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Strongly Correlated Systems

Theoretical Methods

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With 147 Figures

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To Maria Marinaro, who introduced us to the wonderful field of many-body physics

Preface

This volume is the first of three volumes reviewing the main analytical, numerical and experimental techniques specifically devised to study Strongly Correlated Systems. This editorial project builds upon the long-standing experience we have acquired in organizing the "Training Course in the Physics of Strongly Correlated Systems" in Vietri sul Mare (Salerno, Italy) since 1996 and our working scientific experience in the field. Running a school for advanced graduate students and junior post-docs, we realized that this field of condensed matter and solid state physics was missing adequate textbooks and that the whole Strongly Correlated Systems community would benefit by a systematic exposition of the field. The present volume consists of a series of monographs on the most relevant analytical methods currently used to tackle the hoary problem of correlations. Authors have been selected, consulted major experts in the field, among the most world-wide famous scientists who invented or greatly helped to improve/spread the specific method in the community. Each chapter presents the method in a pedagogical way and contains at least one case study where the method has proved to give a substantial leap forward in the knowledge and a very rich bibliography. The book is mainly intended for neophytes, who will find in one single volume all pieces of information necessary to choose and start learning an analytical method. Also more experienced researchers would benefit from this volume as they would gain a deeper understanding of what any single technique can really tell them and what cannot. Accordingly, the accent is more on the ideas behind (origins, pros/cons, perspectives, etc.) than on the technical details, which are left to the comprehensive bibliography.

We wish to thank all authors of this volume as they all joined this editorial project with enthusiasm and provided the whole community with what we hope will become a relevant resource for any researcher in the field as comprehensive and extended reference.

Salerno, October 2011

Adolfo Avella
Ferdinando Mancini

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Foreword

Peter Fulde

It required the discovery of the high-temperature superconducting cuprates before the field of strongly correlated electrons obtained the attention it deserves. Shortly after their discovery it became clear that the normal state properties of these materials and moreover the appearance of superconductivity cannot be understood without better insight into the strong correlations prevailing in these systems [1]. Even before that time, a sizeable amount of research had been devoted to strong correlations. The Kondo effect, intermediate valence systems, and materials with heavy low-energy quasiparticles are areas which required to deal with them. But these efforts were small when compared with those which set in after high-T_c superconductivity was discovered. In a series of three volumes, of which the present is the first, an overall survey is made of the present status of the theory of strongly correlated electrons. Some aspects, like numerical methods, are the subject of the second volume in this series. The last one includes experimental techniques, which are used to study strongly correlated electrons.

When speaking about strongly correlated electrons, the first question which comes to one's mind is, how can we decide whether or not electrons in a given material are strongly correlated. In other words, how can we determine the strength of correlations provided that we know the full many-electron wavefunction $|\psi_0\rangle$ to a reasonable approximation? For that, a simple measure can be introduced, which is based on the degree of suppression of electronic charge fluctuations on different atomic sites compared with those which are obtained when instead of $|\psi_0\rangle$ the uncorrelated or Hartree–Fock counterpart $|\Phi_0\rangle$ is used [2]. This gives rise to a quantity $0 \leq \Sigma_A \leq 1$. It defines the strength of correlations at a site A, so that $\Sigma_A = 0$ is the limit of uncorrelated electrons, while $\Sigma_A = 1$ describes the strong

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correlation limit. More specifically, we define Σ_A through

$$\Sigma_A = \frac{\left\langle \Phi_0 \left| (\delta n_A)^2 \right| \Phi_0 \right\rangle - \left\langle \psi_0 \left| (\delta n_A)^2 \right| \psi_0 \right\rangle}{\left\langle \Phi_0 \left| (\delta n_A)^2 \right| \Phi_0 \right\rangle}, \tag{1.1}$$

where $\delta n_A = n_A^2 - \bar{n}_A^2$ with n_A denoting the electron number operator, e.g., of d electrons on site A and $\bar{n}_A$ its average value with respect to $|\Phi_0\rangle$ or $|\psi_0\rangle$. Note that definition (1.1) deviates slightly from the one given in [2]. Applied to the simple example of a H_2 molecule, one finds $\Sigma_{\mathrm{H}} \approx 0.1$, i.e., rather weak correlations. A wavefunction with a doubly occupied molecular orbital would give $\Sigma_{\mathrm{H}}(\mathrm{MO}) = 0$ while the Heitler-London wavefunction yields $\Sigma_{\mathrm{H}}(\mathrm{HL}) = 1$, since all ionic configurations are suppressed. It is interesting that the π electrons in graphene have $\Sigma_\pi \simeq 0.5$, showing that correlations are fairly strong in that system, while the d electrons on a Cu site in the Cu–O planes of the cuprates have $\Sigma_{\mathrm{Cu}} \simeq 0.8$. Thus, correlations are indeed strong here. But it is also apparent that theories which apply, e.g., a Gutzwiller projector to a wavefunction of electrons in the Cu–O planes overestimate the correlation strength. That projector eliminates charge fluctuations completely and is equivalent to setting $\Sigma_{\mathrm{Cu}} = 1$.

Electronic charge fluctuations at a given atomic site interfere with the formation of intra-atomic Hund's rule correlations. When $\Sigma_A \simeq 1$ the latter can fully form, while with decreasing values of Σ_A they become less important. This shows up in the behavior of $\langle \psi_0 | \mathbf{S}_A^2 | \psi_0 \rangle$ with changing Σ_A where $\mathbf{S}_A$ is the total spin at site A.

1 Ab-Initio Calculations

Ab initio electronic structure calculations are dominated by density functional theory (DFT). They have revolutionized that field. The subject is reviewed in this volume by Jones (see Chap. 8), one of the pioneers in the field. But DFT is a ground-state theory and therefore it is of little surprise that it fails, in particular for strongly correlated systems, when low-energy excitations are calculated from it. The failure is inherent and independent of any approximations which are made for the potential in the Kohn-Sham equation. This is seen by considering the simplest possible system of strongly correlated electrons, i.e., two electrons in two orbitals. As seen below, this model also shows a characteristic feature of strong correlations, namely the appearance of new low-energy scales. In weakly correlated systems the characteristic energy scale is given by the Fermi energy ϵ_{F}, or alternatively, by the electronic hopping matrix elements t_{ij} between neighboring sites i and j. Strong correlations cause additional, much lower energy scales.

The two orbitals are denoted by L (for ligand) and F (for $4f$, for example) and we assume the corresponding orbital energies to be ϵ_l and ϵ_f with $\epsilon_f < \epsilon_l$. Two electrons in the F orbital are expected to repel each other with an energy $U \gg \Delta\epsilon$ with $\Delta\epsilon = \epsilon_l - \epsilon_f$. When both electrons are in the L orbital, or when one electron is in the L and the other in the F orbital, we neglect their Coulomb interaction.

This is justified, if the ligand orbital has a large spatial extent. It applies when, for example, the ligand orbital is that of a large molecule or when it is a Bloch state. We assume that the hybridization t between the two orbitals is small, i.e., $t \ll \Delta\epsilon$. The Hamiltonian of the system is

$$H = \epsilon_l \sum_\sigma l_\sigma^+ l_\sigma + \epsilon_f \sum_\sigma f_\sigma^+ f_\sigma + t \sum_\sigma \left(l_\sigma^+ f_\sigma + f_\sigma^+ l_\sigma \right) + U n_\uparrow^f n_\downarrow^f . \tag{1.2}$$

The $l_\sigma^+(l_\sigma)$, $f_\sigma^+(f_\sigma)$ create (annihilate) electrons with spin σ in the L and F orbitals, respectively; furthermore $n_\sigma^f = f_\sigma^+ f_\sigma$. The Hamiltonian is so simple that it can be easily diagonalized. When $t = 0$, the ground state of the system has energy $E_0 = \epsilon_l + \epsilon_f$ and is fourfold degenerate. One electron is in the F orbital, while the other is in the L orbital. The four states are eigenstates of the total spin S and consist of a singlet $|\Phi_{S=0}\rangle$ and a triplet $|\Phi_{S=1}\rangle$. The system has one excited state of the form

$$|\Phi_{\mathrm{ex}}\rangle = l_\uparrow^+ l_\downarrow^+ |0\rangle . \tag{1.3}$$

The energy of that state is $E_{\mathrm{ex}} = 2\epsilon_l$. The state $f_\uparrow^+ f_\downarrow^+ |0\rangle$ is excluded from further consideration, since its energy is of order U and we assume $U \to \infty$.

When the hybridization is turned on, the singlets $|\Phi_{S=0}\rangle$ and $|\Phi_{\mathrm{ex}}\rangle$ are coupled, while the $S = 1$ states $|\Phi_{S=1}\rangle$ remain unchanged. The coupling leads to the two eigenvalues

$$\begin{aligned} \tilde{E}_0 &= E_0 - \frac{2t^2}{\Delta\epsilon}, \\ \tilde{E}_{\mathrm{ex}} &= E_{\mathrm{ex}} + \frac{2t^2}{\Delta\epsilon}. \end{aligned} \tag{1.4}$$

For small values of t there is a low-lying triplet excitation above the singlet ground state. One can attach a characteristic temperature $T^* = 2t^2/(k_{\mathrm{B}}\Delta\epsilon)$ to the energy gain associated with the singlet formation. It is by a factor $t/\Delta\epsilon$ smaller than the energy scale set by the hopping matrix element t and is an example of the new low-energy scales, which are generated by strong correlations. The same system can be treated using the density functional theory. In fact, that is quite interesting to do so, because one can derive explicitly the exact exchange-correlation potential $v_{\mathrm{xc}}[\rho]$ as function of the density. When the 2×2 Kohn–Sham equation is solved, one finds that the energy difference between the two eigenvalues should *not* be interpreted as the excitation energy, since it is of order t instead of T^*. These findings hold irrespective of approximations to the functional [3].

With the above pointed out, it is clear that treatments of low-energy excitations by Kohn–Sham equations have no sound basis. Nevertheless, semi-empirical methods based on density functional theory have had numerous successes. An excellent example is the renormalized band-structure method [4]. It is the only one which has been able to make detailed predictions for the effective mass anisotropies at the Fermi surface of heavy-quasiparticle systems. The idea hereby is to formulate the quasiparticle dispersions in terms of phase shifts like in an independent electron approach. For these phase shifts, one is using the ones obtained from an LDA, i.e., a local approximation to the density functional, except for those of the strongly correlated electrons. For Ce intermetallic compounds like $CeRu_2Si_2$, $CeSn_3$, $CeCoIn_5$, etc., these are the f electron phase shifts at the Ce sites. For the latter, a phenomenological ansatz is made. It has the effect of reducing the bare bandwidth to a renormalized one of order $k_B T^*$. Take $CeRu_2Si_2$ as an example. The phase shifts near the Fermi energy ϵ_F are

$$\{\eta_l^A(\epsilon)\} = \left\{\eta_l^{\mathrm{Ce}}(\epsilon), \eta_{l'}^{(\mathrm{Ru})_\nu}(\epsilon), \eta_{l''}^{(\mathrm{Si})_\mu}(\epsilon)\right\}, \quad \nu; \mu = 1, 2, \tag{1.5}$$

where l, l', l'' are angular momenta and the indices ν, μ count different atoms within the unit cell. Except for $\eta_{l=3}^{\mathrm{Ce}}(\epsilon)$ all other phase shifts are assumed to be given by the LDA. Regarding the f phase shifts at a Ce site, only the one with $j = 5/2$ (Hund's rule multiplet) is relevant and, more specifically, with the symmetry of the crystalline field ground-state doublet, i.e., $\eta_\tau^{\mathrm{Ce}}(\epsilon)$ with $\tau = 1, 2$. It can be parameterized by the resonant form

$$\eta_\tau^{\mathrm{Ce}}(\epsilon) = \arctan \frac{\Gamma}{\tilde{\epsilon} - \epsilon} \tag{1.6}$$

with two parameters Γ and $\tilde{\epsilon}$. One of them is fixed by the f-electron number at a Ce site, while the remaining one is fixed by requiring that the large γ coefficient of the low temperature specific heat $C = \gamma T$ is reproduced. As mentioned earlier, with these phase shifts not only a Fermi surface but also the strongly anisotropic quasiparticle masses can be determined. They agree well with experiments.

Another extension of density functional theory which is often used is the LDA+U method. Here the LDA is supplemented by adding an on-site Coulomb interaction U and exchange interaction J term to the LDA energy. For example, for d electrons it is

$$E = E_{\mathrm{LDA}} + \frac{U}{2} \sum_{lij\sigma} \delta n_{i\sigma}(l) \delta n_{j-\sigma}(l) + \frac{(U-J)}{2} \sum_{li(\neq j)\sigma} \delta n_{i\sigma}(l) \delta n_{j\sigma'}(l), \tag{1.7}$$

where l is a site index while i and j are d orbital indices. Furthermore, $\delta n_{i\sigma}(l) = n_{i\sigma}(l) - n_0(l)$ where $n_0(l) = n_d(l)/10$ and $n_d(l)$ is the total d electron number at site l. The LDA is an orbital-independent molecular-field approximation and therefore an inclusion of the deviations $\delta n_{i\sigma}(l)$ allows for an improved treatment of correlations. The potential entering the Kohn-Sham equation is obtained from $\delta E / \delta n_{i\sigma}(l)$ as

$$V_{i\sigma}^{\mathrm{eff}}(l) = V_{\mathrm{LDA}} + U \sum_j \delta n_{j-\sigma}(l) + (U-J) \sum_{j \neq i} \delta n_{j\sigma}(l), \tag{1.8}$$

which shows that results different from LDA are obtained if the spin orbitals are differently populated, i.e., when $\delta n_{i\sigma}(l) \neq 0$. An unequal population is favored by a large Coulomb interaction U like in any unrestricted mean-field approximation. As explained earlier, this way charge fluctuations are suppressed and correlation energies (not wavefunctions) are improved. There has also been an approach developed in which the LDA is used for computing Wannier functions and Coulomb parameters as input for a multiband Hubbard Hamiltonian. The latter is treated by a generalized tight-binding method, i.e., one which combines the exact diagonalization of an isolated cluster, i.e., a unit cell, with a perturbation treatment of the intercluster hopping and interactions [5] (see Chap. 4.4). The aim has been to find, e.g., the size of the gap in La_2CuO_4, which in LDA is absent.

Another hybrid method is the LDA+DMFT [6]. The dynamical mean-field theory (DMFT) [7–9] is a dynamical coherent potential approximation (DCPA) [10] which was stimulated by work on the Hubbard model in infinite dimensions [11, 12] (see Chap. 6.5). While the standard coherent potential approximation (CPA) introduced by Hubbard in connection with his Hamiltonian (see below) reduces at temperature $T = 0$ to a self-consistent field (SCA), i.e., Hartree–Fock theory, the DMFT (or DCPA) contain correlation effects in that limit. A site of an infinite lattice with, e.g., d electrons is treated as an impurity in a medium for which an LDA calculation has been done. The electronic self-energy $\Sigma(\omega)$ at the impurity site is computed and the medium is self-consistently modified until the self-energy of the impurity coincides with that of the medium. A shortcoming of the DMFT and DCPA is that only on-site correlations are treated, i.e., any $\mathbf{k}$ dependence of the self-energy is neglected. From quantum chemical calculations it is well known that intersite correlations are important and must be treated if one is interested in quantitative results.

Extensions of the original DMFT to a cluster DMFT [13] go in the right direction, but the clusters one can treat are rather small. Therefore, one cannot distinguish, e.g., between short-range AF correlations and long-range AF order. One possible way of including properly the short-ranged correlations is by using the method of increments in connection with a self-consistent projection operator method. This allows $\Sigma(\mathbf{k}, \omega)$ to be calculated with rather high accuracy. These approaches are still at their infancy as far as realistic calculations for specific materials are concerned, but some promising results have been obtained.

A rather different approach to strongly correlated electron systems is based on wavefunction methods [2]. They are combined with quantum chemical techniques and provide a rigorous theoretical framework for addressing the correlation problem which avoids any uncontrolled approximations. Many-body wavefunctions can be explicitly constructed at levels of increasing sophistication and accuracy. But in order to ensure size extensivity of the modifications induced by correlations the wavefunctions have to be formulated using cumulants. Standard quantum chemical methods thus offer a systematic path to converged results. They provide the right framework for coping with issues like a rigorous treatment of the ubiquitous short-range correlations and of a realistic representation of the crystalline environment. The way to proceed is to cut out a finite atomic cluster C from the infinite solid which is large enough to describe the crucial short-range correlations. Partially filled d-electron shells require a multiconfiguration representation of the correlated many-electron wavefunction, which is achieved using the complete-active-space (CAS) self-consistent field (CASSCF) method. This way, strong correlations can be very well accounted for. The crystalline environment is described by an effective one-electron potential which is extracted from prior Hartree–Fock calculations for the periodic system. Remember that Hartree–Fock calculations describe charge distributions quite well. They are robust against correlation corrections, even when the latter are strong. With this approach the ground state of such strongly correlated systems as $LaCoO_3$ and LiFeAs was determined as well as the Zhang-Rice-like electron removal band for CuO_2 planes in La_2CuO_4 [14].

Wavefunction-based quantum chemical calculations for strongly correlated electrons are a field with high potential for the future. They have been somewhat neglected, because they require investments in program development and time, features not particularly favored by research funding. However, concerning actual calculations, they are the best one can do to obtain insight into the most important microscopic processes.

2 Model Hamiltonians

From Sect. 1 it is apparent that ab-initio calculations for strongly correlated electron systems are still at their beginning. Therefore, simplifying model Hamiltonians are very helpful in order to unravel physical effects caused by them. The one studied most is the Hubbard Hamiltonian [15]

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} . \qquad (1.9)$$

It has one orbital associated with each site i and the Hamiltonian contains a hopping term between nearest-neighbor sites and an on-site Coulomb repulsion term U. The simplifications made by this ansatz as compared with a quantum chemical ab-initio Hamiltonian are enormous. But nevertheless, important insight can be gained by studying (1.9), in particular, when a system is at or close to half filling. Various techniques have been applied to study the Hubbard model with emphasis on two dimensions (2D). This is, because claims have been made that a 2D Hubbard model contains all of the important physics of high-T_c superconductivity.

A large role is being played by cluster approximations. They replace the infinite lattice by a finite cluster which is often embedded in an effective medium. In view of the short range of the correlation hole of an electron, that seems fine even for an infinite system, provided the correlation hole is properly constructed. In order not to limit for computational reasons the cluster to a too-small size, the method of increments can be used as a tool. It can be looked at as an expansion of a (cumulant) scattering matrix in terms of one, two, three etc. site clusters. But that is often not done and in that case translational invariance within a cluster is missing. Established approaches within quantum cluster theory are the dynamical cluster approximation [16, 17] (see Chap. 8.8), the cluster DMFT mentioned earlier [18] (see Chap. 10.7) and the cluster perturbation theory [19] (see Chap. 7.9). In the latter case a perturbation expansion in terms of the hopping matrix element t is combined with the exact diagonalization of small clusters. The dynamical cluster approximation has the advantage of ensuring translational invariance within a cluster. In that respect it differs from the cluster DMFT in which this symmetry is violated. Otherwise, both methods are similar in many aspects. An incremental cluster expansion of the self-energy or scattering matrix has been applied in a fully self-consistent projection operator approach [20].

One can try to find a formalism from which all the different cluster methods derive as special cases, at least as long as they are based on Feynman diagrams. The hope is that this allows for the development of improved cluster methods. Such an attempt has been made with the Self-Energy Functional Theory [21] (see Chap. 9.5). It starts from the generating functional $\Phi[G, U]$ of the Green's function G. The self-energy is required to be given by the derivative of Φ with respect to G, i.e., $\Sigma = \delta\Phi[G]/\delta G$. From the work of Baym and Kadanoff it is known that conservation laws are obeyed if $\Phi[G, U]$ is calculated from all distinct, connected, and closed skeleton diagrams expressed in G and U. One may then specify to which approximations for Φ a given cluster method corresponds to.

Quantum cluster theories are one possibility to find approximate solutions for the Hubbard model. Of course, other methods have been developed too, which treat the infinite system. Thereby special attention is paid to conserving approximations, i.e., approximations which do not violate conservation laws [22] (see Chap. 12.6). Also the functional renormalization group has been applied to the two-dimensional Hubbard model. It works like a microscope with variable resolution. For understanding the low excitation energy sector of the Hubbard model, one eliminates all degrees of freedom of the system which are irrelevant for its behavior in that limit. For that purpose differential equations for the one-particle Green's function are derived which describe the flow of parameters as the degrees of freedom are reduced. Since it is difficult to calculate the renormalization flow for a strongly interacting system, one is starting out from a weakly interacting system in which case the energy scale is given by the kinetics. But as the energy scale decreases, the coupling function increases. This is indicative of possible instabilities, e.g., of magnetic or pair forming origin. In that case one has to switch to a modified description of the system which accounts for these changes [23].

A much studied example is the Mott–Hubbard metal-to-insulator phase transition at half filling when $U \gg t$ [52]. But even now it is not known at which critical ratio of U_c/t this phase transition is taking place at $T = 0$. The value has been steadily increasing with improvements of the approximation schemes. At present the most accurate estimates are obtained when the self-energy is computed with a dynamical CPA in combination with self-consistent projection operator methods. That allows for the calculation of $\Sigma(\mathbf{k}, \omega)$ with an accuracy, which includes effects up to the 12th nearest neighbors. Despite considerable efforts, the topic itself is still wide open. There are several reasons for this. One is that in the Hubbard model we include one orbital per site only. But in a realistic multiorbital system it is likely that criteria for localization are first fulfilled for a single orbital or for two of them (compare with the dual model of $5f$ electrons) before the system becomes an insulator. Also, there may be a redistribution of electrons among different orbitals as the phase transition is approached. The spectral density and in particular the low-energy peak as obtained, e.g., from a DMFT calculation behave quite different when the ground state is paramagnetic and when it has a long-range AF order. An open question is how AF correlations modify the spectral density as the correlation length increases continuously near a metal-insulator transition.

For small deviations from half filling the Hubbard Hamiltonian can be transferred into a $t - J$ model Hamiltonian of the form

$$\begin{aligned} H_{t-J} &= -t \sum_{\langle ij \rangle \sigma} \left(\hat{a}^{+}_{i\sigma} \hat{a}_{j\sigma} + h.c. \right) + J \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{\hat{n}_i \hat{n}_j}{4} \right) \\ &= H_t + H_J, \end{aligned} \tag{1.10}$$

where the operators $\hat{a}^{+}_{i\sigma}$, $\hat{a}_{i\sigma}$ are defined by

$$\begin{aligned} \hat{a}^{+}_{i\sigma} &= a^{+}_{i\sigma}(1 - n_{i-\sigma}), \\ \hat{a}_{i\sigma} &= a_{i\sigma}(1 - n_{i-\sigma}). \end{aligned} \tag{1.11}$$

The spin operators are $\mathbf{S}_i = (1/2) \sum_{\alpha\beta} \hat{a}^{+}_{i\alpha} \boldsymbol{\sigma}_{\alpha\beta} \hat{a}_{i\beta}$ and $\hat{n}_{i\sigma} = \hat{a}^{+}_{i\sigma} \hat{a}_{i\sigma}$. The coupling constant is $J = 4t^2/U$ and defines a low-energy scale caused by the strong correlations. At half filling $H_t = 0$ and we deal with an antiferromagnetic (AF) Heisenberg Hamiltonian. Its excitations involve only spin degrees of freedom and constitute the simplest example of spin-charge separation. The $t - J$ model has been very successful in understanding the motion of doped holes or electrons in an antiferromagnetic surroundings. The bandwidth of a coherent hole motion is of order J and therefore strongly renormalized as compared with the bare hopping matrix element t. The energy dispersion of the coherent quasihole motion strongly resembles that found by ab initio calculations using quantum chemical methods. With the $t - J$ model one can also show that two doped holes attract each other, a possible mechanism for high-T_c superconducting in hole-doped cuprates. One can also study the effects of small hole concentration back on the form of AF order, i.e., the development of spiral spin states [24].

Improved Hubbard Hamiltonians have been applied to the Cu–O planes of the high-T_c cuprates. For example, in addition to a $3d_{x^2-y^2}$ orbital for the Cu ions the $2p$ orbitals of the O ions which hybridize with the $3d_{x^2-y^2}$ Cu orbitals are included.This leads to three-band or five-band Hubbard Hamiltonian depending on whether one includes one or two of the $2p$ oxygen orbitals in the Cu–O plane. A new feature which is not contained in a one-band Hubbard description is the formation of a Zhang–Rice singlet state, when a hole is doped in an otherwise half-filled system. It is mainly located on the oxygen sites and the singlet is formed with the hole on the Cu^{2+} ion [25].

Model Hamiltonians have also been widely used in order to study the microscopic origins of different systems with heavy quasiparticle excitations. The Anderson lattice Hamiltonian has played a prominent role. It is of the form

$$\begin{aligned} H = & \sum_{\mathbf{k}n\sigma} \epsilon_n(\mathbf{k}) a^+_{\mathbf{k}n\sigma} a_{\mathbf{k}n\sigma} + \sum_m \epsilon_{fm} f^+_m(i) f_m(i) \\ & + \frac{1}{\sqrt{N_0}} \sum_{im\mathbf{k}n\sigma} V_{m\sigma}(\mathbf{k}, n) \left[a^+_{\mathbf{k}n\sigma} f_m(i) \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}_i} + h.c. \right] \\ & + \frac{U}{2} \sum_{im \neq m'} n^f_m(i) n^f_{m'}(i). \end{aligned} \tag{1.12}$$

There are conduction electrons with band index n which weakly hybridize with strongly correlated electrons. They are created (destroyed) by f^+, f operators with an orbital index m and are positioned at lattice sites i. Various approximation schemes have been applied to that Hamiltonian. They are of diagrammatic nature like the noncrossing approximation [26, 27], which describes the Anderson lattice as a system of independent impurities. Or they introduce auxiliary fields like slave boson fields [28–30] which allow for mean-field treatments. Also the so-called Gutzwiller approximation has been applied [31–33]. It renormalizes the hybridization matrix element and moves the orbital energy close to the Fermi energy.

The common feature of those approximations is to reproduce the low-energy scales, which strongly correlated electrons generate.

3 Systems with Heavy Quasiparticles

A sizeable number of intermetallic compounds have a high density of fermionic low-energy excitations. Experiments show that their low-temperature thermodynamic properties strongly resemble those of ordinary metals but with a large quasiparticle mass. The latter can become as large as a meson or even proton mass. It is a consequence of the low-energy scales which strong electron correlations create. Systems with heavy quasiparticles involve $4f$ or $5f$ electrons, in one case, i.e., LiV_2O_4 even $3d$ electrons. Much studied examples are $CeAl_3$, $CeRu_2Si_2$, $CeCu_2Si_2$ or Yb_3As_4 with $4f$ electrons and UPt_3, UBe_{13} and UPd_2Al_3 with $5f$ electrons.

After the discovery of the heavy quasiparticles [34] it was generally believed that the Kondo effect is responsible for those low-energy excitations. Indeed, breaking up a Kondo singlet formed between a $4f$ electron, e.g., of Ce, with the conduction electrons requires a small amount of energy only, i.e., of the order of a few meV. However, in the meantime we have learned that heavy quasiparticles may have quite different microscopic origins. In addition to the Kondo effect (e.g., $CeAl_3$,

$CeRu_2Si_2$, $CeCu_2Al_2$) also partial charge order (e.g., Yb_4As_3), partial localization (e.g., UPt_3, UPd_2Al_3) or the Zeeman effect (e.g., $Nd_{2-x}Ce_xCuO_4$) may cause heavy quasiparticles [35]. In LiV_2O_4, a spinel, the frustrated pyrochlore sublattice of the V ions plays an important role in the formation of the large number of low-energy excitations. While the low temperature properties of heavy quasiparticles are reasonably well understood, the transition to higher temperatures $T > T^*$ at which the quasiparticles lose their large effective mass is less understood. Related with it is a transition from a large Fermi surface, in which the strongly correlated f electrons take part to a small Fermi surface at $T > T^*$ where they are excluded. In the latter case, they behave like localized electrons.

A field of its own are quantum critical points and their neighborhood [36]. At a quantum critical point a system undergoes a phase transition at zero temperature as a function of an external parameter like pressure, impurity concentration etc. Clearly, there are many low-lying excitations in the vicinity of quantum critical point. In some cases, e.g., YMn_2 [37] heavy quasiparticle behavior is observed, but more common is a break down of Fermi-liquid theory near such a point.

4 Mean Field Approximations

Whenever mean-field approximations (MFA) can be made to a Hamiltonian, they not only simplify significantly its solution, but in most cases, also provide new physical insight. The simplest MFA to a Hamiltonian of interacting electrons is the Hartree–Fock or SCF approximation. It neglects totally electron correlations. The question arises whether MFAs can be made which take strong correlations reasonably well into account. Of special interest are clearly mean-field solutions with broken symmetries, i.e., with a ground state which has a lower symmetry than the Hamiltonian. However, care must be exercised here. Often only a symmetry breaking occurs, because correlation effects are simulated which otherwise are insufficiently taken into account.

For example, an AF ground state reduces on-site charge fluctuations as do correlations. In that case, one has to decide whether an AF mean-field solution describes the system correctly or whether it is merely favored because it suppresses charge fluctuations. The simplest example is a H_2 molecule with variable bond length. An unrestricted SCF calculation gives a symmetry broken ground state when the bond length exceeds a critical value. Near one proton the electrons have predominantly spin up while near the other proton they have predominantly spin down. In reality, there is, of course, no distinction between the spins on the two sites. But therefore, all ionic configurations are eliminated by the unrestricted MFA in the limit of large bond lengths.

A special object of mean-field investigations has been the Hubbard model on a cubic or square lattice at or near half filling. With hopping limited to nearest neighbors one finds for the half-filled case perfect nesting at the Fermi surface and a spin-density mean-field ground state for any value of $U > 0$.

An interesting variety of MF solutions is obtained when auxiliary slave boson or fermion fields are introduced [38] (see Chap. 3). An example is the replacement

$$a_{i\sigma} = f_{i\sigma} b_i^+, \quad a_{i\sigma}^+ = f_{i\sigma}^+ b_i, \tag{1.13}$$

where the fermion operator $f_{i\sigma}^+$ creates a spinon at site i while the boson b_i^+ creates an empty site (holon). Strong correlations can be taken into account by forbidding double occupancies via the subsidiary condition

$$\sum_\sigma f_{i\sigma}^+ f_{i\sigma} + b_i^+ b_i = 1, \tag{1.14}$$

i.e., a site is either empty or singly occupied. When the $t - J$ Hamiltonian (1.10) is re-expressed in terms of spinons and holons, different MFAs with different order parameters can be made [39]. One of them has the form of a BCS superconducting order parameter, but here in terms of spinons, not electrons, while another is of resonating valence bond (RVB) type (see Chap. 1.6). There are also other MFAs possible, in particular, since the decomposition (1.14) of electrons in form of spinons and holons is not the only possible one. Another decomposition is

$$a_{i\sigma}^+ = f_i b_{i\sigma}^+, \quad a_{i\sigma} = f_i^+ b_{i\sigma}, \tag{1.15}$$

where the spin degree of freedom is represented by a boson field. We want to find a representation of the Hamiltonian in terms of auxiliary fields in terms of which a MFA describes strong electron correlations as well as possible.

5 Deviations from Fermi Liquids

There is no a priori reason why strongly correlated metallic systems should depict Fermi-liquid behavior. But experiments show that in many cases they do. Systems with heavy quasiparticles are an example. However, in dimensions lower than three deviations may easily occur.

In one dimension (1D) a much discussed item is the separation of spin and charge degrees of freedom. An example is trans-polyacetylene where it is known that excitations involving only spin or charge degrees of freedom do exist. Moreover, when heavily doped, those systems can have excitations with fractional charges. Spin-charge separation is also found in Tomonaga-Luttinger liquids, i.e., one-dimensional interacting electron systems. These features are found independent of the strength of correlations.

In 2D, deviations from Fermi-liquid behavior have been observed not only in the high-T_c cuprates, but also most importantly in samples which exhibit a fractional quantum Hall effect [40]. In the latter case, excitations with fractional charges are widely spread and their statistics changes from fermionic to anyonic. We are able to understand in the cuprates a number of deviations from standard Fermi-liquid behavior by a *marginal* Fermi-liquid description [41].

Even in three dimensions, deviations from a Fermi liquid are known. Examples are doped Mott–Hubbard systems, but also, e.g., Yb_4As_3 where due to partial charge order, spin and charge degrees of freedom are nearly separated. The break down of a Fermi liquid near a quantum critical point was mentioned before.

6 Superconductivity

Two features of superconductivity in strongly correlated electron systems need special attention. One is the form of the pair state and the other is the origin of electron-electron attraction resulting in a Cooper pair formation. Before the discovery of the high-T_c cuprates, s-wave pairing was assumed to be ubiquitous, although there were indications that in some of the systems with heavy quasiparticles the pair state was of a more complex form. However, it turned out that in the high-T_c materials, electrons pair in a d wave state. This state is preferred when the electron-electron attractions are caused by electronic excitations rather than phonons. Here, one has to distinguish between excitations within the electron system, which forms the Cooper pairs and those, which take place in another, i.e., localized electron system with which the itinerant electrons are interacting. The first case seems to be realized in the cuprates with spin fluctuations leading to electron attractions [42, 43] (see Chap. 5.8). Their form is though quite different in the underdoped and overdoped regimes. The second case is realized, e.g., in the filled skutterudite compound $PrOs_4Sb_{12}$ where intra-atomic, i.e., crystal field excitations of the $4f^2$ subshell of Pr^{3+} provide for an attraction between conduction electrons. The more recent FeAs superconducting compounds, which came as a complete surprise, re-emphasize the need for a better understanding of strongly correlated electrons.

A main topic of research is to describe the high-T_c cuprates for low and high hole doping concentrations, i.e., in the under- and overdoped regimes. While in the overdoped regime a Fermi liquid description applies, this is different in the underdoped regime, where the system is close to a Mott–Hubbard transition to an insulating state.

Understanding the form of the Fermi surface as function of hole doping is an important issue. Angular-resolved photon emission spectroscopy is an invaluable tool here [44]. For a satisfactory description of the normal state a broad spectrum of methods has been used. At one end, are MFA to the Hubbard Hamiltonian rewritten in terms of auxiliary fields [39], at the other end, are quantum chemical calculations with a basis set of respectable size for the energy dispersion of a hole in a Cu–O plane. A separate question is the form of the wavefunction in the superconducting state. An obvious choice is a BCS wavefunction multiplied by a Jastrow function in order to take the strong correlations into account. A simplified form of the Jastrow factor is a Gutzwiller projector which eliminates all configurations with doubly occupied sites [45] (see Chap. 3.7). This wavefunction relates to an RVB state as mentioned earlier. It is used to estimate the transition temperature in the regime of small hole doping. In the overdoped regime, solving Eliashberg's equations with a spin fluctuation propagator determined within the FLEX approximation has given good results [46].

7 Composite Operator and Projection Techniques

One way of dealing with strongly correlated electrons is to limit the operator or Liouville space within which one wants to describe the many-body system. Stated differently, among all possible degrees of freedom of the system only those are kept, which are considered to be the most important ones. The composite operator method developed by Mancini and Avella [47] and expanded continuously [48–50] (see Chap. 3.7) and the projection operator method (see, e.g., [2]) share this goal. They differ in the way the relevant part of the operator space is chosen. The composite operator method starts from the equation of motion for the single particle Green's function, which generates a new Green's function, this time for composite operators instead of a single electron operator. This procedure is repeated until the sequence of Green's function is terminated at some stage. The projection operator method selects the relevant operator space simply by specifying the microscopic processes which one wants to include, independent of the order in which they appear in the hierarchy of Green's function. This has to do with the lack of a proper expansion parameter, when kinetic energy and Coulomb repulsion are of comparable size. After the space of composite or relevant operators has been chosen, one can diagonalize the matrix of Green's functions. However, there are constants appearing in the solution and different methods differ in the way they are computed They may or may not include couplings to the neglected part of the full operator space. Notwithstanding the possible derivation of low energy scales in certain special cases, like the Kondo problem [51], the selection of a limited number of composite operators is best suited for determining high-energy incoherent excitations of strongly correlated systems. The Zhang–Rice singlet in Cu–O planes or satellite peaks in transition metals serve as examples here. Usually, the lower the considered energy scales are, the more the relevant operator space, i.e., the number of composite operators has to be extended to deal with them.

8 Summary

We have tried to point out a number of features which are characteristic for systems with strongly correlated electrons. Needless to say that neither are they complete nor do they give a historical account of their development. For example, we have not mentioned the effects characteristic for transition metals. The interplay of Hund's rule correlations and the kinetic energy requires a description which interpolates