The Hubbard model with orbital degeneracy and in polarizable media

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Introduction

In this chapter some introductory material to this thesis is given. Briefly the background and motivation for this work is described, completed with a general discussion of the Hubbard model and its possible extensions. The material in this chapter represents just a personal choice out of an intensively studied area in solid state physics.

1.1 Introduction

In the theoretical description of the electronic structure of solids, theories based on the concept of the propagation of one single electron in a periodic field due to the nuclei of the atoms and an average Coulomb field due to the other electrons, have been very successful in calculating and predicting a wide range of properties of those solids. A very attractive aspect of effective one-electron theories is that the electronic structure can be calculated \textit{ab initio}, i.e. without using any free parameters. Already in an early stage, however, it was noted that some systems have properties that cannot be reconciled with the outcome of one-electron theory calculations. A canonical example of a class of such materials are the transition-metal oxides. Many of these oxides, for instance, are predicted to be metals in single electron theory, but are in fact insulators with large band-gaps.

The failure of one-electron theory is caused by the assumption that the electrons propagate in the average field of the other electrons. In order to understand this, it is necessary to examine what the consequences are of the averaging of the Coulomb field. Electrons have a kinetic energy and propagate in the lattice so that an average distance between the electrons can be defined. This average distance and deviations from it determine the potential energy of the electron due to the Coulomb interaction with all other electrons. In transition metal oxides, however, it turns out that the Coulomb interaction gives the dominant contribution to the total energy and that the kinetic energy of the electrons associated with their propagation is of secondary
importance. The consequence of this is that the averaging over distances between electrons provides a wrong starting point for the description of these systems. Rather one would start from the concept that first the potential energy between the electrons is minimized, leading to a state where the position of one electron strongly depends on the position of other electrons. Using this collective, correlated, state as a starting point, one can proceed and take also the propagation of electrons in the lattice into account.

Theoretical models that treat the kinetics and electron-electron interactions of the total system on an equal footing are very hard to handle. On an intuitive level this can be expected since in these models the collective motion of, say, $10^{23}$ electrons cannot be split up in small subsystems anymore without losing the correlation effects. In correlated electron systems the whole is literally more than the sum of the parts.

The lack of success in treating the full effect of correlations has lead to the development of model Hamiltonians. These model Hamiltonians describe highly idealized systems, where most interactions between the electrons are left out. One of the simplest model Hamiltonians is the one proposed by Hubbard in 1963 [1]: it only deals with one band of electrons that only have a Coulomb repulsion when the electrons occupy the same lattice site. The rationale behind considering such an over simplified system is that most interesting physical phenomena occur at a low energy scale, in the order of the temperature, i.e. for room-temperature in the order of 25 meV. Processes that occur at higher energy scales are not interesting in themselves. With a model Hamiltonian one wants to describe only a part of the physical phenomena, only the essential ones, which are mostly the low energy phenomena. So the total -full energy scale- problem is mapped onto a model Hamiltonian that incorporates only some effects on part of the full energy scale. This implies that model Hamiltonians are by definition not suited for ab initio calculations. The parameters used in the model Hamiltonian are thought to be effective parameters determined by a renormalization from the full many-body problem.

The trick of the trade now is to find the relevant model Hamiltonian and to solve it. Both are highly non trivial challenges.

## 1.2 Motivation

In the last decades a wealth of materials was discovered where electron correlation seems to play an essential role. Some of these materials exhibit extraordinary properties, phases and phase transitions. Examples are the colossal magneto-resistance (CMR) compounds with magnetic and non-magnetic phases, the high $T_c$ materials with insulating, magnetic, metallic and superconducting phases and the (intercalated) C$_{60}$ compounds with an equally overwhelming richness in phases. Also the longer established Kondo- and heavy fermion systems, low dimensional organic salts and transition metal oxides in general, are dominated by correlation effects. In spite of the enormous efforts, the behavior of these materials is theoretically not well understood.

It would be surprising if all these classes of different correlated systems could
be described by one, simple, model Hamiltonian. This, however, can also not be excluded and the possibility exists that the low energy excitations of these systems can be explained in terms of such a simple, effective model. As argued above, this generates a force-field where the extrema are given by the full many-body problem on one hand and the simplest model Hamiltonian on the other.

In this thesis interactions between electrons that go beyond the simplest model Hamiltonians are included. For the CMR materials the importance of orbital degeneracy is heavily debated and for \(C_{60}\) and high \(T_c\) compounds the possible relevance of longer range Coulomb interactions is considered. In transition-metal oxides in general and in \(C_{60}\) the screening of the Hubbard \(U\) is surely important. Model Hamiltonians that incorporate these interactions found their way into this thesis. The primary focus is on the relevance and consequences of the inclusion of these interactions.

### 1.3 The Hubbard Model Hamiltonian

The Hubbard Hamiltonian [1] is one of the simplest Hamiltonians incorporating electron correlations and electron bandwidth at an equal footing. The Hamiltonian is as easily written down as it is difficult to solve

\[
H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

where \(n_{i\sigma} \equiv c_{i\sigma}^\dagger c_{i\sigma}\) and \(c_{i\sigma}^\dagger\) \((c_{i\sigma})\) creates (annihilates) an electron on site \(i\) with spin \(\sigma = \uparrow\) or \(\downarrow\). The hybridization is denoted by \(t\) and a nearest-neighbor pair by \(\langle ij \rangle\). If two electrons are on the same lattice site, they repel each-other, raising the energy of the system with an amount \(U\). Let us consider the case where the band is half filled, i.e. the number of electrons in the system is equal to the number of sites. If \(U/t = 0\) the system is metallic because the band is half filled. In the opposite limit \(U/t \rightarrow \infty\) the situation is quite different. As it is very unfavorable for two electrons to be at the same lattice site, there are no doubly occupied sites in the ground-state. Each site is forced to be occupied by exactly one electron and this single electron cannot move to other sites, as it would create a doubly occupied site by doing so. The electrons are thus fully localized, and the system is insulating. This implies that a metal-insulator transition occurs as a function of \(U/t\). This is a very interesting feature of the Hubbard model: it shows that electron-electron repulsion can drive a metallic system into an insulating state. As a bonus the insulating state is also magnetic. In the strong coupling limit, when \(U\) is large and the electrons are (almost) localized, it is favorable for neighboring electrons to have opposite spins so that one electron can be virtually excited to a neighboring site, a process that is obviously forbidden by the Pauli principle when the two electrons have parallel spins. In fact the half filled Hubbard Hamiltonian at strong coupling transforms into a Heisenberg Hamiltonian with an anti-ferromagnetic exchange.
However, one would like to quantify these statements. At what value of $U/t$ does the phase-transition take place, and how does this depend on the dimensionality of the system? Unfortunately it is difficult to solve the Hubbard model. Exact solutions are known only for the 1D and the infinite dimensional system. The more appealing 2D and 3D cases remain to be solved exactly. Because also the formal solution of the 1D Hubbard model does not give easy access to physical quantities, there is a large interest in quite a number of approximations, also in 1D. Some aspects of several approximations are briefly addressed below.

### 1.3.1 Correlation Gap

The metal-insulator (M-I) transition in the Hubbard model is characterized by the formation of a gap $\Delta$ due to the correlation effects. From the exact solution of the Hubbard model in 1D by Lieb and Wu [2], can be proven that the gap is given by

$$\Delta = U - 4 - 8 \sum_{n=1}^{\infty} (-1)^n \left\{ \sqrt{1 + n^2 U^2 / 4} - nU / 2 \right\},$$

(1.2)

where $t$ is set to unity. Note that in the derivation for the gap equation given by Lieb and Wu there is a wrong minus sign\(^1\). The result above is corrected for this inaccuracy. From this expression follows that, in the particular 1D case, there is a finite correlation gap for any non-zero value of $U/t$. Strictly speaking in 1D the M-I transition takes place at $U = 0$, which is in some sense a disappointing result.

In order to get a handle on the Hubbard model also in higher dimensions, Gutzwiller [3] developed a variational method to approximate correlation effects. The idea is to introduce a variational wavefunction where the weight of the doubly occupied states is reduced as $U/t$ increases. The variational wavefunction $|\psi_G>$ proposed by Gutzwiller is

$$|\psi_G> = \prod_i \left[ 1 - (1 - \eta) c_{i,\downarrow}^\dagger c_{i,\downarrow} \right] |\psi_0>, \quad (1.3)$$

where $|\psi_0>$ is the wavefunction of the system in absence of correlations ($U = 0$) and $\eta$ is the variational parameter to be determined by the condition that the ground-state energy is minimized with respect to $\eta$. At half filling the ground-state energy per particle is

$$E_{GS} = Q(\nu)W + \nu U, \quad (1.4)$$

where $W$ is the bandwidth ($W = 2zt$, where $z$ is the number of nearest neighbours in a hyper-cubic lattice) and $\nu$ the average number of doubly occupied sites. $Q(\nu)$ reflects

\(^1\)Expression (23) of Lieb and Wu [2] for the chemical potential $\mu_- \text{ is: } \mu_- - 2 = -4 \int_0^\infty \frac{d\omega}{\sqrt{1 + (\nu + 1)^2 U^2 / 4}}$, which is correct, but which is followed by $\mu_- - 2 = -4 \sum_{n=1}^{\infty} (-1)^n \left\{ \sqrt{1 + n^2 U^2 / 4} - nU / 2 \right\}$. It is easy to convince oneself that the correct result is $\mu_- - 2 = +4 \sum_{n=1}^{\infty} (-1)^n \left\{ \sqrt{1 + n^2 U^2 / 4} - nU / 2 \right\}$. This inaccuracy is consistently overlooked in the literature, for instance in Y. Ren and P. W. Anderson, Phys. Rev. B. 48 16662 (1993).
the narrowing of the effective bandwidth due to correlation. Gutzwiller calculated which $\eta$ minimizes the ground-state energy and how exactly $Q(\nu)$ and $\nu$ depend on $\eta$. In this scheme the effect of $U$ is to reduce the probability for a site to be doubly occupied, which at the same time narrows the bandwidth of the electrons. It was pointed out by Brinkman and Rice [4] that in this variational scheme a metal-insulator transition occurs. The phase transition takes place when $U = U_c = 2W$.

Another method to approach the Hubbard model is to diagonalize the Hubbard Hamiltonian numerically for a small clusters of atoms. The great advantage of this method is that all energies and correlation functions can be evaluated exactly. The disadvantage naturally lies in the fact that a small cluster of atoms is a poor representation of a full lattice in some, but not in all, aspects. Short range correlations are described accurately, where as long wavelength properties are represented only approximately. In this thesis the exact diagonalization method is used frequently. For more details on this method the reader is referred to [5, 6]. In figure 1.1 the gap-values for a 1D system calculated within the three schemes described above is shown. The exact diagonalization is performed for a ring of 12 sites. The figure shows that the results of the exact diagonalization are close to the exact result of Lieb and Wu. The gap obtained with Gutzwiller’s variational method strongly deviates from the previous results.

1.3.2 Infinite Dimensions

The limit of large dimensions can be understood as the limit that each lattice site has a large number of neighbors, so that the coordination number is large. Some years ago it was shown that the theory of correlated fermions on a lattice is greatly simplified
in the limit of infinite dimensions [7-9]. In the one-particle Green’s function
\[ G(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon_f - \epsilon(\mathbf{k}) - \Sigma(\mathbf{k}, \omega)} \] (1.5)
all interaction effects enter via the self-energy \( \Sigma(\mathbf{k}, \omega) \). The major consequence of
\( d \to \infty \) is that the self-energy is independent of the momentum \( \mathbf{k} \) [7]:
\[ \Sigma(\mathbf{k}, \omega) = \Sigma(\omega), \quad d \to \infty. \] (1.6)
This can be understood by realizing that in fact we are dealing with an impurity model, where the self-energy is by definition independent of momentum. Each site can be thought of as an impurity in a bath of all other sites. In fact the Hubbard model transforms into an Anderson-impurity model. The Green’s function then can be found by a self-consistent solution of this coupled impurity problem. Because the self-energy is independent of momentum, it is useful to introduce the local one-particle
Green’s function
\[ G_{\text{loc}}(\omega) = \sum_{\mathbf{k}} G(\mathbf{k}, \omega), \] (1.7)

Let us focus on one particular consequence of the momentum independent self-energy. The spectral density, integrated over momenta, is given by
\[ \rho(\omega) = \frac{1}{\pi} \text{Im} G_{\text{loc}}(\omega) = \int_{-\infty}^{\infty} d\epsilon \rho_0(\epsilon) \text{Im} \left[ \frac{1/\pi}{\omega - \epsilon - \Sigma(\omega)} \right], \] (1.8)
where \( \rho_0(\epsilon) \) is the density if states of the non-interacting system and the frequency \( \omega \) is defined with respect to the Fermi-level: \( \omega = \epsilon_f - \text{Re} \Sigma(0) \).

In the limit \( \omega \to 0 \), we know that since the system has quasiparticle properties
\[ \text{Im} \Sigma(\omega) = O(\omega^2) \quad \omega \to 0, \] (1.9)
because the life-time of the quasi-particles is infinite at the Fermi-level. Combining the last two equations, we obtain
\[ \rho(0) = \rho_0(0), \] (1.10)
that is, the density of states at the Fermi-energy is not renormalized by the interaction [8]. This is a strong implication of the self-energy being independent of momentum. Note that in the argument above, symmetry breaking effects due to for instance magnetic ordering, were not taken into account. The fact that the density of states at the Fermi-level is un-renormalized by the interactions leads to a remarkable evolution of the spectral function with increasing interaction. As the interaction increases a so-called coherence-peak builds up around the Fermi-level. This is shown in figure 1.2 for a system with a 2D density of states in the infinite dimensional approximation. At the same time spectral weight is pushed away from the Fermi-level, forming the precursors of the upper and lower Hubbard band. As \( U \) increases the width of the coherence peak gets smaller, going towards zero for very large \( U \).

\[ ^2 \text{Markus Fleck is gratefully acknowledged for making the data represented in this figure available to the author.} \]
The central theme of this thesis is study the consequences of expanding the Hubbard model beyond its simplest form. The focus is on the relevance and consequences of the inclusion of more interactions than only the on-site Coulomb repulsion. Let us briefly address some of these interactions.

### 1.4.1 Atomic Polarizability

If an atom is put in an electric field, the electrons tend to screen the applied field by polarizing. The atomic polarization $\alpha$, the ratio between the strength of the induced dipole moment and the applied field, was already used in the last century in solid state physics when Clausius and Mossotti (independently) derived a formula relating the index of refraction, and in general the response to electric fields, of ionic materials to the polarizability of the constituent ions.

It is less well known that atomic polarizabilities can even play a crucial role in determining the lattice structure, lattice deformations and even electric properties of materials. Let us illustrate this by an example. The ions $S^{2-}$, $Se^{2-}$ and $Te^{2-}$ have huge polarizabilities, mainly due to the fact that their volume is very large (as a rule of thumb the atomic polarizability is proportional to the volume of the atom). Often materials formed with these ions have layered structures [10]. This can be understood by realizing that if sets of ions form layers, electric fields are generated in the solid in which the large ions can polarize, lowering the energy of the system. This competes with a Madelung term which favors a cubic surrounding, i.e. as many as possible - ions around a + ion. Also distortions of the lattice are favored by the highly polarizable ions, as illustrated in figure 1.3. If the lattice distorts an electric
Figure 1.3: A lattice distortion generates an electric field at the position of the polarizable ion as this ion is surrounded by a non inversion-symmetric charge distribution in presence of the distortion. The field induces a electric dipole moment. The interaction of the induced dipole and the field lowers the total energy of the system.

Field $\mathbf{F}$ is generated which in turn induces a dipole moment $\mathbf{P} = \alpha \mathbf{F}$ on the polarizable ion. The interaction of the induced dipole with the electric field lowers the energy by an amount $\Delta E_{\text{pol}} = -\frac{1}{2} \alpha \mathbf{F}^2$. This energy gain is counterweighted by the energy loss due to the elastic deformation of the lattice. The energy needed to distort the crystal is $\Delta E_{\text{elas}} = \frac{1}{2} c u^2 + du^4 + ......$, where $u$ is the amplitude of the distortion. In the distorted structure the electric field on the atom is, first order, proportional the distortion amplitude so that $F = \beta u$. This leads to a total energy for the deformation given by

$$\Delta E_{\text{deform}} = \frac{1}{2} (c - \alpha \beta^2) u^2 + du^4. \quad (1.11)$$

From this polynomial in $u^2$ it is easy to see that if $\alpha < c/\beta^2$ it always costs energy to deform the lattice: $\Delta E_{\text{deform}} > 0$. If, however, the polarizability is larger than $c/\beta^2$, the minimum of energy is reached for some finite deformation amplitude. This shows that the atomic polarizability can be the driving force for lattice deformations. This line of argument was also used to describe the occurrence of ferroelectric phases. The coefficient $c$ depends on temperature. In the simplest approximation this results in a phase where at $T < T_c$ there is a spontaneous electrical polarization of the system which is lacking above $T_c$. This may serve as an extra argument stressing the importance of a relatively simple concept as the atomic polarizability in physical systems.

The combination of polarizable atoms and the on-site Coulomb repulsion $U$ is discussed in the chapters 2 and 5 in this thesis.
1.4.2 Longer Range Coulomb Interaction

Several authors have stressed the importance of longer range Coulomb interactions for the properties of correlated systems as the High $T_c$ superconductors, (intercalated) C$_{60}$ compounds and the CMR materials [11]. In these systems the importance of the on-site Coulomb interaction is generally accepted, but it should be noted that the fact that the on-site Coulomb repulsion is large does not mean at all that, for instance, the inter-site Coulomb repulsion is large. There are two different length-scales involved in these quantities. The on-site Coulomb repulsion is determined by the expectation value of the Coulomb operator acting on two orbitals on the same atom, so it is related to the atomic radius of these two orbitals. The inter-site Coulomb repulsion is determined by the expectation value of the Coulomb operator acting on two orbitals on neighboring atoms, so that it is related to the lattice constant. This implies that whenever the nearest neighbor Coulomb interaction is important, necessarily also the on-site Coulomb repulsion is important, but not the other way around. This leads to the natural consequence to extend the Hubbard model with (at least) the inter-site Coulomb interaction. The chapters 3, 4 and 5 of this theses are therefor (partially) devoted to this subject.

1.4.3 Orbital Degeneracy

The $d$ wavefunctions of free atoms are, besides spin-degenerate, also 5-fold orbital degenerate. If atoms with open $d$ in a solid, $d$ orbitals retain to a large extend their atomic character because $d$ wavefunctions are very localized around the nucleus. In a crystal the symmetry of the surroundings of an atom with an open $d$ shell is lowered, lifting some orbital degeneracy but not necessarily all. So a partially filled $3d$ level can have both a localized orbital and spin degree of freedom. This problem was already put forward some twenty years ago [12] and attention for it flourishes since the recent discovery of the CMR materials where orbital ordering is important. The excitations of an orbitally degenerate system consist of spin and orbital waves that are coupled. In chapter 6 the nature of the elementary excitations in an orbital degenerate correlated system are examined in detail.

1.5 Scope

The scope of this thesis is for the largest part already described in the previous subsections. The thesis is completed by chapter 7 about the optical conductivity in intercalated C$_{60}$ and chapter 8 about the $t$-$t'$-$t''$-$J$ model for the high $T_c$ compounds. In chapter 7 we take a viewpoint to C$_{60}$ that is opposite to the viewpoint taken in the rest of this thesis. Throughout the thesis the importance of correlations for this material is stressed. It is, however, not generally accepted that correlations are very important for these materials. In chapter 7 we take the approach of neglecting correlations completely. We include phonons and try to explain the measured, very unusual, optical conductivity in this way. The conclusion of this chapter is that the
one-electron theory plus phonons can not account for the measured conductivities, and that most likely correlation effects are needed in order to explain the data. In the last chapter we go beyond the simplest model for the low-energy phenomena for the high $T_c$ compounds, the t-J model. From recent band-structure calculations it is known that the band-structure of the Cu-O$_2$ planes in these materials cannot be described by one hopping parameter $t$ alone. Within the self-consistent Born approximation we calculate the temperature dependence of the quasi-particle peaks as measured in angle-resolved photo-emission and compare our results with the experimental data.

References

[11] See references included in the introductory sections of the chapters 3, 4 and 5.