Introduction

1.1 Strongly Correlated Materials

In last decades main attention of experimental and theoretical studies for metallic systems has shifted to the field of transition and rare-earth elements with partially filled 3d-, 4f-, and 5f-electronic shells and based on them chemical compounds. At the beginning of this process in 1960s, the most intriguing phenomenon in this field was metal–insulator phase transition (\(MI\)) observed for many transition metal oxides with variations in pressure, temperature, or doping. A decade later a new class of rare-earth compounds was discovered where charge carriers have effective mass value tens and hundreds time larger than free electron mass – so called “heavy fermion” (HF) systems. In such systems a great variety of interesting phenomena were found: phase transitions between magnetic order and superconductivity, appearance and disappearance of local magnetic moments, transport properties anomalies.

Such interplay of electric and magnetic properties is typical manifestation of strong coupling for electronic and magnetic degrees of freedom in many 3d- and 4f-elements compounds. Good example of such coupling are manganites with colossal magneto-resistive effect, where moderate magnetic filed can drastically change electronic state of the system from insulating to metallic. However, the most significant and totally unexpected was the discovery of high-temperature superconductivity (\(high-T_c\)) in transition metal oxides. This discovery brought researchers attention to synthesis and physical properties study of new materials and in next 20 years there were found a lot of new compounds with anomalous properties.

It is clear that physical phenomena richness for these compounds is due to the presence of partially filled 3d-, 4f-, or 5f-electronic shells with local magnetic moments preserved in solid. Strong interaction of \(d, f\) electrons with each other and with itinerant electronic states of the material is responsible for its anomalous properties. Such materials with strong electron–electron interaction are called strongly correlated systems (SCS). All the above mentioned
chemical compounds and many others discussed later belong to \textit{SCS} (see e.g.\cite{1}).

Anomalous physical properties of new materials are determined by their electronic structure. Classical band theory works very well for simple metals and semiconductors where interelectron interaction is weak but it is unable to describe \textit{SCS}. In \textit{SCS} a strength of Coulomb interaction among electrons is of the same order as band width for 3\textit{d}-, 4\textit{f}-, or 5\textit{f}-shells or even larger. In this case completely new approach is needed that is beyond perturbation theory. In last 40 years starting from pioneering Hubbard works \cite{2,3} there were proposed many methods to treat \textit{SCS} electronic structure problem. Those methods were based on simple models: Hubbard model, \textit{sd}-model, and periodic Anderson model. Some of the proposed approaches were successful for certain \textit{SCS} classes but they were far from being universal and failed for more complicated models describing real materials.

It seemed that \textit{SCS} theory was doomed to be adequate only for certain limited cases and able to produce not more than semiquantitative results. The breakthrough was achieved when Metzner and Vollhardt \cite{4} in 1989 proposed to study strongly interacting electrons systems in large dimensional \textit{d} space (or equivalently lattices with large number of nearest neighbors \textit{z}). It was shown that in the limit \textit{d} \(\rightarrow\) \(\infty\) (or \textit{z} \(\rightarrow\) \(\infty\)) equations of motion for electrons on lattice are significantly simplified and can be exactly solved for any value of Coulomb interaction strength.

Theory simplification in \textit{d} \(\rightarrow\) \(\infty\) limit is because of the fact that in this case one can neglect spatial fluctuation in the system leaving in consideration only dynamical on-site fluctuations. This discovery led to development of Dynamical Mean-Field Theory (\textit{DMFT}) where lattice problem was mapped to effective impurity problem with correlated electrons feeling time or energy dependent mean-field (hence the name \textit{dynamical} mean-field) but the field dependence on wave vector responsible for spatial correlations is ignored. Solution of the impurity problem is used to build self-energy for lattice Green function that in its turn gives new approximation for dynamical mean-field. So this field is self-consistently determined in \textit{DMFT} calculation scheme. First application of this method was done by Georges and Kotliar \cite{5} and Jarrell \cite{6} for Hubbard model in 1992. There was obtained so called three-peak spectral structure with central quasiparticle peak on Fermi energy and two broad side peaks corresponding to lower and upper Hubbard bands (see also \cite{7}). Such three-peak structure was later found in experimental spectra. Metal–insulator transition with increasing Coulomb interaction strength \textit{U} was described in this picture as spectral weight transferring from quasiparticle band to Hubbard bands with disappearance of quasiparticle peak and energy gap creation for critical \textit{U} value.

Later \textit{DMFT} was applied to basic \textit{SCS} models and results were described in review \cite{8}. In last years \textit{DMFT} developments allowed to treat successfully not only simple systems but also complicated real compounds \cite{8–11}. Some extensions of \textit{DMFT} were proposed to take into account spatial
correlations. Successes of $DMFT$ were recognized when its founders Georges, Kotliar, Metzner, and Vollhardt were awarded in 2006 Agilent Technologies Europhysics Prize \cite{12}.

It is necessary to note that long before $DMFT$ development the importance of taking into account local on-site correlations was recognized. Local correlations has allowed Hubbard \cite{13,14} to describe splitting of noninteracting band on two “Hubbard” sub-bands due to strong Coulomb interaction. The next important step was to use representation of partition function as a functional integral over fluctuating fields that has allowed to Hubbard and Hasegawa to develop “Single-site Spin Fluctuation” theory (SSF) \cite{13,15–17}.

Further progress in this direction was based on using “Coherent Potential Approximation” (CPA) developed originally to treat disordered alloys electronic structure. Later, it was shown that CPA is exact in the limit of infinite dimensions $d \to \infty$. Kakehashi and Fulde \cite{18–25} have developed a number of approaches where CPA calculation scheme was generalized for taking into account dynamical fluctuations. It was done via introduction of frequency dependence in coherent potential corresponding to combined action of all electrons on distinguished lattice site. These approaches resulted in the development of “Dynamical CPA” (din.CPA) \cite{19}, “many-body CPA” (MB-CPA) \cite{26}, and “projection operator CPA” method (PM-CPA) \cite{22}.

As it was shown in \cite{21,27} that MB-CPA and PM-CPA methods are equivalent to $DMFT$. All of them ignore spatial correlations in SCS but take into account local on-site dynamical fluctuations. Extension of those approaches to include spatial correlations was realized in “self-consistent PM-CPA” method (SCPM) \cite{23,24}. Application of SCPM method to Hubbard model has allowed to reproduce all main effects of strong correlations near half-filling including three-peak structure of spectral function that was obtained in $DMFT$.

There is an important technical detail worth mentioning. In contrast to $DMFT$ based on temperature (Matsubara) Green function formalism, in PM–CPA method and its extension SCPM retarded Green functions are used. In the result in those methods one does not need to perform analytical continuation procedure from imaginary frequencies to real energy values as it is the case in $DMFT$ calculation scheme. That could be a significant advantage of SCPM method compared to $DMFT$ because such analytical continuation can be an “ill defined problem”.

Dynamical CPA approaches were developed in parallel to $DMFT$ and the former could be regarded as a supplemental method to the latter. A detailed comparison of those two approaches is presented in Kakehashi review \cite{27}. Later we will consider only $DMFT$ method results for SCS theory.
1.2 Basic Models in Strongly Correlated Systems Theory

Quantum mechanical study of strongly correlated systems is done by two approaches: ab-initio electronic structure calculations and model investigations. In the first case real materials can be described with specifics of their chemical composition and crystal structure fully taken into account. In model approaches such specifics are neglected but more rigorous solution of the problem can be obtained with physical properties dependence on temperature and applied external fields. Sometimes, it is possible to get analytical description of the results with formulas but in general numerical calculations to find equations solutions are unavoidable.

For material with partially filled $d$- or $f$-shells three basic models are used: Hubbard model [2], $sd$-model [28, 29], and periodic Anderson model [30]. In Hubbard model only one group of nondegenerate electrons is considered with repulsive Coulomb interactions for electrons on the same site. Model Hamiltonian describing electrons motion on the lattice and their local Coulomb interaction is:

$$
\mathcal{H} = \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}.
$$

(1.2.1)

As electrons are not degenerate then two electrons can meet on the same site only when their spin directions are opposite to each other. Here $\hat{c}_{i\sigma}$ and $\hat{c}_{i\sigma}^+$ are creation and annihilation operators for electron on site $i$ with spin index $\sigma$ that can have two values: $\uparrow$ and $\downarrow$, $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^+ \hat{c}_{i\sigma}$ is electrons number operator with spin $\sigma$ on site $i$, $t_{ij}$ is hopping matrix element. Usually, it is supposed that hopping is not zero only for nearest neighbors (number of those is $z$). Second term in (1.2.1) describes local Coulomb interaction among electrons with Coulomb parameter $U$ defined as an energy needed to put two electrons on the same atomic site ($U \equiv E(2) + E(0) - 2E(1)$). This term was proposed by Anderson to describe a problem of local magnetic moment on impurity in metal [30]. Such simplified expression for Coulomb interaction was found very convenient for magnetism in metals study. Fundamental investigations performed by Hubbard on the basis of Hamiltonian (1.2.1) gave his name to the model [31].

In Hamiltonian (1.2.1) there are two parameters: $zt$ and $U$ ($t$ is hopping matrix element value for nearest neighbors $t_{ij}$). For various values of their ratio two cases can be distinguished: weak coupling when $U \ll zt$ and strong coupling when $U \geq zt$. First case corresponds to standard itinerant magnetism model (see for example [32]) whereas second one to strongly correlated systems where Hubbard model is usually used. In the limit $U \gg zt$ Hamiltonian (1.2.1) can be reduced to effective $tJ$-model Hamiltonian [31]:

$$
\mathcal{H} = t \sum_{ij\sigma} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + J \sum_{ij} (S_i^e S_j^e).
$$

(1.2.2)
1.2 Basic Models in Strongly Correlated Systems Theory

Hamiltonian (1.2.2) describes correlated motion for electrons on the lattice (correlated means that electrons can hop to the neighboring site only when there is no other electron on this atom); operator \( \hat{c}_{i\sigma}^+ = \hat{c}_{i\sigma}^+(1 - \hat{n}_{i-\sigma}) \) correspond to creation for correlated electrons, electron number operator \( \hat{n}_{i\sigma} \) on the site \( i \) with spin \( \sigma \) assumes that only one electron can occupy the site. Second term in (1.2.2) describes exchange interaction among electrons on neighboring sites. Its parameter value \( J = 4t^2/U \) is determined by Anderson kinetic exchange effect [33]. Exchange interaction in (1.2.2) describes the tendency to antiferromagnetic ordering in the system. Spin operators in (1.2.2) can be expressed via Fermi operators in a standard way [34]:

\[
S_i^\sigma = \sum_{\sigma' \sigma'} c_{i\sigma}^+ s_{\sigma \sigma'} c_{i\sigma'}, \tag{1.2.3}
\]

where \( s \) is a vector build from Pauli matrices:

\[
s^x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad s^y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad s^z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.2.4}
\]

It means that \( tJ \)-model Hamiltonian has purely electron nature and does not include local spin operators as in Heisenberg model.

Let us consider now hybrid models that include two types of electrons. One of them is \( sd \)-exchange model where electrons interact not with each other but with localized magnetic moments. Those moments are formed by atoms with partially filled electronic shells called \( d \)-electrons while itinerant electrons are named \( s \)-electrons. In reality, \( sd \)-model describes rare-earth elements compounds where \( 4f \) electrons are indeed very well localized. \( sd \)-model Hamiltonian is expressed via Fermi operators for itinerant electrons and local spin operators:

\[
\mathcal{H} = \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} - J \sum_{i\sigma\sigma'} (S_i s_{\sigma \sigma'} \hat{c}_{i\sigma}^+ \hat{c}_{i\sigma'}). \tag{1.2.5}
\]

Here \( J \) is so called \( sd \)-exchange integral defining strength of exchange interaction \( JS_i S_i^\sigma \) of local spin \( S_i \) on site \( i \) and electron spin \( S_i^\sigma \) on the same site that is determined by (1.2.3). \( sd \) model Hamiltonian is quadratic for Fermi operators with off-diagonal exchange terms.

\( sd \)-model contains two parameters \( zt \) and \( J \). Depending on their ratio value two cases can be distinguished. For \( J \ll zt \) one has weak coupling and \( sd \)-exchange term can be treated in perturbation theory. In this approximation many interesting physical results were obtained: itinerant electrons magnetization in ferromagnetic metals, electron-band splitting in antiferromagnetic metal, exchange interaction between local spins via itinerant electrons, Kondo effect, connection between magnetic and electron properties in rare-earth metals, and superconductivity destruction by paramagnetic impurities. In strong coupling case \( J \gg zt \) the problem can be reduced to effective double-exchange Hamiltonian [35–37] that describes ferromagnetism in manganites.
Second hybrid model is Periodic Anderson Model (PAM) that includes two type of electrons: itinerant ($s$-electrons) and localized ($d$-electrons). Coulomb interactions is taken into account only for localized electrons on the atomic site. In contrast to $sd$-models $s$- and $d$-electrons are coupled not via exchange interaction by through hybridization term. In general case Periodic Anderson Model Hamiltonian is:

\[
H = \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + \varepsilon_d \sum_{i\sigma} \hat{n}_{i\sigma}^d + \sum_{i\sigma} \hat{n}_{i\uparrow}^d \hat{n}_{i\downarrow}^d + \sum_{ij\sigma} (V_{ij} \hat{c}_{i\sigma}^+ \hat{d}_{j\sigma} + V_{ij}^* \hat{d}_{i\sigma}^+ \hat{c}_{i\sigma}),
\]

(1.2.6)

where $\hat{c}_{i\sigma}(\hat{c}_{i\sigma}^+)$ and $\hat{d}_{i\sigma}(\hat{d}_{i\sigma}^+)$ are Fermi operators for $s$- and $d$-electrons, respectively, and $\hat{n}_{i\sigma}^d = \hat{d}_{i\sigma}^+ \hat{d}_{i\sigma}$ the electron number operators for $d$-electrons with spin $\sigma$ on the site $i$. In Hamiltonian (1.2.6) $\varepsilon_d$ is $d$-electron energy and $V_{ij}$ the hybridization parameter. This model describes appearance of local magnetic moments, Kondo insulators, heavy fermions, and intermediate valence effect.

Models defined by Hamiltonians (1.2.1) and (1.2.6) are basis of strongly correlated systems theory where magnetic and transport properties are studied. Investigation results for those models help to understand metal–insulator phase transition, high-$T_c$ superconductivity, heavy fermion effects in rare-earth and actinides compounds.

### 1.3 Methods for Models Investigation

We will exclude from our consideration one-dimensional Hubbard model where exact analytical solutions can be found. Our main interest will be $d = 3$ (sometimes $d = 2$) systems ($d$ is space dimension) that are directly related to real materials with strong correlations effects.

Initially, models were investigated by simplest methods such as mean-filed theory and perturbation theory when small parameter can be found like $U \ll zt$ for Hubbard and Anderson models or $J \ll zt$ for $sd$ model. In the cases where there is no small parameter ($zt \sim U$ or $zt \sim J$) serious difficulties appear in attempts to obtain analytical solution for the problem. In such cases sometimes another small parameter could be found such as number of electrons, $1/N$ expansion ($N$ is a number of degenerate states), or $1/z$ expansion ($z$ is nearest neighbors number). The last case in the limit of $d \to \infty$ (or $z \to \infty$) led to development of DMFT.

There were also approaches developed not based on perturbation theory for interaction parameter. Among them we mention decoupling method for double-time Green functions starting from pioneering Hubbard works and used in various models. Closely related to it is composite operators method [38] that was successfully applied to strong correlations problem. Rather apart stands variation Gutzwiller method [39] widely used for study strongly correlated systems.

Important development was also auxiliary particle approach: slave boson and auxiliary fermions methods. The idea on the basis of those methods is
to replace general operators (such as Hubbard $X$-operators) by the product of Fermi and Bose operators with additional procedure to exclude unphysical states. Good choice of auxiliary particles can lead to correct low-energy physics of the model in mean-filed approximation. Unfortunately, there is no universal recipe to construct such representation and often it is not clear which of the possible representations is the best one. There are many version of auxiliary particle methods.

In the physical literature there were proposed and used many different theoretical approaches to strong correlations problem. Reader can find their description in reviews [40–43] and monograph [44].

As we will show in this book the most universal method to study basic models is $DMFT$ that allows to calculate electronic spectra and physical properties of strongly correlated systems with arbitrary value of interelectron interaction strength.

1.4 Ab-initio Electronic Structure Calculation Methods

Approach based on basic model study allows to understand electronic states in strongly correlated systems and to plot phase diagrams as a function of model parameters. However, in order to use these results for interpretation of real compounds experimental data one needs to know parameter values characteristic for particular material. For this purpose there are two approaches: empirical and first principles.

The first of them, empirical, is based on using experimental data to determine model parameters. Usually that is spectral data (optical, photoemission, and X-Ray spectra) that can give information about band width. In the case of strongly correlated systems on the edge of the metal–insulator transition (or already in Mott insulator state) it is possible to estimate also value for Coulomb interaction parameter $U$ determined from the energy separation of the spectral peaks interpreted as Hubbard bands.

More often the approach is used where model parameters (such as Coulomb interaction parameter $U$ and band width $W$) are varied to achieve the best agreement between experimental data for some characteristic (resistivity, susceptibility, etc.) and the corresponding value calculated in model solution. In such approach model parameters are considered to be adjustable parameters.

However, the most justified way to determine model parameters is using results of electronic structure calculations from first principles methods (or in other words ab-initio methods). The name first principles is used as opposite to empirical approach. First principles methods are not formally exact ones, because a lot of various approximations were done in their derivation. The key issue is the fact that in these methods construction only the most basic (first) Quantum Mechanics principles were used such as many-electron Schrödinger equation. For atoms and small molecules many-electron methods could be used where wave function is represented as linear combination of
Slater determinants. However for solids the most practical approach is Density Functional Theory (DFT)\cite{45,46} that reduces many-particle problem to one-electron one. In Sect. 2.1.1 the basics of DFT are presented and in Sect. 2.1.2 the main calculation methods based on DFT are described.

In DFT one solves differential equations for one-electron wave functions with effective potential that is in its turn determined by the equation solutions. That results in very effective and practically realized iterative calculation scheme. However that means explicit neglect of correlation effects (all electrons feel the same time and energy independent potential). In the result for Mott insulators (for example transition metal oxides) DFT methods gave wrong metallic ground state (see Sect. 2.1.3).

There were proposed many corrections to DFT overcoming this defect and resulting in correct ground state for Mott insulators (see Sect. 2.1.4). However those correction were not derived from general enough equations and have rather restricted area of applicability.

Better perspectives has approach where electronic structure calculation results by DFT methods are used to calculate parameters for general Hamiltonian and then the problem defined by this Hamiltonian is solved by one of the methods developed in basic models theory (see Sect. 1.2). In Sect. 2.2 we describe how it is possible using Wannier functions formalism to calculate Hamiltonian parameters from eigenfunctions and eigenvalues obtained in DFT. Using constrain DFT (see Sect. 2.2.5) one can calculate also the value of Coulomb interaction parameter $U$.

The problem defined by this Hamiltonian can be solved in the simplest static mean-filed approximation (unrestricted Hartree-Fock). The resulting calculation scheme is called LDA + $U$ method and is described in Sect. 2.3. This method was found to be very successful when applied to systems with long-range spin and orbital order.

However, more general problems of paramagnetic insulator and strongly correlated metal can be solved only by DMFT method that is described in details in Chaps. 3–5. Approach based on solving in DMFT the problem defined by the Hamiltonian with parameters calculated in DFT calculations is called LDA + DMFT method and is described in Chap. 6.
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