\in(\mathrm{BZ}(k)\cap\mathrm{BZ}(-k))} \langle d_{-k+k'}\, c_{k+k'}\rangle \mathrm{e}^{2\mathrm{i}k'\cdot R} \tag{3.8a}$$

$$f_c(R,k) = \int_V C(R,x)\mathrm{e}^{-\mathrm{i}k\cdot x}\,\mathrm{d}^3x = \sum_{k'\in(\mathrm{BZ}(k)\cap\mathrm{BZ}(-k))} \langle c^\dagger_{k-k'}\, c_{k+k'}\rangle \mathrm{e}^{2\mathrm{i}k'\cdot R} \tag{3.8b}$$

$$f_v(R,k) = \int_V D(R,x)\mathrm{e}^{-\mathrm{i}k\cdot x}\,\mathrm{d}^3x = \sum_{k'\in(\mathrm{BZ}(k)\cap\mathrm{BZ}(-k))} \langle d^\dagger_{k-k'}\, d_{k+k'}\rangle \mathrm{e}^{2\mathrm{i}k'\cdot R} \tag{3.8c}$$

where $\mathrm{BZ}(k)$ is the Brillouin zone centred around $k$ and creation and annihilation operators with respect to Bloch functions have been introduced ($c_k = c_{c,k}$, $d_k = c^\dagger_{v,-k}$).

The equations of motion resulting from the Fourier transform are

$$\left[\frac{\partial}{\partial t} - \mathrm{i}\frac{\hbar}{8\mu}\Delta_R + \frac{\hbar}{2}\left(\frac{1}{m_c} - \frac{1}{m_v}\right)k\cdot\nabla_R - \frac{e}{\hbar}[E_\parallel(R,t) + E_\perp(0,t)]\cdot\nabla_k\right]p(R,k)$$
$$= \left(\frac{\partial p(R,k)}{\partial t}\right)_s - \frac{1}{\tau_2}p(R,k) \tag{3.9a}$$

$$\left(\frac{\partial}{\partial t} + \frac{\hbar}{m_c}k\cdot\nabla_R - \frac{e}{\hbar}[E_\parallel(R,t) + E_\perp(0,t)]\cdot\nabla_k\right)f_c(R,k) = \left(\frac{\partial f_c(R,k)}{\partial t}\right)_s$$
$$- \frac{1}{\tau_1}[f_c(R,k) - f_c^{\mathrm{eq}}(k)] \tag{3.9b}$$

$$\left(\frac{\partial}{\partial t} + \frac{\hbar}{m_v}k\cdot\nabla_R + \frac{e}{\hbar}[E_\parallel(R,t) + E_\perp(0,t)]\cdot\nabla_k\right)f_v(R,k) = \left(\frac{\partial f_v(R,k)}{\partial t}\right)_s$$
$$- \frac{1}{\tau_1}[f_v(R,k) - f_v^{\mathrm{eq}}(k)] \tag{3.9c}$$

where the source terms are given by

$$\left(\frac{\partial p(R,k)}{\partial t}\right)_s = \frac{1}{\mathrm{i}\hbar}\left[\left(E_g + \frac{\hbar^2k^2}{2\mu}\right)p(R,k) + er_{vc}^*\cdot[E_\parallel(R,t) + E_\perp(0,t)]\right.$$
$$\left.\times[1 - f_c(R,k) - f_v(R,-k)]\right] \tag{3.10a}$$

$$\left(\frac{\partial f_c(R,k)}{\partial t}\right)_s = \frac{e}{\mathrm{i}\hbar}[r_{vc}^* p^*(R,k) - r_{vc}p(R,k)]\cdot[E_\parallel(R,t) + E_\perp(0,t)] \tag{3.10b}$$

$$\left(\frac{\partial f_v(R,k)}{\partial t}\right)_s = \frac{e}{\mathrm{i}\hbar}[r_{vc}^* p^*(R,-k) - r_{vc}p(R,-k)]\cdot[E_\parallel(R,t) + E_\perp(0,t)]. \tag{3.10c}$$

The optical Bloch equations are again obtained in the case where $p$, $f_c$ and $f_v$ do not depend on $R$ and $k$. Neglecting only the space dependence yields the density matrix dynamics in

the $k$-space formulation as often used in optics (after inclusion of the Coulomb interaction), i.e. apart from the drift terms $\propto \boldsymbol{E} \cdot \nabla_k$ the usual semiconductor Bloch equations. On the other hand, the equations for $f_c$ and $f_v$ coincide in the absence of the source terms with the Boltzmann transport equations in the relaxation time approximation.

## 4. Electrodynamic quantities

In this section we establish a relation between the dynamic variables, i.e. the electron–hole pair amplitude and the electron and hole distributions, and macroscopic quantities of interest such as the interband polarization and the conduction current density. Our scheme will be based on an identification of the expectation value of the Hamiltonian with the classical Hamiltonian in the electric dipole approximation. For that, we use the orthonormality relation of the sampling functions (3.4)

$$\int_V \Delta^*(\boldsymbol{R} - \boldsymbol{R}_l)\Delta(\boldsymbol{R} - \boldsymbol{R}_j)\,\mathrm{d}^3R = \delta_{l,j} \tag{4.1}$$

in order to extend the summation in (2.1$a$) and thus are able to rewrite the expectation value of the Hamiltonian

$$\langle H \rangle = \mathrm{Tr}(\rho H) = \int_V \mathcal{H}(\boldsymbol{R})\,\mathrm{d}^3R \tag{4.2}$$

as an integral over an energy density which is given in terms of the dynamic variables (3.3) and (3.8), respectively, and can be arranged in the form

$$\mathcal{H}(\boldsymbol{R}) = W(\boldsymbol{R}) + \varrho(\boldsymbol{R})[\Phi(\boldsymbol{R}, t) - \boldsymbol{E}_\perp(\boldsymbol{0}, t) \cdot \boldsymbol{R}] - \boldsymbol{P}_{\mathrm{inter}}(\boldsymbol{R}) \cdot [\boldsymbol{E}_\parallel(\boldsymbol{R}, t) + \boldsymbol{E}_\perp(\boldsymbol{0}, t)] \tag{4.3}$$

where the time dependence of the densities is suppressed. In the following we give the definitions of the individual terms in (4.3) and interpret them. The first term

$$\begin{aligned} W(\boldsymbol{R}) = W_c(\boldsymbol{R}) + W_v(\boldsymbol{R}) &= \left(E_g - \frac{\hbar^2}{2m_c}\Delta_x - \frac{\hbar^2}{8m_c}\Delta_R\right) C(\boldsymbol{R}, \boldsymbol{x})|_{\boldsymbol{x}=\boldsymbol{0}} \\ &\quad + \left(-\frac{\hbar^2}{2m_v}\Delta_x - \frac{\hbar^2}{8m_v}\Delta_R\right) D(\boldsymbol{R}, \boldsymbol{x})|_{\boldsymbol{x}=\boldsymbol{0}} \\ &= \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} \left(E_g + \frac{\hbar^2 k^2}{2m_c} - \frac{\hbar^2}{8m_c}\Delta_R\right) f_c(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k \\ &\quad + \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} \left(\frac{\hbar^2 k^2}{2m_v} - \frac{\hbar^2}{8m_v}\Delta_R\right) f_v(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k \end{aligned} \tag{4.4}$$

represents, apart from the band gap, the kinetic energy density of electrons and holes. It can be seen that this energy involves a quantum mechanical correction term, a fact which was first found by Wigner [41] for the case of thermodynamic equilibrium. Our approach for the quasi-particles in a semiconductor, however, holds under arbitrary non-equilibrium conditions, since we did not need to invoke any particular shape of the electron and hole distributions. The quantum correction will be discussed in more detail in section 6. Here, we only consider briefly the limiting case of thermal equilibrium in a non-uniform situation described for non-degenerate electrons by the Maxwellian

$$f_c^{\mathrm{eq}}(\boldsymbol{R}, \boldsymbol{k}) = \exp\left[-\left(E_g + \frac{\hbar^2 k^2}{2m_c} - e\Phi(\boldsymbol{R}) - \mu\right)(k_B T)^{-1}\right] \tag{4.5}$$

where $\mu = E_g/2 + 3k_BT[\ln(m_v/m_c)]/4$ denotes the chemical potential. The energy density of the electrons then becomes

$$\frac{1}{(2\pi)^3}\int_{BZ}\left(\frac{\hbar^2k^2}{2m_c} - \frac{\hbar^2}{8m_c}\triangle_R\right) f_c^{eq}(R,k)\,d^3k = n_c(R)\left(\tfrac{3}{2}k_BT - \frac{\hbar^2e^2}{8m_c}\frac{[\nabla_R\Phi(R)]^2}{(k_BT)^2} - \frac{\hbar^2e}{8m_c}\frac{\triangle_R\Phi(R)}{k_BT}\right) \tag{4.6}$$

with the electron density given by

$$n_c(R) = (2\pi)^{-3}\int_{BZ} f_c(R,k)\,d^3k.$$

This shows that the quantum correction for the mean energy, $W_c(R)/n_c(R)$, vanishes in the limit of high temperatures.

The last term in (4.3) induces via the electric field interband transitions between valence and conduction bands, which can be described by the interband polarization

$$\begin{aligned} P_{inter}(R) &= -er_{vc}Y(R,0) - er_{vc}^*Y^*(R,0) \\ &= \frac{1}{(2\pi)^3}\int_{BZ}[-er_{vc}p(R,k) - er_{vc}^*p^*(R,k)]\,d^3k. \end{aligned} \tag{4.7}$$

On the other hand, the second term in (4.3) accounts for the intraband drift motion. In fact, differentiating the charge density

$$\begin{aligned} \varrho(R) &= \varrho_c(R) + \varrho_v(R) = -eC(R,0) + eD(R,0) \\ &= \frac{1}{(2\pi)^3}\int_{BZ}[-ef_c(R,k) + ef_v(R,k)]\,d^3k \end{aligned} \tag{4.8}$$

with respect to time and using the equations of motion (3.6*b*) and (3.6*c*) yields in the absence of relaxation processes the continuity equation

$$\frac{\partial}{\partial t}\varrho(R) + \nabla_R\cdot j(R) = 0 \tag{4.9}$$

which permits us to identify the conduction current density describing transport processes as

$$\begin{aligned} j(R) &= j_c(R) + j_v(R) = -\frac{e}{m_c}\frac{\hbar}{i}\nabla_x C(R,x)|_{x=0} + \frac{e}{m_v}\frac{\hbar}{i}\nabla_x D(R,x)|_{x=0} \\ &= \frac{1}{(2\pi)^3}\int_{BZ}\left(-e\frac{\hbar k}{m_c}f_c(R,k) + e\frac{\hbar k}{m_v}f_v(R,k)\right)d^3k \end{aligned} \tag{4.10}$$

It has to be stressed that the expression for the conduction current density comprises in general explicitly the vector potential, as does the probability current density in ordinary quantum mechanics. Only the choice of our gauge (see (2.5)) removes the explicit dependence on the vector potential from the expression (4.10) as long as the magnetic field can be neglected.

It has thus been possible to divide the electronic dynamics into band-to-band transitions given by the interband polarization and the drift motion described through the conduction current density. This division is further emphasized by the constitutive relations, which can be derived from the equations of motion for the density matrix. Taking in the limit of

infinite large effective masses the second derivative of the polarization (4.7) with respect to time and using (3.6*a*)–(3.6*c*) leads to

$$\frac{\mathrm{d}^2 P_{\mathrm{inter}}}{\mathrm{d}t^2} + \frac{2}{\tau_2}\frac{\mathrm{d}P_{\mathrm{inter}}}{\mathrm{d}t} + [\omega_{\mathrm{g}}^2 + (1/\tau_2)^2]P_{\mathrm{inter}} = \frac{2\omega_{\mathrm{g}} e^2 r_{\mathrm{vc}} \otimes r_{\mathrm{vc}}}{\hbar} n E(t) \tag{4.11}$$

with $\omega_{\mathrm{g}} = E_{\mathrm{g}}/\hbar$, $n = 1/\Omega_{\mathrm{cell}}$ and $E = E_{\perp} + E_{\parallel}$. Here, the electron and hole densities have been neglected against $n$, and the dipole matrix element is assumed to be real. Equation (4.11), which is usually introduced within the picture of 'bound' charges, represents the constitutive relation for the polarization (after inclusion of the induced electric field) permitting us to calculate the susceptibility $\chi(\omega)$ defined through $\hat{P}_{\mathrm{inter}}(\omega) = \varepsilon_0 \chi(\omega)\hat{E}(\omega)$. On the other hand, the first derivative with respect to time of the conduction current densities (4.10) of electrons and holes yields in spatially homogeneous systems with the help of (3.6*b*) and (3.6*c*) the Drude equations

$$\frac{\mathrm{d}j_{\mathrm{c}}}{\mathrm{d}t} + \frac{1}{\tau_1} j_{\mathrm{c}} = \frac{e^2}{m_{\mathrm{c}}} n_{\mathrm{c}} E(t) \tag{4.12}$$

$$\frac{\mathrm{d}j_{\mathrm{v}}}{\mathrm{d}t} + \frac{1}{\tau_1} j_{\mathrm{v}} = \frac{e^2}{m_{\mathrm{v}}} n_{\mathrm{v}} E(t) \tag{4.13}$$

where $n_{\mathrm{c}}$ and $n_{\mathrm{v}}$ denote the electron and hole densities, respectively, and band-to-band transitions have been neglected. These equations, which correspond in the framework of classical electrodynamics to 'free' charges, determine the frequency-dependent conductivity $\sigma(\omega)$ given by $\hat{j}(\omega) = \sigma(\omega)\hat{E}(\omega)$. Note that the electric field in (4.11) stems from the source term in the equations of motion, whereas in (4.12) and (4.13) it comes from the drift term. It should be stressed as well that even in the simplest case of a static electric field ($\Phi = -E_0 \cdot R$, $A \equiv 0$) the scheme given in (2.7), i.e. using localization properties of the Wannier functions to restrict integrations to an overlap region and relating the position vector in the dipole matrix element to the centre of the overlap region, is necessary within our approach to obtain as the limiting case Ohm's law $j_{\mathrm{c}} = \sigma_0 E$ with $\sigma_0 = e^2 \tau_1 n_{\mathrm{c}}/m_{\mathrm{c}}$.

Finally, we give for the case of a sufficiently localized system an equivalent formulation of the energy density (4.3). Performing another gauge transformation via $\bar{\chi} = \int^t \Phi(\mathbf{0}, t')\,\mathrm{d}t'$ and approximating the longitudinal electric field by its value at the origin (compare (2.6)) results in

$$\bar{\mathcal{H}}(R) = W(R) - [P_{\mathrm{intra}}(R) + P_{\mathrm{inter}}(R)] \cdot E(\mathbf{0}, t) \tag{4.14}$$

with

$$P_{\mathrm{intra}}(R) = -eRC(R, \mathbf{0}) + eRD(R, \mathbf{0}) = \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} [-eRf_{\mathrm{c}}(R, k) + eRf_{\mathrm{v}}(R, k)]\,\mathrm{d}^3k. \tag{4.15}$$

This intraband polarization is related to the conduction current density according to

$$\frac{\partial P_{\mathrm{intra}}(R)}{\partial t} = j(R) \tag{4.16}$$

as can be shown with the help of the continuity equation (4.9) and an integration by parts, if there is no current crossing the surface of the sample.

## 5. Static magnetic field

This section is devoted to the inclusion of a static and uniform magnetic field $\boldsymbol{B}_0$ into the equations of motion. The magnetic field is considered to be so strong that it is no longer justified to neglect the magnetic contributions. The corresponding equations of motion are obtained by the same procedure which led in section 2 to (3.6). However, the expression for the conduction current density resulting from the continuity equation (4.9) now includes explicitly the magnetic field. In order to obtain again the field-independent expression (4.10) one has to apply the transformation

$$\tilde{Y}(\boldsymbol{R}, \boldsymbol{x}) = \mathrm{e}^{\mathrm{i}e\boldsymbol{x}\cdot(\boldsymbol{B}_0\times\boldsymbol{R})/2\hbar}\, Y(\boldsymbol{R}, \boldsymbol{x}) \tag{5.1a}$$

$$\tilde{C}(\boldsymbol{R}, \boldsymbol{x}) = \mathrm{e}^{\mathrm{i}e\boldsymbol{x}\cdot(\boldsymbol{B}_0\times\boldsymbol{R})/2\hbar}\, C(\boldsymbol{R}, \boldsymbol{x}) \tag{5.1b}$$

$$\tilde{D}(\boldsymbol{R}, \boldsymbol{x}) = \mathrm{e}^{-\mathrm{i}e\boldsymbol{x}\cdot(\boldsymbol{B}_0\times\boldsymbol{R})/2\hbar}\, D(\boldsymbol{R}, \boldsymbol{x}). \tag{5.1c}$$

This kind of transformation was first given by Lamb [52] for two-particle problems in the Schrödinger picture (using the centre-of-mass instead of the centre coordinate) and later used by other authors [53, 54]. The corresponding variables in the $k$-space formulation are again obtained by the transformation (3.8) and the total energy density (compare (4.3)) in the new variables is

$$\tilde{\mathcal{H}}_{\mathrm{tot}}(\boldsymbol{R}) = \tilde{\mathcal{H}}(\boldsymbol{R}) - \boldsymbol{M}(\boldsymbol{R})\cdot\boldsymbol{B}_0 + \mathcal{H}_{\mathrm{dia}}(\boldsymbol{R}) \tag{5.2}$$

enabling the identification of the magnetization as

$$\begin{aligned}\boldsymbol{M}(\boldsymbol{R}) = &-\frac{e}{2m_0}\{\boldsymbol{L}_{\mathrm{cc}}\tilde{C}(\boldsymbol{R}, \boldsymbol{0}) - \boldsymbol{L}_{\mathrm{vv}}\tilde{D}(\boldsymbol{R}, \boldsymbol{0}) \\ &+ [\boldsymbol{R}\times\boldsymbol{p}_{\mathrm{vc}} + \boldsymbol{L}_{\mathrm{vc}}]\tilde{Y}(\boldsymbol{R}, \boldsymbol{0}) + [\boldsymbol{R}\times\boldsymbol{p}^*_{\mathrm{vc}} + \boldsymbol{L}^*_{\mathrm{vc}}]\tilde{Y}^*(\boldsymbol{R}, \boldsymbol{0})\} \\ = &\frac{1}{(2\pi)^3}\int_{\mathrm{BZ}}\Bigg(-\frac{e}{2m_0}\{\boldsymbol{L}_{\mathrm{cc}}\tilde{f}_{\mathrm{c}}(\boldsymbol{R}, \boldsymbol{k}) - \boldsymbol{L}_{\mathrm{vv}}\tilde{f}_{\mathrm{v}}(\boldsymbol{R}, \boldsymbol{k}) \\ &+ [\boldsymbol{R}\times\boldsymbol{p}_{\mathrm{vc}} + \boldsymbol{L}_{\mathrm{vc}}]\tilde{p}(\boldsymbol{R}, \boldsymbol{k}) + [\boldsymbol{R}\times\boldsymbol{p}^*_{\mathrm{vc}} + \boldsymbol{L}^*_{\mathrm{vc}}]\tilde{p}^*(\boldsymbol{R}, \boldsymbol{k})\}\Bigg)\mathrm{d}^3k.\end{aligned} \tag{5.3}$$

Here $\mathcal{H}_{\mathrm{dia}}(\boldsymbol{R})$ denotes the diamagnetic contribution, which is quadratic in $\boldsymbol{B}_0$. Note that it is due to the transformation (5.1) that the expression for the magnetization does not include the group velocity defined in (2.9).

Instead of listing the complete equations of motion following from (2.13$a$) and (5.1) we concentrate on the cases that are relevant either for transport theory or for optics. In the former case one can often neglect the electron–hole pair amplitude restricting the dynamics to the Boltzmann transport equations. In the presence of the magnetic field they are

$$\begin{aligned}\Bigg[\frac{\partial}{\partial t} + \frac{\hbar}{m_{\mathrm{c}}}\boldsymbol{k}\cdot\nabla_{\boldsymbol{R}} - \frac{e}{\hbar}[\boldsymbol{E}_{\parallel}(\boldsymbol{R}, t) + \boldsymbol{E}_{\perp}(\boldsymbol{0}, t) + \frac{\hbar}{m_{\mathrm{c}}}\boldsymbol{k}\times\boldsymbol{B}_0]\cdot\nabla_{\boldsymbol{k}} \\ - \frac{e^2}{4\hbar}\left(\frac{1}{m_0} - \frac{1}{m_{\mathrm{c}}}\right)(\boldsymbol{B}_0\times\boldsymbol{R})\cdot(\boldsymbol{B}_0\times\nabla_{\boldsymbol{k}})\Bigg]\tilde{f}_{\mathrm{c}}(\boldsymbol{R}, \boldsymbol{k}) = -\frac{1}{\tau_1}[\tilde{f}_{\mathrm{c}}(\boldsymbol{R}, \boldsymbol{k}) - f_{\mathrm{c}}^{\mathrm{eq}}(\boldsymbol{k})]\end{aligned} \tag{5.4}$$

$$\begin{aligned}\Bigg[\frac{\partial}{\partial t} + \frac{\hbar}{m_{\mathrm{v}}}\boldsymbol{k}\cdot\nabla_{\boldsymbol{R}} + \frac{e}{\hbar}[\boldsymbol{E}_{\parallel}(\boldsymbol{R}, t) + \boldsymbol{E}_{\perp}(\boldsymbol{0}, t) + \frac{\hbar}{m_{\mathrm{v}}}\boldsymbol{k}\times\boldsymbol{B}_0]\cdot\nabla_{\boldsymbol{k}} \\ + \frac{e^2}{4\hbar}\left(\frac{1}{m_0} + \frac{1}{m_{\mathrm{v}}}\right)(\boldsymbol{B}_0\times\boldsymbol{R})\cdot(\boldsymbol{B}_0\times\nabla_{\boldsymbol{k}})\Bigg]\tilde{f}_{\mathrm{v}}(\boldsymbol{R}, \boldsymbol{k}) = -\frac{1}{\tau_1}[\tilde{f}_{\mathrm{v}}(\boldsymbol{R}, \boldsymbol{k}) - f_{\mathrm{v}}^{\mathrm{eq}}(\boldsymbol{k})].\end{aligned} \tag{5.5}$$

Note that without the transformation (5.1) there would be a factor $1/2$ in front of the Lorentz force as well as additional terms leading in particular to a conduction current density that depends explicitly on the magnetic field. As a result, we have found in addition to the usual drift term a contribution that is quadratic in the magnetic field and cancels in the limit of free particles ($m_c \to m_0, m_v \to -m_0$). The equation for the holes is obtained from that for the electrons through the substitution $m_c \to -m_v$ and $k \to -k$. If there were not the term quadratic in $B_0$ (and the band-to-band transitions already neglected), this would be equivalent to the substitution $m_c \to m_v$ and $-e \to +e$ thus permitting the interpretation of holes as positively charged particles.

In contrast, the space dependence can often be neglected in the field of optics. When dealing with a magnetic field it is then advantageous not to perform the Fourier transform according to (3.8), but to use the $x$-space density matrix formulation. The resulting equations in this case (neglecting $eB_0^2(r^2)_{nn}/8m_0$ against $3(B_0 \times x)^2/32\mu$ in view of an expansion of the density matrix in terms of exciton wavefunctions (compare (2.13$a$)) and taking $R = 0$ as the point of reference) are

$$\left(-i\hbar\frac{\partial}{\partial t} + E_g + \frac{e}{2m_0}B_0 \cdot (L_{cc} - L_{vv}) + \tilde{\Omega}_{vc}\right)\tilde{Y}(x) = \left(-er^*_{vc} \cdot E(t) - \frac{e}{2m_0}L^*_{vc} \cdot B_0\right) \times [\delta_B(x) - \tilde{C}(x) - \tilde{D}(-x)] - \frac{e}{4m_0}x \times p^*_{vc} \cdot B_0[\tilde{C}(x) - \tilde{D}(-x)] + \frac{i\hbar}{\tau_2}\tilde{Y}(x) \tag{5.6a}$$

$$\left(-i\hbar\frac{\partial}{\partial t} + \tilde{\Omega}_{cc}\right)\tilde{C}(x) = -e[r^*_{vc}\tilde{Y}^*(-x) - r_{vc}\tilde{Y}(x)] \cdot E(t) - \frac{e}{2m_0}[L^*_{vc}\tilde{Y}^*(-x) - L_{vc}\tilde{Y}(x)] \cdot B_0 - \frac{e}{4m_0}x \times [p^*_{vc}\tilde{Y}^*(-x) + p_{vc}\tilde{Y}(x)] \cdot B_0 + \frac{i\hbar}{\tau_1}[\tilde{C}(x) - C^{eq}(x)] \tag{5.6b}$$

$$\left(-i\hbar\frac{\partial}{\partial t} + \tilde{\Omega}_{vv}\right)\tilde{D}(x) = -e[r^*_{vc}\tilde{Y}^*(x) - r_{vc}\tilde{Y}(-x)] \cdot E(t) - \frac{e}{2m_0}[L^*_{vc}\tilde{Y}^*(x) - L_{vc}\tilde{Y}(-x)] \cdot B_0 - \frac{e}{4m_0}x \times [p^*_{vc}\tilde{Y}^*(x) + p_{vc}\tilde{Y}(-x)] \cdot B_0 + \frac{i\hbar}{\tau_1}[\tilde{D}(x) - D^{eq}(x)] \tag{5.6c}$$

with the total electric field $E(t) = E_\parallel(0, t) + E_\perp(0, t)$ and the drift operators

$$\tilde{\Omega}_{vc} = -\frac{\hbar^2}{2\mu}\Delta_x + eE(t) \cdot x + \frac{e}{2}\left(\frac{1}{m_c} - \frac{1}{m_v}\right)B_0 \cdot x \times \frac{\hbar}{i}\nabla_x + \frac{3e^2}{32\mu}(B_0 \times x)^2 \tag{5.7a}$$

$$\tilde{\Omega}_{cc} = eE(t) \cdot x + \frac{e}{m_c}B_0 \cdot x \times \frac{\hbar}{i}\nabla_x \tag{5.7b}$$

$$\tilde{\Omega}_{vv} = -eE(t) \cdot x - \frac{e}{m_v}B_0 \cdot x \times \frac{\hbar}{i}\nabla_x. \tag{5.7c}$$

Note that $L_{cc}$ and $L_{vv}$ in (5.6$a$) are the only terms to be modified according to $J_{cc} = L_{cc} + S_{cc}$ and $J_{vv} = L_{vv} + S_{vv}$, respectively, when including the spin. This contribution leads to a band-splitting which depends on the strength of the magnetic field. A similar effect occurs in the drift operators (5.7) after projecting the density matrix onto exciton wavefunctions. For a realistic description of the dynamics these equations have to be extended by the Coulomb interaction treated in the literature in the time-dependent Hartree–Fock approximation [8, 11, 16, 18] or beyond [25, 26]. In magneto-optics this has already been done within the density matrix approach by Stafford and co-workers [22]. However, they omitted the magnetic contributions corresponding to the Lorentz force in the drift operators of electrons (5.7$b$) and holes (5.7$c$) as well as the terms associated with a magnetic

dipole on the right-hand sides of (5.6). In addition, the prefactor of the term, which is quadratic in $\boldsymbol{B}_0$, differs from ours in (5.7*a*) (note that there would be still a difference when using the centre-of-mass instead of the centre coordinate within our approach). This difference is supported by former investigations showing that the 'Peierls substitution', i.e. the use of effective operators $\epsilon_n(-\mathrm{i}\nabla + e(\boldsymbol{B}_0 \times \boldsymbol{r})/2\hbar)$, involves an error proportional to $\boldsymbol{B}_0^2$ [55]. Doubts about the validity of the 'Peierls substitution' have also been confirmed recently [35]. Hence, our approach suggests that one should expand the density matrix in terms of exciton wavefunctions instead of projecting it onto Landau orbitals.

## 6. Quantum transport

In this section we concentrate on the intraband drift motion in the presence of a scalar potential and therefore neglect interband transitions described by the electron–hole pair amplitude. On the other hand, we will make no simplifying assumptions about the band structure and consider the full space dependence of the scalar potential. The equations of motion can be found along the same lines as developed in section 3. We only do not apply the effective-mass approximation and retain the complete expansion of the scalar potential in (3.5). The resulting collisionless quantum Boltzmann transport equations are

$$\left(\frac{\partial}{\partial t} + \frac{\mathrm{i}}{\hbar}\{\epsilon_\mathrm{c}(\boldsymbol{k} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) - \epsilon_\mathrm{c}(\boldsymbol{k} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) - e[\Phi(\boldsymbol{R} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{k}}) - \Phi(\boldsymbol{R} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{k}})]\}\right) f_\mathrm{c}(\boldsymbol{R}, \boldsymbol{k}) = 0 \tag{6.1a}$$

$$\left(\frac{\partial}{\partial t} + \frac{\mathrm{i}}{\hbar}\{\bar{\epsilon}_\mathrm{v}(\boldsymbol{k} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) - \bar{\epsilon}_\mathrm{v}(\boldsymbol{k} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) + e[\Phi(\boldsymbol{R} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{k}}) - \Phi(\boldsymbol{R} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{k}})]\}\right) f_\mathrm{v}(\boldsymbol{R}, \boldsymbol{k}) = 0 \tag{6.1b}$$

where we have introduced the hole band structure via $\bar{\epsilon}_\mathrm{v}(\boldsymbol{k}) = -\epsilon_\mathrm{v}(\boldsymbol{k})$ and suppressed the time dependence of the scalar potential and the distribution functions. Expressions of the form $f(\boldsymbol{x} \pm \frac{1}{2}\mathrm{i}\nabla_{\boldsymbol{y}})$ are understood to be expanded into a Taylor series according to

$$f(\boldsymbol{x} \pm \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{y}}) = f(\boldsymbol{x}) \pm \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{x}} f(\boldsymbol{x}) \cdot \nabla_{\boldsymbol{y}} \pm \ldots . \tag{6.2}$$

The corresponding expression for the expectation value of the Hamiltonian (compare (4.2) and (4.3)) is

$$\langle H \rangle = \mathrm{Tr}(\rho H) = \int_V [W(\boldsymbol{R}) + \varrho(\boldsymbol{R})\Phi(\boldsymbol{R})]\,\mathrm{d}^3R \tag{6.3}$$

with the energy density

$$W(\boldsymbol{R}) = W_\mathrm{c}(\boldsymbol{R}) + W_\mathrm{v}(\boldsymbol{R}) = \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} \tfrac{1}{2}[\epsilon_\mathrm{c}(\boldsymbol{k} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) + \epsilon_\mathrm{c}(\boldsymbol{k} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}})] f_\mathrm{c}(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k + \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} \tfrac{1}{2}[\bar{\epsilon}_\mathrm{v}(\boldsymbol{k} + \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}}) + \bar{\epsilon}_\mathrm{v}(\boldsymbol{k} - \tfrac{1}{2}\mathrm{i}\nabla_{\boldsymbol{R}})] f_\mathrm{v}(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k. \tag{6.4}$$

The equations of motion (6.1) yield again the continuity equation (4.9) for the charge density $\varrho(\boldsymbol{R})$ defined in (4.8). However, the conduction current density is now given by

$$\boldsymbol{j}(\boldsymbol{R}) = \boldsymbol{j}_\mathrm{c}(\boldsymbol{R}) + \boldsymbol{j}_\mathrm{v}(\boldsymbol{R}) = -\frac{e}{(2\pi)^3}\int_{\mathrm{BZ}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!}(\tfrac{1}{2}\nabla_{\boldsymbol{R}} \cdot \nabla_{\boldsymbol{k}'})^{2n} \boldsymbol{v}_\mathrm{c}(\boldsymbol{k}')|_{\boldsymbol{k}'=\boldsymbol{k}} f_\mathrm{c}(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k + \frac{e}{(2\pi)^3}\int_{\mathrm{BZ}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!}(\tfrac{1}{2}\nabla_{\boldsymbol{R}} \cdot \nabla_{\boldsymbol{k}'})^{2n} \bar{\boldsymbol{v}}_\mathrm{v}(\boldsymbol{k}')|_{\boldsymbol{k}'=\boldsymbol{k}} f_\mathrm{v}(\boldsymbol{R}, \boldsymbol{k})\,\mathrm{d}^3k \tag{6.5}$$

where $\bar{v}_v(k) = \nabla_k \bar{\epsilon}_v(k)/\hbar$ denotes the hole group velocity. The equations of motion (6.1) together with the expressions for energy density (6.4), charge density (4.8) and conduction current density (6.5) represent a complete description of collisionless quantum transport.

In contrast, concrete applications require tractable formulations that include only the leading quantum corrections. One way of doing this is to introduce the classical momentum $p = \hbar k$ and to retain only terms with the lowest power of $\hbar$ that do not cancel. This correction turns out to be of the order $\hbar^2$ both for the equations of motion and for the energy and conduction current density. Another possibility would be to classify according to the derivatives of the given functions $\epsilon_c(k)$, $\bar{\epsilon}_v(k)$ and $\Phi(R)$. The consideration of zero- and first-order derivatives with respect to $k$ and $R$, respectively, coincides with the formulations in classical transport theory. However, as a result of keeping the second derivatives in the next step, one finds that only the energy density involves a quantum mechanical correction term. Even-order derivatives of $\epsilon_c(k)$, $\bar{\epsilon}_v(k)$ and $\Phi(R)$ cancel in the equations of motion as well as in the expression for the conduction current density. This second approach leads to the formulations presented in sections 3 and 4.

Once a scheme of approximation has been chosen the corresponding equations of motion, together with the expressions for energy and conduction current density, can serve as a starting point for the derivation of quantum hydrodynamic equations for electrons and holes.

## 7. Conclusions

We have presented a derivation of the two-band density matrix dynamics that goes beyond the usual semiconductor Bloch equations and the semiclassical Boltzmann transport equations. Our approach is based on localization properties of the Wannier functions which enables the decomposition of the effect of external fields into transition and transport contributions. The main applications beyond the standard theories concern the 'resonant' Stark effect, which originates from the light field in the drift term of the electron–hole pair amplitude, the emission of THz radiation from semiconductor heterostructures, which is related to the intraband polarization, and quantum transport, where our approach yields a general expression for the quantum correction of the energy density thus representing a rigorous basis for the derivation of quantum hydrodynamic equations. The inclusion of a static magnetic field has led to additional terms so far not considered in the field of magneto-optics and semiclassical transport theory. In concrete cases the simplified equations given in this paper have to be adapted to the situation under consideration (e.g. a heterostructure) and extended by generalization to a multi-band model including the spin as well as the induced transverse fields and the Coulomb interaction.

## Acknowledgments

We would like to thank A Stahl and R Thoma for useful discussions.

## Appendix

In this appendix we show briefly how to pass within the formalism employed in this paper from a semiclassical Hamiltonian in the original gauge to the corresponding Hamiltonian in another gauge.

The system under consideration consists of $N_0$ electrons interacting with a classical external electromagnetic field and subjected to the influence of a potential $U(\mathbf{r})$. It can be

described by the Hamiltonian

$$H(t) = \sum_{s=1}^{N_0} h_s(t) \tag{A1}$$

$$h_s(t) = \frac{1}{2m_0}[p_s + eA(r_s, t)]^2 - e\Phi(r_s, t) + U(r_s). \tag{A2}$$

Under a canonical transformation

$$T(t) = \exp\left(-\frac{\mathrm{i}}{\hbar}e\sum_{s=1}^{N_0}\chi(r_s, t)\right) \tag{A3}$$

the Hamiltonian $H(t)$ and the $N_0$-electron state satisfying the Schrödinger equation $\mathrm{i}\hbar\,\mathrm{d}|\psi(t)\rangle/\mathrm{d}t = H(t)|\psi(t)\rangle$ transform to [46–48]

$$H'(t) = T(t)H(t)T^{\dagger}(t) + \mathrm{i}\hbar\frac{\mathrm{d}T(t)}{\mathrm{d}t}T^{\dagger}(t) \tag{A4}$$

$$|\psi'(t)\rangle = T(t)|\psi(t)\rangle \tag{A5}$$

where $H'(t)$ turns out to be again of the form as given by (A1) and (A2), but in terms of potentials $A'$ and $\Phi'$ which are related to $A$ and $\Phi$ via the usual gauge transformation (2.4).

Rewriting the Hamiltonian (A4) in the occupation number representation (second quantization) then yields

$$H'(t) = \sum_{\nu,\mu}\langle\phi_\nu|h'(t)|\phi_\mu\rangle\, c_\nu^{\dagger}c_\mu \tag{A6}$$

the sums running over a complete set $\{|\phi_\nu\rangle\}$ of one-particle functions. Finally, we pass over to the Hamiltonian in the Heisenberg picture $\hat{H}'(t) = \mathcal{U}'^{\dagger}(t, t_0)H'(t)\mathcal{U}'(t, t_0)$ with the corresponding time evolution operator $\mathcal{U}'(t, t_0)$ given as the solution of $\mathrm{i}\hbar\,\mathrm{d}\mathcal{U}'(t, t_0)/\mathrm{d}t = H'(t)\mathcal{U}'(t, t_0)$. Hence

$$\hat{H}'(t) = \sum_{\nu,\mu}\langle\phi_\nu|h'(t)|\phi_\mu\rangle\,\hat{c}_\nu'^{\dagger}(t)\hat{c}_\mu'(t) \tag{A7}$$

The model used in this paper is then specified by using (2.5) in the canonical transformation (A3), choosing the Wannier functions as the complete set of one-particle functions and as a last step restricting in the two-band approximation the summation over the band indices in (A7) to one valence band and one conduction band. In order to keep the notation as simple as possible we have dropped, in the Hamiltonian (2.1*a*), the primes indicating the gauge and suppressed the time dependence of the Heisenberg operators.

## References


[1] Jacoboni C and Rossi F 1993 *Proc. NATO ASI* series B **314** ed W E Bron (New York: Plenum) pp 287–335
[2] Kadanoff L P and Baym G 1962 *Quantum Statistical Mechanics* (New York: Benjamin)
[3] Haug H 1988 *Optical Nonlinearities and Instabilities in Semiconductors* ed H Haug (San Diego: Academic)
[4] Schmitt-Rink S, Chemla D S and Haug H 1988 *Phys. Rev.* B **37** 941
[5] Henneberger K and Haug H 1988 *Phys. Rev.* B **38** 9759
[6] Zimmermann R 1988 *Phys. Stat. Solidi* b **146** 545
[7] Kuznetsov A V 1991 *Phys. Rev.* B **44** 8721
[8] Schmitt-Rink S and Chemla D S 1986 *Phys. Rev. Lett.* **57** 2752
[9] Zimmermann R and Hartmann M 1988 *Phys. Stat. Solidi* b **150** 365
[10] Zimmermann R 1990 *Phys. Stat. Solidi* b **159** 317
[11] Lindberg M and Koch S W 1988 *Phys. Rev.* B **38** 3342

[12] Kuznetsov A V 1991 *Phys. Rev.* B **44** 8721
[13] Kuhn T and Rossi F 1992 *Phys. Rev.* B **46** 7496
[14] Stahl A and Balslev I 1987 *Electrodynamics of the Semiconductor Band Edge (Springer Tracts in Modern Physics* **110***)* (Berlin: Springer)
[15] Lin J and Chiu L C 1985 *J. Appl. Phys.* **57** 1373
[16] Stahl A 1988 *Z. Phys.* B **72** 371
[17] Schlösser J and Stahl A 1989 *Phys. Status Solidi* b **153** 773
[18] Balslev I, Zimmermann R and Stahl A 1989 *Phys. Rev.* B **40** 4095
[19] Stahl A 1990 *Phys. Status Solidi* b **159** 327
[20] Schlösser J, Stahl A and Balslev I 1990 *J. Phys.: Condens. Matter* **2** 5979
[21] Zimmermann R 1990 *Festkörperprobleme (Advances in Solid State Physics 30)* (Braunschweig: Vieweg) p 295
[22] Stafford C, Schmitt-Rink S and Schaefer W 1990 *Phys. Rev.* B **41** 10000
[23] Victor K, Roskos H G and Waschke C 1994 *J. Opt. Soc. Am.* B to be published
[24] Kuhn T, Binder E, Rossi F, Lohner A, Rick K, Leisching P, Leitenstorfer A, Elsaesser T and Stolz W 1994 *Proc. NATO ASI* series B, ed R Phillips (New York: Plenum) at press
[25] Axt V M and Stahl A 1994 *Z. Phys.* B **93** 195
[26] Axt V M and Stahl A 1994 *Z. Phys.* B **93** 205
[27] Ferry D K and Zhou J-R 1993 *Phys. Rev.* B **48** 7944
[28] Mysyrowicz A, Hulin D, Antonetti A, Migus A, Maaslink W T and Morkoc H 1986 *Phys. Rev. Lett.* **56** 2748
[29] von Lehmen A, Chemla D S, Zucker J E and Heritage J P 1986 *Opt. Lett.* **11** 609
[30] Roskos H G, Nuss M C, Jagdeep S, Leo K, Miller D A B, Fox A M, Schmitt-Rink S and Köhler K 1992 *Phys. Rev. Lett.* **68** 2216
[31] Waschke C, Roskos H G, Schwedler R, Leo K, Kurz H and Köhler K 1993 *Phys. Rev. Lett.* **70** 3319
[32] Fröhlich D, Nothe A and Reimann K 1985 *Phys. Rev. Lett.* **55** 1335
[33] Fröhlich D, Wille R, Schlapp W and Weimann G 1987 *Phys. Rev. Lett.* **59** 1748
[34] Bassani F, Forney J J and Quattropani A 1977 *Phys. Rev. Lett.* **39** 1070
[35] Alexandrov A and Capellmann H 1991 *Z. Phys.* B **83** 237
[36] Jacoboni C and Reggiani L 1983 *Rev. Mod. Phys.* **55** 645
[37] Jacoboni C and Lugli P 1989 *The Monte Carlo Method for Semiconductor Device Simulation* (Berlin: Springer)
[38] Rudan M and Odeh F 1986 *COMPEL* **5** 149
[39] Thoma R, Emunds A, Meinerzhagen B, Peifer H-J and Engl W L 1991 *IEEE Trans. Electron Devices* **ED-38** 1343
[40] Woolard D L, Tian H, Trew R J, Littlejohn M A and Kim K W 1991 *Phys. Rev.* B **44** 11119
[41] Wigner E 1932 *Phys. Rev.* **40** 749
[42] Iafrate G J, Grubin H L and Ferry D K 1981 *J. Physique Coll.* **42** 307
[43] Grubin H L and Kreskovsky J P 1989 *Solid State Electron.* **32** 1071
[44] Zhou J-R and Ferry D K 1992 *IEEE Trans. Electron Devices* **ED-39** 473
[45] Zhou J-R and Ferry D K 1993 *IEEE Trans. Electron Devices* **ED-40** 421
[46] Fiutak J 1963 *Can. J. Phys.* **41** 12
[47] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1989 *Photons and Atoms: Introduction to Quantum Electrodynamics* (New York: Wiley)
[48] Felderhof B U and Adu-Gyamfi D 1974 *Physica* **71** 399
[49] Göppert-Mayer M 1931 *Ann. Phys., Lpz* **9** 273
[50] Kohn W 1959 *Phys. Rev.* **115** 809
[51] Feynman R P, Vernon F L and Hellwarth R W 1957 *J. Appl. Phys.* **28** 49
[52] Lamb W E 1952 *Phys. Rev.* **85** 259
[53] Elliott R J and Loudon R 1959 *J. Phys. Chem. Solids* **8** 382
[54] Shinada M and Tanaka K 1970 *J. Phys. Soc. Japan* **29** 1258
[55] Schnakenberg J 1963 *Z. Phys.* **171** 199