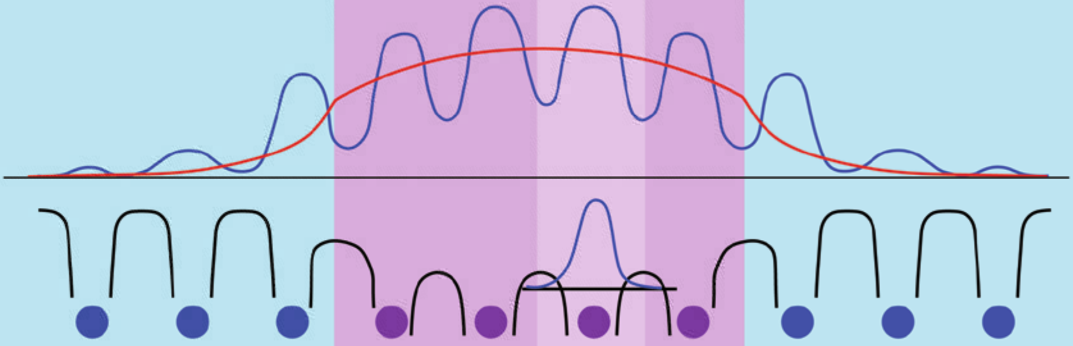

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Matthias Ehrhardt · Thomas Koprucki
Editors

Multi-Band Effective Mass Approximations

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Lecture Notes in Computational Science and Engineering

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Multi-Band Effective Mass Approximations

Advanced Mathematical Models and Numerical Techniques

Springer

Editors

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Foreword

With the rapid development of nano sciences, the structural properties of semiconductors can be arranged on an atomic scale. This has led to massive down scaling of electronic integrated circuits, compact semiconductor light sources with highest power densities, and tiny sensors that monitor various physical properties in complex environments. This development will continue in the future, and with ongoing progress in the synthesis of complex nanostructures, the inclusion of a wider field of chemical elements and as result even more functionality and better performance will be feasible.

At the heart of understanding the electronic, optical, or magnetic properties in nanostructures is the dispersion relation for electrons and holes. It represents a quantum mechanical property of the electron, namely the energy versus its wave vector. The latter can also be viewed as momentum, using the de Broglie relation. The dispersion relation contains a plethora of information, namely the phase velocity (which in classical electromagnetics is related to the refractive index), the group velocity, and the effective mass, only to name few. In free space, solving Schrödinger's equation for a single electron gives the well-known parabolic dispersion relation. Now if the electron is located in a semiconductor crystal, it is surrounded by a periodic arrangement of nuclei, a large number of core and valence electrons. Inclusion of the respective potentials in the Hamiltonian leads to a large coupled many-particle quantum mechanical problem, which, for nanostructures, cannot be solved with current numerical or analytical methods.

It is due to three formidable approximations that we can study the physical properties of nanostructures with the sophisticated mathematical and numerical methods that are presented in this book. First, the core electrons of the fully occupied orbitals can be lumped together with the nuclei, which leads to potentials of ionic cores. This removes all the equations for the core electrons from the system. The next simplification is called Born-Oppenheimer approximation: the ion cores are much heavier than the remaining valence electrons. Therefore, they move much slower and are basically stationary to the electrons. As a consequence, the electronic properties can be calculated using fixed nuclei positions, and the nuclei dynamics can be separated into an interaction Hamiltonian. At last, the so-called mean field approximation treats all valence electrons (except the electron of interest) as average background potential. That way, the electron–electron coupling can be treated by a single uncoupled effective potential, and the remaining equation resembles a single particle Schrödinger equation.

A fundamental property of this single particle equation for crystals is the periodicity of the ionic core potentials, which leads directly to Bloch wave functions as solutions, and a separation of the Hamiltonian into a part independent of the wave vector and dependent on the wave vector, containing a **k·p** term (therefore the name **k·p** is sometimes used for this equation). The presence of the periodic potential introduces band gaps in the dispersion relation and a plethora of significant deviations from the free-electron case. Time-dependent or stationary perturbation theory can be applied to solve the **k·p** Schrödinger equation in an elegant fashion, where the terms containing the wave vector are treated again as perturbation in the Hamiltonian. Hence, the solution is more exact for small wave vector magnitudes, depending on the order of perturbation included. In order to study realistic nanostructures, many more perturbations need to be added to the single particle Hamiltonian. These perturbations and the mathematics and numerics to solve the resulting Schrödinger equation is the subject of this book. They include the band-to-band coupling, spin–orbit interaction, the presence of hetero interfaces, mechanical strain, and surfaces or carrier scattering and their statistics. This way, the electronic dispersion relation (band structure) or even the carrier dynamics of complex semiconductor nanostructures can be calculated with high numerical efficiency. It gives us information such as the effective masses, the strength and energies of optical transitions or the spin–orbit interaction, or the density of states for charge carriers, which are of fundamental importance to understand electronic, optical, or magnetic properties in nano devices.

The book starts with three chapters on the physical models, from a multi-band description aiming at quantum transport properties of carriers within the multi-band formalism, to a focus on state-of-the-art **k·p** models for quantum dots, emphasizing symmetry considerations. The second part is devoted to numerical methods for solving the **k·p** type equation framework, with one chapter on the finite element method, and the second one on the plane wave expansion. In the third part, applications of the **k·p** method are presented, demonstrating the capabilities of the framework for describing challenging but nonetheless realistic situations in band structure calculations. In the final chapter, advanced mathematical topics are discussed, such as a time-dependent effective mass multi-band formalism dealing with carrier dynamics, and the topic of transparent boundary conditions for termination of the simulation domain.

The reader of this book will gain a detailed insight into the status of the multi-band effective mass method for semiconductor nanostructures. Both users of the **k·p** method and advanced researchers who want to advance the **k·p** method further will find helpful information to work with this method and use it as a tool to characterize the physical properties of semiconductor nanostructures.

Kassel, Germany
June 2014

Bernd Witzigmann

Preface

The operational principle of modern semiconductor nanostructures, such as quantum wells, quantum wires, or quantum dots, relies on quantum mechanical effects. The goal of numerical simulations using quantum mechanical models in the development of semiconductor nanostructures is threefold: First, they are needed for a deeper understanding of experimental data and of the operational principle. Second, is to predict and optimize in advance qualitative and quantitative properties of new devices in order to minimize the number of prototypes needed. Semiconductor nanostructures are embedded as an active region in semiconductor devices. Finally, the results of quantum mechanical simulations of semiconductor nanostructures can be used by upscaling methods to deliver parameters needed in semi-classical models for semiconductor devices such as quantum well lasers. This book covers in detail all these three aspects using a variety of illustrating examples.

Multi-band effective mass approximations have been increasingly attracting interest over the last decades, since it is an essential tool for effective models in semiconductor materials. This book is concerned with several mathematical models from the most relevant class of $\mathbf{k}\cdot\mathbf{p}$-Schrödinger Systems. We will present both mathematical models and state-of-the-art numerical methods to solve adequately the arising systems of differential equations. The designated audience is graduate and Ph.D. students of mathematical physics, theoretical physics and people working in quantum mechanical research or semiconductor/opto-electronic industry who are interested in new mathematical aspects.

The principal audience of this book is graduate and Ph.D. students of (mathematical) physics, research lecturer of mathematical physics, and research people working in semiconductor, opto-electronic industry for a professional reference.

Wuppertal, Germany
Berlin, Germany
June 2014

Matthias Ehrhardt
Thomas Koprucki

Contents

Part I Physical Models

Part II Numerical Methods

Part IV Advanced Mathematical Topics

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Part I
Physical Models

Chapter 1
Kinetic and Hydrodynamic Models for Multi-Band Quantum Transport in Crystals

Luigi Barletti, Giovanni Frosali, and Omar Morandi

Abstract This chapter is devoted to the derivation of **k·p** multi-band quantum transport models, in both the pure-state and mixed-state cases. The first part of the chapter deals with pure-states. Transport models are derived from the crystal periodic Hamiltonian by assuming that the lattice constant is small, so that an effective multi-band Schrödinger equation can be written for the envelopes of the wave functions of the charge carriers. Two principal approaches are presented here: one is based on the Wannier-Slater envelope functions and the other on the Luttinger-Kohn envelope functions. The concept of Wannier functions is then generalized, in order to study the dynamics of carriers in crystals with varying composition (heterostructures). Some of the most common approximations, like the single band, mini-bands and semi-classical transport, are derived as a limit of multi-band models. In the second part of the chapter, the mixed-state (i.e. statistical) case is considered. In particular, the phase-space point of view, based on Wigner function, is adopted, which provides a quasi-classical description of the quantum dynamics. After a theoretical introduction to the Wigner-Weyl theory, a two-band phase-space transport model is developed, as an example of application of the Wigner formalism to the **k·p** framework. The third part of the chapter is devoted to quantum-fluid models, which are formulated in terms of a finite number of macroscopic moments of the Wigner function. For mixed-states, the maximum-entropy closure of the moment equations is discussed in general terms. Then, details are given on the

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multi-band case, where “multi-band” is to be understood in the wider sense of “multi-component wave function”, including therefore the case of particles with spin or spin-like degrees of freedom. Three instances of such systems, namely the two-band **k**·**p** model, the Rashba spin-orbit system and the graphene sheet, are examined.

1.1 Introduction

The derivation of mathematical models for particle transport in semiconductor devices of last generation cannot discard quantum effects. In particular, quantum dynamics involving two or several energy bands of a semiconductor, forces to consider “quantum multi-band models”, that are the subject of the present chapter. As an example, particle transitions between the conduction and the valence band states could in some case increase considerably the peak-to-valley ratio of the resonant current through a double-barrier. Resonant interband tunneling diodes (RITD) are examples of devices which exploit this phenomenon; they are of paramount importance in nanotechnology for their applications to high-speed miniaturized systems [101, 118].

Quantum multi-band models have largely been formulated and analyzed in the recent past (see references throughout this chapter). Similarly to other models for semiconductor devices, they can be divided in two main classes: pure-state (non statistical) and mixed-state (statistical) models. The former are based on wave functions, and, therefore, on Schrödinger equation, while the latter require a density-operator framework which can be more conveniently formulated in terms of the phase-space formalism provided by Wigner functions. Such a quasi-classical description provides some advantages in terms of simplicity in the physical interpretation and the availability of feasible method for the inclusion of irreversible processes like thermalization or phase breaking mechanisms. Another category of models is that of quantum-fluid models which, analogously to classical fluids, are formulated in terms of a finite number of macroscopic moments of the Wigner function. The equations of a quantum fluid, therefore, can be deduced from the underlying phase-space description.

In this chapter, we describe the multi-band models that have recently been formulated in both classes (statistical and non-statistical). Attention is given to the definitions of the relevant quantities which characterize each model and to the advantages and disadvantages of each model compared to others. The technical details of the derivations of the various models, as well as the rigorous proofs of consistency and existence of the solutions, are diverted directly to the papers where the models have been described and that are cited in the chapter.

The chapter is organized as follows. In Sect. 1.2 we briefly recall the **k**·**p** envelope-function theory. We first discuss the Wannier-Slater approach and, secondly, the Luttinger-Kohn approach. Since in many practical cases the dynamics of carriers in crystals with varying composition (heterostructures) is of considerable interest, then a section is devoted to non-uniform materials, introducing the concept of generalized Wannier functions. Since the microscopic simulation of the particle transport in a fully quantum many-band context is extremely complex and usually unfeasible, the last part of Sect. 1.2 is devoted to review a few theoretical works where some of the most common approximations, like the single band, mini-bands and semi-classical transport, are derived as a limit of a multi-band model. In Sect. 1.3 we deal with the statistical kinetic models based on the Wigner-function approach. The multi-band **k·p** models can be easily adapted to the Wigner-Weyl framework, providing a quasi-classical description of the quantum motion which offers some advantages in terms of simplicity in the physical interpretation. As an example of the application of the Wigner formalism to the **k·p** framework, a two-band model is considered. Section 1.4 is devoted to quantum fluid models. After a short review of quantum hydrodynamics in the single-band/scalar case, we turn to the multi-band case, indicating by this term a general framework where discrete degrees of freedom are involved. Rather than developing a general theory (which is probably beyond to come), we shall examine three instances, namely the two-band **k·p** model, the Rashba spin-orbit system and the transport of electrons on a graphene sheet.

1.2 Envelope k·p Models

The study of periodic crystalline solids leads naturally to a representation of the electronic ground state in terms of Bloch waves. They are the Schrödinger wave functions of particles with a given momentum that interact with the periodic "frozen" ionic lattice. As an alternative, the particle motion can be represented in terms of localized orbitals or Wannier functions. They are formally defined in terms of a suitable unitary transformation applied to the Bloch orbital. In the simplest case the link between the Bloch and the Wannier waves is the Fourier transform from the reciprocal to the direct lattice space. The Wannier representation is a useful starting point for various formal developments, such as the semiclassical theory of electron dynamics or more generally, the envelope function methods [74].

Many different methods have been employed for the study of the electronic structure and the optical properties of the semiconductors. In particular, the envelope function, the tight-binding, the pseudo-potential, and the density functional methods constitute the most common approaches. For the simplicity and ease of interpretation, the envelope-function method is one of the most developed approach for modeling the electrons motion in bulk semiconductor and in heterostructures. The envelope-function approach is a quite general theory and applies both to periodic and quasi-periodic materials. Various details concerning the physical composition of the sample and the band structures can be easily included. Moreover, the envelope-function method represents the theoretical basis of the common effective-mass approximation [5]. It provides a detailed description of conduction and valence subbands near the center of the Brillouin zone and it is widely used to calculate confined-state energies and subband structure of III–V and II–VI semiconductor systems. A simple and rather complete description of the spectrum of a bulk semiconductor around the band gap includes the conduction band and the three highest valence bands, namely the heavy-hole, light-hole, and spin-split-off bands. More complex semiconductors like strained-layer heterostructures, strained crystals and indirect-gap material are characterized by a more structured valence band. A variety of envelope models, from two to a total of eight bands are found in literature. All the electronic properties of the materials enter in the model via few macroscopic parameters (Luttinger-Kohn parameters) that are easily characterized by direct measurement on the bulk crystals [13, 36].

One of the main interest in the study of multi-band models is the possibility to reproduce the band-to-band tunneling. This phenomenon explains the transition of a particle between two disconnected parts of the band diagram. In many situations, the various branches of the energy spectrum of a semiconductor belong to spectral regions which are separated by a certain energy gap (forbidden region). Particles can travel from one band to one other (for example from the conduction to the valence band) by two distinguished mechanisms: (1) overcoming the energy gap by gaining or loosing energy; (2) tunneling the energy gap. The first mechanism is an incoherent process that involves the interaction of the particle with some other particle or dynamical field. The second mechanism takes place when a static field (and in this case this phenomenon is known as Zener tunneling) or a (usually strong) discontinuity in the ionic lattice is present. The particle transition from one band to the other can be easily characterized from a mathematical point of view. Let Ψ represent the Schrödinger wave function of a particle in the solid. The conservation of the total particle probability is expressed by the normalization of the L^2 norm $\|\Psi(t)\|_{L^2} = 1$ for each time t. The description of the particle motion, in terms of a multi-band approach, requires the projection of the wave function in a suitable orthonormal set of given functions $\phi_{n,\mathbf{R}}$

$$\Psi(\mathbf{x}, t) = \sum_{n,\mathbf{R}} f_n(\mathbf{R}, t)\phi_{n,\mathbf{R}}(\mathbf{x}) .$$

The index n is denoted band index and $\mathbf{R}$ are the vectors of the lattice sites. The new unknowns of the problem $f_n(\mathbf{R}, t)$ are defined envelope functions. The conservation of the total probability and the orthonormality of the $\phi_{n,\mathbf{R}}$ imply that the sum over n and $\mathbf{R}$ of the squared modulus of the envelope functions is constant in time $\sum_n \|f_n\|^2_{\ell^2_{\mathbf{R}}} = 1$, where $\|f_n\|^2_{\ell^2_{\mathbf{R}}} \equiv \sum_{\mathbf{R}} |f_n(\mathbf{R}, t)|^2$. In general $\frac{\partial}{\partial t}\|f_n\|_{\ell^2_{\mathbf{R}}} \neq 0$ holds true. Since $\|f_n\|^2_{\ell^2_{\mathbf{R}}}$ is interpreted as the probability to find the particle in the n-th band, the previous relation is the mathematical formulation of the band transition process. In particular, the situation where there exists an index n such that $\frac{\partial}{\partial t}\|f_n\|_{\ell^2_{\mathbf{R}}} \simeq 0$, is indicated by single band motion.

In the following sections we introduce some of the most common $\mathbf{k}{\cdot}\mathbf{p}$ models.

1.2.1 Wannier-Slater Envelope Functions Approach

The motion of electrons in a semiconductor is governed by the effective one-electron potential $U(\mathbf{x})$, generated by the crystal ions with the periodicity property

$$U(\mathbf{x}+\mathbf{R}) = U(\mathbf{x})$$

for all vectors $\mathbf{R}$ of the Bravais lattice $\mathscr{L}$ of the crystal. The total single particle Hamiltonian is $H = \frac{p^2}{2m} + U(\mathbf{x})$, where $\mathbf{p} = -i\hbar\nabla$ is the momentum operator and $p = |\mathbf{p}|$, m is the electron mass, and $\hbar$ is the Planck's constant over 2π. From the Bloch's theorem it is well-known that the one-electron Hamiltonian H has a complete system of eigenfunctions $|n,\mathbf{k}\rangle$ with eigenvalues $E_n(\mathbf{k})$ (that in the solid state framework are usually defined energy bands)

$$H\,|n,\mathbf{k}\rangle = E_n(\mathbf{k})\,|n,\mathbf{k}\rangle\ . \tag{1.1}$$

In the position representation the Bloch functions can be written in the form

$$b_n(\mathbf{x},\mathbf{k}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}}u_{n,\mathbf{k}}(\mathbf{x}) \equiv \langle\mathbf{x}|n,\mathbf{k}\rangle, \tag{1.2}$$

where $\mathbf{k}$ is the quasimomentum (or crystal momentum) running over the first Brillouin zone B. The first Brillouin zone is a special primitive cell in reciprocal space $\mathscr{L}^*$, defined as all points $\mathbf{k} \in \mathbb{R}^3$ which are closer to the Γ point than to any other point of $\mathscr{L}^*$. The Bloch wave are completely characterized by their behavior in a single Brillouin zone, in fact

$$u_{n,\mathbf{k}}(\mathbf{x}+\mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{x})\,.$$

The Bloch functions are normalized as

$$\int_{\mathbb{R}^3} b_n(\mathbf{x},\mathbf{k}) b_n(\mathbf{x},\mathbf{k}')\ \mathrm{d}\mathbf{x} = |B|\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}')\,,$$

where $|B|$ denotes the measure of the Brillouin zone. Hereafter, the delta function with continuous variable denotes the Dirac's distribution and with discrete suffix denotes the Kronecker's delta. The set of the Bloch functions provides a (generalized) basis of the L^2 space. Any function $\Psi \in L^2$ can be thus expanded as

$$\Psi(\mathbf{x}) = \sum_n \int_B \varphi_n(\mathbf{k}) b_n(\mathbf{x},\mathbf{k})\ \mathrm{d}\mathbf{k}, \tag{1.3}$$

where

$$\varphi_n(\mathbf{k}) = \int_{\mathbb{R}^3} \overline{b}_n(\mathbf{x},\mathbf{k})\Psi(\mathbf{x})\ \mathrm{d}\mathbf{x}\,, \tag{1.4}$$

with the bar denoting complex conjugation.

Following [114], we define the Wannier-Slater envelope functions by the Fourier transform of $\varphi_n(\mathbf{k})$

$$f_n(\mathbf{x}) = \frac{1}{(2\pi)^{3/2}} \int_B \varphi_n(\mathbf{k})\, \mathrm{e}^{i\mathbf{x}\cdot\mathbf{k}}\, \mathrm{d}\mathbf{k}\,. \tag{1.5}$$

If Ψ represents the particle wave function in the crystal, the square modulus of $f_n(\mathbf{x})$ is proportional to the probability to find the particle in the n-th energy band. We remark that, by definition, the Fourier transform of the Wannier envelope functions f_n is compactly supported in the first Brillouin zone. Consequently, any spatial oscillation with wave length smaller than the lattice constant cannot be present in f_n. For that reason, the envelope functions can be considered a class of intrinsically smooth functions. On the contrary, the original function Ψ and the Bloch functions $b_n(\mathbf{x}, \mathbf{k})$ may display high oscillations induced by the periodic ionic potential. When projected on the Wannier-Slater basis, these high frequency oscillations are filtered to high energy bands. One of the advantages of the envelope function theory is that for many purposes, the knowledge of the full wave function is not longer necessary and only few bands have to be considered. The relationship between the Wannier envelope functions and the full wave function is given by

$$f_n(\mathbf{x}) = \int_{\mathbb{R}^3} \overline{a}_n(\mathbf{x}', \mathbf{x})\Psi(\mathbf{x}')\, \mathrm{d}\mathbf{x}'\,, \tag{1.6}$$

where the Wannier functions a_n are defined by

$$a_n(\mathbf{x}, \mathbf{x}') = \frac{1}{(2\pi)^{3/2}} \int_B b_n(\mathbf{x}, \mathbf{k})\mathrm{e}^{-i\mathbf{x}'\cdot\mathbf{k}}\, \mathrm{d}\mathbf{k}\,. \tag{1.7}$$

Conversely, the wave function in terms of the Wannier functions is given by

$$\Psi(\mathbf{x}) = \sum_n \frac{1}{|B|} \int_{\mathbb{R}^3} a_n(\mathbf{x}, \mathbf{x}') f_n(\mathbf{x}')\; \mathrm{d}\mathbf{x}'. \tag{1.8}$$

In this section we discuss the derivation of the Wannier-Slater model, that essentially consists in replacing as unknown of the problem the original wave function Ψ with the envelope functions defined in Eq. (1.5). According to (1.1), an ideal homogeneous material is completely described by the Bloch functions. The utility of the expansion given in (1.8) becomes evident when an external non periodic field is added to the ionic potential. For the sake of simplicity, we consider the effect of a purely electrostatic potential denoted by V. In particular, V may take in account different effects, like the device energy-band offset for the heterojunctions, the bias voltage applied across the device, the contribution from the doping impurities and from the self-consistent field produced by the mobile electronic charge.

The dynamics of the Wannier envelope functions can be deduced from the Schrödinger equation for Ψ and Eq. (1.6). Following [1] (see also [14] for the details of the derivation), we have

$$i\hbar \frac{\partial f_n}{\partial t}(\mathbf{x},t) = \tilde{E}_n(-i\nabla)\, f_n(\mathbf{x},t) + \sum_{n'} \int_{\mathbb{R}^3} V^W_{nn'}(\mathbf{x},\mathbf{x}') f_{n'}(\mathbf{x}',t)\ \mathrm{d}\mathbf{x}'. \tag{1.9}$$

Here,

$$V^W_{nn'}(\mathbf{x},\mathbf{x}') = \frac{1}{|B|} \int_{\mathbb{R}^3} \overline{a}_n(\mathbf{y},\mathbf{x})\, V(\mathbf{y})\, a_n(\mathbf{y},\mathbf{x}')\ \mathrm{d}\mathbf{y} \tag{1.10}$$

are matrix-elements of the external potential with respect to the Wannier functions and $\tilde{E}_n(-i\nabla)$ are pseudo-differential operators associated to the energy bands with a cut-off outside the Brillouin zone, namely

$$\tilde{E}_n(-i\nabla)\, f_n(\mathbf{x}) = \frac{1}{(2\pi)^3} \int_B E_n(\mathbf{k})\, f_n(\mathbf{x}')\, \mathrm{e}^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}\ \mathrm{d}\mathbf{x}'\ \mathrm{d}\mathbf{k}.$$

The system (1.9) defines an infinite hierarchy of coupled equations. As stated before, the envelope function f_n represents the probability to find the electron in the n-th band. This is equivalent to say that the f_n envelope functions describe particles whose energy is around the band edge E_n. For this reason it seems reasonable to ignore the contribution of all the envelope functions of the remote bands $E_{n'}$ such that $|E_n - E_{n'}| \gg 1$. We remark that, despite this argument is roughly correct, in some case the remote bands could influence significatively the particle motion around the Fermi energy [63, 115].

1.2.1.1 Approximated Dynamics

In order to introduce some simple and quite general approximations it is convenient to write the set of equations (1.9) in the Fourier transformed space. We obtain

$$i\hbar \frac{\partial \varphi_n}{\partial t}(\mathbf{k}) = E_n(\mathbf{k})\varphi_n(\mathbf{k}) + \sum_{n'} \int_B \langle n,\mathbf{k}|V|n',\mathbf{k}'\rangle \varphi_n(\mathbf{k}')\, d\mathbf{k}', \tag{1.11}$$

where we use the Dirac's bracket notation in order to compact the notation. After some algebra the previous system can be recast as (see [84] for more details)

$$\begin{aligned} i\hbar \frac{\partial \varphi_n}{\partial t}(\mathbf{k}) &= E_n(\mathbf{k})\varphi_n(\mathbf{k}) + \int_B \tilde{V}(\mathbf{k}-\mathbf{k}')\varphi_n(\mathbf{k}')\, d\mathbf{k}' \\ -i\frac{\hbar^2}{m_0} \sum_{n'\neq n} \int_B \tilde{V}(\mathbf{k}-\mathbf{k}')\varphi_{n'}(\mathbf{k}') &\frac{(2\pi)^3}{\Omega} \int_{\text{u-cell}} \overline{u_{n,\mathbf{k}}}(\mathbf{x}) \frac{\mathbf{k}-\mathbf{k}'}{\triangle E_{n,n'}} \cdot \nabla u_{n'}(\mathbf{k}',\mathbf{x})\, d\mathbf{x}\, d\mathbf{k}', \end{aligned} \tag{1.12}$$

where $\tilde{V}$ denotes the Fourier transform of the potential V, Ω is the volume of the unitary cell (u-cell) and

$$\triangle E_{n,n'}(\mathbf{k},\mathbf{k}') \equiv E_{n'}(\mathbf{k}') - E_n(\mathbf{k}) + \frac{\hbar^2}{2m_0}\left(k'^2 - k^2\right) .$$

This set of equations is still too complex for practical applications. Anyway, it is in a form that can be easily simplified. The idea is to expand with respect to **k** the last term of Eq. (1.12). In particular, at the leading order we get

$$-i \sum_{n' \neq n} \frac{\hbar^2 \mathbf{P}_{n,n'}}{m_0 \triangle E_{n,n'}} \cdot \int_B \left(\mathbf{k} - \mathbf{k}'\right) \tilde{V}(\mathbf{k} - \mathbf{k}') \varphi_{n'}(\mathbf{k}')\, d\mathbf{k}' , \tag{1.13}$$

where

$$\mathbf{P}_{n,n'} = \frac{(2\pi)^3}{\Omega} \int_{\mathrm{u-cell}} \overline{u_{n,\mathbf{0}}}(\mathbf{x}) \nabla u_{n',\mathbf{0}}(\mathbf{x})\, \mathrm{d}\mathbf{x} . \tag{1.14}$$

After the **k** expansion is performed, the set of equations can be restored in terms of the original variable f_n by applying the inverse Fourier transform. We give here the final result in the simplest case where only two bands ("conduction" and "valence") are taken into account and the parabolic band approximation (with positive curvature for the conduction and negative for the valence band) is assumed

$$\begin{cases} i\hbar \dfrac{\partial f_c}{\partial t} = -\dfrac{\hbar^2}{2m_c^*} \Delta f_c + V f_c + E_c f_c - \dfrac{\hbar^2 \mathbf{P}_{c,v} \cdot \nabla V}{m_0 E_g} f_v \\ i\hbar \dfrac{\partial f_v}{\partial t} = \dfrac{\hbar^2}{2m_v^*} \Delta f_v + V f_v + E_v f_v - \dfrac{\hbar^2 \mathbf{P}_{c,v} \cdot \nabla V}{m_0 E_g} f_c \end{cases} . \tag{1.15}$$

Here m_n^* is the effective mass in the n-band. These equations describe the intraband dynamics and contain an interband coupling, proportional to the momentum matrix element **P**, that is responsible for tunneling between different bands induced by the applied electric field proportional to the gradient of V.

1.2.2 Luttinger-Kohn Envelope Functions

A different definition of envelope function was given by Luttinger and Kohn [70] (see also [15, 30]). The crucial observation is that the set of the periodic functions $u_{n,\mathbf{k}}(\mathbf{x})$ is complete for each fixed value of the quasi-momentum **k**. For that reason, all the previous expansion formulae are still valid if we substitute formally $u_{n,\mathbf{k}}(\mathbf{x})$ with $u_{n,\mathbf{0}}(\mathbf{x})$. More precisely, Eq. (1.8) becomes

$$\begin{aligned} u_{n,\mathbf{k}} \quad &: \Psi(\mathbf{x}) = \frac{1}{|B|(2\pi)^{3/2}} \sum_n \sum_j f_n(\mathbf{R}_j) \int_B u_{n,\mathbf{k}}(\mathbf{x}) \mathrm{e}^{-i\left(\mathbf{x}-\mathbf{R}_j\right)\cdot\mathbf{k}} \, \mathrm{d}\mathbf{k} \\ u_{n,\mathbf{k}} \to u_{n,\mathbf{0}} \quad &: \Psi(\mathbf{x}) = \frac{1}{|B|} \sum_n \sum_j f_n(\mathbf{R}_j) u_{n,\mathbf{0}}(\mathbf{x}) \int_B \mathrm{e}^{-i\left(\mathbf{x}-\mathbf{R}_j\right)\cdot\mathbf{k}} \, \mathrm{d}\mathbf{k} \\ \Psi(\mathbf{R}_i) &= \sum_n \sum_j \delta_{i,j} f_n(\mathbf{R}_j) u_{n,\mathbf{0}}(\mathbf{R}_i) = \sum_n f_n(\mathbf{R}_i) u_{n,\mathbf{0}}(\mathbf{R}_i) \end{aligned}$$

where the $\mathbf{R}_i$ denote the atomic sites and we substituted the integral over the space with a sum over the atomic sites (which gives the correct normalization). Interpolation over all the space gives the expansion formula

$$\Psi(\mathbf{x}) = \sum_n f_n(\mathbf{x}) u_{n,\mathbf{0}}(\mathbf{x}) \; . \tag{1.16}$$

This formula is the starting point of the Luttinger-Kohn (L-K) procedure. The Schrödinger equation takes the form

$$i\hbar \frac{\partial \varphi_n(\mathbf{k})}{\partial t} = \sum_{n'} \int_B \mathscr{H}^{kp}_{nn'}(\mathbf{k}, \mathbf{k}') \, \varphi_{n'}(\mathbf{k}') \, \mathrm{d}\mathbf{k}' \tag{1.17}$$

where, coherently with Eq. (1.5), $\varphi_n(\mathbf{k})$ is the Fourier transform of the envelope function $f_n(\mathbf{x})$. The Hamiltonian matrix elements are

$$\mathscr{H}^{kp}_{nn'}(\mathbf{k}, \mathbf{k}') = \left[\left(E_n + \frac{\hbar^2 k^2}{2m_0} \right) \delta_{nn'} + \frac{\hbar}{m_0} \mathbf{k}\cdot\mathbf{P}_{nn'} \right] \delta(\mathbf{k}-\mathbf{k}') + \tilde{V}(\mathbf{k}-\mathbf{k}')\delta_{nn'} \; . \tag{1.18}$$

In order to proceed, it is convenient to consider the quasi-unitary transformation Θ that diagonalizes the Hamiltonian in the momentum space up to second order in $\mathbf{k}$. The new Hamiltonian reads

$$\mathscr{H}^{LK} = \Theta^{-1} \mathscr{H}^{kp} \Theta \; , \tag{1.19}$$

the matrix elements of Θ are

$$\langle n, \mathbf{k} | \Theta | n', \mathbf{k}' \rangle_{kp} = \left(\delta_{nn'} - \frac{\hbar}{m_0} \frac{\mathbf{P}_{nn'}\cdot\mathbf{k}}{\Delta E_{nn'}} \right) \delta(\mathbf{k}-\mathbf{k}') \, , \tag{1.20}$$

where $\langle \mathbf{x} | n, \mathbf{k} \rangle_{kp} = u_{n,0}(\mathbf{x}) e^{i\mathbf{kx}}$. Equation (1.19) defines a basis rotation. The elements of the new basis correspond to an expansion of the $u_{n,\mathbf{k}}(\mathbf{x})$ functions up to the first order in $\mathbf{k}$

$$\langle \mathbf{x} | n, \mathbf{k} \rangle_{LK} = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}} \left(u_{n,\mathbf{0}}(\mathbf{x}) + \mathbf{k} \left. \frac{\partial u_{n,\mathbf{0}}(\mathbf{x})}{\partial \mathbf{k}} \right|_{\mathbf{0}} \right) \, . \tag{1.21}$$

Applying the Fourier transform, we obtain the evolution equation for the Luttinger-Kohn envelope function. As a final result, we report here the complete Luttinger-Kohn four band model (we ignore the spin degeneracy) for direct band gap semiconductors like GaAs. This model takes into account two light and two heavy holes branches. The equation of motion takes the form of a Schrödinger equation with effective Hamiltonian. The expansion given in (1.16) describes the projection of the solution on the four degenerate Bloch wave functions at the center of the Brillouin zone. The set of the four envelope functions can be arranged in a vector

$$F = (f_{3/2}, f_{1/2}, f_{-1/2}, f_{-3/2}) ,$$

where the $\pm 3/2$ and the $\pm 1/2$ components describe the heavy and the light hole band, respectively (see [20] for more details). The Hamiltonian of the system is

$$\mathscr{H}^{LK} = \begin{pmatrix} P+Q & -S & R & 0 \\ -S^* & P-Q & 0 & R \\ R^* & 0 & P-Q & S \\ 0 & R^* & S^* & P+Q \end{pmatrix} , \tag{1.22}$$

where the symbol $*$ denotes the formal adjoint. The matrix elements are given in terms of the Luttinger parameters $\gamma_1, \gamma_2, \gamma_3$ [35]

$$\begin{aligned} P &= \frac{\hbar^2}{2m}\gamma_1 \Delta , \\ Q &= \frac{\hbar^2}{2m}\gamma_2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} - 2\frac{\partial^2}{\partial z^2} \right) , \\ R &= \frac{\hbar^2}{2m}\sqrt{3}\left[-\gamma_2 \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} \right) + 2i\gamma_3 \frac{\partial}{\partial y}\frac{\partial}{\partial x} \right] , \\ S &= \frac{\hbar^2}{m}\sqrt{3}\gamma_3 \left(\frac{\partial^2}{\partial x^2} - i\frac{\partial^2}{\partial y^2} \right) \frac{\partial}{\partial z} . \end{aligned}$$

1.2.3 Non Uniform Materials and Generalized Wannier Functions

In the previous sections, the derivation of the **k·p** models have been focused on the description of a uniform bulk material in the presence of some small perturbation field. In many practical cases, the crystal translation symmetry is broken (or considerably affected) by various factors like the presence of a strong external electric or magnetic field, impurity, or, in graded mixed semiconductor and graded heterojunctions, by the variation of chemical composition. An important theoretical effort was devoted to understand how the simple models based on the effective mass equation should be modified in order to incorporate all the aforementioned effects. The first attempts to describe the dynamics of carriers in crystals with varying composition was based on the phenomenological assumptions of a position-dependent energy gap and of a position-dependent effective mass. In this approach, the particles move in a force field, the strength of which depends on the band they occupy [68, 112]. Although this assumption could be considered reasonable for systems that deviate slightly from the ideal case (like for example in semiconductors with highly diluted impurities), serious problems arise when abrupt junctions between two different materials are considered. In this case, a common approximation consists in discarding the difference between the band edge Bloch functions in the two different materials. The heterostructures are thus characterized in terms of their bulk properties alone. Theoretical studies proved the foundation of such an hypothesis for slowly varying perturbation and for some particular abrupt junctions [48].

The ground properties of a non-uniform material and the study the interface effects could be in principle deduced by a microscopic approach based for example on the density functional theory. Anyway, the computational cost demanded for the solution of such models is extremely high and the inclusion of dynamical effects is still unfeasible. One of the main difficulties connected with the study of the interfaces is to provide an accurate approximation of the Bloch functions between the two media. A number of envelope-function models incorporating this difference have been proposed in recent years, but most of these requires extensive microscopic calculations. A widely used approach assumes a “symmetrized” form of the contact Hamiltonian. Few examples of different solutions to the question are given in [4, 30, 80, 85]. The description of position-dependent material properties is most easily attached by using a localized basis in the direct space such as the Wannier functions presented in the previous section. The Wannier functions play a central role in qualitative as well as quantitative aspects of the one-electron theory of solids. Differing from the elements of the Bloch basis, the Wannier functions are not eigenfunctions of the Hamiltonian. They have the theoretical advantage that in many cases they are exponentially localized around a given lattice cell. This particularly useful property makes the Wannier functions an interesting object for the description of a wide class of complex materials [59]. In particular, based on the theory of ordinary differential equations, Kohn in 1959 showed a rigorous result of exponential localization of the Wannier functions for a one-dimensional lattice [64]. An important contribution toward the generalization to higher dimension was given by Cloizeaux that proved the exponential localization in arbitrary dimension for a single isolated Bloch band [37]. One of the difficulties for a possible extension of this result that consider many bands relies on the lake of regularity around the regions where the bands cross [91]. For more recent achievements for two and three dimensions insulators see [31, 94]. Despite these theoretical results, it is anyway quite difficult to construct such a maximally localized Wannier basis. Indeed, for the application of the envelope function method to complex electronic devices, other approaches are also considered in literature. As an example, in the following, we will discuss the Foreman approach to non-uniform lattices [49]. In this method, the evolution equations for the envelope functions take the form of local, spatially varying, **k**·**p** equations, with additional terms describing the explicit effects of the interface or inhomogeneity. In order to describe a graded crystal, Foreman defined the following quasi-periodic ionic potential

$$\mathscr{W}(\mathbf{x}) = \frac{1}{\Omega(2\pi)^d} \sum_i \mathrm{W}(\mathbf{x}, \mathbf{R}_i) \int_B e^{i(\mathbf{R}_i - \mathbf{x})\mathbf{k}} \, \mathrm{d}\mathbf{k} \,. \tag{1.23}$$

Here, the potential $\mathrm{W}(\mathbf{x}, \mathbf{R}_i)$ is periodic with respect the first variable, $\mathrm{W}(\mathbf{x}+\mathbf{R}_j, \mathbf{R}_i) = \mathrm{W}(\mathbf{x}, \mathbf{R}_i)$ for all i, j and the $\mathbf{R}_i$ run on the atomic sites. The idea of this representation is that the second variable of W labels the macroscopic position on the crystal lattice while the first gives the fine resolution around each Wigner-Seitz cell. The integral on the quasi-momentum in (1.23), can be viewed as a continuous function approximating the Dirac's delta in $\mathbf{R}_j$ (more precisely, it tends to a Dirac's delta when the first Brillouin zone extends to infinity). With this remark, it becomes evident that the real potential $\mathscr{W}(\mathbf{x})$ is nearly equal to the value of the periodic potential $\mathrm{W}(\mathbf{x}, \mathbf{R}_i)$ with $\mathbf{R}_i$ equal to the coordinate of the cell containing $\mathbf{x}$. By using this definition it is possible to describe a large class of non-homogeneous media (more details are given in [48]). In particular, in this approach the existence of a common symmetry group of $\mathrm{W}(\mathbf{x}, \mathbf{R}_i)$ for all $\mathbf{R}_i$ and, consequently, a unique first Brillouin are assumed.

The essential element of the Foreman approach is to obtain a localized-in-space basis that extends the definition given by Luttinger and Kohn. The new basis functions are defined as

$$\chi_n(\mathbf{x}, \mathbf{R}_j) = u_{n,\mathbf{0}}\left(\mathbf{x}, \mathbf{R}_j\right) \frac{1}{(2\pi)^d} \int_B e^{i(\mathbf{R}_j - \mathbf{x})\mathbf{k}} \, \mathrm{d}\mathbf{k} \,, \tag{1.24}$$

where, coherently with (1.16), the periodic function $u_{n,\mathbf{0}}$ is the center-band periodic part of the Bloch wave related to a "virtual" bulk lattice obtained by the periodical rearrangement of the $\mathbf{R}_j$ Wigner-Seitz cells. More precisely, $u_{n,\mathbf{0}}(\mathbf{x}, \mathbf{R}_j)$ is obtained by the eigenvalue equation

$$\left[-\frac{\hbar^2}{2}\Delta_{\mathbf{x}} + \mathrm{W}(\mathbf{x}, \mathbf{R}_i)\right] u_{n,\mathbf{0}}\left(\mathbf{x}, \mathbf{R}_j\right) = E_n^j \, u_{n,\mathbf{0}}\left(\mathbf{x}, \mathbf{R}_j\right) \,. \tag{1.25}$$

It is possible to prove that the wave function ψ can be expanded in the extended L-K basis as

$$\psi(\mathbf{x}, t) = \sum_{n,j} f_n(\mathbf{R}_j, t) \chi_n(\mathbf{x}, \mathbf{R}_j) \,. \tag{1.26}$$

Since the aim of the use of the Foreman approach is to provide a theoretical basis for the description of the particle motion in a graded semiconductor, here we