

# Chapter 2

## Models and Concepts

In condensed matter physics, one is faced with the intricate task of finding an appropriate description of systems consisting of a huge number of particles. Owing to the quantum mechanical nature of the problem and neglecting relativistic effects, we are faced with the task of solving the many-particle Schrödinger equation

$$\tilde{H}\Psi(\mathbf{x}_1 \dots \mathbf{x}_N) = E\Psi(\mathbf{x}_1 \dots \mathbf{x}_N), \quad (2.1)$$

where the number of the particles  $N$  is of the order of the Avogadro constant  $N_A = 10^{23}$ . In a real solid, the electrons interact with each other and move in the field of the nuclei, which in turn interact among themselves and oscillate about their equilibrium positions. As always, we have to employ physical intuition, which here tells us that the fact that the nuclei are much heavier than the electrons,  $m_e/M_n \approx 10^{-4} - 10^{-6}$ , will cause the electrons to move rather independently of the motion of the nuclei. In other words, the motion of electrons and nuclei is decoupled, which is true up to terms of order  $m_e/M_n$ . If we are only interested in the excitations of the electronic system, we may regard the nuclei as frozen in their equilibrium positions and solve the electronic problem in a static background potential of the nuclei. This is the essence of the Born-Oppenheimer approximation, which leaves us with the Hamiltonian of the electronic system subject to an external potential  $V$ :

$$\tilde{H} = \tilde{H}_0 + \tilde{V}_{ee} = \sum_{i=1}^N \left( -\frac{\hbar^2}{2m} \nabla_{\mathbf{x}_i}^2 + V_{\text{ext}}(\mathbf{x}_i) \right) + e^2 \sum_{i<j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}. \quad (2.2)$$

What we neglect are the excitations of the system of the nuclei – the phonons – and their interaction with electrons, but we still have the freedom to introduce phonons and the electron-phonon coupling perturbatively afterwards<sup>1</sup>. By distinguishing core and

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<sup>1</sup>The fact that the electron-phonon interaction is a small perturbation does not imply that it has a small effect. It may break symmetries and lift the associated selection rules, as for example recently observed in the case of phonon mediated tunneling into graphene [42].

valence electrons, the problem is further simplified. The former are tightly bound to the nuclei and do not participate in bonding. The Hamiltonian (2.2) then describes the system of valence electrons moving in the external potential of the ion cores. Despite these simplifications, an exact solution of the many-particle Schrödinger equation is impossible and one has to resort to approximations. Two main routes have evolved to deal with the Hamiltonian (2.2): the density functional theory and a description in terms of quantum lattice models.

## 2.1 Density Functional Theory

The density functional theory (DFT) is a very successful *ab-initio* theory to describe the band features of weakly correlated materials. Its applications range from the description of molecules to solids, within quantum chemistry and solid state physics and it is widely used in science and industry. A thorough introduction can e.g. be found in Ref. [43].

The theory is based on the two Hohenberg-Kohn theorems. The first theorem states that for an interacting electron system in an external potential  $V_{\text{ext}}$ , this potential is uniquely determined (up to a constant) by the ground state density  $n_0(\mathbf{x})$ . This statement is nontrivial, for it implies that the ground state properties of the interacting  $N$ -particle system, including the many-body wavefunction, are uniquely determined through the ground state density only. Instead of dealing with the full wavefunction which depends on  $3N$  particle coordinates, it is sufficient to use the density. A recipe of how to calculate the ground-state density is provided by the second Hohenberg-Kohn theorem.

In the formulation by Levy and Lieb, a functional of the density is constructed on the space of densities that can be represented by  $N$ -body wavefunctions. It is defined as the minimum of the expectation values of the exact kinetic and electron-electron interaction, taken over the class of wavefunctions that yield the density  $n(\mathbf{x})$ :  $F[n] := \min_{\Psi_n} \langle \Psi | T + V_{\text{ee}} | \Psi \rangle$ . By the Ritz variational principle, the ground-state density  $n_0(\mathbf{x})$  minimizes  $F[n]$  and the functional of the total energy is given by

$$E[n] = F[n] + \int d\mathbf{x} v_{\text{ext}}(\mathbf{x})n(\mathbf{x}) . \quad (2.3)$$

In order to find the ground state density of the system, one therefore needs to solve the constrained variational problem

$$\frac{\delta E[n]}{\delta n(\mathbf{x})} = \mu , \quad (2.4)$$

where  $\mu$  plays the role of a Lagrangian multiplier (chemical potential) which fixes the particle number  $N = \int d\mathbf{x} n(\mathbf{x})$ . In practice, this is achieved by considering a noninteracting auxiliary system in an effective potential described by the Schrödinger equation

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{x}) \right) \psi_i(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}) , \quad (2.5)$$

where the effective potential is chosen such that the Kohn-Sham orbitals  $\psi_i$  reproduce the density of the interacting many-body system:

$$n(\mathbf{x}) = \sum_{i=1}^N |\psi_i(\mathbf{x})|^2 . \quad (2.6)$$

This yields the correct particle number given that the Kohn-Sham orbitals fulfill the orthonormality constraint  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ ,  $i, j = 1, \dots, N$ . In order to identify the effective potential, the energy functional is written in the form

$$E[n] = T_0[n] + E_H[n] + E_{\text{ext}}[n] + E_{\text{xc}}[n] , \quad (2.7)$$

where the kinetic energy functional  $T_0$  of the noninteracting system, the Hartree functional  $E_H$  and the corresponding potential  $v_H$  are known explicitly. The exchange correlation functional contains the many-particle effects. Variation gives

$$\frac{\delta E[n]}{\delta n} \frac{\delta n}{\delta \psi^*} = \frac{\delta T_0}{\delta \psi^*} + (v_H + v_{\text{ext}} + v_{\text{xc}}) \frac{\delta n}{\delta \psi^*} = 0 . \quad (2.8)$$

Solving (2.5) is hence equivalent to (2.4) provided that  $v_{\text{eff}} = v_H + v_{\text{ext}} + v_{\text{xc}}$ . The Kohn-Sham eigenvalues play the role of Lagrange-multipliers which ensure the orthonormality constraints. Since the effective potential depends on the density and also determines the density through the solution of the Kohn-Sham equations, these have to be solved self-consistently.

The energy functional (2.7) is known except for the exchange-correlation functional. Knowing  $E_{\text{xc}}[n]$  would imply that the ground state properties of all interacting electron systems were known. Various approximations to the exchange-correlation functional have been devised, the most common being the local density- (LDA) or generalized gradient approximations (GGA). The LDA (GGA) are known to over(under)-estimate bond strengths. The local spin-density approximation includes the electron spin and a relativistic formulation of DFT has been developed. The available electronic structure codes mainly differ in the construction of the basis set and potential used to solve the Kohn-Sham equations. Pseudopotential methods allow a very fast solution of large systems. In the augmented wave methods partial solutions within atomic spheres and interstitial regions have to be matched such that the solution is continuously differentiable at the boundary for all energies. The related computational effort could be significantly reduced by linearizing the matching condition in the LMTO formalism introduced by Anderson [44]. Recent augmented wave codes are very accurate, but the construction of the basis set (APW, FLAPW) in these codes (WIEN2k, FLEUR) is rather involved. A compromise between speed and accuracy is the projector augmented wave method implemented in VASP.

## 2.2 Quantum Lattice Models

Methods of quantum field theory are widely used in condensed matter physics. They provide a convenient way to treat systems consisting of many particles. This includes cases where the particle number is allowed to fluctuate, as in superconductivity. The difficulty to construct and deal with (anti-)symmetrized (fermionic) bosonic many-particle wave functions for identical particles is circumvented by introducing operators that create or annihilate a particle in a given state. The proper (fermion) boson statistics are imposed through the (anti-)commutation relations of the field operators:

$$[\psi_\alpha(\mathbf{x}), \psi_\beta(\mathbf{x}')]_{(\pm)} = 0, \quad [\psi_\alpha(\mathbf{x}), \psi_\beta^\dagger(\mathbf{x}')]_{(\pm)} = \delta_{\alpha\beta} \delta(\mathbf{x} - \mathbf{x}'). \quad (2.9)$$

Instead of considering the many-particle Schrödinger equation  $H|\psi\rangle = E|\psi\rangle$  in a particular representation, such as the position representation (2.1), with a fixed number of particles, the Hamiltonian itself is expressed in terms of field operators. This corresponds to replacing the wavefunction by an operator acting on a quantum field with a fluctuating particle number and is referred to as second quantization. As described in standard textbooks, the Hamiltonian is expressed in terms of field operators as

$$H = \sum_{\alpha\beta} \int d\mathbf{x} \psi_\alpha^\dagger(\mathbf{x}) \left( -\frac{\hbar^2}{2m} \nabla_{\mathbf{x}}^2 + V_{\text{ext}}(\mathbf{x}) \right) \psi_\alpha(\mathbf{x}) + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \int d\mathbf{x} \int d\mathbf{x}' \psi_\alpha^\dagger(\mathbf{x}) \psi_\beta^\dagger(\mathbf{x}') V(\mathbf{x} - \mathbf{x}') \psi_\delta(\mathbf{x}') \psi_\gamma(\mathbf{x}). \quad (2.10)$$

A representation which is more convenient for practical calculations can be obtained by considering Wannier functions. These are localized around a given lattice site  $\mathbf{X}_i$  and can be chosen as

$$\phi_{i\alpha}(\mathbf{x} - \mathbf{X}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{X}_i} \psi_{\mathbf{k}\alpha}(\mathbf{x}), \quad (2.11)$$

where the  $\psi_{\mathbf{k}\alpha}(\mathbf{x})$  are Bloch functions of the noninteracting Hamiltonian. The index  $\alpha$  labels spins and orbitals. Defining the (creation) annihilation operator of a Wannier state as  $(c_{i\alpha}^\dagger) c_{i\alpha}$ , the field operators can be expressed in the form  $\psi_\alpha(\mathbf{x}) = \sum_i \phi_{i\alpha}(\mathbf{x}) c_{i\alpha}$  and the Hamiltonian takes the form of a lattice model

$$H = \sum_{ij} \sum_{\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + \frac{1}{2} \sum_{ijkl} \sum_{\alpha\beta\gamma\delta} U_{ijkl}^{\alpha\beta\gamma\delta} c_{i\alpha}^\dagger c_{j\beta}^\dagger c_{l\delta} c_{k\gamma}, \quad (2.12)$$

where the matrix elements are given by

$$t_{ij}^{\alpha\beta} = \int d\mathbf{x} \phi_\alpha^*(\mathbf{x} - \mathbf{X}_i) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{x}) \right) \phi_\beta(\mathbf{x} - \mathbf{X}_j),$$

$$U_{ijkl}^{\alpha\beta\gamma\delta} = e^2 \int d\mathbf{x} \int d\mathbf{x}' \frac{\phi_\alpha^*(\mathbf{x} - \mathbf{X}_i) \phi_\beta^*(\mathbf{x}' - \mathbf{X}_j) \phi_\gamma(\mathbf{x} - \mathbf{X}_k) \phi_\delta(\mathbf{x}' - \mathbf{X}_l)}{|\mathbf{x} - \mathbf{x}'|}. \quad (2.13)$$

The second quantization representation is essentially a reformulation of the original problem and the task of reliably calculating the properties of the general Hamiltonian (2.12) is theoretically challenging. Instead of attempting a full diagonalization of the problem, one concentrates on the causal single-particle (and sometimes two-particle) Green function,

$$G_{\alpha\beta}(\mathbf{x} - \mathbf{x}', \tau - \tau') := -\langle T_{\tau} c_{\alpha}(\mathbf{x}, \tau) c_{\beta}^{\dagger}(\mathbf{x}', \tau') \rangle. \quad (2.14)$$

which takes the place as the central quantity similar to the density in DFT. The remainder of this thesis is mainly concerned with finding approximations to the Green function, or the self-energy. In reciprocal space, the latter is defined through  $G(\mathbf{k}, i\omega)^{-1} = i\omega + \mu - h_{\mathbf{k}} - \Sigma(\mathbf{k}, i\omega)$ . Here  $h_{\mathbf{k}}$  is the Fourier transform of the hopping, the bare dispersion. The self-energy contains information about the electronic correlations. Spatial correlations – which are of particular interest here – manifest themselves in an explicit wavevector dependence of the self-energy. Approximate results should be examined to whether a feature is inherent to the model or an artefact of the particular approximation. This is difficult for the complex Hamiltonian (2.12). For the study of the basic physical mechanisms, simpler model Hamiltonians are traditionally used. These are derived from the general Hamiltonian by reducing the number of matrix elements to the dominant contributions, often assuming a short-range Coulomb interaction.

A prominent example obtained in this way is the single-band Hubbard model (or multi-orbital generalizations thereof). In a tight-binding approximation, the hopping matrix element in (2.13) is taken with respect to the atomic orbitals, which have little overlap with their neighbors. Therefore, the matrix elements are usually restricted to nearest-neighbor hopping  $t$  and next-nearest-neighbor hopping  $t'$ . Due to screening, the local intraatomic matrix elements  $U_{iii}^{\alpha\beta\gamma\delta}$  are expected to strongly dominate. Hubbard proposed to restrict the Coulomb matrix to these elements [45, 46]. For a single band-model, the resulting Hamiltonian reads

$$H = \sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (2.15)$$

where  $t_{ij} = t$  if  $i$  is a nearest neighbor of  $j$ ,  $t_{ij} = t'$  for next-nearest-neighbors and zero otherwise. Despite the approximate nature of the model it is still under current active research. An exact (Bethe-Ansatz) solution is available only for the one-dimensional model [47, 48], which is a Luttinger liquid [49]. The two-dimensional square lattice model is a minimal model to study the phenomenon of high-temperature superconductivity. It is believed to capture the low energy physics of the cuprates [50]. Another aspect is the Mott transition [14, 9] which arises due to the interplay between the kinetic energy and Coulomb repulsion. The orbital selective Mott transition was studied in the two-orbital model [51]. The model was investigated on the Kagomé lattice to elucidate the effect of frustration [52]. The abundance of numerical results make the Hubbard model an ideal benchmark system for testing new theoretical approaches.