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Ultrafast Optics and Relaxation Dynamics
Ermin Malic and Andreas Knorr

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Ermin Malic and Andreas Knorr

Graphene and Carbon Nanotubes
Ultrafast Relaxation Dynamics and Optics

With a Contribution by Stephan Winnerl

WILEY-VCH Verlag GmbH & Co. KGaA
To

Kati
Yvette, Paula, and Hannah
Claudia and Noah
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Preface

In this book, we review recent progress in the field of optics and ultrafast processes in carbon nanostructures. The focus lies on the intensive theoretical research on graphene and carbon nanotubes performed at the Technische Universität Berlin combined with a number of collaborations with experimental groups worldwide. Parts of the book are based on the habilitation theses of the authors.

The key for designing and engineering novel carbon-based optoelectronic devices is a microscopic understanding of their pronounced optical properties as well as of the ultrafast carrier relaxation dynamics. The presented density matrix formalism offers microscopic tools to reveal an optical fingerprint, which unambiguously characterizes each carbon nanostructure. Furthermore, it enables us to track the path of optically excited carriers towards equilibrium – resolved in time, momentum, and angle. It treats carrier–light, carrier–carrier, and carrier–phonon interactions on the same microscopic footing allowing a study of the coupled carrier, phonon, and coherence dynamics. Combined with tight-binding wave functions, it does not rely on further adjustable parameters. A comparison with modern high-resolution experiments leads to new insights into the underlying elementary processes, which is a crucial prerequisite for exploiting the exceptional application potential of carbon-based materials.

The main part of the book introduces the reader to the ultrafast nanoworld of graphene and carbon nanotubes including their unique properties and future perspectives. It offers a theoretical foundation based on equations derived within an in-depth appendix. Furthermore, it reviews recent experimental techniques on pump-probe spectroscopy accessing ultrafast carrier relaxation within a guest contribution by Stephan Winnerl. The combination of theory and experiment throughout the book as well the connection between the main results and detailed theoretical derivations in the appendix only requiring knowledge of basic quantum mechanics makes the book suitable for theoreticians and experimentalists, for researchers and graduate students, and for physicists and engineers.

We would like to use this opportunity to thank a number of people, who contributed to the accomplishment of this book. First of all, we would like to thank our students for their exemplary carbon research – without them, this book would not exist. Especially, we are grateful to Torben Winzer for his excellent work on the relaxation behavior of excited electrons in graphene; Eike Verdenhalven, Evge-
ny Bobkin, and Faris Kadi, who helped us reveal the optical fingerprint of carbon nanostructures; Christopher Köhler and Matthias Hirtschulz for shedding light on the nonequilibrium dynamics in carbon nanotubes; Stephan Butscher for his initial study on carrier relaxation in graphene. Special thanks go to Faris, who helped us type the comprehensive appendix. Furthermore, we thank Frank Milde, Torben, Eike as well as Marten Richter, Florian Wendler, and Gunnar Berghäuser for careful reading of various chapters of the book. Their suggestions contributed to a clearer and better presentation.

The progress of this work has substantially benefited from close scientific collaborations with experimental and other theoretical groups. Here, our thanks go to Stephanie Reich (Freie Universität Berlin), who introduced us to the fascinating world of carbon nanotubes, Manfred Helm (Helmholtz-Zentrum Dresden-Rossendorf) for new insights into the relaxation behavior of graphene electrons close to the Dirac point, Tony F. Heinz (Columbia University, New York) for many stimulating discussions on carbon nanotubes and graphene, Thomas Elsaesser (Max-Born Institut Berlin) and Jürgen Rabe (Humboldt Universität Berlin) for the joint high-resolution study on the carrier and phonon dynamics in graphene, Theodore E. Norris (University of Michigan) and John E. Sipe (University of Toronto) for the successful collaboration on current decay in graphene, Ulrike Woggon (Technische Universität Berlin) for revealing efficient relaxation channels in carbon nanotubes, Rolf Binder (University of Arizona) for fruitful discussions on many-particle screening in carbon nanostructures, Pablo Ordejon, Carlos F. Sanz-Navarro (CIN2, Barcelona), Peter Saalfrank, and Tillmann Klamroth (Universität Potsdam) for scientific collaboration on the ab initio description of functionalized carbon nanotubes, and last but not least Janina Maultzsch and Christian Thomsen (Technische Universität Berlin) for valuable input on carbon nanostructures since the beginning of our research. We also thank Vera Palmer and Anja Tschörtner from Wiley-VCH for their support.

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Berlin, October 2012

Ermin Malic, Andreas Knorr
1

Introduction – The Carbon Age

The continuing trend towards miniaturization of optoelectronic devices leads to fundamental physical limits of conventional silicon-based materials. The search for new concepts has moved low-dimensional carbon nanostructures into the focus of current research [1–5]. They are represented by a variety of different metallic and semiconducting materials with unique optical, electronic, and mechanical properties [2, 3].

The main carbon material is graphite. It consists of multiple flat layers of sp²-hybridized carbon atoms arranged in a hexagonal lattice [6]. While the σ-bonds between the carbon atoms are very strong, the Van der Waals coupling between different layers is rather weak and can be easily broken. Therefore, graphite is a suitable material for example for pencils.

In 1985, a new carbon structure named fullerene was discovered [7]. Its most common form C_{60} is a spherical carbon molecule with a mean diameter of 0.68 nm, cp. Figure 1.1c. Since the charge carriers are spatially confined in all directions, fullerenes are zero-dimensional carbon nanostructures. For their discovery, Richard Smalley, Robert Curl, and James Heath obtained the Nobel Prize in Chemistry in 1996.

Carbon nanotubes (CNTs) represent another low-dimensional carbon nanostructure, which was found for the first time in 1991 by Iijima [8, 9] and has attracted large scientific and technological interest. Nanotubes are tiny, hollow cylinders constructed by rolling up a single layer of graphite, cp. Figure 1.1b. They have diameters in the range of one nanometer, while their length can reach several micrometers. As a result, they are prototypical one-dimensional systems, in which carriers can move freely only along the axis of the cylinder. Arising from a specific geometry quantum confinement, they can be either metallic or semiconducting with a tunable bandgap. This makes them excellent materials for various technological applications.

In 2004, graphene was discovered – a perfect two-dimensional carbon nanostructure consisting of a monolayer of carbon atoms [10]. Graphene can be considered as the basic carbon material and it can be rolled up into a one-dimensional carbon nanotube, wrapped into a zero-dimensional fullerene, and stacked into a three-dimensional graphite, cp. Figure 1.1. Up to its discovery, graphene was considered as an academic material [6] that could not exist in reality due to thermodynamic
instabilities of two-dimensional structures on a nanometer scale [11–13]. However, Konstantin Novoselov and Andre Geim from the University of Manchester succeeded to mechanically exfoliate a single layer of graphite and revealed a completely new structure with exceptional properties. They were awarded the Nobel Prize for Physics in 2010.

Meanwhile, also carbon-based hybrid materials consisting of a nanostructure functionalized with molecules have moved into the focus of current research [16–18], cp. Figure 1.1d. Carbon materials offer a variety of metallic and semiconducting substrates, which show a large sensitivity to changes in their surrounding environment. Thus, they are excellent structures for functionalization with molecules [17, 19], which offers the possibility to control and optimize certain properties. As a result, functionalization is a promising strategy to exploit the great application potential of carbon nanostructures [18, 20, 21].

Figure 1.1 Schematic illustration of different carbon-based nanostructures. (a) Graphene as a two-dimensional material consisting of a single layer of carbon atoms can be rolled up into (b) one-dimensional carbon nanotubes, wrapped into (c) zero-dimensional fullerenes, or stacked into three-dimensional graphite (multilayered graphene). (d) Exemplary carbon-based hybrid nanostructure consisting of a nanotube functionalized with merocyanine molecules. The latter creates a strong dipole field giving rise to changes in the optical and electronic properties of the nanotube. Figure parts (a) and (b) adapted from [14], part (c) from [15].
1.1 Graphene

Properties Since its discovery [10], graphene has attracted tremendous interest in fundamental research and industry [5, 22]. Graphene has an exceptional band structure exhibiting crossing points between the valence and the conduction band at the six corners of the Brillouin zone [6]. Around these so-called Dirac points, the energy dispersion is linear giving rise to unique optical and electronic properties [3, 15]. The electrons behave like relativistic massless particles and can be described by a Dirac-like equation [15]. One consequence is for example the anomalous fractional quantum Hall effect [23].

Consisting of just a single layer of carbon atoms, graphene is the thinnest known material. Because of the sp2-bonds between the hexagonally arranged carbon atoms, it is also one of the strongest structures that we know of [24]. Furthermore, it is an excellent conductor of electricity and heat, which can be traced back to its excellent carrier mobility at room temperature. The carriers can move freely without scattering events over length scales of some hundreds of nanometers (ballistic transport) [3, 25, 26]. Moreover, graphene is flexible and almost transparent in the optical frequency range [27–29]. As a result, it is a promising material for applications in nanoelectronics and optoelectronics [3, 30].

Synthesis Graphene was first obtained by mechanical exfoliation [10]. Konstantin Novoselov and Andre Geim used a common adhesive tape to repeatedly split graphite crystals into increasingly small flakes, cp. Figure 1.2. Then, they transferred the thinnest flakes onto a SiO2 substrate of a specific width. Finally, they could visualize monolayers of carbon atoms under a simple optical microscope. The procedure is known as the scotch tape or drawing method, since the mechanical exfoliation resembles writing with a pencil. Such exfoliated graphene exhibits a high crystal quality resulting in a large carrier mobility. This method is ideal

![Figure 1.2](image-url)
for producing samples for fundamental research. However, the sample size is too small (around 10 μm) for technological applications. Thus, other methods allowing large-scale exfoliation are required to exploit the great application potential of graphene [30]. The most promising growth technique for the mass production of large area graphene films is chemical vapor deposition (CVD). Graphene samples with a size of over 75 cm have already been reported [31]. However, the structural quality of the produced graphene layers is so far lower compared to exfoliated or epitaxially grown samples.

The crystalline quality of graphene grown epitaxially on silicon carbide or metal substrates via high-temperature annealing is very high [32, 33]. However, the growth strongly depends on which side of the SiC graphene layers are grown. On the Si-face a single layer of highly doped graphene is formed on top of a buffer layer [34]. On the C-face rotationally twisted graphene multilayers are produced, which do not exhibit Bernal stacking order but are rotationally twisted against each other resulting in a negligible coupling and a graphene-like behavior [32]. A more detailed discussion of growth methods can be found in Section 3.4.

**Applications** Graphene is considered a very promising future material for nanoelectronics [3, 5, 30, 35]. It is characterized by huge carrier mobilities, optical transparency, flexibility, robustness, and environmental stability giving rise to a large variety of applications ranging from solar cells and light-emitting devices to touch screens, photodetectors, and ultrafast lasers [30, 35].

In particular, the observed ballistic transport and the resulting exceptional carrier mobility can be exploited to build highly efficient transistors. Recently, IBM researchers reported on a graphene-based field-effect transistor with an on–off rate of 100 GHz exceeding the speed of corresponding silicon transistors [36, 37], cp. Figure 1.3a. Since graphene is almost transparent and at the same time an excellent conductor it is also a promising material for transparent electrodes required in touch screens and displays. Its mechanical strength and flexibility make it more suitable than indium tin oxide [5, 30, 38].

The exceptional carrier mobility and absorption over a large spectral range from terahertz to ultraviolet also suggest application as ultrafast, spectrally broad photodetectors [35, 39]. Recently, terahertz emission and amplification was observed in optically pumped graphene demonstrating the feasibility of active graphene-based terahertz devices [30]. Furthermore, graphene can be applied as a broadband and fast saturable absorber in ultrafast laser systems [40, 41] due to its ultrafast carrier dynamics, broadband absorption, and efficient Pauli blocking — in contrast to conventional materials with a narrow spectral range requiring costly bandgap engineering. Finally, graphene has already been applied in composite materials to achieve improved mechanic and electric properties [42].

**Challenges** Despite the impressive progress in the short time since its discovery, there are still substantial challenges on the way to graphene-based nanoelectronics. In particular, further progress in epitaxial growth techniques is needed to obtain high-quality graphene films complying with industrial standards including suffi-
1.2 Carbon Nanotubes

Properties

The discovery of carbon nanotubes has opened a new research field [1, 2]. CNTs are ideal model systems to study the fundamental physics of one-dimensional nanostructures. CNTs can be considered as a piece of graphene rolled up into a cylinder with a diameter of approximately one nanometer, cp. Figure 1.1. The diameter of the cylinder and the chiral angle $\phi$ (rolling-up angle) determine the microscopic structure of each specific nanotube [1]. Because of the hexagonal shape of the Brillouin zone of graphene, the angles can reach values between $0^\circ$–$30^\circ$. The two distinguished angles correspond to zigzag nanotubes with $\phi = 0^\circ$ and armchair nanotubes with $\phi = 30^\circ$. The names reflect zigzag- and armchair-like chains at the edge of their unit cells, cp. Figure 1.4.

Similarly to graphene, carbon nanotubes are one of the strongest known materials due to the covalent sp$^2$-bonds between the carbon atoms [47]. At the same time, they are very light, because they consist of a single layer of carbon atoms. The extraordinary crystal quality gives rise to a ballistic conduction of current and heat at room temperature. As a one-dimensional material with an extreme length-to-
Figure 1.4 The classification of nanotubes according to the chiral angle \( \phi \) describing the orientation of carbon hexagons relative to the nanotube axis: (a) zigzag tubes with \( \phi = 0^\circ \), (b) armchair tubes with \( \phi = 30^\circ \), and (c) chiral tubes \( (n_1, n_2) \) with \( 0^\circ < \phi < 30^\circ \). The names reflect the armchair- and zigzag-like edges of the corresponding unit cells (emphasized area). Figure adapted from [1].

diameter ratio, CNTs also exhibit pronounced optical properties [48]. In contrast to graphene, the further spatial confinement gives rise to a variety of metallic and semiconducting nanostructures with distinct physical properties. Depending on the chiral angle, one third of all possible nanotubes are metallic [1]. Furthermore, the bandgap of the semiconducting CNTs is tunable with the diameter of the tube. This variety of one-dimensional nanostructures with distinct physical properties accounts for the huge potential of carbon nanotubes for technological applications [2, 4, 49].

Synthesis Carbon nanotubes can be grown by chemical vapor deposition, laser ablation, and arc discharge [14]. All methods have in common that first a carbon plasma is generated and then metal catalysts are added, which induce the growth of nanotubes. The type of catalyst and the growth conditions determine the number of nanotube walls, their diameter, and length [14].

Figure 1.5a shows an SEM image of CNT bundles grown by arc discharge [50]. Each bundle consists of 20–100 single-walled carbon nanotubes, as indicated in the high-resolution TEM image in Figure 1.5b. To obtain single-walled CNTs, the bundles are broken apart by ultrasonification and the single tubes are coated by a surfactant to prevent them from rebundling. Furthermore, CNT forests can be produced via water-assisted chemical vapor deposition [51], cp. Figure 1.5c. Additionally, the CVD technique enables the growth of CNTs in well-defined positions on patterned substrates [51], as shown in Figure 1.5d.

While the diameter and the length of CNTs can be controlled during growth, the control of the chiral angle remains a major challenge in current research. Usually, CNT samples exhibit a homogeneous distribution of chiral angles. Separation of metallic and semiconducting carbon nanotubes was successfully achieved by using i.a. (i) density-gradient ultracentrifugation (DGU), which separates surfactant-wrapped CNTs by the difference in their density [52], (ii) alternating current dielectrophoresis, which exploits the difference in the relative dielectric constants resulting in an opposite movement of metallic and semiconducting tubes along the electric field gradient [53], and (iii) agarose gel electrophoresis, where the rela-
1.2 Carbon Nanotubes

**Figure 1.5** Carbon nanotubes obtained with different growth techniques including (a) CNT bundles grown by arc discharge [50], (b) cross section of such a bundle, (c) mm-thick CNT forests grown by water-assisted chemical vapor deposition [51], (d) CNTs grown in predefined places on a patterned substrate [51]. Figure taken from [14].

Effective mobility through a gel is used for separation of CNTs with different molecular weights [54]. Recently, progress has also been made allowing enrichment of CNTs with a specific chirality for example by exploiting chirality-dependent wrapping of CNTs with the DNA leading to enrichments of up to 90% and more [55].

**Applications** The variety of one-dimensional metallic and semiconducting carbon nanotubes with a tunable bandgap makes CNTs promising candidates for various technological applications [2, 4, 49]. In particular, nanotube-based field-effect transistors have already been demonstrated based on room-temperature ballistic transport [4, 46], cp. Figure 1.3b. Furthermore, metallic CNTs can be used in integrated circuits to conduct current and high-speed signals [56]. Consisting of a single layer of carbon atoms, CNTs exhibit a large surface-to-volume ratio, which is favorable for application as chemical or gas sensors [57]. Functionalization of CNTs can be used to improve their sensitivity and selectivity to specific chemical substances or biomolecules [58].

The strength and flexibility of CNTs on the one hand and their extraordinary conductivity on the other hand suggest engineering of transparent, electrically conductive films of CNTs for application in touch screens and flexible displays [49, 59]. CNTs have already been used in composite materials to improve their mechanical, thermal, and electronic properties [60]. Their mechanical strength is already exploited in everyday items, such as cloths, sports gear, cars and so on.

**Challenges** Most technological applications require an almost perfect separation of metallic and semiconducting nanotubes. For some applications, even a separation by chiral angle is necessary. Therefore, further progress in growth and selection techniques remains the major challenge in current nanotube research [2].
Furthermore, the unambiguous characterization and identification of specific CNTs is an important issue. In this context, the well-pronounced optical transitions can be seen as an optical finger print for each individual nanotube. Optical spectroscopy methods, such as absorption, photoluminescence, Rayleigh and Raman scattering can be used for structural assignment of CNTs [61–65]. This aspect is addressed in detail in Chapter 6.

For applications in nanoelectronics, a microscopic understanding of the Coulomb- and phonon-induced ultrafast relaxation dynamics of optically excited carriers is required, in particular addressing different relaxation channels and their diameter and chirality dependence. Microscopic investigations on the carrier dynamics in CNTs are presented in Chapter 5.
2 Theoretical Framework

In this chapter, the basic theoretical methods applied in this book are presented. All investigations are based on a many-particle density-matrix framework – an established technique for quantum-mechanical treatment of solid-state many-particle systems [66–68]. Applying the Heisenberg equation, we obtain graphene/CNT Bloch equations describing the coupled dynamics of carrier and phonon occupations as well as of the microscopic polarization. The approach provides microscopic tools for the investigation of optical and electronic properties of low-dimensional nanostructures including excitonic effects in optical spectra as well as the ultrafast many-particle kinetics in a nonequilibrium situation. More details on the theoretical approach can be found in the comprehensive appendix. In particular, if the reader is not experienced with the theoretical description of many-particle effects within the second quantization, we suggest reading Appendix C.

Main questions addressed in this chapter

- What are optical graphene/CNT Bloch equations?
- What does the second-order Born–Markov approximation mean?
- Which characteristics does the electronic band structure of graphene and carbon nanotubes (CNTs) exhibit?
- Can an analytic expression be obtained for the optical matrix element?
- How important is the many-particle screening of the Coulomb potential in metallic and semiconducting carbon nanotubes and graphene?
- Which processes does the Boltzmann-like kinetic equation include?
- How can microscopic quantities be related to macroscopic observables, such as optical absorption and differential transmission?
2 Theoretical Framework

2.1 Many-Particle Hamilton Operator

To obtain the graphene/CNT Bloch equations, we first need the many-particle Hamilton operator \( H \), which determines the energy of a carrier–phonon system interacting with an electromagnetic field [68]. We apply a semiclassical approach treating the carriers and phonons quantum mechanically and the electrical field classically. The formalism is expressed in second quantization based on the introduction of Heisenberg field operators

\[
\Psi(r) = \sum_l a_l \Phi_l(r), \quad \Psi^+(r) = \sum_l a_l^+ \Phi_l^*(r)
\] (2.1)

with \( \Phi_l(r) \) as single-particle wave functions and \( a_l^+ \) and \( a_l \) as the creation and annihilation operators, respectively [68]. In analogy, the corresponding bosonic operators \( b_u^+ \) and \( b_u \) are introduced, which create or annihilate a phonon in the state \( u \), respectively. The introduced compound index \( l = (\lambda, k, s) \) contains the electron momentum \( k \), the band index \( \lambda \), and the spin \( s \), while \( u = (j, q) \) describes the phonon momentum \( q \) and the phonon mode \( j \). The advantage of the second quantization is that the symmetry conditions are expressed in fundamental commutation relations between these operators and therefore the tedious symmetrization of wave functions can be omitted. A detailed description of the second quantization and the many-particle Hamilton operator is provided in Appendix C.6.

In this book, the many-particle Hamilton operator \( H = H_0 + H_{c,f} + H_{c,c} + H_{c,p} \) contains the free-carrier and phonon contribution \( H_0 \), carrier–field \( H_{c,f} \), the carrier–carrier \( H_{c,c} \), and the carrier–phonon interaction \( H_{c,p} \), cp. Appendix C. The noninteraction part \( H_0 \) reads

\[
H_0 = \sum_l \varepsilon_l a_l^+ a_l + \sum_u \hbar \omega_u \left( b_u^+ b_u + \frac{1}{2} \right)
\] (2.2)

with the electronic single-particle energy \( \varepsilon_l \) and the phonon energy \( \hbar \omega_u \). The carrier–field interaction \( H_{c,f} \) is expressed within the radiation gauge [69] \((\nabla \cdot A = 0, \Phi = 0)\) as

\[
H_{c,f} = i\hbar \frac{e_0}{m_0} \sum_{l_1, l_2} M_{l_1, l_2} \cdot A(t) a_{l_1}^+ a_{l_2}
\] (2.3)

with the elementary charge \( e_0 \), the free electron mass \( m_0 \), and the vector potential \( A(t) \). The strength of this carrier–light coupling is given by the optical matrix element \( M_{l_1, l_2} \). The contribution proportional to the square of the vector potential has been neglected, since it is small within the limit of linear optics and it does not contribute to the dynamics of nonequilibrium carriers after an optical excitation.

The carrier–carrier interaction \( H_{c,c} \) is given by

\[
H_{c,c} = \frac{1}{2} \sum_{l_1, l_2, l_3, l_4} V_{l_1, l_2}^{l_3, l_4} a_{l_1}^+ a_{l_2}^+ a_{l_4} a_{l_3}
\] (2.4)
including the Coulomb matrix element \( V^{\lambda_1,\lambda_2}_{l_1,l_2} \). Finally, the last contribution \( H_{c,p} \) of the Hamilton operator describes the interaction between carriers and phonons and reads

\[
H_{c,p} = \sum_{l_1,l_2} \sum_{u} \left( g^{l_1,l_2}_{u} a_{l_1}^+ b_{u} + g^{l_1,l_2}_{u} a_{l_1} b_{u}^+ \right)
\]  

(2.5)

with the carrier–phonon matrix elements \( g^{l_1,l_2}_{u} \).

The Hamilton operator becomes specific by inserting the dispersion relations and the coupling elements for the material to be investigated. In Sections 2.3–2.7, we discuss in detail these material-specific quantities in the case of graphene and carbon nanotubes.

### 2.2 Microscopic Bloch Equations

With the Hamilton operator \( H \), we have microscopic access to the temporal evolution of an arbitrary quantity \( O(t) \) within the Heisenberg equation of motion [66]

\[
i\hbar \frac{d}{dt} O(t) = [O(t), H] = O(t) H - H O(t).
\]  

(2.6)

In this book, we focus on the carrier and phonon dynamics in a nonequilibrium situation. Therefore, the quantities of interest are: (i) the coherence or microscopic polarization \( p_k = \langle a_{\lambda k}^+ a_{\lambda k} \rangle \), (ii) the carrier occupation probability \( \rho^c_k = \langle a_{\lambda k}^+ a_{\lambda k} \rangle \) in the state \( k \) within the band \( \lambda \), and (iii) the phonon occupation \( n^j_q = \langle b_{jq}^+ b_{jq} \rangle \) in the mode \( j \) and with the momentum \( q \). Figure 2.1 illustrates these quantities in a system with a linear electronic band structure. First, an optical pulse described by the vector potential \( A(t) \) is applied to perturb the carrier system. In the strong excitation regime, a nonequilibrium carrier distribution is generated by lifting electrons

![Figure 2.1](image_url)

**Figure 2.1** Illustration of the microscopic quantities of interest \( (\rho^c_k, p_k, \text{ and } n^j_q) \) for describing the carrier and phonon dynamics in nonequilibrium. The optical excitation is described by the vector potential \( A(t) \), which lifts electrons from the valence (v) into the conduction band (c). A measure for the transition probability is given by the microscopic polarization \( p_k \). The Coulomb- and phonon-induced scattering changes the occupation probabilities \( \rho^c_k(t) \) and \( \rho^v_k(t) \) in the involved bands as well as the phonon occupation \( n^j_q(t) \). Figure adapted from [70].
from the valence into the conduction band. The microscopic polarization $p_k$ is a measure for the transition probability between the two bands. The optical excitation and the subsequent scattering dynamics changes the occupation probabilities $\rho^v_k$ and $\rho^c_k$ in the involved bands. The phonon-induced scattering also changes the phonon occupation $n^q_k$. Therefore, knowledge of the temporal evolution of $\rho^v_k$, $p_k$, and $n^q_k$ is required to microscopically access the nonequilibrium carrier dynamics.

Applying the Heisenberg equation of motion and exploiting the fundamental commutator relations for fermionic and bosonic operators, we obtain optical Bloch equations (cp. Appendix D [70, 71]):

\begin{equation}
\dot{\rho}^v_k(t) = (i \Delta \omega_k + \Omega_k) p_k(t) - i \Omega_k^v [\rho^v_k(t) - \rho^c_k(t)] + \dot{\rho}^v_k(t)_{|_{HF+s}},
\end{equation}

\begin{equation}
\dot{\rho}^c_k(t) = -2 \text{Im} \left[ \Omega_k^{vc} \rho^v_k(t) \right] + \dot{\rho}^v_k(t)_{|_{HF+s}},
\end{equation}

\begin{equation}
\dot{n}^q_k(t) = -\gamma_j \left[ n^j_q(t) - n_B \right] + \dot{n}^j_q(t)_{|_s}.
\end{equation}

Here, $\hbar \Delta \omega_k = (\epsilon^v_k - \epsilon^c_k)$ is the momentum-dependent energy difference between the valence and the conduction band, $\Omega_k^{vc} = i e_0 / m_0 M_k^{vc}$. $\Delta \omega(t)$ is the Rabi frequency, $\gamma_j^{-1}$ corresponds to the experimentally accessible phonon lifetime [72, 73], and $n_B$ denotes the equilibrium distribution of phonons, which is given by the Bose–Einstein distribution at room temperature. The intraband contribution of the carrier–field interaction is proportional to $\Omega_k(t) = i e_0 / m_0 (M_k^{vc} - M_k^{vc})$. $\Delta \omega(t)$ is nonlinear in the vector potential (cp. Eq. (2.7)) and since it is also connected to $p_k$, it gives rise to the generation of higher harmonics in a strong-excitation regime [74]. Because of the symmetry of the valence and conduction band around the $K$ point, the carrier occupations in the two bands are related via $\dot{\rho}^v_k = -\dot{\rho}^c_k$. Within the electron–hole picture, we obtain $\dot{\rho}^h_k = \dot{\rho}^c_k$ with $\rho^h_k = 1 - \rho^v_k$ and $\rho^c_k = \rho^v_k$, that is, electrons in the conduction band and holes in the valence band show the same dynamics.

Many-particle interactions in Eqs. (2.7)–(2.9) can be separated into a Hartree–Fock ($p_k|_{HF}$, $\rho^v_k|_{HF}$) and a scattering part ($\dot{\rho}^v_k|_{S}$, $\rho^c_k|_{S}$, $n^q_k|_{S}$), cp. Appendix E. The many-particle interactions couple the dynamics of single-particle elements $p_k$, $\rho^v_k$, $n^q_k$ to higher-order terms describing the correlation between carriers, that is, $d/dt \langle a^+_1 a_2 \rangle \propto \langle a^+_A a^+_B a_C a_D \rangle$. The equation of motion for the appearing two-particle quantities depends on three-particle terms $\langle a^+_1 a^+_2 a^+_3 a_4 a_5 a_6 \rangle$, which couple to four-particle quantities, and so on. The resulting set of equations is not closed and an infinite hierarchy of quantities with increasing number of involved particles appears [66].

At some level, this infinite hierarchy needs to be systematically truncated. In this book, we apply the correlation expansion and consider only contributions from a certain order assuming that higher-order terms are negligibly small, cp. Appendix E for more details [75, 76]. This factorization technique leads to a closed set of equations for the single-particle elements. To give an example, a two-particle quantity is factorized into products of single-particle terms yielding

\[ \langle a^+_1 a^+_2 a_3 a_4 \rangle = \langle a^+_1 a_4 \rangle \langle a^+_2 a_3 \rangle - \langle a^+_1 a_3 \rangle \langle a^+_2 a_4 \rangle + C_{12}^{12}, \]
where \( C_{12}^{34} = \left( a_1^+ a_2^+ a_3 a_4 \right) \) denotes the correlation term beyond the Hartree–Fock approximation. Neglecting \( C_{12}^{34} \) in the first order corresponds to the Hartree–Fock factorization or the mean-field approximation [66, 67]. Considering the second-order terms in the carrier–carrier and carrier–phonon interaction, that is, explicitly calculating the dynamics of \( C_{12}^{34} \) and neglecting the three-particle correlation quantities, allows the investigation of two-particle scattering processes [77]. This is called second-order Born approximation [68].

2.2.1 Hartree–Fock Approximation

Here, we discuss the Hartree–Fock approximation applied to the Coulomb interaction. This approximation already describes well the formation of excitons [66], which are known to dominate the linear spectra of carbon nanostructures, as discussed in Chapters 6 and 7. Neglecting the carrier–phonon coupling for now, the Bloch equations read within the Hartree–Fock approximation:

\[
\dot{\rho}_k(t)_{\text{HF}} = \frac{i}{\hbar} \sum_{k'} \left\{ \left( V_{k'c,kv}^{kc,k'v} - V_{k'v,kv}^{k'v,k'} \right) \rho_k(t) \left[ \rho_{k'}(t) - \rho_{k'}^*(t) \right] \right. \\
- \left. \left[ V_{k'c,kv}^{k'v,kc} \rho_k(t) + V_{k'v,kv}^{k'v,k} \rho_{k'}(t) \right] \left[ \rho_k(t) - \rho_{k'}^*(t) \right] \right\}, \tag{2.10}
\]

\[
\dot{\rho}_k(t)_{\text{HF}} = -\dot{\rho}_k(t)_{\text{HF}} = \frac{2}{\hbar} \sum_{k'} \left( V_{k'c,kv}^{k'v,kc} \rho_k(t) \rho_{k'}(t) \right). \tag{2.11}
\]

We observe two different Coulomb-induced contributions to the dynamics of the microscopic polarization: the term proportional to \( p_k(t) \) (first line of Eq. (2.10)) describes the repulsive electron–electron interaction giving rise to a renormalization of the single-particle energy in Eq. (2.7). The second Coulomb contribution is proportional to \( p_{k'}(t) \) (second line in Eq. (2.10)) and induces a redistribution of the momentum. It leads to a renormalization of the Rabi frequency \( \Omega_k(t) \) in Eq. (2.7) accounting for the formation of excitons. The strength of the renormalization is given by the involved material-specific Coulomb matrix elements \( V_{AB}^{CD} \).

In a many-particle system, it is of crucial importance to take into account the intrinsic screening of the Coulomb potential. The Coulomb matrix elements entering the Bloch equations are screened via the momentum-dependent dielectric function \( \varepsilon(q) \) resulting in

\[
W_{CD}^{AB} = \frac{V_{CD}^{AB}}{\varepsilon(q)}. \tag{2.12}
\]

The dielectric function \( \varepsilon(q) \) can be derived self-consistently within the presented equation of motion approach by taking into account higher-order contributions in the correlation expansion, cp. Appendix E.2.3.

The Coulomb-induced change in absorption spectra of carbon nanostructures is investigated in detail in Chapters 6 and 7.
2.2.2 Second-Order Born–Markov Approximation

The access to the carrier relaxation dynamics requires an extension of the Bloch equations beyond the mean-field level. The scattering contributions $\dot{\rho}_k|_s$, $\dot{\rho}_k^2|_s$, and $\dot{n}_k^j|_s$ in Eqs. (2.7)–(2.9) are obtained by considering the carrier–carrier and the carrier–phonon interaction within the second-order Born–Markov approximation [68]. The introduced Markov approximation neglects quantum-mechanic memory effects and accounts for a conservation of energy, as discussed below.

This approach results in a microscopic Boltzmann-like kinetic equation for the carrier occupation probabilities

$$\dot{\rho}_l(t)|_s = \Gamma_l^\text{in}(t)\left[1 - \rho_l(t)\right] - \Gamma_l^\text{out}(t)\rho_l(t) \quad (2.13)$$

with the compound index $l = (k, \lambda)$. The time- and momentum-dependent scattering rates $\Gamma_l^\text{in/out}(t)$ include both carrier–carrier (cc) as well as carrier–phonon (cp) relaxation channels, that is, $\Gamma_l^\text{in/out}(t) = \Gamma_{l,cc}^\text{in/out}(t) + \Gamma_{l,cp}^\text{in/out}(t)$. More details on the derivation of this equation are provided in Appendix E.

2.2.2.1 Detailed Balance

In equilibrium, the in- and out-scattering processes compensate each other leading to $\dot{\rho}_l = \Gamma_l^\text{in}(1 - \rho_l) - \Gamma_l^\text{out} \rho_l = 0$. Here, the carrier distribution $\rho_l$ corresponds to a Fermi function $f_l = \int f(\varepsilon_l, T, \mu)$, which depends on the energy $\varepsilon_l$, the temperature $T$, and the chemical potential $\mu$. As a result, in equilibrium we can derive a fixed relation between the in- and out-scattering rate with

$$\Gamma_l^\text{in} = \Gamma_l^\text{out} \exp\left[\frac{(E_l - \mu)}{k_B T}\right] \quad (2.14)$$

The initial carrier distribution before the optical excitation as well as the final, thermalized carrier distribution fulfill this relation.

2.2.2.2 Markov Approximation

The presented Boltzmann-like kinetic equation is obtained by applying a Markov approximation. Within the second-order Born approximation, equations of motion for two-particle quantities $C_{12}^{12}$ need to be evaluated, cp. Appendix E. For reasons of simplicity, we neglect the quantum numbers in this paragraph. Applying the Heisenberg equation and considering only the free-carrier part and the Coulomb interaction yields

$$\frac{d}{dt} C(t) = -\frac{i}{\hbar} \Delta \varepsilon C(t) - \frac{i}{\hbar} Q(t) - \gamma C(t) \quad (2.15)$$

with the energy difference $\Delta \varepsilon = (\varepsilon_3 + \varepsilon_4 - \varepsilon_1 - \varepsilon_2)$ of all involved states and the inhomogeneous part $Q(t)$ containing the integrals over all scattering and dephasing contributions, cp. Appendix E.2.2. The solution of this inhomogeneous differential