A 3BS Approach to Electron-Electron Correlations in Solids

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Introduction

One of the main challenges of theoretical condensed matter physics is the understanding and the development of tools for the calculation of material properties. One of the most important and revolutionary steps that have been made in the last century toward this goal was the introduction of density functional theory (DFT) [1], [2], which together with the local density approximation (LDA) [3] established itself as the par excellence method for realistic solid state calculations. Despite of its drastic approximation to the interacting electrons problem, that is replaced by an effective mean field and further simplified by the employment of a functional that would properly describe a weakly interacting system, DFT-LDA calculations of both ground state energies and band structures turn out to be satisfactory for many materials, implying that correlations, which are rudimentarily treated in the LDA, are rather weak in such systems.

Materials for which DFT is successful have broad energy bands associated with large values of the kinetic energy of the electrons: this implies that these are highly itinerant, or delocalized, and therefore it is reasonable to describe them using a wave-like picture in which interactions become in some sense smooth and can be averaged out.

On the contrary when bands are narrower and the associated kinetic energy smaller, namely when electrons tend to localize around lattice ions, they “see each other” more as individual point charges and the correlation between their motion becomes important.

One striking consequence of electron-electron correlations is the emergence of insulating behaviour in systems with partially filled bands, a feature that according to band theory is precisely the definition of a metal. Nevertheless, “it is quite possible that the electrostatic interaction between the electrons prevents them from moving at all. At low temperatures the majority of the electrons are in their proper places in the ions. The minority which have happened to cross the potential barrier find therefore all the other atoms occupied, and in order to get through the lattice have to spend a long time in ions already occupied by other electrons. This needs a considerable addition
of energy and so is extremely improbable at low temperatures” (Peierls, 1937, cited in [4]). In other words, as the ratio of the Coulomb repulsion energy and the available kinetic energy increases delocalising the valence electrons over the whole solid becomes less and less energetically favorable, and a point can be reached where electrons remain completely localized: if this happens to all the electrons close to the Fermi level the solid becomes an insulator (in other cases the electron localization affects only a part of the valence band and the solid remains a metal: but its properties are frequently quite different from those of ordinary metals, and define what is called an anomalous metallic phase). The insulating phase, which depends not on the lack of accessible electronic states but on the Coulomb repulsion that “freezes” the system, was first understood by Peierls and Mott [5], [6], and such insulators are therefore called Mott insulators; prototype examples are NiO and V$_2$O$_3$.

It is apparent that a Mott insulator can be hardly depicted in terms of a wave-like picture with an average electron-electron interaction borrowed from a homogeneous electron gas: the Mott physics indeed is completely missing in the LDA. One can think to stay within the single-particle approach, but to adopt a particle-like picture involving wavefunctions localized around specific atomic sites: retain DFT, but improve the functional. This is the idea behind the LDA+U method [7], which indeed succeeds in capturing the insulating character of Mott systems, with two sets of bands (Hubbard bands) separated by a local Coulomb repulsion $U$. The drawback is that the energy gain due to the formation of Hubbard bands is so large in LDA+U that for realistic values of $U$ it almost automatically yields an insulating behaviour, even if this is not correct. If in LDA “everything is metallic”, in LDA+U conversely “everything is insulating”: the problem remains of how to properly treat the whole range of electron-electron correlations in a unified manner, and even more so because the interesting physics often occurs for intermediate regimes (think for instance to high-temperature superconductivity in cuprates, colossal magnetoresistance in manganites, mass renormalization effects in heavy fermion compounds).

Although the quest for better and better DFT functionals is still open, the alternative route of leaving single-particle approaches and switching to many-body ones is also widely followed. In particular the search for non-perturbative methods, applicable to all regimes of correlations, has been intense in the last fifteen years, leading now to some widely accepted results, the first and most important one being the choice of the Hubbard model [8], [9] as the general framework to describe strong electron-electron correlations. The idea is to replace the exact hamiltonian of the interacting electron system with a model one which explicitly (i.e. beyond mean-field approximation) contains the Coulomb repulsion between electrons sitting on the same lattice.
site, namely the part of the electron-electron interaction which is considered to dominate the physics of strongly correlated materials (the Hubbard hamiltonian will be presented in more details in Sec. 1.1 of the present work). This model captures the competition between electron localization and delocalization that gives rise to the interesting phenomena observed in such systems, but still is hard to be solved, and a variety of techniques have been proposed at this purpose, ranging from exact diagonalizations to Monte Carlo simulations to different kinds of approximations [10].

One method in particular is here worth to be mentioned, due to its several common features with the three-body scattering theory (3BS) that will be presented in this thesis: the dynamical mean field theory (DMFT) [11], [12]. In DMFT the lattice problem of the Hubbard model is mapped onto a single-impurity model, for which very powerful non perturbative methods of solution are available [13]. This quantum impurity model consists of a single correlated site embedded in a fermionic bath whose structure has to be determined self-consistently. Although originally designed for model systems, this method can be combined with DFT-LDA band structures to describe real materials: the resulting LDA+DMFT scheme [14], [15] is presently one of the most widely used and successful techniques to compute electronic structures of strongly correlated solids. The comparison between DMFT and 3BS will be addressed in Sec. 4.2.1 of this thesis.

One limitation of the original formulation of DMFT, and of 3BS as well, is that it results in a purely local self-energy, thus missing non-local effects that would be crucial in the context of spectral properties which vary across the Brillouin zone. Many efforts have been made to extend the theory taking into account at least finite-range interactions via the substitution of the single impurity with a cluster-impurity, but so far with severe problems and drawbacks [16]. The inclusion of non-local effects is an important current topic of research for 3BS as well.

As previously mentioned the Hubbard model explicitly contains the interaction between electrons only when they are at the same lattice site, thus to a large extent neglecting the long-range part of the Coulomb interaction. A promising approach which has been recently proposed [17] to overcome this limitation is to combine DMFT with the GW approximation [18],[19], [20]. This last, one of the most widely used methods based on many-body perturbation theory, amounts to a first order expansion of the self-energy in terms of the dynamically screened Coulomb interaction \( W \) and is believed to quite adequately describe the long-range part of the electron-electron repulsion: excited state properties of \( sp \) metals and semiconductors are indeed well reproduced by GW. Short-range correlations, on the other side, are not properly taken into account, and this is the reason of its failure in the de-
scription of $d$ and $f$-electron materials. To address these strongly correlated systems therefore one can think to use DMFT to compute the local part of the self-energy, and to take from GW the long-range contribution. This could be an interesting outlook for 3BS theory as well.

The 3BS theory discussed and employed in this thesis belongs to the approximate methods devised to solve non-perturbatively the Hubbard model. Its basic idea dates back to the 80’s from the pioneering work of Igarashi [21], [22], [23]: mapping the many-body problem on an effective three-body one, for whose solution the general method developed by Faddeev [24] is adapted and exploited.

3BS appears for the first time in the literature in its present form, suitable for the inclusion of correlation effects into electronic structures of realistic systems, in 1994 [25]. Its applications include the prediction of the correct insulating character of NiO [26], the study of valence and core states photoemission from ferromagnetic nickel [27], [28], the calculation of low-energy excitations and Fermi surface of YBa$_2$Cu$_3$O$_7$ [29], the reproduction of the quenching of majority spin quasi-particles in cobalt [30]. Moreover it has been used to address the issue of the relevance of electronic correlations in transport properties (see Refs. [31], [32], [33]).

3BS theory is currently at a stage of active development. Several extensions of the method have been pursued in the present work, including the account for five-body corrections beyond the original three-body formulation and the introduction of an iterative self-consistent procedure.

Self-consistency seems to be a very general requirement, fundamental both in DMFT (to link, as previously mentioned, the starting lattice model with the effective single-impurity model) and in many-body perturbation theory, where the calculation of the Green’s function $G$ requires the knowledge of the self-energy $\Sigma$ which in turn is a functional of $G$. A vast discussion about self-consistency indeed exists in the context of the GW method (recent advances can be found for instance in Refs. [34]-[35]). In the following we will show that a self-consistent procedure is needed also in our approach and we will present a way to achieve it.

Moreover, the five-body generalization of 3BS opens the way to a reformulation of the whole theory in terms of a variational method based on the Luttinger-Ward functional [36], [37], in which the total ground state energy $E$ is expressed as a functional of the interacting one-particle Green function $G$, and the self-energy as the derivative of $E$ with respect to $G$. The interesting point is that any self-energy which can be obtained with this procedure guarantees conservation of total energy, particle number and of all the other quantities that must be conserved according to the symmetry of the Hamiltonian, in contrast with generic approximations to the self-energy that
may introduce some symmetry breaking and lead to unphysical violations of conservation laws.

While 3BS theory is described, in its present five-body version, in Chapt. 1 of this thesis, Chapt. 2 is devoted to a reformulation of the theory in terms of Feynman diagrams which makes it possible to link it with the Luttinger-Ward functional formalism and thus to establish its conserving properties; Chapt. 3 focuses on the self-consistency issue, which is illustrated considering applications to model systems.

Finally in Chapt. 4 as a prototype example of applicability to real systems we present the study of the quasi-particle spectra of the late transition metals iron, cobalt and nickel, with a specific eye to the comparison with recent experimental results of spin-resolved photoemission spectroscopy [38], [39]. While these systems can be considered as moderately correlated, still they show some important correlation effects such as the shrinking of the 3d band and the formation of non-coherent satellites in their photoemission spectrum. If observed down to the very details with modern tools they look less and less conventional, and despite their vital importance for nearly all fields of technology it turns out that we still lack a full, quantitative understanding of these materials.
Chapter 1

Three-body scattering theory

In this chapter we present the basis of the 3BS theory for the calculation of ground state total energy $E_G$ and self-energy $\Sigma$ of a strongly correlated system. We show how from the Hubbard model it is possible to derive an effective hamiltonian which describes the effect of correlations on one-electron removal energies in terms of interactions between, essentially, 3-body configurations. This first step relies on a configuration-interaction expansion of the exact many-body state, and the truncation of this expansion at the level of two electron-hole pairs added to the Fermi sea. Then expressions of both $E_G$ and $\Sigma$ in terms of a 3-body resolvent related to the effective hamiltonian are derived, under the additional approximation of neglecting electron interactions within the ground state of the system (a scheme to go beyond this approximation will be presented in Chapter 3); the Faddeev method to compute the 3-body resolvent is illustrated. Concerning the self-energy, the result is a complex, energy dependent quantity that is evaluated at zero temperature on the real energy axis. Finally we describe how the various formulas have been practically implemented, exploiting a local approximation which removes the dependence of all the involved quantities on $k$-vector.

The whole theory is developed in the simple case of a single band solid; only in the last section we mention the necessary extensions to deal with realistic systems.

1.1 Hubbard hamiltonian

The Hubbard model has been extensively used to study electronic correlations both in model system and in real materials. It describes the competition, in a solid system, between electronic delocalization due to the interaction with the lattice potential and localization due to Coulomb repulsion.
The simplest Hubbard hamiltonian assumes that at most two electrons of opposite spins can sit on each lattice site (just one orbital per site); its representation in a localized basis \( \{ | \varphi_{i\sigma} \rangle \} \) (\( i \) = lattice site index, \( \sigma \) = spin index) is:

\[
\hat{H} = \sum_{i\sigma} \epsilon_i \hat{n}_{i\sigma} + \sum_{\sigma} \sum_{ij} t_{ij} \hat{c}_{i\sigma} \hat{c}_{j\sigma} + U \sum_{i\sigma} \hat{n}_{i\sigma} \hat{n}_{i-\sigma} \quad (1.1)
\]

where \( \hat{c}_{i\sigma} ^\dagger \), \( \hat{c}_{i\sigma} \) and \( \hat{n}_{i\sigma} \) are respectively the creation, annihilation and number operators relative to the state \( | \varphi_{i\sigma} \rangle \), and the superscript “′” means that terms with \( i = j \) are excluded from the summation.

The first two terms of the hamiltonian describe a system of non interacting, delocalized electrons; the last term, the Hubbard term, describes the interaction between two electrons with opposite spins sitting on the same lattice site. This is assumed to be the most relevant part of the electron-electron interaction and is the only one which is explicitly included as a many-body term in the hamiltonian; the reminder long range Coulomb interaction is neglected (or treated by mean field approximation: this is the case when the Hubbard model is exploited to correct single particle band structure results obtained by \emph{ab-initio} methods. See Sec. 1.9).

We can give an alternative representation of the Hubbard hamiltonian in terms of extended single particle states characterized by the lattice vector \( k \):

\[
\hat{H} = \sum_{k\sigma} \epsilon_k \hat{n}_{k\sigma} + \frac{U}{N} \sum_{kk'q} \hat{c}_{k+q} \uparrow \hat{c}_k \uparrow \hat{c}_{k'q} \downarrow \hat{c}_{k'q} \downarrow \quad (1.2)
\]

here \( N \) is the number of lattice sites and of \( k \) points. Now the first term describes the set of non interacting electrons with dispersion \( \epsilon_k \), while the last is the electron-electron interaction in an extended states representation.

1.2 Effective hamiltonian

The core of our approach is the expansion of the interacting \( M \)-particle ground state \( | \Psi_0^M \rangle \) in terms of (all, in principle) the excited states of the corresponding non interacting system:

\[
| \Psi_0^M \rangle = \sum_n | \Phi_n^M \rangle \quad (1.3)
\]

where \( n \) is the number of electron-hole pairs added to the Fermi sea \( | \Phi_0^M \rangle \) (non-interacting ground state); each term with fixed \( n \) actually consists of a
Figure 1.1: Pictorial representation of the configuration-interaction expansion of a many-body state $|\Psi_0^M\rangle$, Eq. (1.3). The dashed area represents the interacting electrons; the same area, when blank instead, the non-interacting Fermi sea; empty and filled circles denote respectively single hole and electron states.

sum over momenta and spins of single electrons and holes, with the condition of momentum and spin conservation (see Fig. 1.1).

As in any configuration-interaction scheme we have to cut the expansion, and we do this including configuration with up to two added electron-hole pairs. In particular, the configurations appearing in the neutral $N$-particle system will be indicated as follows (see Fig. 1.2):

$$
|o\rangle \equiv |\Phi_0^N\rangle \\
|f\rangle \equiv |\Phi_2^N\rangle = \hat{c}_{k_1}^\dagger \hat{c}_{k_3}^\dagger \hat{c}_{k_0}^\dagger |\Phi_0^N\rangle \\
\text{with } -k_1 + k_2 - k_3 + k_4 = 0 ;
$$

(1.4)

those for the $N - 1$-particle system (with a removed spin down electron of momentum $q$) as:

$$
|u\rangle \equiv |\Phi_0^{N-1}\rangle = \hat{c}_{q}^\dagger |\Phi_0^N\rangle \\
|t\rangle \equiv |\Phi_1^{N-1}\rangle = \hat{c}_{k_2}^\dagger \hat{c}_{k_1}^\dagger |\Phi_0^N\rangle \\
\text{with } -k_0 - k_1 + k_2 = -q \\
|v\rangle \equiv |\Phi_2^{N-1}\rangle = \hat{c}_{k_4}^\dagger \hat{c}_{k_3}^\dagger \hat{c}_{k_1}^\dagger |\Phi_0^N\rangle \\
\text{with } -k_1 + k_2 - k_3 + k_4 = -q \\
\text{and } k_3 \neq q ;
$$

(1.5)

similar expressions, but with creation operators replaced by the corresponding annihilation ones and vice versa, hold for the $N + 1$-particle system with a spin down electron of momentum $q$ added.

Notice that, in principle, 2-body configurations of the type $\hat{c}_{k_2\sigma_2}^\dagger \hat{c}_{k_1\sigma_1}^\dagger |\Phi_0^N\rangle$ have to be additionally included in the $N$-particle basis set Eq. (1.4). Nev-
Figure 1.2: Pictorial representation of the basis states for the N- and N − 1- particle systems, Eqs. (1.4) and (1.5) (for the N + 1 system just replace each electron state with a hole one of the same name, and vice versa). Arrows represent the two different spin channels.

Nevertheless, due to momentum and spin conservation which demands \( k_2 = k_1 \) and \( \sigma_1 = \sigma_2 \), such configurations are identical to \( |o\rangle \).

Notice also that within all the possible 5-body configurations
\[
\hat{c}_{k_4 \downarrow} \hat{c}_{k_3 \downarrow} \hat{c}_{k_2 \uparrow} \hat{c}_{k_1 \uparrow} \hat{c}_{k_0 \downarrow} |\Phi^N_0\rangle
\]
only those having fixed \( k_0 = q \) appear in the \( N − 1 \)-particle basis set Eq. (1.5). Configurations with \( k_0 \neq q \) are neglected since they give no contribution to the self-energy of the system.\(^1\)

The configurations \( |o\rangle \) and \( |u\rangle \) are the ground states of the non interacting \( N \)-particle and \( N − 1 \)-particle system respectively; we define the quantities

\[
W_0 \equiv \langle o | \hat{H} | o \rangle = \sum_{k} \epsilon_k + \frac{U}{N} N_\uparrow N_\downarrow \tag{1.6a}
\]

\[
W_1 \equiv \langle u | \hat{H} | u \rangle = \sum_{k} \epsilon_k - \epsilon_q + \frac{U}{N} N_\uparrow (N_\downarrow - 1) = W_0 - \epsilon_q - \frac{U}{N} N_\uparrow. \tag{1.6b}
\]

Assuming \( \{|o\rangle, |f\rangle\} \) and \( \{|u\rangle, |t\rangle, |v\rangle\} \) as complete basis sets for, respect-

\(^1\)As it will be shown in the following (see Eq. (1.31)) 5-body configurations enter the calculation of the self-energy only via the matrix elements of the potential \( V'' \) (the definition of \( V'' \) is given in the end of the present Section). It can be easily shown that such matrix elements \( V''_{uv} = \langle \Phi^N_0 | \hat{c}_{q \downarrow} \hat{c}_{k_4 \downarrow} \hat{c}_{k_3 \downarrow} \hat{c}_{k_2 \uparrow} \hat{c}_{k_1 \uparrow} \hat{c}_{k_0 \downarrow} |\Phi^N_0\rangle \) vanish unless \( k_0 = q \).
tively, the \( N \)-particle and the \( N \pm 1 \)-particle system, we can express the action of \( \hat{H} \) on these systems by means of the following effective hamiltonians:

\[
\hat{H}^N = \langle o | \hat{H} | o \rangle \langle o | + \sum_{f f'} \langle f | \hat{H} | f' \rangle \langle f' | + \sum_{f} \langle f | \hat{H} | o \rangle \langle o | \equiv \hat{H}_0 + \hat{H}_4 + \hat{V}'
\]

\[
\hat{H}^{N\pm 1} = \langle u | \hat{H} | u \rangle \langle u | + \sum_{tt'} \langle t | \hat{H} | t' \rangle \langle t' | + \sum_{vv'} \langle v | \hat{H} | v' \rangle \langle v' | + \sum_{t} \langle t | \hat{H} | u \rangle \langle u | + \sum_{v} \langle v | \hat{H} | u \rangle \langle u | \equiv \hat{H}_1 + \hat{H}_3 + \hat{H}_5 + \hat{V} + \hat{V}''.
\]

From Eq. (1.6) we see that \( \hat{H}_0 \) and \( \hat{H}_1 \) give the energy of \( |o\rangle \) and \( |u\rangle \) including the interaction term treated in mean field approximation; \( \hat{V}' \), \( \hat{V} \) and \( \hat{V}'' \) couple the different basis configurations; \( \hat{H}_4 \), \( \hat{H}_3 \) and \( \hat{H}_5 \) can be further decomposed into diagonal terms \( \hat{H}^D \) accounting for the energy of the reminder basis states \( |f\rangle \), \( |t\rangle \) and \( |v\rangle \) (always with the Coulomb repulsion treated by mean-field approximation), and off-diagonal terms \( \hat{H}^{ND} \) which describe all the allowed scattering processes between the different particles of the basis configurations (we adopt a notation in which the superscript denotes the number of particles of the configuration at issue, while the subscript indicates the pair of interacting particles - see Fig. 1.3):

\[
\hat{H}_4^{ND} = \hat{V}_{13} + \hat{V}_{24} + \hat{V}_{23} + \hat{V}_{14} \\
\hat{H}_3^{ND} = \hat{V}_{10} + \hat{V}_{20} \\
\hat{H}_5^{ND} = \hat{V}_{13} + \hat{V}_{24} + \hat{V}_{23} + \hat{V}_{14}
\]

The matrix elements of the effective hamiltonians are known [25] and summarized in Appendix A.

### 1.3 Ground state energy

Given the \( N \)-particle hamiltonian \( \hat{H}^N \), with exact (interacting) ground state \( |\Psi_0^N\rangle \), and introduced the resolvent operator related to \( \hat{H}^N \) as

\[
\hat{G}^N(z) = \frac{1}{z - \hat{H}^N},
\]

the energy \( E_G \) of \( |\Psi_0^N\rangle \) is given by the lowest-lying pole of \( \hat{G}^N \), that is the pole of the function [40], [41]

\[
\langle \Psi_0^N | \hat{G}^N(z) | \Psi_0^N \rangle = \frac{1}{z - \langle \Psi_0^N | \hat{H}^N | \Psi_0^N \rangle}.
\]
To proceed in the actual calculation of $E_G$ we need to replace in the previous equation the unknown interacting ground state $|\Psi_N^{\text{N}}\rangle$ with the non-interacting one: that is, we define the exact ground state energy of the $N$-particle system as the pole of the function $\langle o|\hat{G}^N(z)|o \rangle$. This is a drastic approximation that will require a specific correction - see Chapter 3.

To perform the calculation we start from the identity

$$\langle o|(z - \hat{H}^N)\hat{G}^N(z)|o \rangle = 1 \quad (1.12)$$

and insert the unity decomposition in terms of our reduced $N$-particle basis set:

$$\hat{1} = |o\rangle\langle o| + \sum_f |f\rangle\langle f| ; \quad (1.13)$$

this way eq. (1.12) becomes

$$\langle o|(z - \hat{H}^N)|o\rangle\langle o|\hat{G}^N|o\rangle - \sum_f \langle o|\hat{H}^N|f\rangle\langle f|\hat{G}^N|o\rangle = 1 . \quad (1.14)$$

Now exploiting the decomposition (1.7) of $\hat{H}^N$ as $\hat{H}_4 + (\hat{H}_0 + \hat{V}')$ and introducing the 4-body resolvent related to $\hat{H}_4$, that is $\hat{F}_4 = \frac{1}{z-\hat{H}_4}$, we can easily
derive the following relation:

\[ \hat{G}^N = \hat{F}_4 + \hat{F}_4(\hat{H}_0 + \hat{V}')\hat{G}^N, \]  
(1.15)

that can be used to write the off-diagonal elements in eq. (1.14) as

\[ \langle f|\hat{G}^N|o \rangle = \sum_{f'} \langle f|\hat{F}_4|f' \rangle \langle f'|\hat{V}'|o \rangle \langle o|\hat{G}^N|o \rangle. \]  
(1.16)

Therefore, after some algebra, we get from eq. (1.14)

\[ \langle o|\hat{G}^N(z)|o \rangle = \frac{1}{z - W_0 - \sum_{f'f} V'_{of} F_{4ff'} V'_{f'o}}, \]  
(1.17)

where the shorthand notation \( V'_{of} \equiv \langle o|\hat{V}'|f \rangle \), etc., has been used. From this last equation we finally recognize the \( N \)-particle ground state energy as

\[ E_G = W_0 + \sum_{ff'} V'_{of} F_{4ff'} V'_{f'o}. \]  
(1.18)

Notice that the ground state energy of the \( N \)-particle system includes corrections due to 4-body correlations.

### 1.4 Self-energy

The propagation of an added or removed particle of momentum \( q \) into a many-body \( N \)-particle state \( |\Psi_0^N \rangle \) is described by the one-particle Green’s function \( G(q, \omega) \), which in turn is related to the \( N \pm 1 \)-particle resolvents \( \hat{G}^{N\pm1}(z) = \frac{1}{z - H_N^{\pm1}} \) by [40], [41]:

\[
G(q, \omega) = G^+(q, \omega) + G^-(q, \omega) \]  
(1.19a)

\[
G^+(q, \omega) = \langle \Psi_0^N | \hat{c}_q \hat{G}^{N+1}(z) \hat{c}_q^\dagger | \Psi_0^N \rangle \]  
(1.19b)

\[
G^-(q, \omega) = -\langle \Psi_0^N | \hat{c}_q^\dagger \hat{G}^{N-1}(z) \hat{c}_q | \Psi_0^N \rangle, \]  
(1.19c)

where the functions \( \hat{G}^{N\pm1}(z) \) are computed for, respectively, \( z = E_G \pm \omega + i\delta \), and the limit \( \delta \to 0^+ \) is taken afterwards (always implied in the following).

If we again substitute the interacting ground state \( |\Psi_0^N \rangle \) with the non-interacting one \( |o \rangle \), we see that what is required in order to obtain the Green’s function are the matrix elements \( \langle u|\hat{G}^{N\pm1}|u \rangle \):

\[ G^\pm(q, \omega) = \pm \langle u|\hat{G}^{N\pm1}(z)|u \rangle. \]  
(1.20)
Let us focus on the $N - 1$-particle case. The procedure is the same as outlined in the previous section for $\langle o | \hat{G}^N | o \rangle$. Starting from the identity
\[
\langle u | (z - \hat{H}^{N-1}) \hat{G}^{N-1}(z) | u \rangle = 1
\] (1.21)
and using the unity decomposition
\[
\hat{1} = |u\rangle\langle u| + \sum_t |t\rangle\langle t| + \sum_v |v\rangle\langle v|
\] (1.22)
we get
\[
\langle u | (z - \hat{H}^{N-1}) \hat{G}^{N-1} | u \rangle - \sum_t \langle u | \hat{H}^{N-1} | t \rangle \langle t | \hat{G}^{N-1} | u \rangle - \sum_v \langle u | \hat{H}^{N-1} | v \rangle \langle v | \hat{G}^{N-1} | u \rangle = 1
\] (1.23)
We now introduce the 3-body and 5-body resolvents
\[
\hat{F}_3(z) = \frac{1}{z - \hat{H}_3}
\] (1.24)
\[
\hat{F}_5(z) = \frac{1}{z - \hat{H}_5}
\] (1.25)
which are related to $\hat{G}^{N-1}$ by
\[
\hat{G}^{N-1} = \hat{F}_3 + \hat{F}_3(\hat{H}_1 + \hat{H}_5 + \hat{V} + \hat{V}''\hat{G}^{N-1} + \hat{F}_5 + \hat{F}_5(\hat{H}_1 + \hat{H}_5 + \hat{V} + \hat{V}''\hat{G}^{N-1})
\] (1.26)
This relation allow us to write the off-diagonal elements of Eq. (1.23) as follows:
\[
\langle t | \hat{G}^{N-1} | u \rangle = \sum_{t'} \langle t | \hat{F}_3 | t' \rangle \langle t' | \hat{V} | u \rangle \langle u | \hat{G}^{N-1} | u \rangle
\] (1.27)
\[
\langle v | \hat{G}^{N-1} | u \rangle = \sum_{v'} \langle v | \hat{F}_5 | v' \rangle \langle v' | \hat{V}'' | u \rangle \langle u | \hat{G}^{N-1} | u \rangle
\] (1.28)
Now after some algebra we obtain the matrix elements of the $N - 1$-particle resolvent as:
\[
-\langle u | \hat{G}^{N-1}(z) | u \rangle = \frac{1}{z - W_1 - \sum_{tt'} V_{ut} F_{3tt'} V_{t'u} - \sum_{vv'} V_{uv'} F_{5vv'} V_{v'u'}}
\] (1.29)
This expression, computed for $z = E_G - \omega + i\delta$, is formally analogous to the Dyson equation obeyed by the hole Green’s function:
\[
G^-(q, \omega) = \frac{1}{\omega - \epsilon_q - \Sigma(q, \omega)},
\] (1.30)
with the quantity (remember the expression (1.18) of $E_G$ and the definition (1.6) of $W_0$ and $W_1$)

$$\Sigma(\omega) = \frac{U}{N} N_\uparrow - \sum_{tt'} V_{ut} F_{3tt'} V_{t'u} + \sum_{ff'} V_{of} F_{4ff'} V_{f'0} - \sum_{vv'} V_{uv} F_{5vv'} V_{v'u} \quad (1.31)$$

playing the role of the hole self-energy. We point out that the constant $\frac{U}{N} N_\uparrow$ amounts to the mean Coulomb interaction of the removed spin down electron with the reminder electronic system.

If following an analogous procedure we derive the $N+1$-particle resolvent and consider the Dyson equation obeyed by the electron Green’s function $G^+$, we obtain for the self-energy an alternative expression in terms of the resolvents $\hat{F}_3$, $\hat{F}_4$ and $\hat{F}_5$ related to the $N+1$-particle system. It can be shown that this is equivalent to Eq. (1.31).

On the other hand, had we excluded 5-body states from our configuration-interaction expansion, we would have obtained from the Dyson equation for $G^-$ and for $G^+$ two different “self-energies” accounting for just 3-body scattering processes:

$$\Sigma^\pm_{\text{BS}}(\omega) = \frac{U}{N} N_\uparrow \pm \sum_{tt'} V_{ut} F_{3tt'} V_{t'u} \quad (1.32)$$

These quantities have no direct physical meaning; we will call them effective electron and hole self-energies and interpret them as auxiliary objects. They will be important in the following.

The determination of the resolvents $\hat{F}_3$, $\hat{F}_4$ and $\hat{F}_5$ which enter the previous equations is by no means trivial. We will now proceed by two steps: first we will introduce the Faddeev approach for the calculation of the 3-body resolvent $\hat{F}_3$; then we will show that, under certain approximations, the computation of $\hat{F}_4$ and $\hat{F}_5$ can be brought back to that of $\hat{F}_3$.

### 1.5 Faddeev approach to the 3-body scattering problem

The basic idea beneath Faddeev approach to the 3-body scattering problem [42], [24] is to decompose the 3-body interaction in terms of 2-body ones, which are more easily tractable. So the system in which a spin down hole labeled 0 interacts with a spin up 1-2 hole-electron pair is separated into a first subsystem where hole 0 interacts only with hole 1, and a second where it interacts only with electron 2. For each of these three systems we can
define the corresponding hamiltonian, resolvent operator and scattering op-
ertator, and set up the Lippmann-Schwinger equations (in all of the following
relations, $\hat{F}_D$ is the diagonal, free resolvent related to $\hat{H}_0$: $\hat{F}_D = \frac{1}{z - \hat{H}_0}$), as
summarized in Fig. 1.4.

The conceptual route to follow in order to solve the 3-body problem, that
is to compute the resolvent $\hat{F}_3$, is the following: we divide the hamiltonian $\hat{H}_3$
into diagonal ($\hat{H}_0$) and off-diagonal ($\hat{V}_3$) parts, and define the free resolvent
$\hat{F}_3^D$ corresponding to the diagonal part; this is linked to the full resolvent by
the relation

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D \hat{V}_3 \hat{F}_3^D .$$  

(1.33)

Next we introduce the scattering operator $\hat{S}_3$, on which all the non trivial
information about the interaction is concentrated:

$$\hat{V}_3 \hat{F}_3 = \hat{S}_3 \hat{F}_3^D .$$  

(1.34)

Eq. (1.33) can therefore be formally simplified and becomes

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D \hat{S}_3 \hat{F}_3^D ,$$  

(1.35)
and the problem of finding $\hat{F}_3$ now amounts to the computation of $\hat{S}_3$.

The standard way to achieve this task would be to solve the Lippmann-Schwinger equation for $\hat{S}_3$ (see Fig. 1.4). But unfortunately, once projected into a specific representation, this integral equation cannot be addressed with standard techniques, due to the fact that its kernel $\hat{V}_3\hat{F}_3^D$ is not modulus integrable neither compact. The alternative approach proposed by Faddeev is to exploit the 2-body scattering operators, whose Lippmann-Schwinger equations do not have the drawbacks of the 3-body one. We therefore introduce two partial 3-body scattering operators which sum up to $\hat{S}_3$:

$$\hat{S}_3 = \hat{S}_{3,10} + \hat{S}_{3,20}. \quad (1.36)$$

These are closely linked to 2-body scattering operators, and in particular it can be showed that [25], as a consequence of the Lippmann-Schwinger equations for $\hat{T}_{10}$, $\hat{T}_{20}$ and $\hat{S}_3$, they obey the following Faddeev equations:

$$\begin{cases} 
\hat{S}_{3,10} = \hat{T}_{10} + \hat{T}_{10}\hat{F}_3^D\hat{S}_{3,20} \\
\hat{S}_{3,20} = \hat{T}_{20} + \hat{T}_{20}\hat{F}_3^D\hat{S}_{3,10}.
\end{cases} \quad (1.37)$$

These two coupled integral equations carry the same physical information as the Lippmann-Schwinger equation for $\hat{S}_3$, but can be practically solved. Solving the Faddeev equations enables us to compute the 3-body resolvent $\hat{F}_3$ and therefore to get directly the 3-body-scattering part Eq. (1.32) of the effective self-energy of the system. For the determination of the full self-energy $(1.31)$, which involves $\hat{F}_4$ and $\hat{F}_3$ too, some additional steps are required.

### 1.6 Reduction of the 4-particle problem to the 3-particle one

Let us now focus on the 4-particle system described by the hamiltonian $\hat{H}_4 = \hat{H}_4^D + \hat{H}_4^{ND}$ and its resolvent $\hat{F}_4$. Similarly to what we have done in the previous section for the 3-particle system (see fig. 1.4), we can write the following Lippmann-Schwinger equation for $\hat{F}_4$:

$$\hat{F}_4 = \hat{F}_4^D + \hat{F}_4^D\hat{H}_4^{ND}\hat{F}_4, \quad (1.38)$$

which can be formally simplified with the introduction of the scattering operator $\hat{S}_4$, resulting in

$$\hat{F}_4 = \hat{F}_4^D + \hat{F}_4^D\hat{S}_4\hat{F}_4^D. \quad (1.39)$$
The operator \( \hat{S}_4 \) itself obeys a Lippmann-Schwinger equation:

\[
\hat{S}_4 = \hat{H}_4^{ND} + \hat{H}_4^{ND} \hat{F}_4^D \hat{S}_4 .
\]  

(1.40)

Now the idea is to decompose the scattering between particles 1, 2, 3 and 4, described by \( \hat{S}_4 \), into two parts (see Fig. 1.5):

- electron 2 interacting with electron-hole pair 3-4: this is a 3-body problem in the \( N + 1 \)-particle system where electron 2 has been added; we will indicate with \( \hat{S}^p_3 \) the corresponding scattering operator;

- hole 1 interacting with electron-hole pair 3-4: this is a 3-body problem in the \( N - 1 \)-particle system where electron 1 has been removed; we will indicate with \( \hat{S}^h_3 \) the corresponding scattering operator.

This task is formally achieved expressing \( \hat{S}_4 \) in terms of the 3-body scattering operators \( \hat{S}^p_3 \) and \( \hat{S}^h_3 \) as follows (we just substitute the decomposition (1.9) of \( \hat{H}_4^{ND} \) into eq. (1.40), leaving out the superscript “4”):

\[
\hat{S}_4 = (\hat{V}_{23} + \hat{V}_{24}) + (\hat{V}_{13} + \hat{V}_{14}) \hat{F}_4^D \hat{S}_4 + (\hat{V}_{13} + \hat{V}_{14}) \hat{F}_4^D \hat{S}_4 \\
\equiv \hat{S}^p_3 + \hat{S}^h_3 ,
\]  

(1.41)

and neglecting terms containing mixtures of a hole operator with interactions of electron type and viceversa, which amounts to decouple the hole problem.

Figure 1.5: Decomposition of the scattering processes in 4-body configurations.
from the electron one:

\[
\hat{S}_3^p = (\hat{V}_{23} + \hat{V}_{24}) + (\hat{V}_{23} + \hat{V}_{24}) \hat{F}_4^p (\hat{S}_3^p + \hat{S}_3^h) \approx (\hat{V}_{23} + \hat{V}_{24}) + (\hat{V}_{23} + \hat{V}_{24}) \hat{F}_4^p \hat{S}_3^p
\]

(1.42)

\[
\hat{S}_3^h = (\hat{V}_{13} + \hat{V}_{14}) + (\hat{V}_{13} + \hat{V}_{14}) \hat{F}_4^p (\hat{S}_3^p + \hat{S}_3^h) \approx (\hat{V}_{13} + \hat{V}_{14}) + (\hat{V}_{13} + \hat{V}_{14}) \hat{F}_4^p \hat{S}_3^h
\]

(1.43)

Note that the second rows of eqs. (1.42) and (1.43) are just the Lippmann-Schwinger equations for \(\hat{S}_3^p\) and \(\hat{S}_3^h\). This means that due to approximation (1.42) and (1.43) we are able to write the 4-body operator \(\hat{S}_4\) as a sum of 3-body operators, which in turn can be separately computed via the Faddeev method as described in the previous section. The Faddeev equations for \(\hat{S}_3^h\) and \(\hat{S}_3^p\) are:

\[
\hat{S}_3^h = \hat{S}_{3,13}^h + \hat{S}_{3,14}^h
\]

(1.44a)

\[
\begin{align*}
\hat{S}_{3,13}^p &= \hat{T}_{13} + \hat{T}_{13} \hat{F}_3^p \hat{S}_{3,14}^p \\
\hat{S}_{3,14}^p &= \hat{T}_{14} + \hat{T}_{14} \hat{F}_3^p \hat{S}_{3,13}^p
\end{align*}
\]

(1.44b)

\[
\hat{S}_3^p = \hat{S}_{3,23}^p + \hat{S}_{3,24}^p
\]

(1.45a)

\[
\begin{align*}
\hat{S}_{3,23}^p &= \hat{T}_{23} + \hat{T}_{23} \hat{F}_3^p \hat{S}_{3,24}^p \\
\hat{S}_{3,24}^p &= \hat{T}_{24} + \hat{T}_{24} \hat{F}_3^p \hat{S}_{3,23}^p
\end{align*}
\]

(1.45b)

Now, according to (1.39) and (1.41), in the expression (1.18) for \(E_G\) no 4-body scattering operators appear anymore, all the significant information about scattering processes being carried by the 3-body operators \(\hat{S}_3^h\) and \(\hat{S}_3^p\):

\[
E_G = W_0 + \sum_f V_{of} F_{4ff}^p V_{f'o} + \sum_{ff'} V_{of} F_{4ff}^p \hat{S}_3^p F_{4f'f}^p V_{f'o} \\
+ \sum_{ff'} V_{of} F_{4ff}^p \hat{S}_3^h F_{4f'f}^p V_{f'o}
\]

(1.46)

1.7 Reduction of the 5-particle problem to the 3-particle one

The case of the 5-particle system is completely analogous to that of the 4-particle one: this can be easily understood observing that interactions within \(|v\rangle\) states never involve the hole labeled 0 (see the decomposition (1.9) of \(\hat{H}_5^{ND}\)}
and fig. 1.3). This means that the 5-particle scattering operator \( \hat{S}_5 \) does not carry any additional information with respect to its 4-particle counterpart.

Formally we consider the resolvent \( \hat{F}_5 \), linked to \( \hat{S}_5 \) by

\[
\hat{F}_5 = F^D_5 + F^D_5 \hat{S}_5 F^D_5 ,
\]

(1.47)

and the Lippmann-Schwinger equation for \( \hat{S}_5 \):

\[
\hat{S}_5 = \hat{H}^{ND}_5 + \hat{H}^{ND}_5 \hat{F}^D_5 \hat{S}_5 .
\]

(1.48)

After substituting the expression (1.9) of \( \hat{H}^{ND}_5 \) into eq. (1.48) we can introduce, as in the 4-particle case, 3-body scattering operators \( \hat{S}^p_3 \) and \( \hat{S}^h_3 \); this time they sum up to \( \hat{S}_5 \), and obey the following Lippmann-Schwinger equations:

\[
\hat{S}^p_3 = (\hat{V}_{23} + \hat{V}_{24}) + (\hat{V}_{23} + \hat{V}_{24}) F^D_5 (\hat{S}^p_3 + \hat{S}^h_3)
\]

\[
\cong (\hat{V}_{23} + \hat{V}_{24}) + (\hat{V}_{23} + \hat{V}_{24}) F^D_5 S^p_3
\]

(1.49)

\[
\hat{S}^h_3 = (\hat{V}_{13} + \hat{V}_{14}) + (\hat{V}_{13} + \hat{V}_{14}) F^D_5 (\hat{S}^p_3 + \hat{S}^h_3)
\]

\[
\cong (\hat{V}_{13} + \hat{V}_{14}) + (\hat{V}_{13} + \hat{V}_{14}) F^D_5 S^h_3
\]

(1.50)

where the only difference with respect to Eqs. (1.42) and (1.43) is the appearance of \( \hat{F}^D_5 \) instead of \( \hat{F}^D_4 \).

We can now come back to the expression (1.31) of the self-energy. Recalling Eq. (1.35) for \( \hat{F}_3 \) (since we are dealing with a \( N-1 \)-particle problem we can indicate the corresponding scattering operator as \( \hat{S}^h_3 \)):

\[
\hat{F}_3 = F^D_3 + F^D_3 \hat{S}^h_3 F^D_3
\]

and given the results we have just derived for \( \hat{F}_4 \) and \( \hat{F}_5 \), that is

\[
\hat{F}_4 = F^D_4 + F^D_4 (\hat{S}^h_3 + \hat{S}^p_3) F^D_4
\]

\[
\hat{F}_5 = F^D_5 + F^D_5 (\hat{S}^h_3 + \hat{S}^p_3) F^D_5 ,
\]

we can express \( \Sigma \) as follows (the matrix element subscripts are implied):

\[
\Sigma = - \sum \hat{V} \hat{F}^D_3 \hat{V} + \sum \hat{V} \hat{F}^D_4 \hat{V} - \sum \hat{V} \hat{F}^D_5 \hat{V} - \sum \hat{V} \hat{F}^D_4 (\hat{S}^h_3 + \hat{S}^p_3) \hat{F}^D_4 \hat{V} - \sum \hat{V} \hat{F}^D_5 (\hat{S}^h_3 + \hat{S}^p_3) \hat{F}^D_5 \hat{V} .
\]

(1.51)

where we see that only 3-body scattering operators appear.
As a last step, we want now to show that this amounts to

\[ \Sigma = \Sigma_{3BS}^+ + \Sigma_{3BS}^- . \]  

(1.52)

We will explicitly perform the calculation within the approximation \( \hat{F}_3 = \hat{F}_3^D \), \( \hat{F}_4 = \hat{F}_4^D \), \( \hat{F}_5 = \hat{F}_5^D \), that is for the first three terms of Eq. (1.51); dealing with the complete resolvents does not require any further effort.

So what is to be evaluated is the sum (recalling that \( \langle \hat{V} \rangle = \langle \hat{V}' \rangle = \langle \hat{V}'' \rangle = -\frac{U}{N} \))

\[
\left( \frac{U}{N} \right)^2 \left( - \sum F_{3tt}^D + \sum F_{4ff}^D - \sum' F_{5vv}^D \right),
\]  

(1.53)

where the resolvents are to be computed for \( z = E_G \) (with regard to \( \hat{F}_4^D \)) and \( z = E_G - \omega \) (for \( \hat{F}_3^D \) and \( \hat{F}_5^D \)). Essential in order to obtain the result (1.52) are the approximations

\[
E_G \approx W_0 \quad \omega \approx \epsilon_q + \frac{U}{N} N_\uparrow
\]  

(1.54)

to be set in the resolvents arguments. Exploiting these last, after some algebra we get

\[
\begin{align*}
\sum F_{3tt}^D & \approx \sum_{012} \frac{1}{\epsilon_0 + \epsilon_1 - \epsilon_2 - \epsilon_q} \\
\sum F_{4ff}^D & \approx \sum_{1234} \frac{1}{\epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4} \\
\sum (1 - \delta_{k\eta\epsilon}) F_{5vv}^D & \approx \sum_{1234} \frac{1}{\epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4} - \sum_{124} \frac{1}{\epsilon_1 - \epsilon_2 - \epsilon_4 + \epsilon_q}
\end{align*}
\]  

(1.55)

Now we note that the term (1.55b) exactly cancels with the first of (1.55c); what remains of (1.55c) is nothing but the particle \( \hat{F}_3^D \) resolvent, computed between the states \( |t^{N+1} \rangle = \hat{c}^\dagger_1 \hat{c}^\dagger_2 \hat{c}^\dagger_3 |o\rangle \), so that at the end the sum (1.53) amounts to

\[
\sum (F_{3tt}^D)^{N-1} + \sum (F_{3tt}^D)^{N+1} ;
\]  

(1.56)

that is, exactly the result (1.52).

In the same way it can be shown that also the expression of the self-energy obtained from the \( N + 1 \)-particle resolvent amounts to \( \Sigma_{3BS}^+ + \Sigma_{3BS}^- \).

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1.8 Implementation

From a conceptual point of view we are now able, exploiting Eqs. (1.46), (1.52) and (1.32), to compute the ground state energy and the self-energy of the system. However, the cited equations have to be further developed into a form suitable for practical calculations. Here we will sketch the route to be followed and report the basic equations that have been implemented.

We would like to stress that, contrary to most many-body implementations which exploit the Matsubara imaginary frequencies formalism [12] and therefore need some analytical continuation method to come back to real energies, here all the energy dependent quantities are computed directly on the real axis (even if in the numerical implementation we are forced to keep a finite but small imaginary energy $i\delta$ in order to avoid singularities). In the following analytical formulas, whenever the quantity $i\delta$ appears the limit $\delta \to 0$ is implied.

1.8.1 Self-energy

We recall, from eqs. (1.32) and (1.52), that what is needed to compute the self-energy in 5-body approximation are the matrix elements of the 3-body resolvent $\hat{F}_3$ (both for $N-1$ and for $N+1$ systems) between the 3-body configurations $|t\rangle$. We have also seen that $\hat{F}_3$ can be decomposed into a simple diagonal term $\hat{F}_3^D$ and an off-diagonal term $\hat{F}_3^D \hat{S}_3 \hat{F}_3^D$, where the scattering operator $\hat{S}_3$ carries all the relevant information about the scattering processes and is computed via the Faddeev equations (see Sec. 1.5). Correspondingly, two terms can be recognized in the 3BS self-energy: the first, which involves only $\hat{F}_3^D$ and does not require to solve the Faddeev equations, is called Kanamori self-energy; we will name the second and most computationally demanding term Faddeev self-energy. It turns out (see the following) that Kanamori self-energy involves only scattering in the particle-particle channel (hole-hole for the $N-1$-particle system, electron-electron for the $N+1$ one), and therefore coincides with the self-energy coming from the so-called $t$-matrix approach: this also relies on a configuration expansion truncated at the level of one added electron-hole pair, but with the additional assumption that the electron-hole scattering can be neglected, and then applies under the condition that the band is nearly full [43], [44], [45], [46].

First of all, the matrix elements of the diagonal 3-body resolvent for the $N-1$-particle system are easily found to be:

$$F_{3ut}^D(z) = \frac{1}{z - \langle t | \hat{H}_3^D | t \rangle} = \frac{1}{z - W_0 + \frac{U}{N} N_\uparrow + \epsilon_0 + \epsilon_1 - \epsilon_2}.$$ 

(1.57)
It is now convenient to introduce some auxiliary objects. First, we consider sums of $\hat{F}_D^3$ over different momenta and define the following quantities:

$$G_3(k_2) \equiv -\frac{1}{N} \sum_{k_0, k_1} \bar{F}_{3tt}^{D} \delta_{k_0 + k_1 - k_2 - q} \quad (1.58a)$$

$$G_1(k_1) \equiv -\frac{1}{N} \sum_{k_0, k_2} \bar{F}_{3tt}^{D} \delta_{k_0 + k_1 - k_2 - q} \quad (1.58b)$$

$$G_2(k_1, k_2) \equiv -\frac{1}{N} \sum_{k_0} \bar{F}_{3tt}^{D} \delta_{k_0 + k_1 - k_2 - q} ; \quad (1.58c)$$

notice that $G_3$ and $G_1$ are related to the free propagation of, respectively, an electron of momentum $k_2$ and a hole of momentum $k_1$ (the reverse is true for the $N + 1$-particle system).

Second, we consider sums of $\hat{F}_D^3$ multiplied by 2-body scattering matrices:

$$\sum_{k_0', k_1'} T_{10}^{tt'} \bar{F}_{3tt'}^{D} \delta_{k_0' + k_1' - k_2 - q} = -T_3(k_2) G_3(k_2) \delta_{k_0 + k_1 - k_2 - q} \delta_{k_2 - k_2'} \quad (1.59a)$$

$$\sum_{k_0', k_1'} T_{20}^{tt'} \bar{F}_{3tt'}^{D} \delta_{k_0' + k_1' - k_2 - q} = -T_1(k_1) G_1(k_1) \delta_{k_0 + k_1 - k_2 - q} \delta_{k_1 - k_1'} ; \quad (1.59b)$$

these relations follow from the Lippmann-Schwinger equations for $\hat{T}_{10}$ and $\hat{T}_{20}$ (see Fig. 1.4), with the definitions

$$T_3(k_2) \equiv \frac{U}{1 + U G_3(k_2)} \quad (1.60a)$$

$$T_1(k_1) \equiv \frac{-U}{1 - U G_1(k_1)} . \quad (1.60b)$$

$T_3$ describes the interaction between two holes (two electrons if we are dealing with the $N + 1$ system), while $T_1$ is related to electron-hole scattering.

Third, another quantity which involves the scattering operator $\hat{S}_{3,20}$ will be useful:

$$A(k_2) = \frac{1}{N} \sum_{k_0, k_1} \sum_{t'} F_{3tt}^{D}(S_{3,20})_{tt'}^{D} \bar{F}_{3tt'}^{D} \delta_{k_0 + k_1 + k_2 - q} \delta_{k_0' + k_1' - k_2' - q} . \quad (1.61)$$

Obtaining $A$ is the most demanding part of the whole calculation, because the resolution of Faddeev equations (1.37) is implied. Indeed it can be shown [25] that from Faddeev equations one can derive the following integral equation...
for $A$:

$$A(k_2) = B(k_2) + \sum_{k_2'} K(k_2k_2') A(k_2') \quad (1.62a)$$

where

$$B(k_2) = \sum_{k_1} G_2(k_1k_2) T_1(k_1) \left( G_1(k_1) - \sum_{k_2'} G_2(k_1k_2') T_3(k_2') G_3(k_2') \right) \quad (1.62b)$$

$$K(k_2k_2') = \sum_{k_1} G_2(k_1k_2) T_1(k_1) G_2(k_1k_2') T_3(k_2') \quad (1.62c)$$

In terms of these auxiliary quantities the 3-body-scattering term of the self-energy, separated into Kanamori (subscript "K") and Faddeev (subscript "F") parts, turns out to be:

$$\Sigma_{3BS} = -UN_1 + \Sigma_K + \Sigma_F$$

$$\Sigma_K = \frac{1}{N} \sum_{k_2} T_3(k_2)$$

$$\Sigma_F = \frac{U}{N} \sum_{k_2} A(k_2) T_3(k_2) \quad ;$$

notice that $\Sigma_K$ includes contributions from the hole-hole scattering channel alone, and therefore corresponds to the $t$-matrix approach of Refs. [43], [44], [45], [46]. Identical expressions hold also for $\Sigma_{3BS}$, but with the exchange of empty and filled states.

As a last step, all the sums appearing in the previous equations can be converted into continuous expressions by means of the following important local approximation [47] ($R_j$ denotes the position of the $j$th lattice site):

$$\delta_{k_0+k_1-k_2-q} = \frac{1}{N} \sum_{j} e^{iR_j \cdot (k_0+k_1-k_2-q)} \cong \frac{1}{N} ; \quad (1.64)$$

this amounts to neglect the explicit dependence on $k$-vectors, averaging it out.

In particular the $G$-objects of Eq. (1.58) become integrals (here we explicit the two cases $N-1$-particle and $N+1$-particle using superscripts "h" and "p"; for each energy label, the corresponding integration extrema follow the fact that it denotes a filled or empty state):

$$G_h^1(\omega, \epsilon_1) = \int_{-\infty}^{\epsilon_F} d\epsilon_0 \int_{\epsilon_F}^{+\infty} d\epsilon_2 \frac{n(\epsilon_0)n(\epsilon_2)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 - i\delta} \quad (1.65a)$$

$$G_p^1(\omega, \epsilon_1) = -\int_{\epsilon_F}^{+\infty} d\epsilon_0 \int_{-\infty}^{\epsilon_F} d\epsilon_2 \frac{n(\epsilon_0)n(\epsilon_2)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 + i\delta} \quad (1.65b)$$
\[ G_h^2(\omega, \epsilon_1, \epsilon_2) = \int_{-\infty}^{\epsilon_F} d\epsilon_0 \frac{n(\epsilon_0)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 - i\delta} \] (1.66a)

\[ G_p^2(\omega, \epsilon_1, \epsilon_2) = -\int_{\epsilon_F}^{+\infty} d\epsilon_0 \frac{n(\epsilon_0)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 + i\delta} \] (1.66b)

\[ G_h^3(\omega, \epsilon_2) = \int \int_{-\infty}^{\epsilon_F} d\epsilon_0 d\epsilon_1 \frac{n(\epsilon_0)n(\epsilon_1)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 - i\delta} \] (1.67a)

\[ G_p^3(\omega, \epsilon_2) = -\int \int_{\epsilon_F}^{+\infty} d\epsilon_0 d\epsilon_1 \frac{n(\epsilon_0)n(\epsilon_1)}{\omega - \epsilon_0 - \epsilon_1 + \epsilon_2 + i\delta} \] (1.67b)

and the continuous version of the integral equation (1.62) can be written as follows (for the \( N = 1 \) system; for the \( N + 1 \) one just change the integration extrema as in the above equations for \( G \)-integrals):

\[ \int_{-\infty}^{\epsilon_F} d\epsilon_j [E(\omega, \epsilon_i, \epsilon_j) - \delta(\epsilon_i - \epsilon_j)]A(\omega, \epsilon_j) = -C(\omega, \epsilon_i) \] (1.68a)

with

\[ \Phi(\omega, \epsilon_j, \epsilon_2) = -n(\epsilon_j)T_1(\omega, \epsilon_j)G_2(\omega, \epsilon_j, \epsilon_2) \] (1.68b)

\[ \Psi(\omega, \epsilon_i, \epsilon_2) = -n(\epsilon_2)T_3(\omega, \epsilon_2)G_2(\omega, \epsilon_2, \epsilon_i) \] (1.68c)

\[ E(\omega, \epsilon_i, \epsilon_j) = \int_{\epsilon_F}^{+\infty} d\epsilon_2 \Psi(\epsilon_i, \epsilon_2)\Phi(\epsilon_j, \epsilon_2) \] (1.68d)

\[ B(\omega, \epsilon_2) = \int_{-\infty}^{\epsilon_F} d\epsilon_0 n(\epsilon_0)G_1(\omega, \epsilon_0)G_2(\omega, \epsilon_0, \epsilon_2)T_1(\omega, \epsilon_0) \] (1.68e)

\[ -\int_{\epsilon_F}^{+\infty} d\epsilon'_2 n(\epsilon'_2)G_3(\omega, \epsilon'_2)F_3(\omega, \epsilon_2, \epsilon'_2) \]

\[ F_3(\omega, \epsilon_2, \epsilon'_2) = T_3(\omega, \epsilon'_2) \int_{-\infty}^{\epsilon_F} d\epsilon_0 n(\epsilon_0)T_1(\omega, \epsilon_0) \]

\[ \cdot G_2(\omega, \epsilon_0, \epsilon_2)G_2(\omega, \epsilon_0, \epsilon'_2) \]

\[ C(\omega, \epsilon_i) = \int_{\epsilon_F}^{+\infty} B(\omega, \epsilon_2)\Psi(\omega, \epsilon_i, \epsilon_2) \] (1.68f)

Finally we report the continuous formulas for the 3BS hole self-energy Eq. (1.63) (again, for the electron self-energy just change the integration

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extrema):

\[ \Sigma_{3BS}^h(\omega) = -UN + \Sigma_K^h(\omega) + \Sigma_F^h(\omega) \]  
(1.69a)

\[ \Sigma_K^h(\omega) = \int_{\epsilon_F}^{+\infty} d\epsilon_2 n(\epsilon_2) T_3(\omega, \epsilon_2) \]  
(1.69b)

\[ \Sigma_F^h(\omega) = U \int_{\epsilon_F}^{+\infty} d\epsilon_2 n(\epsilon_2) T_3(\omega, \epsilon_2) \cdot \{ B(\omega, \epsilon_2) + \int_{\epsilon_F}^{+\infty} d\epsilon_3 \Phi(\omega, \epsilon_3, \epsilon_2) A(\omega, \epsilon_3) \} \]  
(1.69c)

As appears from the above Equations, the only input ingredients of a 3BS self-energy calculation are the electron density of states \( n(\epsilon) \) and the Hubbard interaction \( U \).

### 1.8.2 Ground state energy

Let us move on now to the expression of the interacting ground-state energy, eq. (1.46). Here again we have a first term involving the free resolvent \( \hat{F}^D_4 \) alone, plus two other terms which also contain \( \hat{S}^p_3 \) and \( \hat{S}^h_3 \) respectively, therefore demanding for the resolution of the Faddeev equations.

First of all, the matrix elements of the diagonal 4-body resolvent are:

\[ F^D_{4ff}(z) = \frac{1}{z - W_0 + \epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4}. \]  
(1.70)

The first term appearing in eq. (1.46) can be written more explicitly as \((z = E_G + i\delta)\):

\[ \sum_f V'_{of} F^D_{4ff} F'_{fo} = \left( \frac{U}{N} \right)^2 \sum_{k_1 k_2 k_3 k_4} \frac{\delta_{k_1 - k_2 + k_3 - k_4}}{E_G - W_0 + \epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4 + i\delta} \]  
(1.71)

Assuming in the denominator \( E_G = W_0 \) and adopting the local approximation we get

\[ \sum_f V'_{of} F^D_{4ff} F'_{fo} = -\frac{U^2}{2\pi} \int_{-\infty}^{+\infty} d\omega G^h_3(\omega) G^p_3(\omega) \]  
(1.72)

To compute the third term of eq. (1.46), that is

\[ \sum_{ff'} V'_{of} F^D_{4ff} \hat{S}^h_3 \hat{T}_{13} \hat{F}^D_3 \hat{S}^h_3 \hat{T}_{14} F^D_{4ff'} F'_{fo} = \sum_{ff'} V'_{of} F^D_{4ff} (\hat{S}^h_3 + \hat{T}_{13} + \hat{T}_{14} \hat{S}^h_3 \hat{T}_{14}) f_{ff'} F^D_{4ff'} F'_{fo} , \]  
(1.73)
we have to solve the integral equation for the function $A^h$ associated to $\hat{S}^h_{3,14}$ (see eqs. (1.61) and (1.62)); then eq. (1.73) becomes

$$\sum_{ff'} V'_{of} F^D_{4ff} \hat{S}^h_{3ff} F^D_{4f'o} V'_{f'o} =$$

$$U^2 \left( \int_{\epsilon_F}^{+\infty} \epsilon_2 d\epsilon_2 n(\epsilon_2) n(\epsilon_4) A^h(\epsilon_2 + \epsilon_4) + \int_{\epsilon_F}^{+\infty} \epsilon_2 d\epsilon_2 n(\epsilon_2) n(\epsilon_4) G^h_3(\epsilon_2 + \epsilon_4) \frac{U G^h_3(\epsilon_2 + \epsilon_4)}{1 + G^h_3(\epsilon_2 + \epsilon_4)} + \int_{\epsilon_F}^{+\infty} \epsilon_2 d\epsilon_2 n(\epsilon_2) n(\epsilon_4) \frac{(U G^h_3(\epsilon_2 + \epsilon_4))^2}{1 + G^h_3(\epsilon_2 + \epsilon_4)} A^h(\epsilon_2 + \epsilon_4) \right).$$

Finally, the second term of eq. (1.46) is identical to the last one except for the substitution of filled states (electrons) with empty ones (holes).

### 1.9 From model to real systems

When we move from model systems to real ones we have to take into account that, in general, more than two electronic states per lattice site are present. We need therefore to replace the simple Hubbard Hamiltonian (1.1) with a generalized multi-orbital Hamiltonian:

$$\hat{H} = \sum_{i\alpha} \epsilon_{i\alpha} \hat{n}_{i\alpha} + \sum_{i\alpha j\beta} t_{i\alpha j\beta} \hat{c}_{i\alpha}^{\dagger} \hat{c}_{j\beta} + U \sum_{i\alpha j\beta} \hat{n}_{i\alpha} \hat{n}_{i\beta} + (U - J) \sum_{i\alpha j\beta} \hat{n}_{i\alpha} \hat{n}_{i\beta}$$

(1.75)

(with $\alpha, \beta$ orbital indexes) which, via the term proportional to $(U - J)$, includes also interactions between parallel spins sitting on the same lattice site, but in different orbitals. Here we have written the Hamiltonian in a localized states representation, and assumed the Hubbard parameters $U$ and $J$ to be site- and orbital-independent; they can be generalized without any other modification to matrices $U_{\alpha\beta}$ and $J_{\alpha\beta}$.

As a consequence of the presence of interactions between parallel spins, additional configurations appear in the many-body states expansion (see Fig. 1.6), and correspondingly additional terms in the effective Hamiltonian. Taken this into account the theory is developed in exactly the same way as for the single orbital case; the final formulas are analogous, with the only difference that now all quantities, from $G$-integrals Eqs. (1.65)-(1.67) to self-energy Eq. (1.69), have additional orbital dependences coming from the fact that the orbital-projected density of states $n_{\alpha}(\omega)$ is given as input. The result is an orbital-dependent self-energy $\Sigma_{\alpha}(\omega)$ which carries many-body
corrections to each specific orbital. The correction to a band eigenvalue of wave vector $k$ and band index $n$ is found projecting the orbital self-energy onto Bloch states, that is to say:

$$\Sigma_{kn}(\omega) = \sum_{\alpha} |C_{k\alpha}^{kn}|^2 \Sigma_{\alpha}(\omega) , \quad (1.76)$$

where $C_{k\alpha}^{kn}$ are the expansion coefficients of Bloch states in terms of localized Wannier orbitals. More details about the multi-orbital version of 3BS theory can be found in Ref. [27].

It is now worth spending a few words about the connection between the multi-orbital model hamiltonian (1.75) and the single-particle hamiltonian that defines the usual band structure of a solid. If among the various terms that form the electron-electron interaction we retain only the on-site one, we can write a mean-field hamiltonian

$$\hat{H}^{MF} = \sum_{i \alpha \sigma} \epsilon_{i \alpha \sigma}^{MF} \hat{n}_{i \alpha \sigma} + \sum_{i \alpha \beta \sigma} t_{i \alpha \beta}^{ij} \hat{c}_{i \alpha \sigma}^\dagger \hat{c}_{j \beta \sigma} \quad (1.77)$$

where the only difference between the energies $\epsilon_{i \alpha \sigma}^{MF}$ and the bare $\epsilon_{i \alpha \sigma}$ of Eq. (1.75) is that the former include the on-site Coulomb repulsion as a mean-field:

$$\epsilon_{i \alpha \sigma}^{MF} = \epsilon_{i \alpha \sigma} + \sum_{\beta} U \langle n_{i \beta \sigma} \rangle + (U - J) \langle n_{i \beta \sigma} \rangle . \quad (1.78)$$

In this case Eq. (1.78) defines unambiguously the relation between the Hubbard and the mean-field hamiltonian.

When we derive the hole and electron propagators for the multi-orbital hamiltonian it turns out, analogously to the one-orbital case developed in Sec. 1.4, that the mean-field Hubbard interaction of Eq. (1.78) explicitly appears as a constant term in the self-energy: at this level we can subtract it from the self-energy and include it into single particle energies, so that the self-energy carries the corrections to the mean-field eigenvalues.
In practice the situation is more complicated. It is known that the band structure is in many cases a good zero-order approximation to the excitation spectrum of a solid, and it seems reasonable to use it as a starting point for the inclusion of correlation effects: the implicit assumption is that among all the many-body terms responsible for correlations the on-site Coulomb repulsion is the one which needs to be treated explicitly. But two different kinds of problem arises.

First of all, which specific mean-field theory should we choose? Hartree-Fock theory would be the method of election to treat Coulomb interaction at first order, with a complete control over the successive higher order terms. This is true for instance of the GW approximation: to be consistent with the iterative solution of the Hedin’s equations, the GW self-energy should be evaluated starting from the Hartree-Fock Green’s function (see for instance [18]). Nevertheless the state of the art method to compute band structures is density functional theory (DFT), and this is the commonly preferred starting point for the inclusion of correlation effects as well (also in the GW framework). One of the reasons why DFT is preferable to Hartree-Fock is that most of the approaches used to go beyond the single particle picture, and most of the current implementations, renormalize the eigenvalues leaving the eigenfunctions unaltered: they therefore need the best possible single particles wavefunctions. On the other hand choosing DFT gives rise to the problem of which approximation to the exchange correlation functional is to be selected among the vast variety of proposed functionals, including LDA [48], [49], GGA [50], [51], Hybrids [52], LDA+U [7], Self-Interaction Corrected (SIC) [53], Exact Exchange (EEX) [54], etc. A growing interest on this issue exists in the GW community too: see for instance [20].

The other problem is the proper subtraction of any double counting of the electron-electron interaction included in the DFT calculation via the exchange-correlation potential. This problem is solved quite simply in the GW approach by defining an effective self-energy as $\Sigma_{GW} - \langle \psi_{kn} | V_{XC} | \psi_{kn} \rangle$, but presents more difficulties when a matching between DFT and the Hubbard model is involved, since DFT eigenvalues do not have the simple shape (1.78); moreover the choice of the double counting correction should in principle depend on the chosen functional. At present no definite and universally accepted answer exists for this problem. This aspect will be further discussed in Sec. 4.2.1.
Chapter 2

A different perspective on 3BS: diagrammatic analysis and the Luttinger-Ward functional

In the previous chapter we have outlined the derivation of an approximate solution of the Hubbard model in terms of the 3BS self-energy. We want now to reformulate this derivation in terms of a variational method based on the Luttinger-Ward functional ([36] as reported by [37]). The key point of this approach is the definition of the total ground state energy $E_G$ as a functional of the interacting one-particle Green function $G$:


Here $T[G]$ is the single particle contribution to the total energy (kinetic energy plus interaction with external fields) and $\Phi[G]$, the Luttinger-Ward functional, contains all the remaining many body terms. While the first term can be explicitly written down as

$$T[G] = E_0 + \text{tr}[G_0^{-1}G - 1] - \text{tr}[\ln G - \ln G_0],$$ (2.2)

the second term is obviously unknown and has to be approximated. What is interesting about $\Phi$ is that its functional derivative with respect to the Green function is exactly the self-energy $\Sigma$:

$$\frac{\delta \Phi[G]}{\delta G} = \Sigma[G].$$ (2.3)

The advantage of this procedure is that any approximate $\Sigma$ obtained as the functional derivative of an approximate $\Phi$ guarantees conservation of total energy, particle number and of all the other quantities that must be
conserved according to the symmetry of the Hamiltonian [55]. This very important property is not always preserved: while, in general, approximations may introduce some symmetry breaking and lead to unphysical violations of conservation laws, this is automatically avoided when using $\Phi$-derivable approximations.

Only recently, thanks to a generalization of the Luttinger-Ward approach (see [56]) and to the progress in computer technology, approaches based on $\Phi$ functionals have been implemented and applied to real materials, both to address ground state total energies in atoms and diatomic molecules [57] [37] and to obtain quasi-particle excitations in Si and Ge [58]. All these studies use an approximate form of the functional based on the weak-coupling skeleton-diagram expansion depicted in Fig. 2.1. This is nothing else than the random phase approximation (RPA), where only ring diagrams are included; in fact, by performing the functional derivative of $\Phi$, one gets for the self-energy the self-consistent GW approximation.

The advantage of reformulating the GW approximation in terms of the Luttinger-Ward functional is twofold: on one hand it has been possible to establish the importance of conserving approximations in calculating total energy within many body perturbation theory, and in particular to verify that only self-consistent GW gives reliable results [57]. The second and even more important advantage is that focusing on the $\Phi$ functional it is possible to build up $\Phi$-derivable conserving approximations that are non-perturbative, i.e. do not employ truncations of the skeleton diagram expansion, and thus can be applied to the regime of high correlation. Along this line of thought we mention the works of Pottohoff [59], [60] and of Aryasetiawan and coworkers [61] that have shown how the Luttinger-Ward approach can open the way for constructing a novel class of approximations (self-energy functionals as a generalization of DMFT or GW+DMFT).

It is in this spirit that we now derive the 3BS self-energy as the functional derivative of a Luttinger-Ward functional. We need first of all to write down our interacting total energy in terms of Feynman diagrams, extracting from it the many body part, namely the $\Phi$ functional. We do this by giving

\[ \Phi = \Phi_G + \Phi_{\text{ring}} + \Phi_{\text{other}} + \ldots \]

Figure 2.1: Diagrammatic representation of the Luttinger-Ward functional $\Phi[G]$ in random phase approximation.
a step-by-step diagrammatic analysis of all the significant quantities which enter 3BS theory. The second point is to perform a functional derivative of $\Phi$ to obtain again the 3BS self-energy. We will be able in this way to establish the conserving properties of the 3BS self-energy, opening also a route for a merging of 3BS with other first principle approaches such as the GW approximation.

2.1 Free propagations and interaction lines

We start our diagrammatic analysis from the diagonal resolvents $\hat{F}^{D}_3$, $\hat{F}^{D}_4$, $\hat{F}^{D}_5$. Exploiting the elementary formula of complex-field integration

$$\int_{-\infty}^{+\infty} d\epsilon \frac{f(\epsilon)}{\omega - \epsilon} = i\pi f(\omega)$$

it is easy to give an expression of the 3-body resolvent on the $N-1$-particle state $|t\rangle$ (see previous chapter, Eq. (1.57))

$$F^{D}_{3tt}(\omega) = \lim_{\delta \to 0} \frac{1}{\omega - W_0 + \frac{U}{N} N_1 + \epsilon_0 + \epsilon_1 - \epsilon_2 - i\delta}$$

as a convolution (indicated with $\otimes$) of the three free one-particle Green’s functions $G_0(\omega, k_0) = \frac{1}{\omega + \epsilon_0 - i\delta}$, $G_0(\omega, k_1) = \frac{1}{\omega + \epsilon_1 - i\delta}$, $G_0(\omega, k_2) = \frac{1}{\omega - \epsilon_2 - i\delta}$ (the limit $\delta \to 0$ is always implied), that is:

$$F^{D}_{3tt}(\omega) \propto \int_{-\infty}^{+\infty} d\epsilon d\epsilon' \frac{1}{\epsilon + \epsilon_0 - i\delta} \cdot \frac{1}{\epsilon' + \epsilon_1 - i\delta} \cdot \frac{1}{\omega - \epsilon' - \epsilon_2 - i\delta}$$

$$= G_0(\omega, k_0) \otimes G_0(\omega, k_1) \otimes G_0(\omega, k_2)$$

This means that the time Fourier transform of $F^{D}_{3tt}(\omega)$ amounts to the direct product of three free time-dependent Green’s function, and therefore (apart from $i\pi$ multiplicative factors) $\hat{F}^{D}_3$ is nothing but a free three-particle Green’s function. Analogously it can be shown that $F^{D}_{4oo}(\omega)$ and $F^{D}_{5vv}(\omega)$ are respectively four-particle and five-particle free propagators in the energy-momentum space. Thus we will represent the diagonal resolvents as shown in Fig. 2.2.

We now move to the analysis of the interaction terms that enter the effective hamiltonians $\hat{H}^N$ and $\hat{H}^{N\pm 1}$, whose explicit form is given in Appendix A. Let us start from the operator $\hat{V}$. Noticing that (recall Eq. (1.5) of the previous chapter)

$$|u\rangle \langle t| = \hat{c}_{q_1} |o\rangle \langle \hat{c}^\dagger_{k_2} \hat{c}^\dagger_{k_1} \hat{c}_{k_0} |o\rangle = \hat{c}_{q_1} \hat{c}^\dagger_{k_0} \hat{c}^\dagger_{k_1} \hat{c}^\dagger_{k_2} |o\rangle \langle o|$$

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Figure 2.2: Diagrammatic representation of the diagonal resolvents $\hat{F}^D_3$, $\hat{F}^D_4$ and $\hat{F}^D_5$ as free propagators.

It is apparent that the matrix elements $V_{ut}$ and $V_{tu}$ can be represented as two-points interactions as depicted in Fig. 2.3, with a single interaction line standing for the Hubbard repulsion $U/N$. The analogous representation of $V'_{of}$ and $V'_fo$ is given in Fig. 2.4; all the other interaction terms of the hamiltonians can be analysed the same way, and we will skip the details.

Figure 2.3: Diagrammatic representation of the interactions $V_{ut}$ and $V_{tu}$. The diagrams has been deformed in order to make explicit that $\hat{V}$ couples 1-body and 3-body configurations.

Figure 2.4: Diagrammatic representation of the interactions $V'_{of}$ and $V'_fo$. The diagrams has been deformed in order to make explicit that $\hat{V}'$ couples the vacuum with 4-body configurations.

### 2.2 Scattering operators

In order to give a diagrammatic representation of the various scattering operators which enter 3BS it is useful to start from the 2-body $\hat{T}$ operators introduced in the previous chapter, Sec. 1.5. The first perturbative orders of
Figure 2.5: The first perturbative orders of the infinite expansion of 2-body scattering operators $\hat{T}_{10}$ and $\hat{T}_{20}$ based on the Dyson equation (2.8).

Their expression, based on the Dyson equation (see Fig. 1.4)

$$\hat{T} = \hat{V} + \hat{V} \hat{F}^D \hat{T}$$  \hspace{1cm} (2.8)$$

is given in Fig. 2.5. With this in mind, we can solve the Faddeev equations (1.37) which give the 3-body scattering operator $\hat{S}_3$ and obtain the result shown in picture 2.6.

We can now move to the 4-body operator $\hat{S}_4$. We recall that according to Eq. (1.41) it is decomposed into a sum of two operators $\hat{S}^p_3$ and $\hat{S}^h_3$; these in turn, in the approximation that neglects coupling of hole operators with interactions of electron type and vice versa, turn out to be 3-body scattering operators in a 4-body system where a hole (or, respectively, an electron) does not undergo any scattering process: this way the problem of four interacting particles is brought back to a double 3-body scattering one.

The approximate expansion of $\hat{S}^p_3$ and $\hat{S}^h_3$ relies on their definition Eq. (1.42) and (1.43) and is depicted in Fig. 2.7; Fig. 2.8 explicitly shows the series of diagrams which have been neglected within the mentioned approximation.

Finally, the approximate expansion of $\hat{S}_4$ in terms of 3-body scattering operators is given in Fig. 2.9.

Figure 2.6: The first perturbative orders of the infinite expansion of 3-body scattering operator $\hat{S}_3$ based on Faddeev equations (1.37).
Figure 2.7: A few diagrams of the infinite expansion of the operators $S^p_3$ and $S^h_3$ (Eqs. (1.42) and (1.43)), in the approximation which decouples the 2-electrons-1-hole problem from the 2-holes-1-electron one.

Figure 2.8: Some diagrams which have been neglected in the approximate expansion of $S^p_3$.

Figure 2.9: Approximate expansion of $\hat{S}_4$ in terms of 3-body scattering operators.
2.3 Ground state energy and Self-energy

Having pursued in the previous sections a diagrammatic analysis of all the ingredients entering 3BS, it is now possible to establish the expression of the two main results of the theory: ground state energy and self-energy. The form of \( E_G - W_0 \) follows from Eqs. (1.18) and (1.46) and is given in Fig. 2.10; 3BS hole and electron auxiliary self-energies Eqs. (1.32), whose sum amounts according to Eq. (1.52) to the proper self-energy of the system, are shown in Fig. 2.11.

![Diagram of ground state energy](image1)

**Figure 2.10:** Diagrammatic expression of the ground state energy \( E_G - W_0 \).

![Diagram of self-energies](image2)

**Figure 2.11:** Diagrammatic expression of the 3BS hole and electron self-energies.
2.4 The Luttinger-Ward theorem: 3BS self-energy regained

According to the previous analysis we may identify the Luttinger-Ward functional \( \Phi \) obtained within 3BS as the interacting part of the total energy

\[
\Phi[G] = E_G - W_0
\]

namely as the summation of diagrams reported in Fig. 2.10. By performing its functional derivative we obtain the corresponding \( \Phi \)-derivable self-energy. Our goal now is to show that this functional derivative coincides with the expression that we have already obtained independently by the Faddeev method and whose diagrammatic expression is given in Fig. 2.11, in this way assuring that the 3BS is a “conserving” approach.

The functional derivative is most easily performed diagrammatically. To show how this works we start by writing down explicitly the first diagram (second order in \( U \)) that appears in Fig. 2.10:

\[
\sum_f V'_o F'_{A_{ff}} V'_o = \left( \frac{U}{N} \right)^2 \sum_{k_1, k_2, k_3, k_4} \frac{\delta_{k_1 - k_2 + k_3 - k_4}}{E_G - W_0 + \epsilon_1 - \epsilon_2 + \epsilon_3 - \epsilon_4 + i\delta} \tag{2.9}
\]

Assuming in the denominator \( E_0 = W_0 \) and adopting the local approximation we get

\[
\sum_f V'_o F'_{A_{ff}} V'_o = \frac{U^2}{2\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\Omega \int_{-\infty}^{\infty} d\Omega' \int_{-\infty}^{\infty} d\Omega'' G^h(\Omega) G^p(\Omega - \omega) G^h(\Omega') G^p(\Omega' + \omega) \tag{2.10}
\]

with

\[
G^h(\omega) = \int_{-\infty}^{E_f} d\epsilon \frac{n(\epsilon)}{\omega - \epsilon - i\delta}, \quad G^p(\omega) = \int_{E_f}^{\infty} d\epsilon \frac{n(\epsilon)}{\omega - \epsilon + i\delta} \tag{2.11}
\]

We then observe that the first diagram of Fig. 2.10 corresponds to an integral over \( \omega \) of a double convolution of one-particle Green functions; thus we may express the variation \( \delta \Phi \) as follows:

\[
\delta \Phi = \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\Omega \int_{-\infty}^{\infty} d\Omega' \left( \delta G^h G^p G^h G^p + G^h \delta G^p G^h G^p + G^h G^p \delta G^h G^p + G^h G^p G^h \delta G^p \right) \tag{2.12}
\]
By comparing Eq. (2.12) with the identity

\[ \delta \Phi = \int \frac{\delta \Phi}{\delta G} \cdot \delta G \, d\omega \]  

(2.13)

we see that to get the functional derivative \( \frac{\delta \Phi}{\delta G} \) we have simply to i) divide by the variation in \( G \), and ii) eliminate the corresponding integral. In diagrammatic terms this corresponds to cut one propagator line. The result is therefore the second-order diagrams reported in Fig. 2.11. We may continue this analysis with higher order diagrams to show that the functional derivative always amounts to this diagrammatic procedure: cutting of one “external” propagator line. In this way we easily recover all the self-energy diagrams of Fig. 2.11.
Chapter 3

Model systems and the self-consistent procedure

Metal-insulator transitions driven by correlation effects associated with the electron-electron interaction are named Mott-Hubbard transitions [4]. They take place, even in partially filled bands materials which according to band structure theory would be metallic, under the control of key parameters such as band filling, bandwidth and dimensionality, that are experimentally varied by doping, pressure, magnetic fields. Near the transition point the metallic phase shows properties that are frequently quite different from those of ordinary metals: we then speak of anomalous metallic phases, or strongly correlated metals. Experimentally, these unusual properties have been most extensively studied in $d$ and $f$-electron systems; in particular there is a revived interest in transition-metal oxides motivated by the finding of high temperature superconductivity in cuprates and colossal magnetoresistance in manganites. From a theoretical point of view, Mott-Hubbard transitions represent one of the most striking failures of weakly interacting electron system based theories, and their description demands for non-perturbative many-body methods able to capture the whole range of strength of electron-electron interaction.

In this Chapter we address the study of the Mott metal-insulator transition in a simple model single-band system under the control of the ratio $U/W$ between the local Coulomb repulsion and the bandwidth: with increasing $U/W$ the system is expected to go from a weakly correlated metal to a strongly correlated one, and finally to a Mott insulator. The transition is reflected by the spectral function: for a strongly correlated metal we observe a quasi-particle peak at the Fermi energy, for a Mott insulator instead two Hubbard bands separated by $U$.

It turns out that essential in order to get the metal-insulator transition
is the introduction of an iterative self-consistent procedure which updates the non-interacting ground state density of states (DOS) needed as input for the self-energy computation. This is reminiscent of the self-consistent cycle of DMFT: also in DMFT self-consistency, which in that context is required to link the starting lattice model with the effective single-impurity model, is fundamental to obtain the transition from a weakly interacting metal to a Mott insulator. As reported in Ref. [62], “in a single DMFT iteration a metallic input produces a metallic solution, irrespective of the value of $U$ […]. It is only through the requirement of a self-consistent solution that the critical value in the Hubbard model is shifted from $\infty$ to a finite value”.

3.1 Adjusting the ground state approximation

We now come back to a major approximation which has been used in deriving both the ground state energy and the self-energy of the many-body system in Secs. 1.3 and 1.4: that is the substitution of the exact ground state of the system with its non-interacting counterpart. Our purpose is to overcome this approximation and we do that by self-consistently updating the non-interacting ground state.

Let us start rewriting the Dyson equation for the energy and momentum dependent one-particle Green’s function:

$$ G(k,\omega) = G_0(k,\omega) + G_0(k,\omega)\Sigma(k,\omega)G(k,\omega) ; \quad (3.1) $$

from this the two exact and equivalent relations follow:

$$ G(k,\omega) = \frac{1}{G^{-1}_0(k,\omega) - \Sigma(k,\omega)} \quad (3.2) $$

$$ G_0(k,\omega) = \frac{1}{G^{-1}_0(k,\omega) + \Sigma(k,\omega)} . \quad (3.3) $$

The imaginary part of $G(k,\omega)$ gives the spectral function of the system:

$$ A(k,\omega) = \frac{1}{\pi} \text{Im} \ G(k,\omega) ; \quad (3.4) $$

the imaginary part of $G_0(k,\omega)$ amounts to the $k$-resolved density of states, of which $A(k,\omega)$ is the generalization to the case of interacting electrons, and whose average over $k$ gives the usual, $k$-independent, DOS of the system:

$$ A_0(k,\omega) = \frac{1}{\pi} \text{Im} \ G_0(k,\omega) \quad (3.5) $$

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\frac{1}{N_s} \sum_k A_0(k, \omega) = n(\epsilon) \quad (3.6)

(with \( N_s \) = number of lattice sites, or of \( k \) points).

Given the energy-momentum relationship \( \epsilon_k \) of the free particle we can compute the free Green’s function \( G_0 \) and therefore, supposed that the self-energy is known, obtain the interacting \( G \) from the Dyson equation (3.2) (in a solid the band structure \( \epsilon_{kn} \) plays the role of a free particle dispersion, and we have a different Green’s function for each band \( n \)). Conversely, given \( G \) and \( \Sigma \) we come back to \( G_0 \) applying Eq. (3.3).

If we consider the \( k \)-averaged counterparts of all the above mentioned quantities, the Dyson equation is replaced by the following continuous representation:

\[ G(\omega) = \frac{1}{N_s} \sum_k G(k, \omega) = \int_{-\infty}^{+\infty} d\epsilon \frac{n(\epsilon)}{\omega - \epsilon - \Sigma(\omega)} \quad (3.7) \]

which can be exploited to compute \( G \) starting from the density of states and the self-energy - notice that the DOS is the quantity entering the calculation of \( \Sigma \) in Eqs. 1.69, and no explicit knowledge of \( \epsilon_{kn} \) is required.

Now we observe that Eq. (3.3) does not hold anymore if we consider \( k \)-averaged quantities: \( \frac{1}{G^{-1}(\omega) + \Sigma(\omega)} \) indeed is obviously different from \( G_0(\omega) \). Therefore its imaginary part does not reproduce the DOS of the system. Rather it is an object we interpret as a modified density of states which includes to a certain extent the effect of correlations into the ground state of the system:

\[ n_{\text{EFF}}(\omega) = \frac{1}{\pi} \text{Im} \frac{1}{G^{-1}(\omega) + \Sigma(\omega)} \quad (3.8) \]

Now we can define a self-consistent cycle setting this “effective DOS”, which follows after a first 3BS self-energy calculation, as the input for a second calculation. At each step we use \( n_{\text{EFF}} \) to compute the self-energy, and then the initial non-interacting DOS \( n \) to compute \( G \) by Eq. (3.7), since we believe that the ground state correction is already carried by the self-energy and we do not want to count it twice. As a matter of fact, if in Eq. (3.7) we replace \( n \) with \( n_{\text{EFF}} \) the iterative procedure would not converge. A sketch of the self-consistent scheme is given in Fig. 3.1.

We want to stress that this procedure is well defined only if the self-energy is independent, or at most weakly dependent, on \( k \).
3.2 Study of the Mott-Hubbard transition in a model constant-DOS system

In this Section we illustrate the results obtained for the model system defined by a single paramagnetic band with a constant density of states of width $W$. The occupation of the band is set to 0.5.

The interest in studying such a system in the context of the 3BS method is that for a constant DOS the objects appearing in the theory can be analytically computed. In particular at half occupation the integrals $G_1$ and $G_3$ are identical and reduce to (from direct integration of Eqs. (1.65), (1.66), (1.67)):

\[
\begin{align*}
\text{Re} G_1^+(x) &= \text{Re} G_3^+(x) = -\frac{1}{W^2} \left\{ x \ln |x| + (x - W) \ln |x - W| + (x - W/2)^2 \ln |x - W/2| \right\} \\
\text{Im} G_1^+(x) &= \text{Im} G_3^+(x) = -\pi \frac{1}{W^2} \left\{ |x| + |x - W| - 2|x - W/2| \right\} \\
\text{Re} G_1^-(x) &= \text{Re} G_3^-(x) = \frac{1}{W^2} \left\{ x \ln |x| + (x + W) \ln |x + W| + (x + W/2)^2 \ln |x + W/2| \right\} \\
\text{Im} G_1^-(x) &= \text{Im} G_3^-(x) = \pi \frac{1}{W^2} \left\{ |x| + |x + W| - 2|x + W/2| \right\}
\end{align*}
\]

Recalling the definition of $T$-matrices, Eq. (1.60), we see that $T_3$ develops a singularity for

\[
\begin{cases}
\text{Im} G_3 = 0 \\
\text{Re} G_3 = -\frac{1}{U}
\end{cases}
\]

condition that is fulfilled, both for $T_3^+$ and for $T_3^-$, when the ratio between
the Hubbard interaction and the bandwidth assumes the critical value

\[ \frac{U}{W} = \frac{1}{\ln 2} \approx 1.443 . \]

(3.11)

Since \( T_3 \) describes interactions between electron-electron or hole-hole couples, a singularity in \( T_3 \) marks the appearing of a bound state in this scattering channel.

Analogously a pole in the \( T_1 \) matrix is found when

\[
\begin{align*}
\text{Im} G_1 &= 0 \\
\text{Re} G_1 &= \frac{1}{U};
\end{align*}
\]

(3.12)

from this we obtain the same critical \( U \) of Eq. (3.11), which therefore denotes the emergence of a bound excitation also in the electron-hole scattering channel described by \( T_1 \).

We have computed the self-energy and the spectral function at half occupation for different values of the Hubbard interaction \( U \), applying the self-consistent procedure described at the beginning of the present Chapter. All the energy-dependent quantities have been calculated directly on the real energy axis, retaining only a small imaginary part \( i\delta \) of the energy in order to numerically avoid singularities; throughout the present Chapter, where not explicitly mentioned, \( \delta = 0 \).

We introduce our results starting from the behaviour of the 3BS self-energy at the first iterative step, therefore neglecting any ground state correction; subsequently we will analyze the substantial changes introduced by self-consistency.

In Fig. 3.2 we compare the behaviour, as a function of \( U \), of the imaginary part of the full self-energy \( \Sigma \) with that of the \( t \)-matrix (Kanamori, Eq. (1.69b)) contribution \( \Sigma_K \) alone, keeping \( W \) fixed. Both Im\( \Sigma \) increase with increasing \( U \), but with different dependences, as explicitly shown in the last part of the figure: \( \Sigma_K \) is a smoother function of \( U \) than \( \Sigma \).

A second interesting feature is that while the maxima of \( \Sigma_K \) move with varying \( U \) the full self-energy ones do not: their position seems to be fixed by the density of states. To precise this last observation, in Fig. 3.3 the imaginary part of the full self-energy is shown as a function of the bandwidth \( W \), for a fixed Hubbard parameter \( U = 2 \) eV. The ratio between the peaks distance and the bandwidth turns out to be a constant, which means that the maxima of Im\( \Sigma \) always occur for the same energy, in units of \( W \): we can say that \( W \) sets the energy scale of the system. With this in mind, from now on we will keep \( W \) fixed at the value of 2.5 eV.

Let us now come back to the behaviour of the 3BS full self-energy as a function of \( U \). An interesting effect we can see from Fig 3.2 is that while
Figure 3.2: Trend of $\text{Im}\Sigma$ vs Hubbard interaction $U$. Left: the full 3BS self-energy; right: the $t$-matrix contribution alone. At the bottom an explicit comparison between the maximum value assumed by $\text{Im}\Sigma$ and $\text{Im}\Sigma_K$ as functions of $U$ is made. All the calculation refer to the same starting constant DOS with $W = 2.5$ eV, shown as a dotted line (not in scale) in the two upper side figures.

Figure 3.3: Trend of $\text{Im}\Sigma$ vs bandwidth $W$: for each $\Sigma$ the corresponding non interacting DOS is shown as a dotted line of the same color. In all the calculations $U = 2$ eV has been used.
Figure 3.4: Imaginary part of the full 3BS self-energy for two different values of $U$ near to the critical point where $T$-matrices become singular, for a constant DOS of width $W$ at half occupation. In the inset an enlargement of the region close to the Fermi energy. For the calculations shown in this picture a distance from the real energy axis $\delta = 0.01$ eV has been adopted.

For small $U$ values the imaginary part of $\Sigma$ goes to zero at the Fermi energy, with increasing $U$ a point is reached after which we have $\text{Im}\Sigma(\epsilon_F) \neq 0$. We have studied this point in more details and found that for a critical $U$ ($U_c$) whose value lies between $1.44W$ and $1.48W$ a small peak at $\epsilon_F$ appears in $\text{Im}\Sigma$. The shape of $\text{Im}\Sigma$ close to this critical point is shown in Fig. 3.4. Since for a Fermi liquid $\text{Im}\Sigma(\epsilon_F) = 0$ (see the next Chapter for a more detailed discussion), this critical $U$ value marks a substantial change in the behaviour of the system. It is significant that the numerical value of $U_c$ corresponding to $\text{Im}\Sigma(\epsilon_F) \neq 0$ coincides with the predicted point in which the $T$-matrices become singular, $U = W/\ln 2$ (for occupations different from 0.5 the symmetry between particle and hole excitations breaks and we would obtain that $U_c$ would correspond to the emergence of a singularity of $T_1$ at $\omega = \epsilon_F$).

Let us now move to the analysis of the role of the ground state self-consistent correction. First of all we have checked that for small values of $U/W$ the picture is essentially unaffected by such a correction. This is illustrated in Fig 3.5, where the self-energy and the spectral function are shown for $U/W = 0.4$: no substantial differences between the first-step quantities and the converged ones can be noticed. For such small values of the interaction the system behaves like a usual metal, and no incoherent features are present in its spectral function.

The situation changes when the interaction becomes more intense, for instance $U/W = 1.4$ as reported in Fig. 3.6. Concerning the effective density
Figure 3.5: Imaginary part of the self-energy (left), effective DOS (middle) and spectral function (right) for a constant non-interacting DOS of width W with $U/W = 0.4$ at half occupation. Results obtained both neglecting (grey) and including (black) the ground state self-consistent correction are shown.

of states, its width gradually decreases as iterations go on, meaning that the effectiveness of electron-electron interaction increases. The result on the self-energy is that the maxima in $\text{Im} \Sigma$ come closer, for an effect similar to the one shown in Fig. 3.3. Through the enhancement of $\text{Im} \Sigma(\epsilon_F)$, in particular, spectral weight is removed from the Fermi level. The system is now in an anomalous metallic phase; its spectral function shows the typical three-peak structure with upper and lower Hubbard bands centered at $\pm \frac{U}{2}$ and a quasiparticle peak at the Fermi level.

Beyond the critical $U$ the effect of self-consistency is even more pronounced. In Fig. 3.7 we report the data referring to $U/W = 1.6$, that is $U = 1.1U_c$: after iteration only a very small peak at $\epsilon_F$ still remains, of negligible spectral weight with respect to the Hubbard bands. Nevertheless, we would expect the system to undergo a metal-insulator transition at $U_c$, and thus to be an insulator for this value of $U$. This is what happens

Figure 3.6: The same as in Fig. 3.5 but for $U/W = 1.4$. 

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for instance in the DMFT calculations by Bulla Ref. [62], where the metal-insulator transition is studied in two different single-band model systems and an insulating behaviour is found in the spectral function beyond the critical point $U/W = 1.46$. In Fig. 3.8 the DMFT spectral functions for the Bethe lattice (corresponding to a semi-elliptical DOS) are shown and directly compared with 3BS results for a constant DOS, for the same values of $U/W$. We have to remark that Bulla defines $U_c$ as the point where the spectral

Figure 3.7: The same as in Figs. 3.5 and 3.6 but for $U/W = 1.6$ ($U > U_c$).

Figure 3.8: Left: DMFT spectral functions for a semi-elliptical DOS for various values of $U/W$ (adapted Figure from Ref. [62]). Right: corresponding 3BS results for a constant DOS. In both cases $W$ denotes the bandwidth; $U_c = 1.46W$ in DMFT calculations, $U_c = 1.44W$ in 3BS ones.
weight at $\epsilon_F$ vanishes; despite the different definitions, the agreement between DMFT and 3BS concerning $U_c$ is significant. On the other hand we believe that the discrepancies in the spectral function, and in particular the enduring of a small peak at $\epsilon_F$ in the 3BS results, could depend on the numerical implementation and on the computational details of the calculations. The main point here is that we are working at a finite distance $\delta$ from the real energy axis; the corresponding broadening which is introduced in all the energy-dependent quantities could hide a discontinuous behaviour like that of the DMFT spectral function and could fictitiously shift the transition to higher values of $U$.

As a last point, in Figs. 3.9 and 3.10 we study the $t$-matrix approximation of 3BS in the cases $U/W = 1.4$ and $U/W = 10$. The iterative procedure converges very rapidly giving only minor corrections both to the self-energy and to the spectral function; the narrowing of the effective DOS and the increase of $\text{Im}\Sigma(\epsilon_F)$ in Figs. 3.9 are considerably smaller than for the full self-energy (Fig. 3.6), and the main quasi-particle peak at $\epsilon_F$ cannot be suppressed irrespectively of the strength of the electron-electron interaction - see 3.10. We conclude that there is no chance to reproduce the Mott-Hubbard transition by means of the $t$-matrix approximation.

In summary we have examined the role of a self-consistent ground state correction in the description of the metal-insulator transition in a model single-band system, comparing 3BS results with similar DMFT calculations. Although the current 3BS implementation has shown severe limitations when treating the delicate regime of $U \gtrsim W$, we have strong evidence that, analogously to what happens in DMFT, self-consistency is essential in order to
properly describe the metal-insulator transition. Additionally, we have shown that the inclusion of all the scattering channels is of fundamental importance as well: within the $t$-matrix approximation, indeed, no insulating phase can be reached, irrespectively of the value of $U$.

Figure 3.10: The same as in Fig. 3.9 but for $U/W = 10$. 
Chapter 4

Correlation effects in the electronic structure of Fe, Co, Ni

Within the Landau Fermi liquid theory [63], [64] it is possible to establish a one-to-one correspondence between elementary excitations of a many-body system and single-particle states of a corresponding non-interacting system. In particular the quasi-particle linked to the non-interacting state $\epsilon_{kn}$ of a solid is described by the following spectral density, or spectral function, defined as the imaginary part of the one-particle Green’s function:

$$A_{kn}(\omega) = -\frac{1}{\pi} \text{Im} G_{kn}(\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\omega - \epsilon_{kn} - \Sigma_{kn}(\omega)} ;$$  \hspace{1cm} (4.1)

the energy $\omega^*$ and the lifetime $\tau$ of the quasi-particle are defined as follows:

$$\omega^* = \epsilon_{kn} + \text{Re} \Sigma_{kn}(\omega^*)$$

$$\tau = \frac{\hbar}{\text{Im} \Sigma_{kn}(\omega^*)} .$$  \hspace{1cm} (4.2)

We see from Eq. (4.1) that if the self-energy $\Sigma_{kn}$ does not actually depend on the energy $\omega$ the spectral function reduces to a Lorentzian peak of half-width-half-maximum $2\text{Im} \Sigma$ around the position $\omega = \epsilon_{kn} + \text{Re} \Sigma$. In the general case of an energy-dependent self-energy the spectral function is a more complicated, asymmetric and maybe multiply peaked function; possibly a clear major peak cannot be identified, or its width $1/\tau$ can be of the same order of the bandwidth of the system, and the quasi-particle picture breaks down.

One major feature of a Fermi liquid system, i.e. a system for which the above quasi-particle description holds, is that the elementary excitations...
acquire an infinite lifetime infinitesimally close to the Fermi energy, since there conservation of energy and momentum makes the scattering processes unlikely. This means that $\text{Im} \Sigma(\epsilon_F) = 0$ for a Fermi liquid.

For weakly correlated systems the quasi-particles are well defined over a wide range of energy, and the electronic properties are satisfactorily described by usual band structure theory. In strongly correlated systems conversely quasi-particles become short-lived and incoherent features such as Hubbard bands and satellites can appear in the excitation spectrum, with the result that a Fermi liquid description still holds only close to the Fermi energy or even completely breaks down.

Fe, Co and Ni are rather strongly correlated systems. They have partially filled shells of fairly localized $3d$ electrons giving rise to a narrow $d$ band which exhibits both atomic-like and free-electron-like behaviour. While the magnetic moments of these transition metals are quite well reproduced by single-particle approaches, the same is not true for their excitation spectra: a comparison with the experimental results of photoemission spectroscopy shows that the width of the majority spin $3d$ band is overestimated as well as the spin splitting, while the $-6 \text{ eV}$ satellite in nickel, an essentially incoherent feature, is not reproduced at all [65], [66], [67].

In this Chapter we will investigate the electronic structure of these materials by means of the 3BS theory in a detailed comparison with experimental results and other theoretical approaches, and we will come to the conclusion that correlation effects based on a full many-body treatment, as well as a detailed description of the photoemission process, need to be included in order to properly describe iron, cobalt and nickel.

### 4.1 Computational details

The starting point for the simulation of the electronic structure of bulk bcc iron, hcp cobalt and fcc nickel has been a DFT calculation performed with the WIEN2k code [68]. This program is based on a Augmented Plane Wave method, in which the unit cell is divided into atomic spheres and interstitial region and different basis sets are used in the two types of regions: a linear combination of radial functions times spherical harmonics inside each atomic sphere, a plane waves expansion in the interstitial region. The ionic potential is expanded in a similar way, with no shape approximations (“full potential” method). The calculations have been checked for convergence with respect to both the number of plane waves used in the above cited expansion, and the number of $\mathbf{k}$ points used to sample the Brillouin zone.

The PBE-GGA functional [69] has been used; for the lattice constants
the experimental values have been adopted, that is

- bcc iron: \( a = 5.417 \) a.u.
- hcp cobalt: \( a = 4.738 \) a.u. and \( c = 7.690 \) a.u.
- fcc nickel: \( a = 6.637 \) a.u.

No spin-orbit coupling has been used.

Once the band structure has been obtained, an orbital dependent density of states is computed projecting the band eigenvalues onto a basis of localized Wannier functions:

\[
n_\alpha(\omega) = \sum_{kn} |C^{kn}_\alpha|^2 \epsilon_{kn}
\]  

(4.3)

where \( C^{kn}_\alpha \) are the expansion coefficients of Bloch states in terms of Wannier orbitals, the same appearing in Eq. (1.76).

The orbital DOS’s (4.3) are the starting ingredients of the subsequent 3BS calculation by which an orbital dependent self-energy \( \Sigma_\alpha(\omega) \) has been computed for 3d electronic states (in all the figures of the present chapter for simplicity we will show its average over orbital indices); \( \Sigma_\alpha(\omega) \) is then projected back over Bloch states according to Eq. (1.76) to give a \( k \) and \( n \) dependent quantity which is finally plugged into Eq. (4.1) to compute the correlated band structure of the system.

All the energy dependent quantities appearing in the 3BS calculation have to be practically evaluated at a finite distance \( \delta \) from the real energy axes: here we have adopted \( \delta = 25 \) meV for the self-energy calculation, and \( \delta = 100 \) meV (a typical experimental resolution) for the spectral function calculation.

Finally, no self-consistent ground state corrections have been made for these materials due to their small ratio \( U/W \), which makes this procedure unnecessary.

## 4.2 Iron

The electronic structure of bulk bcc iron has been investigated by means of the combined GGA+3BS approach described in the previous section. Different values of the local Coulomb repulsion \( U \) have been tried; the order of magnitude is the one commonly accepted in the literature (see for instance [70], [71], [72]). For the \( J \) parameter the atomic value of 0.9 eV has been chosen.

In Figs. 4.1 and 4.2 the average orbital self-energy is reported for two different values of \( U \), that is \( U = 1.5 \) eV and \( U = 3 \) eV. On the right side
Figure 4.1: Self-energy (left) and correlated band structure (right) of bcc iron for two different values of the Hubbard parameter $U$, for majority spin. The starting DFT-GGA dispersion is also shown (red lines) for reference.

The band structure obtained with the corresponding self-energy correction is shown for various high-symmetry directions in the first Brillouin zone.

From Eqs. (4.1) and (4.2) we see that the width of the peaks appearing in the spectral function is essentially defined by the imaginary part of the self-energy, and inversely related to the lifetime of the corresponding quasi-particle. Consistently with the Landau Fermi liquid theory, $\text{Im}\Sigma$ in Figs. 4.1 and 4.2 goes to zero near the Fermi energy: in this region of the spectrum we can see well-defined lines of band structure, corresponding to the long-lived quasi-particles. Conversely between about 3 eV and 6 eV binding energy $\text{Im}\Sigma$ assumes its maximum values, and correspondingly in this region the
bands are substantially damped.

The effect of the real part of the self-energy is to renormalize quasi-particle energies, shifting the real poles of the Green’s function in Eq. 4.1. As a result the electronic states in the region between the Fermi energy and $-5 \text{ eV}$, where $\text{Re}\Sigma$ is positive, are pushed upwards: the net effect is a shift and a narrowing of the bands, as can be seen in the corresponding spectral functions.

From the previous Figures it is apparent that in the filled part of the spectrum majority spin states are more affected by correlations then minority spin ones, while the reverse is true for empty states. In the framework of 3BS theory this can be understood taking into account two points. First of all we notice that the leading interactions are those between opposite spins, while
the processes involving parallel spins are much smaller being proportional to $U - J$ (and $J$ is of the order of $U$ in most cases: see the discussion of Ref. [28]).

The second point is that the efficiency of the scattering processes depends on the number of states accessible for the scattering itself; this number is related for direct photoemission to the overall number of empty states, and to the number of filled states for inverse photoemission. We may see this more formally looking at the self-energy Eq.(1.69): it contains an integral over the empty DOS for direct photoemission and over the filled DOS for inverse photoemission. By these arguments we expect the most effective scattering channels to be those involving an added majority spin hole with a minority spin electron-hole pair, and an added minority electron with a majority electron-hole pair, resulting in filled majority and empty minority spin states to be most affected by electron-electron correlation.

Finally we note that increasing $U$ the self-energy increases, still maintaining the same structure: the effects on the band structure remain qualitatively the same but with enhanced importance.

4.2.1 3BS, Dynamical Mean Field Theory and the double counting issue

The dynamical mean field theory is presently one of the most popular and successful theories to study electronic correlations in solids. A review of this method can be found in [11]. Its starting point is, as for the 3BS method, a generalized Hubbard hamiltonian of the type of Eq. (1.75); the Hubbard problem in a periodic lattice is then mapped into a correlated impurity coupled to a self-consistent bath, and this last is addressed by means of a variety of different solvers.

Due to the fact that both DMFT and 3BS are many-body non perturbative methods founding their description of electronic correlation on the Hubbard model, the two are expected to describe basically the same physics: the interesting point of their comparison will be addressed in this section using the case of iron as a benchmark.

In particular we consider the results of [73], where the adopted solver for the impurity problem is the spin-polarized $t$-matrix fluctuation-exchange (SPTF), suitable for the case $U \leq W$ [74]. The parameters of the self-energy 3BS calculation presented in this section are the same as in [73], that is $U = 2.3$ eV, $J = 0.9$ eV and a distance from the real energy axes $\delta = 60$ meV. There are instead some differences in the DFT starting point: while the same lattice constant $a = 5.417$ a.u. has been adopted, for the DMFT calculation the LDA functional has been used, and the implementation is based on full-
potential linear muffin-tin orbital (FP-LMTO) method. Anyway concerning the orbital densities of states, which are the input ingredient both in 3BS and in DMFT, the two DFT calculations result only in minor differences.

Before we present the results a few words need to be spent about a delicate issue, that is the double counting problem. Due to the fact that DFT describes, although in a mean field fashion, the whole electron-electron interaction, and in the Hubbard model one-site Coulomb repulsion is explicitly considered, when we put the two worlds together in a single Hamiltonian of the type of Eq. (1.75) we found contributions due to the additional Hubbard term that have already been included in the DFT eigenenergies, and which should be removed in order to avoid to count them twice.

In DMFT this is done by means of a correction to the self-energy, i.e. subtracting from Σ a “double counting” term; however such a correction is not unique and its choice represents an open question. In particular in the results reported here the double counting was taken into account shifting the real part of each orbital self-energy in such a way that their average passes through zero at the Fermi energy. This means that the LDA is assumed to properly describe the Fermi surface of the system, which is left identical to that of its uncorrelated counterpart (unless the density of states used in the DFT parent calculation is self-consistently updated after the self-energy is computed, which is not carried out here). This result can be reasonable in the case of transition metals, but would be questionable for more strongly correlated materials such as high $T_C$ superconductors; a whole branch of research indeed is involved in the calculation of the complicated Fermi surfaces of strongly correlated materials [75], [76], [29], [77].

Anyway, for consistency with the DMFT procedure here the same prescription is adopted for 3BS self-energy: that is we set $\text{Re}(\Sigma_{3BS}(\epsilon_F)) = 0$.

We can now proceed and analyze the results, starting from a comparison between 3BS and DMFT self-energy, Figs. 4.3 and 4.4.

First of all we observe that the scale of the self-energy functions is the same, which means that the two methods give similar estimations of the strength of correlation effects; the overall shape of Σ is also comparable, while some differences arise going down to the details. In particular it is interesting to observe that the position of the maxima both for $\text{Im}\Sigma_{DMFT}$ and $\text{Re}\Sigma_{DMFT}$ well agrees with $t$-matrix self-energy one, but not with the full 3BS Σ. Recalling that $t$-matrix approximation only includes the contribution of electron-electron and hole-hole scattering, this circumstance suggests that the SPTF solver of DMFT may reduce, with respect to 3BS, the role of electron-hole interaction. Still some details of $\Sigma_{DMFT}$ are not present in 3BS results, such as the shoulder in $\text{Im}\Sigma$ at about 2 eV and the double peak of $\text{Re}\Sigma$ for majority spin.
Figure 4.3: Imaginary part of the self-energy of bcc bulk iron: comparison between DMFT (left, reprinted figure with permission from A. Grechnev, I. Di Marco, M. I. Katsnelson, A. I. Lichtenstein, John Wills and Olle Eriksson, Phys. Rev. B 76, 35107 (2007)) and 3BS (right). Majority spin is shown at the top, minority one at the bottom. For DMFT the various lines refer to different sets of correlated orbitals and different temperatures; for 3BS we show both the complete self-energy and the t-matrix contribution.

Figure 4.4: Real part of the self-energy of bcc bulk iron: DMFT (left, reprinted figure with permission from A. Grechnev, I. Di Marco, M. I. Katsnelson, A. I. Lichtenstein, John Wills and Olle Eriksson, Phys. Rev. B 76, 35107 (2007)) and 3BS (right) results, for both spins.
Figure 4.5: Comparison between spin-resolved (top: majority; bottom: minority) 3BS (left) and DMFT (right) correlated density of states of bcc iron. For 3BS both the complete self-energy (black) and the t-matrix approximation (orange) are shown. The bare DFT-GGA result is also reported for reference.

Looking at the spin-resolved density of states in Fig. 4.5 we see that at this level the differences between DMFT and 3BS self-energy practically disappear, giving rise to a DMFT DOS that is quite the same as the t-matrix one: in particular they both show a satellite at about 8 eV binding energy. Due to the shift in Im$\Sigma$, the complete 3BS theory sets the satellite position at about $-6$ eV instead.

4.2.2 Photoemission from the theoretician’s point of view

Angle-resolved photoemission spectroscopy (ARPES) is a powerful technique to determine the electronic structure of solid systems [78]. It exploits photoelectric effect to extract from the sample electrons whose energy and momentum distribution reflects the $\epsilon_k$ dispersion of the material.

A theoretical model of the photoemission process is needed in order to establish a correspondence between the measured photocurrent and the electronic properties of the solid. In a single-particle view, photoelectrons outside the solid are free:

$$k^{OUT} = \frac{\sqrt{2m\epsilon_{KIN}}}{\hbar},$$

and the surface-parallel component of their momenta is conserved at surface crossing: so we can immediately obtain the parallel momentum an electron had inside the solid as a function of its measured kinetic energy $\epsilon_{KIN}$ and
angle of emission $\theta$:

$$k_{\|}^{IN} = k_{\|}^{OUT} = \frac{\sqrt{2m\epsilon_{KIN}}}{\hbar} \sin \theta .$$  \hfill (4.5)

Concerning the perpendicular component $k_{\perp}^{IN}$ of momentum inside the solid, the situation is more complicated. We are forced to make some hypothesis about the state of the photoelectron after its excitation, but still inside the sample; the simpler one is of course that of a free final state, whose energy can be written (leaving $E_0$ as a free fitting parameter):

$$\epsilon_f = \frac{\hbar^2 k_{IN}^2}{2m} + E_0 .$$  \hfill (4.6)

From here the desired formula for $k_{\perp}^{IN}$ follows:

$$k_{\perp}^{IN} = \frac{1}{\hbar} \sqrt{2m\epsilon_{KIN} \cos^2 \theta - V_0}$$  \hfill (4.7)

where $V_0$, the so called inner potential, is given by $E_0$ minus the work function of the material.

Eqs. (4.5) and (4.7) are the basic formulas of ARPES and demonstrate how measuring the energy- and angle-dependent photocurrent one can obtain the momentum distribution of electrons inside the solid.

In particular, in normal emission ($\theta = 0$) only the $k$-space line normal to the emission surface is sampled; Eq. (4.7) reduces to (with the further assumption that the energy of the electron in its initial state is negligible with respect to $\hbar \omega$, which is reasonable for photoemission from the valence band):

$$k_{\perp}^{IN} \approx \frac{1}{\hbar} \sqrt{2m(\hbar \omega - E_0)} .$$  \hfill (4.8)

We see from the previous Equation that in normal emission the value of $k_{\perp}^{IN}$ is selected varying the incoming photon energy.

We can make a step forward in the theoretical description of photoemission giving a many-body treatment [79] which relies on the Fermi golden rule. This gives the probability that under the effect of a perturbation hamiltonian $\hat{H}_{PS}$ the system undergoes a transition from the initial state $|\Psi_i\rangle$ to the final state $|\Psi_f\rangle$:

$$J_k(\omega) = \sum_s |\langle \Psi_f | \hat{H}_{PS} | \Psi_i \rangle|^2 \delta(\epsilon_k - \epsilon_s - \hbar \omega) .$$  \hfill (4.9)

In the context of photoemission $\hat{H}_{PS}$ describes the interaction between the incoming photon and the electrons inside the solid; $|\Psi_i\rangle = |N; \hbar \omega\rangle$ amounts
to the $N$-particle ground state plus one photon, and has the energy $E_i = E_G + \hbar \omega$; while $|\Psi_f\rangle = |N - 1, s; k\rangle$ is the $s$-excited state of the $N - 1$-particle system plus a free electron of momentum $k$ and its energy is given by $E_f = E_{N-1}^s + \epsilon_k$. The delta function in Eq. 4.9 ensures energy conservation:

$$E_f = E_i \Rightarrow \hbar \omega = \epsilon_k - \left( E_{N-1}^s - E_G \right) \tag{4.10}$$

where we have denoted with $\epsilon_s$ the electron binding energy in the excited state $s$. Overall Eq. (4.9) is proportional to the detected photocurrent as a function of the energy $\omega$ and electron momentum $k$.

The only approximation made until now is the one implicit in the Fermi golden rule: namely that is appropriate to treat the photon-solid interaction within second order perturbation theory. To proceed we have two options and we can rely on the so-called three-step or one-step models of photoemission.

The three-step model [80], although purely phenomenological, has proven to be rather successful [81], [82]. Within this approach the photoemission process is subdivided into three independent and sequential steps:

(i) optical excitation of the electron inside the bulk;

(ii) travel of the excited electron to the surface;

(iii) escape of the photoelectron into vacuum.

Correspondingly the total photoemission intensity is given by the product of three independent terms: the probability for the optical transition, the scattering probability for the electrons traveling within the solid (which can be phenomenologically taken into account via an effective mean free path), the transmission probability through the surface potential barrier. We are interested in evaluating step (i), which contains all the information about the electronic structure of the material. To do this it would be convenient to decouple the photoelectron from the reminder $N - 1$-electron system. This, however, is far from trivial because during the photoemission process the system relaxes. The problem simplifies within the so-called sudden approximation, which is extensively used in many-body calculations of photoemission spectra: the photoemission process is assumed to be instantaneous, with no post-collisional interaction between the photoelectron and the system left behind. Formally, within the sudden approximation we can write the final photoemission state as

$$|\Psi_f\rangle = \hat{c}_k^\dagger |N - 1, s\rangle, \tag{4.11}$$

where $\hat{c}_k^\dagger$ creates a free electron with momentum $k$. 69
Next we write the interaction hamiltonian in second quantization, with $\hat{c}_i^\dagger/\hat{c}_i$ = creation/annihilation operator relative to the single particle state $|\psi_i\rangle$ and $i$ denoting a complete set of single particle quantum numbers:

$$\hat{H}_{PS} = \sum_{f_i} \Delta_{f_i} \hat{c}_i^\dagger \hat{c}_i, \quad \text{with}$$

$$\Delta_{f_i} = \langle \psi_f | \hat{H}_{PS} | \psi_i \rangle;$$

introducing the energy- and $i$-dependent spectral function as

$$A_i(\omega) = \sum_s |\langle N - 1, s | \hat{c}_i | N \rangle|^2 \delta(\omega - \epsilon_s) \quad (4.13)$$

after a few algebra Eq. (4.9) is turned into

$$J_k(\omega) = \sum_i |\Delta_{ki}|^2 A_i(\epsilon_k - \omega) \quad (4.14)$$

which establishes the relation between photocurrent and spectral function within the simple model adopted. We see that the measured current is given by the spectral function modulated by the matrix elements of the photon-solid interaction; these can be worked out within different approximations and have basically the effect of modifying the intensity of the peaks observed in the photoemission spectrum.

The one-step model is a more refined approach in which the whole process of photoemission, that is the excitation of the photoelectron, its transport within the solid and its escape through the surface into the vacuum, is treated as a single coherent process [82], [83], [84], [85]. In this case bulk, surface, and vacuum have to be included in the Hamiltonian describing the crystal, which implies that not only bulk states have to be considered, but also surface and evanescent states, as well as surface resonances. A main difference with respect to three-step model is the definition of the final state of the photoelectron inside the solid, which is assumed to be a time-reversed Low Energy Electron Diffraction (LEED) state and can be computed using Korringa-Kohn-Rostocker (KKR) theory [86], [87], [88], [89], therefore taking into account all the possible multiple-scattering processes. Moreover, an extension of the original theory has been developed which allows to take into account correlation effects in the initial electron state by means of many-body self-energy corrections [90]. This version of the one-step model of photoemission has been applied to various systems: see for instance [91], [92], [93], [94].

In the present experiment the energy of the incoming photons (25-110 eV) was within the UV region, where ARPES is quite sensitive to the surface electronic structure: a bulk and surface combined theoretical study is therefore
necessary in order to analyze the experimental results. But before going to the simulation of ARPES spectra within the one-step model, let us consider the spectral functions.

A six-slab GGA simulation of the Fe(100) surface has been performed, and checked for convergence with respect to the number of slabs, in the same implementation used for bulk calculations and discussed in the previous sections.

Let us start focusing on the bare GGA surface spectral function, shown in Fig. 4.6 for the $\bar{\Gamma}$ point of the surface Brillouin zone (we recall that $\bar{\Gamma}$ resumes the information about the whole $\Gamma N$ bulk line). Concerning majority spin, we see that several bulk states show a degenerate or nearly-degenerate surface component; among these, it is worth noting that the $-2.25$ eV bulk state is substantially shifted to $-2.48$ eV at the surface. In addition two pure, although small, surface contributions are visible at $-0.43$ eV and $-1.69$ eV.

The surface spectrum for minority spin is essentially continuous, and degenerate with the bulk one, up to $-1.5$ eV. We recall that while bulk states move along the $\Gamma N$ direction following their $\epsilon_k$ relation, because of the lost surface-normal symmetry surface states do not disperse, and should appear in the experiment at the same energy for every $k$ point; therefore, depending on the specific position in $k$ space, they can be completely hidden by a degenerate bulk state, or superimpose with a close-lying one, just enlarging its width, or appear as isolated peaks.

Now we have to face the delicate point of how surface states are affected by correlation effects. In principle two mechanisms should enhance correlations at the surface: due to the reduced correlation number, on one side the bands

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**Figure 4.6:** Comparison between bulk, sub-surface and surface GGA spectral function at the $\bar{\Gamma}$ point of the surface Brillouin zone of bcc iron, for both spins.
Figure 4.7: The same as in Fig. 4.6, but here the correlated 3BS spectral function is shown.

become narrower, on the other the screening of the electron-electron interaction is less effective. This last effect could be simulated with an increased $U$ value for surface atoms; nevertheless, since no estimate of a “surface $U$” for iron is available in the literature, we prefer to use the same value $U = 1.5$ eV for all the atoms in the supercell. $J = 0.9$ eV has been adopted for each atom too.

The 3BS surface spectral function is shown in Fig. 4.7 with the same notation as Fig. 4.6. While the minority spin spectrum is very similar to the bare GGA one, the majority spin one is considerably simpler; it exhibits just two main features, one at $-2.15$ eV, shifted of about $-20$ meV with respect to its bulk counterpart and of $+40$ meV with respect to the GGA calculation, and one at $-1$ eV, degenerate with the bulk. Two additional small peaks are visible at $-0.12$ eV and $-0.4$ eV.

Let us now move to the analysis of experimental spectra. Several ARPES studies have been presented in the literature for ferromagnetic bcc iron [95], [96], [97], [98], [99]; here we consider recent spin-resolved ARPES experiment performed with synchrotron radiation on a 20 ML thick iron film epitaxially grown on W(110) and magnetized along the [1 0 1̅] easy axis [38]. Photoemission spectra from the Fe(110) surface have been taken in normal emission, that is the ΓN direction of the Brillouin zone is investigated; different k points are selected varying the photon energy $h\omega$ according to Eq. (4.8), with $E_0 = 14.5$ eV. Both p-polarized and s-polarized photons were used; due to dipole selection rules in matrix elements [100] in the first case only $\Sigma_1$ and $\Sigma_4$ symmetry states are detectable, while in the second one only $\Sigma_3$ ones; $\Sigma_2$ symmetry corresponds to forbidden transitions in the present experimental setup (in practice the light polarization is never pure, so that residues of the
“forbidden” symmetry can be visible). The energy resolution was 100 meV.

In Figs. 4.9 and 4.10 we compare experimental spectra at various fixed \( \mathbf{k} \) points with the corresponding \( \mathbf{k} \)-dependent bulk spectral function. The bare GGA band structure along the \( \Gamma N \) direction is reported for reference in Fig. 4.8, with the explicit indication of the bands symmetry. We recall (see Eq. (4.14)) that the spectral function is expected to reproduce photoemission spectra only to a limited extent, since matrix element effects are not taken into account; moreover the final-state broadening due to the scattering the photoelectron undergoes during its way out of the sample, and its interaction with the surface, are neglected too.

For majority spin, the main feature in the experimental \( p \)-polarization spectra is a peak close to the Fermi energy, dispersing from \( \sim 1.1 \text{ eV} \) to \( \sim 0.8 \text{ eV} \) binding energy going from \( \Gamma \) to \( N \). This peak can be asigned to nearly degenerate \( \Sigma_1 \) and \( \Sigma_4 \) bulk states and its position is systematically improved by 3BS corrections with respect to the bare GGA calculation, even if the accuracy of the matching with the experiment depends on the \( \mathbf{k} \) point.

The \( s \)-polarization spectra show two additional features: a broad non-dispersive peak at \( \sim 2.2 \text{ eV} \), which nicely matches the \( -2.15 \text{ eV} \) surface state of Fig. 4.7; and a shoulder near the Fermi energy which we interpret as related to the surface too (at about \( 2/3 \Gamma N \) a \( \Sigma_3 \) bulk state overlaps with
Figure 4.9: Comparison between photoemission spectra, bare GGA bulk spectral function and GGA+3BS bulk spectral function of bcc iron, for majority spin. The various panels refer to different incoming photon energies, corresponding to different points of the Brillouin zone along the $\Gamma N$ direction (with $\Gamma N = 1.55\,\text{Å}$). We have explicitly marked $\Sigma_2$ states appearing in the spectral functions, which are experimentally forbidden, and surface resonances appearing in the experiment but not included in the theoretical calculation.

For minority spin, according to theoretical calculations three degenerate bands are present at the $\Gamma$ point close to the Fermi energy, together with a surface resonance. One of the bands has $\Sigma_2$ symmetry thus is not visible in the experiment; of the remaining two, the $\Sigma_3$ band crosses the Fermi level at about $1/3\,\Gamma N$ (notice the corresponding reduction of the experimental s-polarization signal in the 40 eV spectrum), while the $\Sigma_1$ one at about $4/5\,\Gamma N$; at this point the underlying surface contribution becomes visible (see 70 eV spectrum). In the case of minority spin no significant differences
arise between GGA and GGA+3BS calculation and the agreement with the experiment is excellent.

As a last observation about Figs. 4.9 and 4.10 we notice that the width of the experimental peaks seems to be systematically underestimated by the theory. To better precise this point the experimental spectra have been fitted as a sum of Lorentzian functions plus a background, and from the width of the Lorentzian peaks an “experimental” \( \text{Im}\Sigma \) has been extracted as a function of the binding energy. The result is shown in Fig. 4.11, in comparison with the imaginary part of the 3BS average orbital self-energy (already presented in Figs. 4.1 and 4.2). While the trend of the experimental line-widths is fairly well reproduced by the theory, from a quantitative point of view the agreement is actually poor, especially for minority spin. Concerning this point we have to underline that the shown theoretical self-energy takes into account lifetime effects only due to electronic correlations in bulk states; while additional contributions like scattering with defects can affect the experiment. Moreover we have seen how the iron spectrum is influenced by surface effects:

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Figure 4.10: *The same as in Figure 4.9 but for minority spin.*
we believe that the presence of surface states quasi-degenerate with bulk ones can explain, to a certain extent, the additional peaks broadening observed in the experiment.

This hypothesis seems to be confirmed by the following study of iron spectrum within the one-step model of photoemission. Both 3BS and DMFT self-energies have been used to include correlations into the photoemission spectra, leading to pretty similar results. In Figs. 4.12 and 4.13 we report the DMFT-based calculation, that is the one shown in [38].

Concerning majority spin, the two $\Sigma_3$ surface resonances are reproduced in the one-step spectra, even if the $-2.2$ eV one with much lower intensity than in the experiment. A new feature appears at $\sim 0.5$ eV binding energy for p-polarization, which could contribute to the broadening of the main experimental peak, whose position, moreover, is now exactly reproduced along the whole $\Gamma N$ line. On the other hand, the intensity of the deeper $\Sigma_1$ band is overestimated in the 40 eV spectrum, while the interpretation of the main s-polarization peak remains uncertain.

For minority spin, we observe that the surface resonance which dominates the 70 eV spectrum is correctly reproduced; moreover the theoretical
Figure 4.12: Iron: comparison between ARPES and theoretical one-step model spectra, both for p- and s-polarized incident photons of various energies. Majority spin. We have explicitly marked surface resonances.

p-polarization spectrum for 56 eV photon energy is broader than the corresponding spectral function in Fig. 4.10 and thus better reproduces the experimental peak width, probably due to the underlying presence of the same surface resonance.

In short, the agreement between experiment and one-step theoretical spectra is good for p-polarization, with improvements with respect to the bare spectral functions concerning both the position and the linewidth, even if this last point still is not completely satisfactory. The s-polarization majority spin spectra show some puzzling issue too. Globally it seems that our approaches, although leading to important improvements when compared to DFT-GGA calculations, still cannot reach a fully quantitative understanding of the photoemission spectra of iron, thus demanding for more refined many-body techniques, possibly with non local schemes which take into account non local fluctuations in multiband systems.
Figure 4.13: The same as in Figure 4.12 but for minority spin.

Figure 4.14: Real part of the self-energy for bcc Fe, hcp Co and fcc Ni, both for majority (left) and for minority (right) spin. Notice the different energy scales.

4.3 Cobalt and nickel

The other itinerant ferromagnets with a partially filled 3d shell are cobalt and nickel.

3BS theory has been already used in the past [30] to study the quasi-
particle band structure of cobalt. In a comparison with angle-resolved, spin-integrated photoemission on hcp Co(0001) it succeeded in reproducing the essentially incoherent spectrum in the energy region deeper than $-2$ eV, where in contrast to standard DFT-based predictions no sharp quasi-particle peak is detected.

Concerning nickel, previous 3BS calculations [27], [28] have been proved successful in reproducing various feature of the experimentally observed electronic structure. 3BS could reproduce the narrowing of the 3$d$ band with respect to standard DFT calculations, and the existance and position of the $-6$ eV satellite. Moreover in comparison with angle-resolved, spin-integrated photoemission from Ni(110) surface a quantitative agreement was reached between $\mathbf{k}$-resolved experimental spectra and theoretical spectral functions; subsequently a DMFT-based study combined with the one-step model of photoemission [92] showed that matrix element effects could further improve the interpretation of photoemission data.

Here we present the study of the electronic structure of Co and Ni within the the extended 5-body version of 3BS. The choice of the Hubbard parameters have been made following previous 3BS studies: $U = 2.3$ eV, $J = 0.9$ eV for cobalt [30], and $U = 1.95$ eV, $J = 0.5$ eV for nickel [28]. First we present our theoretical results concerning self-energy, spectral density and correlated DOS, subsequently moving to a detailed comparison with recent spin-resolved ARPES experiments.

In Figs. 4.14 and 4.15 we report a comparison between the self-energies of the three transition metals Fe, Co, and Ni, and in Figs. 4.16 and 4.17 the corresponding correlated band structures of respectively cobalt and nickel are shown in comparison with the bare GGA ones. We notice that, while...
the maximum of $\text{Im}\Sigma$ sets the position of a possible satellite (about $-6$ eV for nickel - as it appears from the correlated density of states, Fig. 4.18 - in excellent agreement with experiments), the energy region significant for the $3d$ band renormalization is the one between the Fermi level and about $-3$ eV: here, with the chosen values of the Hubbard parameters, the imaginary part of the self-energy is maximum for cobalt, resulting in a most pronounced damping of quasi-particles states.
Figure 4.18: Correlated density of states (solid line) of fcc Ni from the 3BS approach with $U = 1.95$ eV and $J = 0.5$ eV, for both spins. For reference the uncorrelated DOS is also shown (dotted line).

We now move to the analysis of photoemission spectra. The experimental results we refer to have been performed with synchrotron radiation on hcp Co(0001) and fcc Ni(111) surfaces in normal emission (ΓA and ΓL directions of the Brillouin zone respectively), both with p-polarized and s-polarized light [39].

In Fig. 4.19 the experimental spectra for various points along the ΓA direction of the hcp Brillouin zone of cobalt are compared with the corresponding $k$-dependent bulk spectral function. In the majority spin channel the differences between DFT and 3BS calculations are evident: the low binding energy states are substantially shifted towards the Fermi level and shrunk, thus leaving the region under $-2$ eV empty; while the deeper state at $-5$ eV is suppressed by lifetime effects. 3BS results well agree in both aspects with experiment, with the exception of the main peak at Γ point, whose shift towards Fermi energy is underestimated.

For minority spin 3BS self-energy brings no significant corrections to DFT calculation, and both theoretical spectra fairly agree with the experimental ones.

In Fig. 4.20 we show ARPES spectra and bulk spectral function of fcc nickel for various points along the ΓL direction of the Brillouin zone, for majority spin. It clearly appears that correlation effects can account for the main difference between experiment and DFT calculation in this energy region: that is, the nearly rigid shift of the states towards the Fermi level. For all the considered $k$ points, 3BS peaks positions agree with experimental ones within 25 meV concerning the first state below the Fermi energy, within
Figure 4.19: Comparison between ARPES spectra and 3BS bulk spectral function for various points along the ΓA direction of the Brillouin zone of hcp Co, for both spin channels. Red crosses mark transitions which are symmetry-prohibited in the present experimental setup (for selection rules in hcp lattice see Ref. [101]).

50 meV for the others. We notice that the relative peaks spectral weight, being influenced by matrix element effects, is not expected to be reproduced by the spectral function.

Analogous effects, even if less significant, are present also in minority spin spectra, Fig. 4.21.
Figure 4.20: Comparison between ARPES spectra and spectral functions (both GGA and GGA+3BS) for various points along the ΓL direction of the Brillouin zone of fcc Ni, for majority spin.

Figure 4.21: The same as in Figure 4.20 but for minority spin.
Summary

It is well established that density functional theory, the major nowadays method for realistic solid state calculations, even within rather simple approximations such as the LDA lead to excellent agreement between theory and experiment concerning electronic, magnetic, transport properties for a wide variety of materials, labeled as weakly correlated. On the other side it is not surprising that the LDA, having been derived from the weakly interacting homogeneous electron gas, does not work well for strongly interacting electrons.

This thesis aims to contribute to the very active field of research in strong correlations beyond DFT-LDA, that has led for instance to the introduction of the DMFT method, with the development of a many-body non-perturbative approach devised to solve the Hubbard model, which in the last years established itself as a general framework to study strong electron-electron correlations.

The method, named Three-body Scattering (3BS) theory, has been presented in the first two Chapters of this thesis. The focus has been on how to go beyond the original three-body formulation by including so called five-body corrections: a development which opens the way to a different derivation of the whole theory in terms of a variational method based on the Luttinger-Ward functional. The interest in such a reformulation is that it guarantees conservation of total energy, particle number and of all the other quantities that must be conserved according to the symmetries of the Hamiltonian. In order to link 3BS with the Luttinger-Ward formalism an analysis of the theory in terms of Feynman diagrams has been carried out (in Chapter 2); this also represents the basis on which in the future 3BS could be combined with the GW approximation, analogously to the recently proposed DMFT+GW method, in order to overcome one of its main limitations: the neglecting of the long-range part of the Coulomb interaction, implicit in the Hubbard model on which the theory is based.

Once the formal basis of 3BS theory has been established, its implementation for calculations of self-energy and total energy has been discussed. Then
it has been shown how correlation effects can be included for real systems starting from the corresponding DFT calculations.

Chapter 3 is centered on a second extension of the theory, namely the introduction of an iterative self-consistent procedure which updates the non-interacting ground state DOS needed as an input for the self-energy computation. The effect of self-consistency is investigated within a model single-band system, results are compared to corresponding DMFT data, and it is shown that self-consistency is needed to describe the Mott-Hubbard metal-insulator transition occurring for increasing values of the electron-electron interaction.

The last section of this thesis is dedicated to calculations of the electronic structure of 3d-transition metals. Bulk Fe, Co and Ni and their surfaces have been chosen as prototype examples to discuss the application of the above described 3BS formalism to realistic systems. Corresponding 3BS spectral functions have been compared with DMFT based calculations and to recent angle- and spin-resolved photoemission spectra, within a collaboration with the experimental group at BESSY synchrotron in Berlin. The interpretation of photoemission data, relying on correlation effects within the 3BS method as well as on a detailed description of the photoemission process within the one-step model, is overall satisfactory; nevertheless a quantitative reproduction of the experimental linewidths is still missing, demanding for more refined many-body calculations, possibly including non-local effects.
Appendix A

Effective hamiltonian matrix elements

Here we resume the effective hamiltonians $\hat{H}^N$ and $\hat{H}^{N-1}$ derived in Sec. 1.2, explicitly listing the involved matrix elements (see Ref. [25] for their derivation). The trivial extension to the case of $N + 1$ particles is omitted.

Please notice that the scattering processes that take place within 5-body configurations $|v\rangle$, represented by the operator $\hat{H}_5^{NP}$, are the same occurring within 4-body states $|f\rangle$ and described by $\hat{H}_4^{ND}$: the only difference is the presence of a spectator hole with momentum $\mathbf{q}$ and spin $\downarrow$. For this reason we don’t give their expressions.
$N$-particle hamiltonian

$$\hat{H}^N = \hat{H}_0 + \hat{H}_4 + \hat{V}'$$

with:

$$\hat{H}_0 = \sum_o W_0 |o\rangle \langle o|$$

$$\hat{H}_4 = \hat{H}_4^D + \hat{H}_4^N D$$

$$\hat{H}_4^D = \sum_f \delta_{k_1-k_2+k_3-k_4} \left( W_0 - \epsilon_1 + \epsilon_2 - \epsilon_3 + \epsilon_4 \right) |f\rangle \langle f|$$

$$\hat{H}_4^{ND} = \hat{V}_{13}^4 + \hat{V}_{24}^4 + \hat{V}_{23}^4 + \hat{V}_{14}^4$$

$$\hat{V}_{13}^4 = \frac{U}{N} \sum_{k_1,k_2,k_3,k_4} \sum_p |k_1 - p, k_2, k_3 + p, k_4\rangle \langle k_1, k_2, k_3, k_4|$$

+ hermitean conjugate (hc)

$$\hat{V}_{24}^4 = -\frac{U}{N} \sum_{k_1,k_2,k_3,k_4} \sum_p |k_1, k_2 + p, k_3, k_4 - p\rangle \langle k_1, k_2, k_3, k_4| + \text{hc}$$

$$\hat{V}_{23}^4 = -\frac{U}{N} \sum_{k_1,k_2,k_3,k_4} \sum_p |k_1, k_2 + p, k_3 + p, k_4\rangle \langle k_1, k_2, k_3, k_4| + \text{hc}$$

$$\hat{V}_{14}^4 = \frac{U}{N} \sum_{k_1,k_2,k_3,k_4} \sum_p |k_1 - p, k_2, k_3, k_4 - p\rangle \langle k_1, k_2, k_3, k_4| + \text{hc}$$

$$\hat{V}' = -\frac{U}{N} \sum_{o,f} \left( |o\rangle \langle f| + |f\rangle \langle o| \right)$$
\textbf{N} - 1-particle hamiltonian

\[ \hat{H}^{N-1} = \hat{H}_1 + \hat{H}_3 + \hat{H}_5 + \hat{V} + \hat{V}'' \]

with:

\[ \hat{H}_1 = \sum_u W_u |u\rangle \langle u| \]

\[ \hat{H}_3 = \hat{H}_3^D + \hat{H}_3^{ND} \]

\[ \hat{H}_3^D = \sum_t \delta_{k_0 + k_1 - k_2, \ q} \left( W_0 - \frac{U}{N} N_1 - \epsilon_0 - \epsilon_1 + \epsilon_2 \right) |t\rangle \langle t| \]

\[ \hat{H}_3^{ND} = \hat{V}_1^3 + \hat{V}_2^3 \]

\[ \hat{V}_1^3 = -\frac{U}{N} \sum_{k_0, k_1, k_2} \sum_p |k_0, k_1, k_2\rangle \langle k_0 - p, k_1 + p, k_2| + \text{hc} \]

\[ \hat{V}_2^3 = \frac{U}{N} \sum_{k_0, k_1, k_2} \sum_p |k_0, k_1, k_2\rangle \langle k_0 + p, k_1, k_2 + p| + \text{hc} \]

\[ \hat{H}_5 = \hat{H}_5^D + \hat{H}_5^{ND} \]

\[ \hat{H}_5^D = \sum_v \delta_{k_1 - k_2 + k_3 - k_4, \ q} \left( W_1 - \epsilon_1 + \epsilon_2 - \epsilon_3 + \epsilon_4 \right) |v\rangle \langle v| \]

\[ \hat{H}_5^{ND} = \hat{V}_1^5 + \hat{V}_2^5 + \hat{V}_3^5 + \hat{V}_4^5 \]

\[ \hat{V} = -\frac{U}{N} \sum_{ut} \left( |u\rangle \langle t| + |t\rangle \langle u| \right) \]

\[ \hat{V}'' = -\frac{U}{N} \sum_{uv} \left( |u\rangle \langle v| + |v\rangle \langle u| \right) \]
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