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Introduction to the physics of metallic systems

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Foreword

The idea of making these Lecture Notes had a series of motivations, associated to four different occasions. The starting point was a very simplified Mini-Course, lectured by A. G. Gomes, around 1981 at the Solid State Physics Department of the Universidade Federal do Rio do Janeiro, on basic aspects of metal physics.

Later on, these previous notes together with some introduced improvements, were used to give a Metal Physics Course in the Centro Brasileiro de Pesquisas Físicas, around 1982. The main motivation at that moment were to present a series of theoretical lectures, emphasizing the close connection to experimental facts. In that occasion it was born the idea of working, in close collaboration with students in experimental Solid State Physics at the Universidade Federal do Rio Grande do Sul. The idea was to introduce, in their scientific formation, a clear difference between the use by experimental people, of theory and formalism. Such a clear distinction, turns out to be essential for a good development of the experimental work.

During a three years stay in the Institute of Physics of the Universidade Federal do Rio Grande do Sul, at least three PhD thesis were supervised and the beginning of the work started always with the study of the 1982 version of these Metal Physics Lectures. It became very clear in this supervising work, in particular with C. M. da Silva and R. L. Sommer, that perfectioning the 1982 version of these Lectures were fundamental. Concerning the discussed subjects, it turned out the need of two distinct series of Lectures. One on Metal Physics, including recent results and methods like the Recursive and LMTO. The other important series of Lectures should consider the macroscopic properties and microscopic theories of Magnetism. In this third occasion, besides their thesis work, the development of these Lectures Notes constituted part of the work of C. M. da Silva and R. L. Sommer.

The idea of producing these Notes, in a more complete form and in the most self contained way as possible, was devised in order to simplify the beginning of the work of young students. This fourth and the more important step is associated to the decision of the Physics Department of the Universidade Federal de Santa Maria, to start a MSc degree.

The absence of specific standard text books, necessary for the future research of the MSc starting students, pushed us, C. M. da Silva, R. L. Sommer and A. G. Gomes, to increase substantially the content of these Lectures and presented in the form of two complementary text books.

Having ensured the strategical support of the Centro Brasileiro de Pesquisas Físicas, through the Monografias de Física, made available to the authors in 1992, this work has been started. In the present volume, considering the Physics of Metallic Systems, the authors tried to overview the basic fundamental ideas and also recent aspects of modern electronic structure theory. Together with the magnetism theory volume, we hope that the students can have a basic text to start their research work.

The authors would like to thank Prof. Delmar Brandão, Professor of Physics at the Instituto de Física of the Universidade Federal do Rio Grande do Sul, for a detailed and careful revision of the manuscript. One of the authors (AGG) would like to thank the CNPq for a grant covering his travel expenses to Santa Maria. The authors thank the Universidade Federal de Santa Maria for the continuous support during the time these notes are written.

Contents

Chapter 1

GENERAL CONSIDERATIONS

The physics of metallic materials is an extensive subject. In this course we have tried to synthesize some aspects in these series of lectures. We started in a very fundamental level discussing the elements of the description of the electronic structure, since this course is expected to be self-contained.

As it will be stressed in all chapters a great emphasis will be given in the description of the experimental aspects and for that we follow closely the classification of the metals as given by the Periodic Table. Examples are the following three large groups. In the first group let us quote the transition ferromagnetic metals like Fe, Co and Ni; paramagnetic metals like Pd and Pt; the noble metals Cu, Ag and Au; and the $s-p$ metals like Cd, In and Sb. The rare earth group is subdivided into two subgroups: the stable rare earths like Gd, Tb and Dy and the unstable ones like Ce, Eu and Sm. Finally the third group is composed by the actinide metals which in certain aspects exhibit close similarities with the anomalous rare earths. These are the pure metals and now we should mention typical examples of their alloys or intermetallics. Since this is a very extensive subject, we will restrict ourselves to examples close to our experience in the description of their electronic structure.

Among the transition metal intermetallics let us quote the Laves phase ones and the Heusler alloys, thus materials exhibiting a two sub lattice structure. Examples of transition metal intermetallics are $ZrFe_2$, YFe_2, $HfFe_2$, $LuFe_2$. These materials are ferrimagnetic, since besides the large magnetic moment at the Fe atoms of the B sub lattice, a small moment anti parallel to the total magnetization, exists in the A sub lattice, as detected by neutron diffraction techniques. In contrast to these ferrimagnetic materials, YCo_2, YAl_2 are paramagnetic materials, requiring the application of external magnetic fields to produce a non zero magnetization. The Laves phase structure produces a very rich collection of materials since the atoms at the A sub lattice can also be rare earths. Compounds like $GdAl_2$, $GdCo_2$, $GdFe_2$, are examples of these materials, again with very interesting magnetic properties. Mostly interesting, this Laves structure has selective properties in producing alloys or more precisely, pseudo binary compounds. The term selective means that impurities can be introduced only in a preferred sub lattice. Examples are Al or Si impurities dissolved in the B sub lattice, replacing Fe for example. In general these compounds have the general form $(A_{1-x}A'_x)(B_{1-y}B'_y)_2$, where B and B' are transition metals and A, A' can be transition metals or rare earths. This shows the great richness of these compounds with a large variety of electronic structures and magnetic properties. Along these lectures, such materials will be quoted as examples for the applications of the theories presented.

Another class of compounds can be mentioned is the Heusler alloys. Examples of these compounds, which exhibit a large list of possibilities are among the most classical are Co_2MnAl and Pd_2MnAl. These materials show almost all possible combinations of elements: transition metals, rare earths, actinides and sp metals. Then the models and theories presented below will certainly be useful in the description of this collection of compounds.

In the first chapter we follow closely the very simple Mott's version of the Tight Binding (TB) description of the electronic structure, starting with a non degenerate picture. The so derived bands are supposed to be non hybridized sp, d, or f character. This provides a first description of the pure metals. After that, the Friedel's version of the TB approximation is presented including degeneracy, and this is very important to describe pure transition metals and actinides. Next we introduce some fundamental concepts like densities of states, the imaginary part theorem and Friedel's version of the cohesion energy of metals. In particular the important theorem associating the maximum of the cohesive energy to the half of the $3d$ transition series is presented together with the concept of bonding and anti-bonding states, as borrowed from chemistry and applied to itinerant states.

The study of the electronic structure has been made, among other ways, by probing the electron states introducing impurities in the dilute limit. Historically this study started with normal metal - normal metal alloys, and after that, involving transition metal alloys. This order was dictated mainly by metallurgical problems suggested by technological activities.

The question of a dilute impurity in a TB host was firstly considered by Slater and Koster. Historically these impurity problems were considered also by Friedel starting from a free electron gas and describing the impurity perturbation through a square well potential. In these lectures however we give more emphasis to the Slater-Koster (SK) problem in order to establish notation and to introduce the solution of Dyson's equation for a localized potential. We discuss also the cases where the impurity potential is constituted of two terms, the solution of the problem involving the first term being exactly known. With this formalism, the effect of an extended potential with low strengths of the "wings", can be made using the Born series.

The important concepts introduced by Friedel, like the phase shifts, as applied to the impurity problem and the sum rule connecting these to the excess charge, are then introduced within the SK picture. The existence of bound states above or below the conduction band, their amplitude at the impurity site or outside it, their connection to the electronic structure of the host metal are also discussed. These topics give a rather general and complete view of the SK problem.

Starting again from the free electron gas and a localized potential well, Friedel was also able to introduce, together with the phase shifts, a particular behavior of the $l = 2$ phase shift. The resonating level was then introduced in the dilute impurity scenario, his properties studied and applied to transition impurities in simple hosts. Later the same problem was considered by P. W. Anderson, using the Green's function method. The possibility of magnetic moment formation was then discussed within the one-electron Hartree-Fock approximation. Later the same problem was reconsidered by Moriya, extending the way of treating the electronic structure of the host. We thus call the Section dedicated to this problem the Friedel-Anderson-Moriya problem. Still later this formalism was applied to the case of rare earths by Coqblin and Blandin, following the ideas developed by Rocher, which in turn were based in Friedel's description of these rare earths.

The reason for beginning with an extensive discussion of the SK problem is to provide the mathematical basis to the deal with a Green's function approach for these two problems. Finally the third problem considered in this dilute limit is how to extend the SK problem to transition metal hosts including explicitly the existence of $s - d$ bands in a non hybridized limit. The scattering problem involves now three matrix elements, namely the $d - d$, the $s - s$ and the $s - d$ or $d - s$ elements. The solution is again very similar to the original SK problem, but in terms of effective matrix elements which are expressed in terms of the starting ones and the suitable resolvents describing the electron propagation in unhybridized bands.

In a later Section the dilute limit is extended to consider the case of concentrated alloys of A and B elements. The Coherent Potential Approximation (CPA) enables one to interpolate the electronic structure from pure elements to concentrated alloys. Two cases are considered: the simplest diagonal disorder (only the values of the energy band centers are different for A and B metals) and the off-diagonal case including different band widths.

In the next Chapter we consider the magnetic properties of the pure metals for which the electronic structure was presented in the first chapter. We start discussing the simplest case namely that of the localized states carrying a magnetic moment. Two different classes are considered separately: the metallic cases and the insulating ones. We firstly derived the Zener interaction between the localized and itinerant spins and emphasize the Pauli principle origin of the exchange interaction. Next we derive the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between localized magnetic moments. We then turn to the opposite limit of itinerant electrons, including the Pauli principle and the Coulomb interaction among pairs of electrons. We derived the so-called Hubbard Hamiltonian and then discussed the Hartree-Fock approximation. We recover the same previous comments about the origin of the magnetic moment formation in the impurity problem case. Remarks are then made about the difficulties involved in the solution of the Hubbard model due to the competition between kinetic effects and the local electron-electron interaction. In that Chapter, both in the derivation of the RKKY interaction and for applications of the itinerant model, the important concept of generalized susceptibility is presented. This is the response of an applied field at the site R_i, measured by the magnetization induced at site R_j. In these cases we use the formulation introduced by Gautier.

In the next Chapter we generalize, via the CPA approximation, the impurity description in alloys including the magnetic properties. It is shown in detail that this approximation interpolates between pure metals A and B in these simple AB alloys. Some remarks are also presented for the application of the CPA pseudo binary compounds, where a two sub-lattice scenario is clearly identified. These remarks are motivated by the Laves phase or Heusler compounds mentioned before.

We want to emphasize that up to this lecture the densities of states invoked in the description of these materials in the dilute limit are model density of states. The magnetic properties of the concentrated alloys can be discussed within the Hartree-Fock approximation including only the spin dependence of the band centers, which in turn are self-consistently determined in terms of the occupation numbers as extracted from the perturbed densities of states. The entry data of all these calculations are the host density of states, the total number of electrons and the Coulomb interaction parameters. Clearly, the obtained results are model dependent, these parameters being fitted to experimental data.

The one electron structure can however be determined in a quite independent and rigorous way in terms of the crystalline structure and some TB parameters, as introduced in the classical paper by Slater and Koster. Given these parameters, a closed and well defined quantum mechanical problem determines the local density of states, through the calculation of the resolvent function. A very general method to solve this problem, the recursive or Lanczos method, is presented in the next Chapter. Initially conceived to be applied for the atomic function TB method, these calculations suffer from the drawbacks of the classical TB method.

Because of that, in the following Chapter we introduce the Linear Muffin Tin Orbitals (LMTO) Method which after Andersen and Jepsen, provides a rigorous foundation for the TB approach, and its drawbacks are thus removed. With this Chapter, the one electron view of these pure metals and alloys have been presented in a quite completely way.

Some other problems must be considered separately due to their many body character. These are the Kondo effect, the intermediary valence problem and finally the heavy fermions and the exotic superconductivity. These are much more complex problems and will be discussed only in a very simplified way in the last Chapter.

Chapter 2

ELEMENTARY DESCRIPTION OF THE ELECTRONIC STRUCTURE

2.1 Tight binding: Mott's formulation

First of all a brief recall of Bloch's theorem is important. This theorem concerns the motion of electrons in periodic potentials. Thus this theorem is useful to describe pure materials, where translation invariance is present:

$$\psi_k(r) = \mu_k(r)e^{ikr}; \quad \mu_k(r+a) = \mu_k(r), \tag{2.1}$$

Bloch theorem states that the $\mu_k(r)$ is a periodic function. We want to emphasize that no degeneracy is present in this formulation, this being valid strictly only for s states. Later on we will introduce explicitly degeneracy, for example, in the case of d wave functions. Since we intent to describe a linear combination of atomic orbitals (LCAO), let us first define R_λ the positions of the atoms in the lattice. Introduce now $\phi(r - R_\lambda)$, the non degenerate atomic wave functions centered at the sites R_λ, see fig. 2.1.

We adopt to the wave function, in this periodic lattice, the following combination:

$$\psi_k(r) = \frac{1}{N^{1/2}} \sum_\lambda a_\lambda(k)\phi(r - R_\lambda), \tag{2.2}$$

where we take for the coefficients the values $a_\lambda(k) = e^{ikR_\lambda}$ and N is the number of

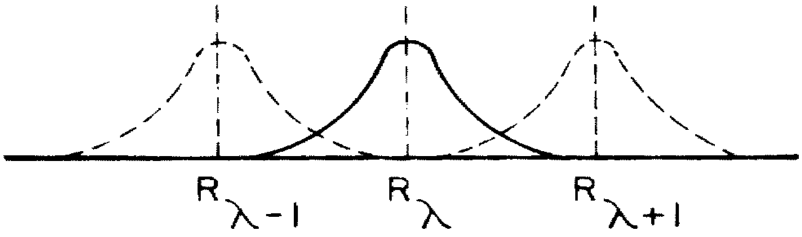


Figure 2.1 Atomic wave functions centered at sites R_λ.

atoms. Let us verify that such combination satisfies Bloch's theorem; in fact:

$$\begin{aligned}\psi_k(r) &= \frac{1}{N^{1/2}}\sum_\lambda e^{ikr}e^{-ik(r-R_\lambda)}\phi(r-R_\lambda) \\ &= e^{ikr}\frac{1}{N^{1/2}}\sum_\lambda e^{-ik(r-R_\lambda)}\phi(r-R_\lambda). \qquad (2.3)\end{aligned}$$

Note that the wave function obtained summing over λ is periodic, thus this function correspond $\mu_k(r+a)=\mu_k(r)$ in Bloch theorem. Then:

$$\psi_k(r) = \frac{1}{N^{1/2}}\sum_\lambda e^{ikR_\lambda}\phi(r-R_\lambda). \qquad (2.4)$$

Let now introduce the following hypothesis:

$$< \phi(r-R_\lambda) \mid \phi(r-R_{\lambda'}) >= \delta_{\lambda\lambda'}, \qquad (2.5)$$

which implies:

$$< \psi_k \mid \psi_k >= \frac{1}{N}\sum_{\lambda\lambda'} e^{ik(R_\lambda - R_{\lambda'})} < \lambda|\lambda' >= 1. \qquad (2.6)$$

The one electron periodic Hamiltonian is:

$$H = T + \mathbf{V}(\vec{r}) \qquad (2.7)$$

where $\mathbf{V}9\vec{r})$ is a periodic potential function and the kinetic energy operator is given by:

$$T = -\frac{\hbar^2}{2m}\nabla^2. \qquad (2.8)$$

The expectation value of the Hamiltonian is then given by:

$$E_k =< \psi_k \mid H \mid \psi_k >, \qquad (2.9)$$

where

$$H \mid \psi_k >= \frac{1}{N^{1/2}}\sum_\lambda e^{ikR_\lambda} H \mid \phi(r-R_\lambda) > . \qquad (2.10)$$

Let rewrite the Hamiltonian as:

$$H = T + v(r-R_\lambda) + \mathbf{V}(\mathbf{r}) - v(r-R_\lambda), \qquad (2.11)$$

where $v(r-R_\lambda)$ is the atomic potential as obtained in any Table for atomic functions, illustrated in fig. 2.2.

Since $v(r-R_\lambda)$ is the atomic potential one has:

$$\left(T + v(r-R_\lambda)\right)\left|\phi(r-R_\lambda)\right\rangle = E_0\left|\phi(r-R_\lambda)\right\rangle, \qquad (2.12)$$

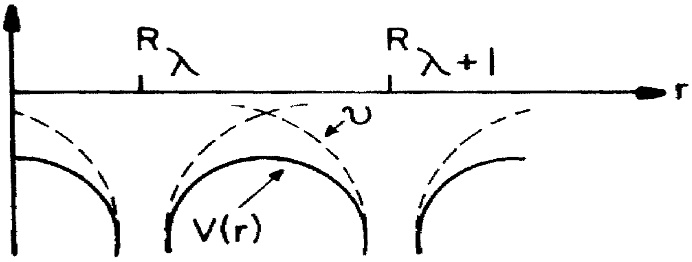


Figure 2.2 The atomic potential functions in the sites R_λ

this following from the atomic function construction. Thus the effect of acting the Hamiltonian on the TB function, implies:

$$H\left|\psi_k\right\rangle = \frac{1}{N^{1/2}}\sum_{\lambda} e^{ikR_\lambda} E_0 \left|\phi(r-R_\lambda)\right\rangle + \frac{1}{N^{1/2}}\sum_{\lambda} e^{ikR_\lambda}\left(\mathbf{V}(\vec{r})-v\right)\left|\phi(r-R_\lambda)\right\rangle \quad (2.13)$$

and the expectation value E_k becomes:

$$\begin{aligned} E_k &= \left\langle\psi_k\left|H\right|\psi_k\right\rangle = E_0\frac{1}{N}\sum_{\lambda\lambda'} e^{ik(R_{\lambda'}-R_\lambda)}\left\langle\lambda'|\lambda\right\rangle \\ &+ \frac{1}{N}\sum_{\lambda\lambda'} e^{ik(R_{\lambda'}-R_\lambda)}\left\langle\phi(r-R_{\lambda'})\left|\mathbf{V}(\vec{r})-v\right|\phi(r-R_\lambda)\right\rangle \end{aligned} \quad (2.14)$$

Using (2.6), one gets:

$$E_k = E_0 + \frac{1}{N}\sum_{\lambda\lambda'} e^{ik(R_\lambda-R_{\lambda'})}\left\langle\phi(r-R_{\lambda'})\left|\mathbf{V}\vec{r})-v\right|\phi(r-R_\lambda)\right\rangle . \quad (2.15)$$

By geometry considerations $R_{\lambda'} = R_\lambda + \Delta R_{\lambda'}$, $\Delta R_{\lambda'}$ being the vector connecting the neighboring atoms. Using symmetry considerations the sum over λ can be performed giving a factor N; one finally gets:

$$E_k = E_0 + \sum_{\lambda'} e^{ik\Delta R_{\lambda'}}\left\langle\phi(r-\Delta R_{\lambda'})\left|\mathbf{V}(\vec{r})-v\right|\phi(r)\right\rangle \quad (2.16)$$

In figure 2.3 we illustrate the contribution to $\mathbf{V}(\vec{r})-v$, overlapping with the atomic functions.

Introducing the following two terms with usual notation:

$$\alpha = -\int \phi^*(r)\left(\mathbf{V}(\mathbf{r})-v(r)\right)\phi(r)dr \quad (2.17)$$

where we have considered the case $\Delta R_{\lambda'} = 0$, and

$$\beta = -\int \phi^*(r-\Delta R_0)\left(\mathbf{V}(\mathbf{r})-v(r)\right)\phi(r)dr \quad (2.18)$$

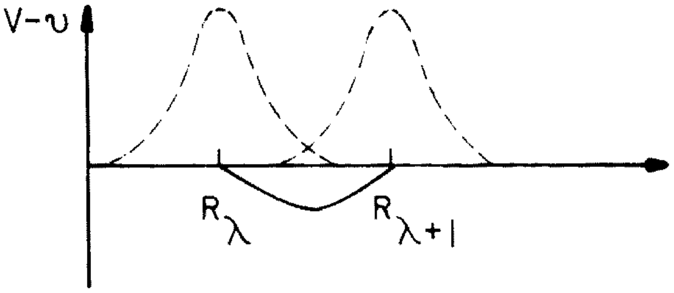


Figure 2.3 Wave functions and the $\mathbf{V}(\vec{r}) - v$ potentials

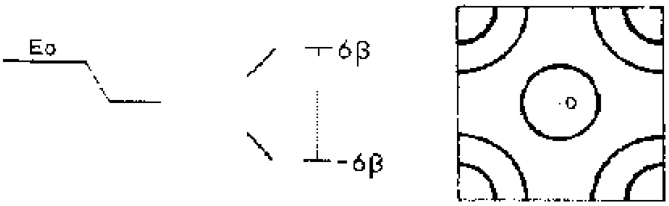


Figure 2.4 (a) Illustration of the three terms of the energy levels. (b) The Sketch of the energy curves

where we only included the nearest neighbors. Usually one has α and $\beta > 0$. If ΔR_0 is the position of any of next neighbors, one gets for the energy:

$$E_k = E_0 - \alpha - \beta \sum_{\Delta R} e^{ik\Delta R_0}. \tag{2.19}$$

If we apply this results to simple cubic lattice, one gets:

$$\Delta R_0 \equiv (\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a), \tag{2.20}$$

in this way

$$E_k = E_0 - \alpha - 2\beta(cosk_x a + cosk_y a + cosk_z a). \tag{2.21}$$

If the $\vec{k} = 0$ the energy is given by

$$E_k = E_0 - \alpha - 6\beta, \tag{2.22}$$

but if $\vec{k} = \frac{\pi}{a}\vec{n}$, $\vec{n}$ is a vector with integer components, the energy is:

$$E_k = E_0 - \alpha + 6\beta. \tag{2.23}$$

The effect of these three terms of (2.19) are illustrated in fig. 2.4a.

For small values of k_i the cosine is $\cos k_i a \cong 1 - \frac{1}{2}k_i^2 a^2$, one gets:

$$\begin{aligned} E_k &= E_0 - \alpha - 2\beta\left(3 - \frac{1}{2}a^2(k_x^2 + k_y^2 + k_z^2)\right) \\ &= E_0 - \alpha - 6\beta + \beta a^2 k^2 \end{aligned} \tag{2.24}$$

For k_i near the $\frac{\pi}{a}$, $\cos(k_i a \cong -\left(1 - \frac{1}{2}k_i^2 a^2\right)$. In the same form, one gets:

$$\begin{aligned} E_k &= E_0 - \alpha - 2\beta\left(-3 + \frac{1}{2}a^2(k_x^2 + k_y^2 + k_z^2)\right) \\ &= E_0 - \alpha + 6\beta - \beta a^2 k^2. \end{aligned} \tag{2.25}$$

A sketch of the constant energy curves for this simple case is shown if fig. 2.4b.

To illustrate the use of the simple Mott's picture to understand four different types of metals in the Periodic Table we have presented figures 2.5. In the left side of the figures we present the expected form of the density of states. In figure 2.5a we illustrate the situation for transition metals. In figure 2.5b the case of noble metals is presented. As compared with the transition metal case, the main difference is the complete filling of the d band. In figure 2.5c we show the case of sp metals. Again a completely filled d band is shown, but the p band are explicitly shown. Finally in fig. 2.5d the case of normal rare earth is presented. Note the existence of the $4f$ localized level at the low energy part of the figure.

2.2 Density of states

The definition of the density of states (DOS), $N(\epsilon)$, between ϵ and $\epsilon + d\epsilon$ is given by:

$$N(\epsilon)d\epsilon = \frac{\Omega}{(2\pi)^3}\int d\vec{k}, \tag{2.26}$$

where the integrations are over $\vec{k}$ values such that the corresponding energies lie in the interval between ϵ and $\epsilon + d\epsilon$, and Ω is the unit cell volume. To obtain the traditional form of the density of states, let us start from:

$$d\vec{k} = dS_k dk_\perp, \tag{2.27}$$

where dS_k and $dk_\perp$ are indicated in figure 2.6. In this way:

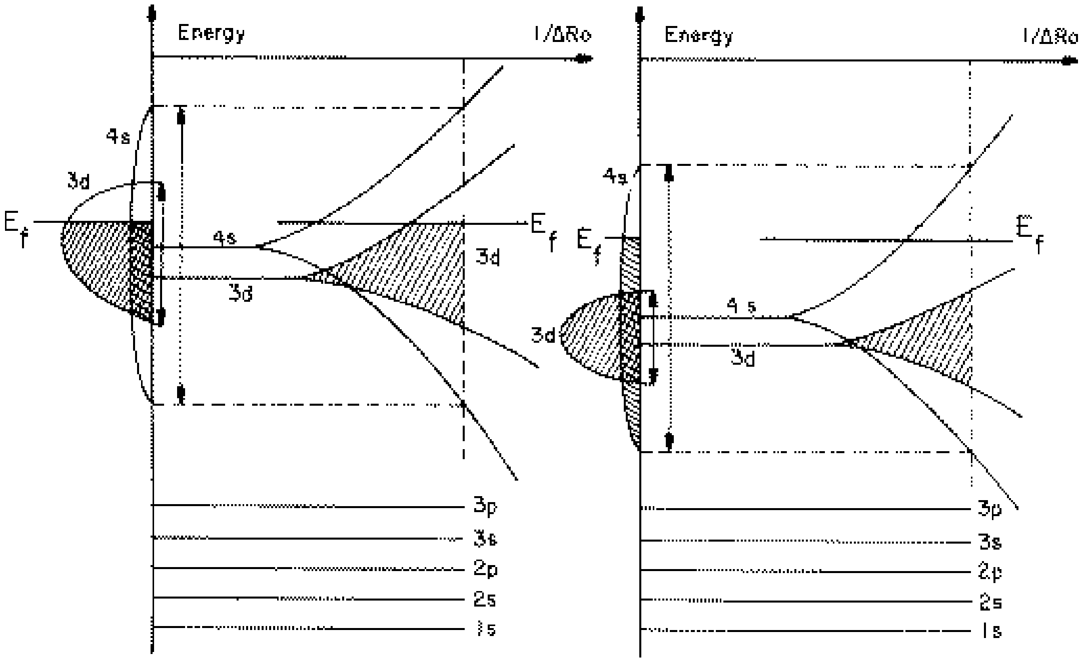
$$d\epsilon = |\nabla_k \epsilon_k|\, dk_\perp \longrightarrow dk_\perp = \frac{d\epsilon}{|\nabla_k \epsilon_k|} \rightarrow d\vec{k} = d\epsilon \frac{dS_k}{|\nabla_k \epsilon_k|}, \tag{2.28}$$

then,

$$N(\epsilon) = \frac{\Omega}{(2\pi)^3}\int_{S(\epsilon)} \frac{dS_k}{|\nabla_k \epsilon_k|}. \tag{2.29}$$

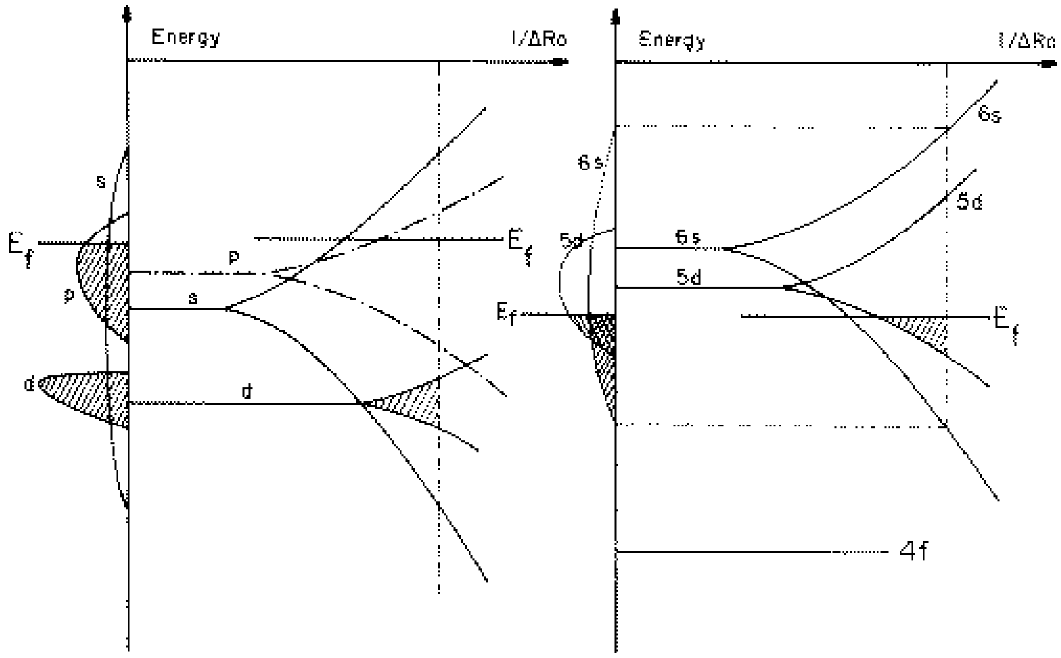
Additional remarks on the density of states; let us start from:

$$\sum_k \delta(\epsilon - \epsilon_k) = \frac{\Omega}{(2\pi)^3}\int d\vec{k}\delta(\epsilon - \epsilon_k), \tag{2.30}$$



TRANSITION METAL

NOBLE METAL



sp METAL

NORMAL RARE EARTH

Figure 2.5 Sketch of the energy bands for several materials

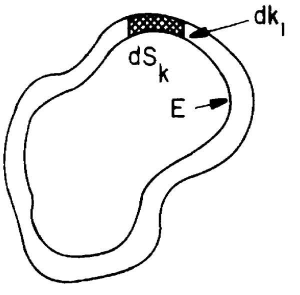


Figure 2.6 Elementary volume for the calculation of the DOS

using the previous representation for the $d\vec{k}$,

$$\begin{aligned}\sum_k \delta(\epsilon-\epsilon_k) &= \frac{\Omega}{(2\pi)^3}\int d\epsilon' \int_{S(\epsilon')} \frac{dS_k}{|\nabla_k \epsilon_k|}\delta(\epsilon-\epsilon') \\ &= \int d\epsilon' \delta(\epsilon-\epsilon') \frac{\Omega}{(2\pi)^3}\int_{S(\epsilon')} \frac{dS_k}{|\nabla_k \epsilon_k|_{\epsilon'}} \\ &= \frac{\Omega}{(2\pi)^3}\int_{S(\epsilon)} \frac{dS_k}{|\nabla_k \epsilon_k|_{\epsilon}}. \end{aligned} \tag{2.31}$$

Then we have verified that:

$$N(\epsilon) = \sum_k \delta(\epsilon-\epsilon_k). \tag{2.32}$$

The imaginary theorem Let us start from the classical Cauchy formula:

$$\lim_{\delta\to 0_+} \frac{1}{\epsilon-\epsilon_k+i\delta} = P\left\{\frac{1}{\epsilon-\epsilon_k}\right\} - i\pi\delta(\epsilon-\epsilon_k) \tag{2.33}$$

where P is the principal part.

Let us first give the definition of the resolvent $G(z)$. For a given complex number z we define the resolvent by:

$$G(z) = (z-H)^{-1}, \tag{2.34}$$

where H is the Hamiltonian. Let $|k>$ be an eigenstate of H, defined by:

$$H|k>= \epsilon_k|k> . \tag{2.35}$$

The states $\mid k >$ are given, for example, by the TB approximation. The matrix elements of $G(z)$ are then:

$$< k \mid G(z) \mid k >= \frac{1}{z-\epsilon_k}. \tag{2.36}$$

Let us take $z = \epsilon + i\delta$ and let us make $\delta \to 0_+$. Then

$$-\frac{1}{\pi} Im\,[Tr_k G(z)] = -\frac{1}{\pi}\sum_k Im < k \mid G(z) \mid k >= -\frac{1}{\pi}\sum_k Im\frac{1}{\epsilon - \epsilon_k + i\delta}. \qquad (2.37)$$

Then,

$$-\frac{1}{\pi} Im\,[Tr_k G(z)] = \sum_k \delta(\epsilon - \epsilon_k) = N(\epsilon). \qquad (2.38)$$

Thus the theorem, which from now on will be called the imaginary theorem valid for an arbitrary resolvent $G(z)$ with $z = \epsilon + i\delta$, connects the imaginary part of the trace of $G(z)$ with the density of states $N(\epsilon)$:

$$N(\epsilon) = -\frac{1}{\pi} Im\,[Tr_k G(z)]\,. \qquad (2.39)$$

2.3 Tight-binding: Friedel's formulation

The principles of the calculation are the following: (a) consider the superpositions of the atomic potentials $\mathbf{V} \simeq \sum_i v_i$ where v_i is the Hartree potential centered at the site i; (b) taking into account the degeneracy one should consider the atomic states $\mid \mathrm{im} >, m = 1 \ldots 2l + 1$, for each site i; the angular momentum l takes the values $l = 0$ (s), $l = 1$ (p), $l = 2$ (d), $\ldots$. By construction these atomic states satisfy:

$$(T + v_i) \mid im >= E_0 \mid im >\,. \qquad (2.40)$$

The states $\{\mid im >\}$ form a complete and orthonormal set,

$$< im \mid jm' >= \delta_{ij}\delta_{mm'}. \qquad (2.41)$$

Let us search a solution for the problem in terms of an expansion in terms of the atomic orbitals:

$$|\psi(\epsilon) >= \sum_{i,m} a_{im} \mid im >, \qquad (2.42)$$

i corresponds to the sites and the degeneracy is given by $m = 1, \ldots 2l + 1$, and ϵ is the energy of the state. The condition for normalization, in this case is:

$$\begin{aligned} < \psi(\epsilon) \mid \psi(\epsilon) > &= \sum_{i,j}\sum_{m,m'} a^*_{im} a_{jm'} < im \mid jm' > \\ &= \sum_{i,j}\sum_{m,m'} a^*_{im} a_{jm'} \delta_{ij}\delta_{mm'} = \sum_{i,m} |a_{im}|^2 = 1. \end{aligned} \qquad (2.43)$$

In the matrix elements $< im \mid v_l \mid jm' >$ we retain only contributions from near neighbors, v_l being the atomic potential at the site l. The crystalline potential

$\mathbf{V}(\vec{r})$ is taken as a superposition of atomic potentials $\mathbf{V}(\vec{r}) = \sum_l v_l$, as stated in (a). The problem to be solved is

$$(T + \mathbf{V}(\vec{r})) \mid \psi(\epsilon) >= \epsilon \mid \psi(\epsilon) >, \tag{2.44}$$

or alternatively:

$$\sum_{i'm'} a_{i'm'} \left(T + \mathbf{V}(\vec{r})\right) |i'm' >= \sum_{i'm'} a_{i'm'}\epsilon \mid i'm' >, \tag{2.45}$$

Multiply in the left by $< im \mid$ to get:

$$\sum_{i'm'} a_{i'm'} < im \mid (T + \mathbf{V}(\vec{r})) \mid i'm' >= a_{im}\epsilon. \tag{2.46}$$

Now it remains to calculate $< im \mid (T + \sum_l v_l) \mid i'm' >$:

$$\begin{aligned} \left\langle im \mid T + \sum_l v_l \mid i'm' \right\rangle &= \; < im \mid T + v_i + \sum_{l\neq i} v_l \mid i'm' > \\ &= \; < im \mid T + v_i \mid i'm' > + \sum_{l\neq i} < im \mid v_l \mid i'm' > \\ &= \; E_0 \delta_{ii'} \delta_{mm'} + \sum_{l\neq i} < im \mid v_l \mid i'm' > . \end{aligned} \tag{2.47}$$

From the matrix elements $\sum_{l\neq i} < im \mid v_l \mid i'm' >$ we retain only the following terms:

$$\delta_{ii'}\delta_{mm'} < im| \sum_{l\neq i} v_l |im >= \delta_{ii'}\delta_{mm'}\alpha_{im} \tag{2.48}$$

and

$$\beta_{im}^{jm'} = \sum_{j\neq i} < im|v_j|jm' > . \tag{2.49}$$

We get then the set of $(2l+1)N$ coupled linear equations, where N is the number of sites:

$$(E_0^{(l)} + \alpha_{im} - \epsilon)a_{im} + \sum_{m'} \sum_{j\neq i} \beta_{im}^{jm'} a_{jm'} = 0 \tag{2.50}$$

which is the general solution for our problem. Note that α_{im} is the crystal field contribution associated to the neighbor atoms to a site i, whereas $\beta_{im}^{jm'}$ is the tunneling between sites i, j and states m and m'. Equating to zero the determinant of the coefficients of the linear equations fixes the energy ϵ; a systematic way to solve the equations like (2.50) is discussed in detail within the recursive method in Chapter 4.

Let us now calculate the expectation value of the energy:

$$E \; = \; \frac{< \psi |H| \psi >}{< \psi \mid \psi >} =< \psi \mid H \mid \psi >$$

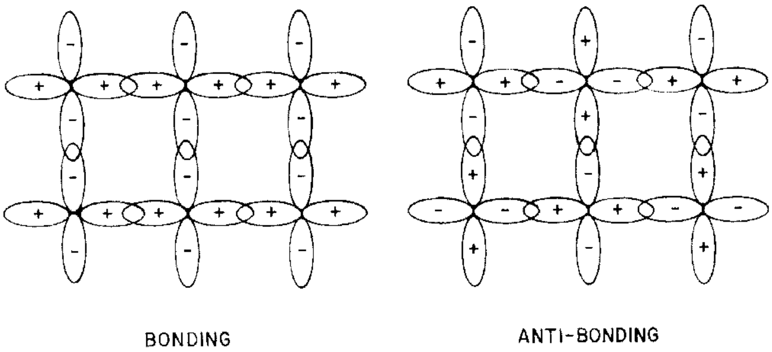

BONDING ANTI-BONDING

Figure 2.7 Bonding and anti-bonding orbitals

$$
\begin{aligned}
&= \sum_{i,i'} \sum_{mm'} < im \mid T + \mathbf{V}(\vec{r}) \mid i'm' > a^*_{im} a_{i'm'} \\
&= \sum_{i,i'} \sum_{mm'} < im \mid T + v_{i'} + \sum_{l \neq i'} v_l \mid i'm' > a^*_{im} a_{i'm'} \\
&= \sum_{i,i'} \sum_{mm'} E_0 \delta_{ii'} \delta_{mm'} a^*_{im} a_{i'm'} + \sum_{ii'} \sum_{mm'} \sum_{l \neq i'} < im \mid v_l \mid i'm' > a^*_{im} a_{i'm'} \qquad (2.51) \\
&= E_0 \sum_{i,m} |a_{im}|^2 + \sum_{i,m} \mid a_{im} \mid^2 < im \mid \sum_{l \neq i} v_l | im > + \sum_{imm'} \sum_{j \neq i} < im | v_j | jm' > a^*_{im} a_{jm}.
\end{aligned}
$$

Recalling the definitions of the crystal fields and the tunneling contribution, one finally gets:

$$E = E_0 + \sum_{i,m} \mid a_{im} |^2 \alpha_{i,m} + \sum_{i,m} \sum_{j \neq i,m'} a^*_{im} a_{jm'} \beta^{jm'}_{im}. \qquad (2.52)$$

At this point let us introduce the bonding and anti-bonding orbitals, as illustrated in figure (2.7). For bonding orbitals the coefficients β^{jm}_{im} are negative due to the potential $\mathbf{V}(\vec{r})$. On the contrary the anti-bonding states are positive due to the combined effect of the potential $\mathbf{V}(\vec{r})$ and the plus or minus signs of the angular lobes of the function.

2.4 The cohesion energy: Friedel's version

Let us start by defining the cohesion energy through the expression

$$E_c = nE_0 - 2 \int_{\epsilon_{bot}}^{\epsilon_f} \epsilon N(\epsilon) d\epsilon. \qquad (2.53)$$

Here E_0 is the atomic levels at infinite separation, n is the total number of electrons, $N(\epsilon)$ the density of states per spin direction (then the factor 2 in the definition) and ϵ_{bot} is the lowest energy of the band. We note that for infinite separation the density of states reduces to a delta function at energy E_0; the second term cancels then exactly the first one, that means there is no cohesion. The Fermi level is determined through

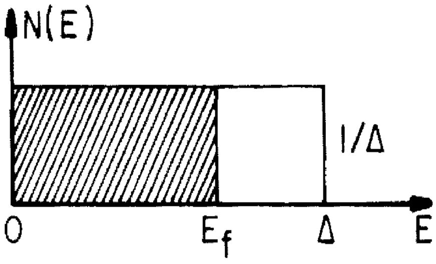


Figure 2.8 Constant density of states

the following equations:

$$n = 2\int_{\epsilon_{bot}}^{\epsilon_F} N(\epsilon)d\epsilon. \tag{2.54}$$

For a constant density of states, figure (2.8), of width Δ, one obtains for a band normalized to 1, that $N(\epsilon)$ is equal to $\frac{1}{\Delta}$ and the occupation number is given by:

$$n = \frac{2}{\Delta}\epsilon_F, \tag{2.55}$$

then $\epsilon_F = n\frac{\Delta}{2}$.

Using this result in the definition above one has:

$$E_c = nE_0 - 2\int_{\epsilon_{bot}}^{\epsilon_F} \epsilon\frac{1}{\Delta}d\epsilon = nE_0 - \frac{\epsilon_F^2}{\Delta}, \tag{2.56}$$

Neglecting crystal field effects we can take the center of the band at $E_0 = \Delta/2$:

$$\frac{E_c}{\Delta} = \frac{n}{2} - \frac{n^2}{4}. \tag{2.57}$$

We have then obtained the cohesion energy (in units of the band width) in terms of the occupation number.

Several limits can be thus obtained: for an empty band ($n = 0, E_c = 0$), for completely filed band, $n = 2$ again $E_c = 0$. Finally the maximum cohesion energy is obtained for $n = 1$, that means a half filled band. This results suggest to interpret the lowest half of band states to be of bonding nature and the second half of anti-bonding nature, this is illustrated in fig. 2.9.

2.5 The Slater-Koster problem

The Slater-Koster (SK) problem concerns the calculation of the resolvent for a system in presence of a localized perturbation. Applications of these results will be presented in following paragraphs, in particular Section 2.7.

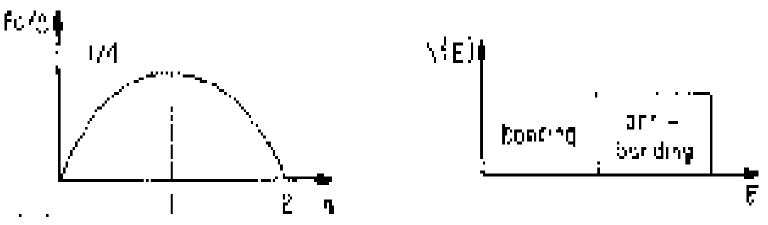


Figure 2.9 Cohesion energy as a function of the occupation number.

First of all let us derive a general equation for the resolvent in presence of a perturbation. The resolvent for a general Hamiltonian is given by:

$$G(z) = (z - H)^{-1}. \tag{2.58}$$

We start from $H = H_0 + V$, where V is a general perturbation and H_0 is the Hamiltonian for the pure metal. The idea is to obtain an identity separating the terms of the pure systems (resolvent of the pure system) and the perturbation. The simple proof is:

$$\begin{aligned} G &= (z-H)^{-1} = (z-H_0-V)^{-1} = (z-H_0)^{-1}(z-H_0)(z-H_0-V)^{-1} \\ &= (z-H_0)^{-1}(z-H_0-V+V)(z-H_0-V)^{-1} \\ &= (z-H_0)^{-1}\left[(z-H_0-V)+V\right](z-H_0-V)^{-1} \\ &= (z-H_0)^{-1} + (z-H_0)^{-1}V(z-H_0-V)^{-1}. \end{aligned} \tag{2.59}$$

Defining $g_0 = (z - H_0)^{-1}$, the above equation becomes:

$$G = g_0 + g_0 V G. \tag{2.60}$$

This is Dyson's equation in a operator form.

Let define now the matrix elements associated to sites i and j, in a TB representation:

$$G_{ij}(z) =< i \mid \frac{1}{z - H_0 - V} \mid j > \tag{2.61}$$

and

$$g_{ij}(z) =< i \mid \frac{1}{z - H_0} \mid j > . \tag{2.62}$$

The Lipmann-Schwinger version of this equation can be written then

$$G_{ij}(z) = g_{ij}(z) + < i \mid gVG \mid j > . \tag{2.63}$$

Introducing the complete and orthonormal set $\sum_l \mid l >< l \mid = 1$, one obtains:

$$\begin{aligned} G_{ij}(z) &= g_{ij}(z) + \sum_{l,m} < i \mid g \mid l >< l \mid V \mid m >< m \mid G \mid j > \\ &= g_{ij}(z) + \sum_{lm} g_{il}(z) V_{lm} G_{mj}(z), \end{aligned} \tag{2.64}$$

this is the general solution of the perturbation problem using that basis set.

The resolvent for the pure metal

$$g_{ij}(z) =< i \mid \frac{1}{z - H_0} \mid j >, \tag{2.65}$$

is calculated by using of the non-degenerated TB method:

$$H_0 \mid k >= \epsilon_k \mid k > \qquad \mid k >= \sum_l e^{i\vec{k}.\vec{R}_l} \mid l > . \tag{2.66}$$

Introducing the complete set in the definition of $g_{ij}(z)$, one has:

$$g_{ij}(z) = \sum_k < i| \frac{1}{z - H_0} |k >< k|j >= \sum_k \frac{< i|k >< k|j >}{z - \epsilon_k} \tag{2.67}$$

using

$$< i|k >= e^{i\vec{k}.\vec{R}_i} \quad \text{and} \quad < k|j >= e^{-i\vec{k}.\vec{R}_j}, \tag{2.68}$$

one gets:

$$g_{ij}(z) = \sum_k \frac{e^{ik(R_i - R_j)}}{z - \epsilon_k}. \tag{2.69}$$

As a particular case, let us calculate the local propagator:

$$g_{ii} = \sum_k \frac{1}{z - \epsilon_k}. \tag{2.70}$$

Using the imaginary theorem, remembering that $z = \epsilon + i\delta$, one gets for the density of states of the pure metals the following expression:

$$\rho(E) = -\frac{1}{\pi} Im \left(g_{ii}(E) \right) \tag{2.71}$$

In the case of localized potential at the origin, let us come back to the general equation (2.64) and take the particular case:

$$V_{lm} =< l \left| V \right| m >= \delta_{lm} \delta_{l0} V_0, \tag{2.72}$$

then

$$\begin{aligned} G_{ij}(z) &= g_{ij}(z) + \sum_{l,m} g_{il}(z) \delta_{lm} \delta_{l0} V_0 G_{mj}(z) \\ &= g_{ij}(z) + g_{i0}(z) V_0 G_{0j}(z). \end{aligned} \tag{2.73}$$

To solve this system of equations let us first take $i = 0$, then:

$$G_{0j}(z) = g_{0j}(z) + g_{00}(z)V_0G_{0j}(z), \tag{2.74}$$

or

$$[1 - g_{00}V_0]G_{0j}(z) = g_{0j}(z), \tag{2.75}$$

then:

$$G_{0j}(z) = \frac{1}{1 - V_0g_{00}(z)}g_{0j}(z) \tag{2.76}$$

and the final result is:

$$G_{ij}(z) = g_{ij}(z) + g_{i0}(z)\frac{V_0}{1 - V_0g_{00}(z)}g_{0j}(z). \tag{2.77}$$

Given a value for V_0 (its determination will be made in 2.7) and given the band structure ϵ_k, and the result of (2.69) the resolvent $G_{ij}(z)$ is completely determined. Using the imaginary theorem it is then possible to calculate the density of states as perturbed by the potential V_0. To make contact with the usual scattering theory let us introduce the T matrix as defined by the formula:

$$T(z) = \frac{V_0}{1 - V_0g_{00}(z)} \tag{2.78}$$

and consequently:

$$G_{ij}(z) = g_{ij}(z) + g_{i0}(z)T(z)g_{0j}(z). \tag{2.79}$$

To the case of the perturbation with two potentials, let us suppose that perturbation V can be written as a sum of two terms

$$V = V_1 + V_2. \tag{2.80}$$

An interesting way to solve the problem is the following: introduce the resolvent $\tilde{g}$ which includes only the effect of the perturbation V_1:

$$\tilde{g} = g + gV_1\tilde{g} \tag{2.81}$$

$\tilde{g}$ is then the complete solution for the scattering by the potential V_1. The complete resolvent should then satisfy:

$$G = \tilde{g} + \tilde{g}V_2G. \tag{2.82}$$

To prove this statement from the first equation one gets:

$$(1 - gV_1)\tilde{g} = g, \tag{2.83}$$

multiply to the left the equation (2.82) by $(1 - gV_1)$ to get:

$$(1 - gV_1)G = (1 - gV_1)\tilde{g} + (1 - gV_1)\tilde{g}V_2G, \tag{2.84}$$

using (2.83), one gets:

$$(1 - gV_1)G = g + gV_2G, \tag{2.85}$$

then:

$$G = g + g(V_1 + V_2)G. \tag{2.86}$$

Let us show that from this equation it follows the previous (2.81) involving only the potential V_1 and the equation (2.82):

$$G = g + gV_1G + gV_2G; \qquad (1 - gV_1)G = g + gV_2G. \tag{2.87}$$

Defining:

$$\tilde{g} = (1 - gV_1)^{-1}g, \tag{2.88}$$

or

$$(1 - gV_1)\tilde{g} = g, \tag{2.89}$$

alternatively

$$\tilde{g} - gV_1\tilde{g} = g, \tag{2.90}$$

from which we recover equation (2.81:

$$\tilde{g} = g + gV_1\tilde{g} \tag{2.91}$$

and from (2.87):

$$G = (1 - gV_1)^{-1}g + (1 - gV_1)^{-1}gV_2G, \tag{2.92}$$

or finally using (2.88), one comes back to equation (2.82)

$$G = \tilde{g} + \tilde{g}V_2G. \tag{2.93}$$

An application of this theorem is suppose that V_2 is a small perturbation and also that one can exactly solve the equation

$$\tilde{g} = g + gV_1\tilde{g}. \tag{2.94}$$

The complete equation for G can be solved formally within the Born approximation:

$$G = \tilde{g} + \tilde{g}V_2G \cong \tilde{g} + \tilde{g}V_2\tilde{g}. \tag{2.95}$$

Note that the Born series can be written as:

$$G = \tilde{g} + \tilde{g}V_2\tilde{g} + \tilde{g}V_2\tilde{g}V_2\tilde{g}\ldots, \tag{2.96}$$

the above approximation corresponds to stop the Born series at the first term, which is justified in certain cases. A very concrete and useful applications of this theorem is the scattering by a central potential and the next neighbor sites, as in moderately concentrated systems and in view of applications to hyperfine interactions.

2.5.1 More details about the SK problem and Friedel sum rule

In this paragraph we discuss the important point of the one electron impurity problem, namely the Friedel's rule. Let us start calculating the total change in electronic density of states as a function of energy. Beginning with the general solution of the SK problem for one localized potential at the origin, where the energy ω contains a small positive imaginary part, ($\omega = \epsilon + i\delta$):

$$G_{ij}(\omega) = g_{ij}(\omega) + g_{i0}(\omega)\frac{V_0}{1 - V_0 g_{00}(\omega)} g_{0i}(\omega), \tag{2.97}$$

in particular

$$\sum_i G_{ii}(\omega) = \sum_i g_{ii}(\omega) + \sum_i g_{i0}(\omega)\frac{V_0}{1 - V_0 g_{00}(\omega)} g_{0i}(\omega). \tag{2.98}$$

The variation in the density of states induced by the impurity as a function of the energy ω can be calculated from:

$$\sum_i \left[G_{ii}(\omega) - g_{ii}(\omega)\right] = \frac{V_0}{1 - V_0 g_{00}(\omega)} \sum_i g_{i0}(\omega) g_{0i}(\omega). \tag{2.99}$$

Using the general result for the resolvent $g_{ij}(\omega)$ one has

$$g_{i0}(\omega) = \sum_k \frac{e^{ik.R_i}}{\omega - \epsilon_k}, \qquad \text{end} \qquad g_{0i}(\omega) = \sum_{k'} \frac{e^{-ik'.R_i}}{\omega - \epsilon_{k'}}, \tag{2.100}$$

this follows that:

$$\begin{aligned} \sum_i g_{i0}(\omega) g_{0i}(\omega) &= \sum_{k,k'} \frac{1}{(\omega - \epsilon_k)(\omega - \epsilon_{k'})} \sum_i e^{i(k-k')R_i} \\ &= \sum_{k,k'} \frac{1}{(\omega - \epsilon_k)(\omega - \epsilon_{k'})} \delta_{k,k'} = \sum_k \frac{1}{(\omega - \epsilon_k)^2}. \end{aligned} \tag{2.101}$$

Remembering that:

$$g_{00}(\omega) = \sum_k \frac{1}{\omega - \epsilon_k}, \tag{2.102}$$

then

$$\frac{\partial}{\partial \omega} g_{00}(\omega) = -\sum_k \frac{1}{(\omega - \epsilon_k)^2}. \tag{2.103}$$

In this way:

$$\sum_i g_{i0}(\omega) g_{0i}(\omega) = -\frac{\partial}{\partial \omega} g_{00}(\omega), \tag{2.104}$$

then:

$$\sum_i \left(G_{ii}(\omega) - g_{ii}(\omega)\right) = \frac{-V_0 \frac{\partial}{\partial \omega} g_{00}(\omega)}{1 - V_0 g_{00}(\omega)} = \frac{\partial}{\partial \omega} \log\left(1 - V_0 g_{00}(\omega)\right) \tag{2.105}$$

It is easily proved from (2.33) that:

$$\lim_{\delta\to 0_+} g_{00}(\omega) = F_{00}(\epsilon) - i\pi\rho(\epsilon), \tag{2.106}$$

where

$$F_{00}(\epsilon) = \mathcal{P}\int d\epsilon'\rho(\epsilon')\frac{1}{\epsilon-\epsilon'}, \tag{2.107}$$

is the Cauchy principal part and $\rho(\omega)$ is the pure metal density of states. Let us define the complex number Z by:

$$Z = 1 - V_0 g_{00} = Z^R + iZ^I, \tag{2.108}$$

where

$$Z^R = 1 - V_0 F_{00}(\epsilon) \quad \text{and} \quad Z^I = \pi V_0 \rho(\epsilon). \tag{2.109}$$

Let us call $Z_1 = logZ$ and introduce $Z_1 = Z_1^R + iZ_1^I$. This implies that $Z = e^{Z_1} = e^{Z_1^R + iZ_1^I} = e^{Z_1^R}(cosZ_1^I + isinZ_1^I) = Z^R + iZ^I$, consequently one obtain the following results:

$$Z^R = e^{Z_1^R}cos(Z_1^I) \quad \text{and} \quad Z^I = e^{Z_1^R}sin(Z_1^I) \tag{2.110}$$

and

$$tg(Z_1^I) = \frac{Z^I}{Z^R} = \frac{\pi V_0\rho(\epsilon)}{1 - V_0F_{00}(\epsilon)}. \tag{2.111}$$

Finally:

$$Z_1^I = arctg\left\{\frac{\pi V_0\rho(\epsilon)}{1 - V_0F_{00}(\epsilon)}\right\}. \tag{2.112}$$

On the other hand one knows from the imaginary theorem:

$$\begin{aligned}\Delta\rho(\epsilon) &= -\frac{1}{\pi}I_m\sum_i\left(G_{ii}(\omega) - g_{ii}(\omega)\right) = -\frac{1}{\pi}I_m\frac{\partial}{\partial\omega}\log\left(1 - V_0 g_{00}(\omega)\right)\\ &= -\frac{1}{\pi}Im\frac{\partial}{\partial\omega}log(Z).\end{aligned} \tag{2.113}$$

In the $\lim_{\delta\to 0_0}$, one gets:

$$\Delta\rho(\epsilon) = -\frac{1}{\pi}Im\frac{\partial}{\partial\epsilon}log(Z) = -\frac{1}{\pi}Im\frac{\partial}{\partial\epsilon}Z_1, \tag{2.114}$$

then:

$$\Delta\rho(\epsilon) = -\frac{1}{\pi}\frac{\partial Z_1^I}{\partial\epsilon}. \tag{2.115}$$

In conclusion, the change in density of states is given by:

$$\Delta\rho(\epsilon) = -\frac{1}{\pi}\frac{\partial}{\partial\epsilon}\left(arctg\frac{\pi V_0\rho(\epsilon)}{1 - V_0F_{00}(\epsilon)}\right). \tag{2.116}$$

At this point we introduce the important concept of phase shift defined by:

$$\delta(\epsilon) = -\frac{1}{\pi} arctg \frac{\pi V_0 \rho(\epsilon)}{1 - V_0 F_{00}(\epsilon)}. \tag{2.117}$$

With a convenient choice of the definition range of the arc tangent we can write

$$\mid \delta(\epsilon) \mid = \frac{1}{\pi} arctg \frac{\pi V_0 \rho(\epsilon)}{1 - V_0 F_{00}(\epsilon)}. \tag{2.118}$$

From these phase shifts one finally gets the famous Friedel's theorem:

$$\Delta\rho(\epsilon) = \frac{\partial}{\partial\epsilon}\delta(\epsilon). \tag{2.119}$$

More explicitly indicating its dependence on the potential strength V_0:

$$\Delta\rho(\epsilon, V_0) = \frac{\partial}{\partial\epsilon}\delta(\epsilon, V_0) \tag{2.120}$$

This theorem states that, giving only the density of states $\rho(\epsilon)$, characterizing the pure metal in consideration, it is possible to describe the perturbation introduced by the impurities in the metal only by the knowledge of the phase shift (via its derivative). See figure (2.10) for illustration, for several values of the potential strength V_0.

In figure (2.10b), the phase shift is shown as a function of the energy E and for several strengths of the impurity potential. This curve is constructed using (2.118) from the density of states and its Hilbert transform shown in figure (2.10a). From these schematic results, using (2.119) we can describe qualitatively the effect on the electronic structure of increasingly strong repulsive potential.

From figure (2.10b) one sees that, for impurity potentials less strong than $V_0^{crit} = 1/F(\epsilon_t)$, the derivativ of the phase shift change sign as a function of the energy. This corresponds physically to the piling-up of states at the high energy side of the band, that means positive values of $\Delta\rho(\epsilon)$. The negative values, at lower energies correspond to the extracted states which a piled-up above.

However, if a bound state exists above the top of the band, a monotonous behaviour of the phase shift is observed. The slope is always negative, meaning that states are extracted from the band in order to build-up the bound state. This follows from the completeness of the set of states: perturbed extended and localized.

2.5.2 Existence of bound states in the SK problem

Let us start from the general solution of the problem of one localized potential at the origin. Again ω includes a small imaginary part. The resolvent is given by:

$$G_{ij}(\omega) = g_{ij}(\omega) + g_{i0}(\omega)\frac{V_0}{1 - V_0 g_{00}(\omega)} g_{0i}(\omega), \tag{2.121}$$

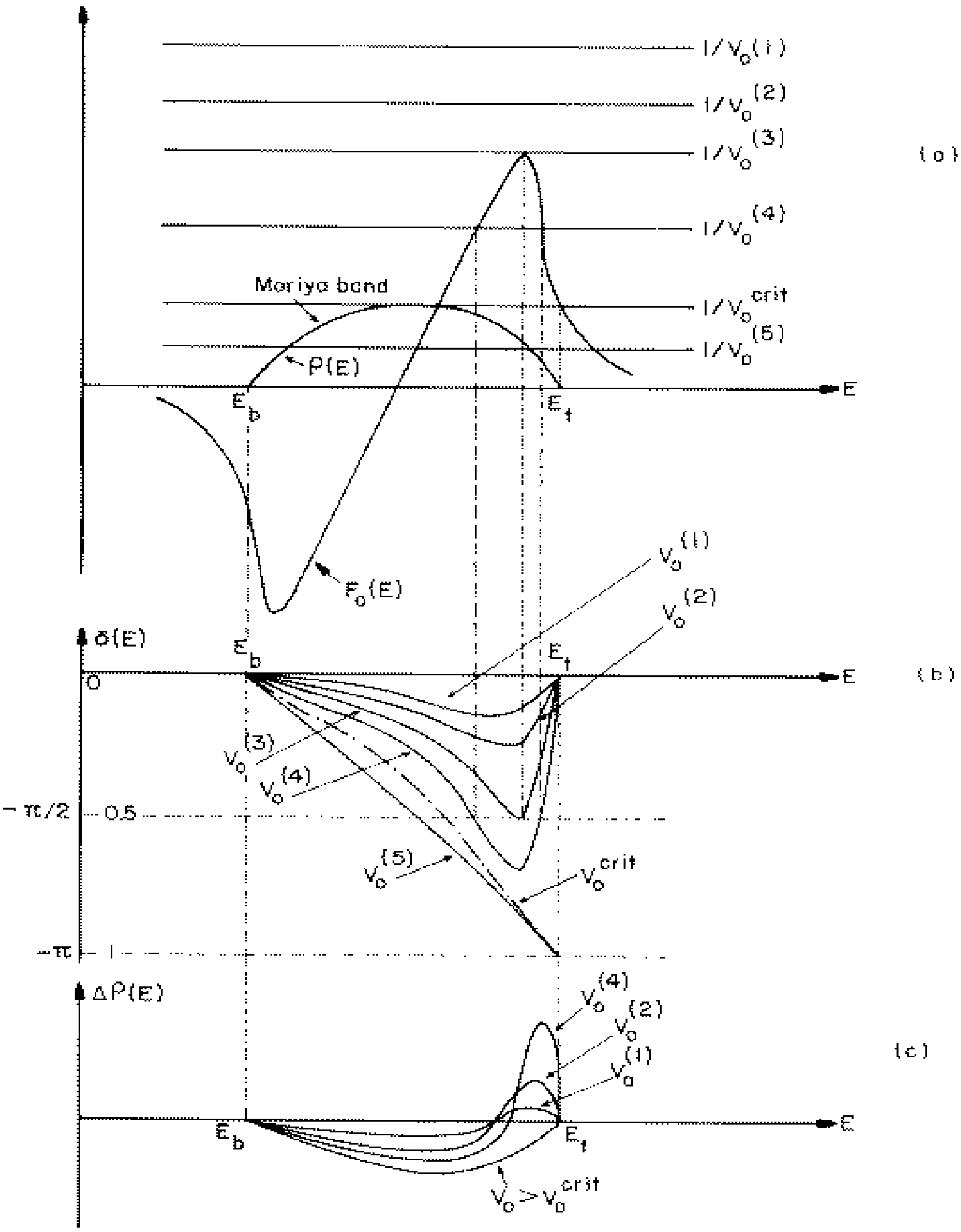


Figure 2.10 (a) Density of states ($\rho(\epsilon)$) and its Hilbert transform ($F_0(\epsilon)$). (b) Phase shift as a function of the energy. (c) Derivative of the phase shift respect to energy.

in the particular case of the same site

$$G_{ii}(\omega) = g_{ii}(\omega) + g_{i0}(\omega)\frac{V_0}{1 - V_0 g_{00}(\omega)} g_{0i}(\omega). \tag{2.122}$$

For ω values outside the unperturbed band, the imaginary part of $g_{ii}(\omega)$ vanishes according with (2.71). We thus discuss, for these energies, the following propagator:

$$G_{ii}(\omega) = g_{i0}(\omega)\frac{V_0}{1 - V_0 g_{00}(\omega)} g_{0i}(\omega). \tag{2.123}$$

Let us start from $g_{ii}(\omega)$ in the limit $\delta \leftarrow 0_+$:

$$g_{ii}(\omega) = \mathcal{P}\int d\epsilon' \frac{\rho(\epsilon')}{\epsilon - \epsilon'} - i\pi\rho(\epsilon) = F_{00}(\epsilon) - i\pi\rho(\epsilon). \tag{2.124}$$

For the considered energies since the density of states vanishes, one has: $g_{00}(\omega) = F_{00}(\epsilon)$. Consequently $1 - V_{00}F_{00}(\epsilon)$ may vanish for a given energy ϵ_{bs}, outside of the electron band.

Consider a metal with a band width 2Δ and suppose that ω is higher than the energy of the top of the band (or conversely lower than the botton). Let us study the properties of the following general propagator:

$$G_{ii}(\omega) = \frac{V_0 g_{i0}(\omega) g_{0i}(\omega)}{1 - V_0 F_{00}(\epsilon)} \tag{2.125}$$

Let us first consider the case of the resolvent at the origin:

$$G_{00}(\omega) = \frac{V_0 g_{00}^2(\omega)}{1 - V_0 F_{00}(\epsilon)} = \frac{V_0 F_{00}^2(\epsilon)}{1 - V_0 F_{00}(\epsilon)}. \tag{2.126}$$

For energies close to ϵ_{bs} it is possible to write

$$G_{00}(\epsilon) = \frac{V_0 F_{00}^2(\epsilon)}{1 - V_0 F_{00}(\epsilon)} = \frac{A}{\epsilon - \epsilon_{bs}}. \tag{2.127}$$

The value of A, the amplitude at the origin for the propagator, is given by:

$$A_{00} = \lim_{\epsilon \longrightarrow \epsilon_{bs}} \frac{(\epsilon - \epsilon_{bs}) V_0 F_{00}^2(\epsilon)}{1 - V_0 F_{00}(\epsilon)}. \tag{2.128}$$

Using L'Hospital rule one finally gets:

$$A_{00} = \frac{F_{00}^2}{\left| \frac{\partial F_{00}}{\partial \epsilon} \right|_{\epsilon_{bs}}}. \tag{2.129}$$

The amplitude of the bound state at the origin is then easily calculated in terms of the band quantities. The next step is to prove that the total amplitude of the bound state including all sites is one, that is the bound state is normalized.

Let us come back to equation (2.125) and sum over all sites i

$$\sum_i G_{ii} = \frac{V_0}{1 - V_0 g_{00}} \sum_i g_{i0} g_{0i} = \frac{-V_0 \partial g_{00}/\partial\omega}{1 - V_0 g_{00}(\omega)} = \frac{-V_0 \partial F_{00}(\epsilon)/\partial\epsilon}{1 - V_0 F_{00}(\epsilon)(\epsilon)}. \tag{2.130}$$

Again we study the bahaviour of $\sum_i G_{ii}$ near the bound state energy, and similarly to the case of the origin we write:

$$\sum_i A_{ii} = \lim_{\epsilon \to \epsilon_{bs}} -\frac{(\epsilon - \epsilon_{bs}) V_0 \frac{\partial F_{00}}{\partial \epsilon}}{1 - V_0 F_{00}}. \tag{2.131}$$

Using again L'Hospital, one gets:

$$\sum_i A_{ii} = 1, \tag{2.132}$$

thus the bound state is normalized, as we indeed expected.

For a general site i, one gets:

$$G_{ii} = \frac{V_0 g_{0i} g_{i0}}{1 - V_0 F_{00}}. \tag{2.133}$$

Using the general formula for g_{0i} one has:

$$g_{0i} = \sum_k \frac{e^{-ik.R_i}}{\omega - \epsilon_k} = \sum_k \frac{e^{ik.R_i}}{\omega - \epsilon_k} = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \frac{e^{-ik.R_i}}{\omega - \epsilon_k}, \tag{2.134}$$

also

$$g_{0i} = \frac{\Omega}{(2\pi)^3} \int d\epsilon' \int_{S(\epsilon')} \frac{dS_k}{\mid \nabla_k \epsilon_k \mid} \frac{e^{ik.R_i}}{\omega - \epsilon'} = \int d\epsilon' \frac{1}{\omega - \epsilon'} \frac{\Omega}{(2\pi)^3} \int_{S(\epsilon')} \frac{dS_k e^{ik.R_i}}{\mid \nabla_k \epsilon_k \mid}. \tag{2.135}$$

This suggests the definition of a "generalized density of states ":

$$\rho(\epsilon', R_i) = \frac{\Omega}{(2\pi)^3} \int_{S(\epsilon')} \frac{dS_k e^{ik.R_i}}{\mid \nabla_k \epsilon_k \mid}, \tag{2.136}$$

then

$$g_{i0} = \int \frac{d\epsilon' \rho(\epsilon', R_i)}{\omega - \epsilon'}.$$

Introducing the small imaginary part($\omega = \epsilon + i\delta$), one has:

$$\begin{aligned} g_{i0}(\omega) &= \mathcal{P} \int \frac{d\epsilon' \rho(\epsilon', R_i)}{\epsilon - \epsilon'} - i\pi\rho(\epsilon, R_i) \\ &= F(\epsilon, R_i) - i\pi\rho(\epsilon, R_i). \end{aligned} \tag{2.137}$$

For energies larger than the top of the band it is reasonable to take $\rho(\epsilon, R_i) \cong 0$. One gets for the G_{ii} amplitude (like in (2.127) to (2.129):

$$A_{ii} = \frac{V_0 F^2(\epsilon, R_i)}{-V_0 \frac{\partial F_{00}}{\partial \epsilon}} = \frac{F^2(\epsilon, R_i)}{\left| \frac{\partial F_{00}}{\partial \epsilon} \right|}. \tag{2.138}$$

Again the amplitude of the bound state at the general site i can be calculated provided one can perform the integration in (2.136).

2.6 The Friedel-Anderson-Moriya model

2.6.1 The classical version

In order to give the first approach to the magnetism of impurities in metals, let us start with the classical Friedel-Anderson-Moriya model. The advantage of this picture is that two kinds of states are present: the localized states in space and energy, the conduction states and mixing between them. This contrasts with the previously discussed SK model where only itinerant states were present and the magnetism is associated to spin dependent scattering at the impurity site.

The ingredients of this model are:

i) The free electron gas, usually s or sp states describing a simple metal like Al or Cu. This subsystem is described by the Hamiltonian:

$$H = \sum_{i,j,\sigma} T_{ij} c^{+}_{i\sigma} c_{j\sigma}, \tag{2.139}$$

where $c^{+}_{i\sigma}$ $(c_{j\sigma})$ are the creation (annihilation) operators for electron in sites i and j respectively and T_{ij} is the hopping between this sites, corresponding to an energy band ϵ_k. For such system the resolvent g_{ij} is given by (2.69, $g_{ij}(\omega) = \sum_k \left(e^{ik.(R_i - R_j)}/\omega - \epsilon_k \right)$. This resolvent is supposed to be known from the beginning.

ii) The impurity introduces a localized level that we call hereafter a d state, and this is described by the following Hamiltonian:

$$H_{imp} = \sum_{\sigma} \epsilon_d d^{+}_{0\sigma} d_{0\sigma} + U_{dd} n^{(d)}_{0\uparrow} n^{(d)}_{0\downarrow}. \tag{2.140}$$

In this Hamiltonian $d^{+}_{0\sigma}$ and $d_{0\sigma}$ are respectively the creates/annihilates operators of the one electron in the localized d states at the origin; the position in energy of the localized level is given by ϵ_d; U_{dd} corresponds to the Coulomb interaction between electrons at the same site. This localized Hamiltonian, involving a electron-electron interaction can be solved exactly only in the limit where the hybridization with conducting states is completely disregarded. The simplest approximation one can make is to use the Hartree-Fock approximation:

$$\begin{aligned} H_{imp} &\cong \sum_{\sigma} \epsilon_d d^{+}_{0\sigma} d_{0\sigma} + U_{dd} \left\langle n^{(d)}_{0_\uparrow} \right\rangle n^{(d)}_{0\downarrow} + U_{dd} \left\langle n^{(d)}_{0\downarrow} \right\rangle n^{(d)}_{0_\uparrow} \\ &= \sum_{\sigma} \left(\epsilon_d d^{+}_{0\sigma} d_{0\sigma} + U_{dd} < n^{(d)}_{0-\sigma} > n^{(d)}_{0\sigma} \right). \end{aligned} \tag{2.141}$$

Let us introduce the Hartree-Fock renormalized energy of the d level:

$$\epsilon_{d\sigma} = \epsilon_d + U_{dd} < n^{(d)}_{0-\sigma} >, \tag{2.142}$$

then approximately:

$$H_{imp} \cong \sum_{\sigma} \epsilon_{d\sigma} d^{+}_{0\sigma} d_{0\sigma}. \tag{2.143}$$

iii) Let us introduce finally the possibility of mixing the localized states with the conduction states; we thus take the hybridization term:

$$H_{hib} = \sum_{\sigma} (V_{cd} c^{+}_{0\sigma} d_{0\sigma} + V_{dc} d^{+}_{0\sigma} c_{0\sigma}). \tag{2.144}$$

Then the Anderson Hamiltonian in its one electron version can be written:

$$H = \sum_{i,j,\sigma} T_{ij} c^{+}_{i\sigma} c_{i\sigma} + \sum_{\sigma} \epsilon_{d\sigma} d^{+}_{0\sigma} d_{0\sigma} + \sum_{\sigma} (V_{cd} c^{+}_{0\sigma} d_{0\sigma} + V_{dc} d^{+}_{0\sigma} c_{0\sigma}). \tag{2.145}$$

The Hartree-Fock approximation reduced the complex Anderson Hamiltonian to a one electron problem. We can introduce alternatively a state vector representation for the itinerant and localized states instead of creation and annihilation operators. This is

$$\begin{aligned} H \;=\; & \sum_{i,j,\sigma} T_{ij} \mid c_{i\sigma} >< c_{j\sigma} \mid + \sum_{\sigma} \epsilon_{d\sigma} \mid d_{0\sigma} >< d_{0\sigma} \mid + \\ & \sum_{\sigma} (V_{cd} \mid c_{0\sigma} >< d_{0\sigma} \mid + V_{dc} \mid d_{0\sigma} >< c_{0\sigma} \mid). \end{aligned} \tag{2.146}$$

The general Dyson equation can be again invoked to calculate the complete problem; one has:

$$G = g + gVG. \tag{2.147}$$

Contrary to the SK problem now we have matrix elements between localized states d and the itinerant ones c. For the pure metal $g^{cd}_{ij} = g^{dc}_{ij} = 0$, since there is no hybridization between d and c states in the pure metal. Therefore:

$$G^{dd}_{00} =< d_0 \mid G \mid d_0 >= g^{dd}_{00} + < d_0 \mid gVG | d_0 >, \tag{2.148}$$

where

$$g^{dd}_{00} =< d_0 \mid \frac{1}{\omega - H_{\text{imp}}} \mid d_0 >= \frac{1}{\omega - \epsilon_{d\sigma}}. \tag{2.149}$$

The last term for G^{dd}_{00} can be transformed introducing the unit operator:

$$< d_0 \mid \mathrm{g}V\mathrm{G} \mid d_0 >=< d_0 \mid g \mid d_0 >< d_0 \mid V \mid c_0 >< c_0 \mid G \mid d_0 >, \tag{2.150}$$

since the mixing potential V has only matrix elements between d and c states. We get then:

$$G^{dd}_{00}(\omega) = g^{dd}_{00}(\omega) + g^{dd}_{00}(\omega) V_{dc} G^{cd}_{00}(\omega). \tag{2.151}$$

The hybridization has introduced a new matrix element for the resolvent, namely the last one, it is then necessary to obtain this new element in terms of the diagonal ones. To do that, again we introduce the unit operator to get:

$$G^{cd}_{00}(\omega) =< c_0 \mid g \mid d_0 > + < c_0 \mid g \mid c_0 >< c_0 \mid V \mid d_0 >< d_0 \mid G \mid d_0 >, \tag{2.152}$$

the first term of the right hand site is equal to zero in the absence of hybridization in the pure host, one then gets:

$$G^{cd}_{00}(\omega) = g^{cc}_{00}(\omega)V_{cd}G^{dd}_{00}(\omega). \tag{2.153}$$

Recall the resolvent for the pure metal:

$$g^{cc}_{ij}(\omega) = \sum_k \frac{e^{ik(R_i - R_j)}}{\omega - \epsilon_k}.$$

Combining these equations one has:

$$\begin{aligned} G^{dd}_{00}(\omega) &= g^{dd}_{00}(\omega) + g^{dd}_{00}(\omega) \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)G^{dd}_{00}(\omega) \\ &= \frac{g^{dd}_{00}(\omega)}{1 - g^{dd}_{00}(\omega) \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} = \frac{1}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)}. \end{aligned} \tag{2.154}$$

In terms of the band structure ϵ_k for the conduction states c one has:

$$g^{cc}_{00}(\omega) = \sum_k \frac{1}{\omega - \epsilon_k}.$$

In summary: the *dd* resolvent is given by:

$$G^{dd}_{00\sigma}(\omega) = \frac{1}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)}. \tag{2.155}$$

From this equation we can extract all the relevant information for the localized d state. Let us now proceed to determine the resolvent $G^{cc}_{ij}(\omega)$. Again we start from Dyson's equation and introduce the unit operator; one gets then:

$$\begin{aligned} G^{cc}_{ij}(\omega) &= < c_i \mid g \mid c_j > + < c_i \mid \mathrm{g}V\mathrm{G} \mid c_j > \\ &= < c_i \mid g \mid c_j > + < c_i \mid g \mid c_0 > V_{cd} < d_0 \mid G \mid c_j >, \end{aligned} \tag{2.156}$$

or

$$G^{cc}_{ij}(\omega) = g^{cc}_{ij}(\omega) + g^{cc}_{i0}(\omega)V_{cd}G^{ds}_{0j}(\omega). \tag{2.157}$$

Again a new matrix element is generated by *ds* hybridization namely $G^{ds}_{0j}(\omega)$. Introducing the unit operator one has:

$$G^{ds}_{0j}(\omega) =< d_0 \mid g \mid c_j > + < d_0 \mid g \mid d_0 >< c_0 \mid G \mid c_j >, \tag{2.158}$$

or

$$G^{ds}_{ij}(\omega) = g^{dd}_{00}(\omega)V_{dc}G^{cc}_{0j}(\omega). \tag{2.159}$$

Combining these equations one obtains:

$$G^{cc}_{ij}(\omega) = g^{cc}_{ij}(\omega) + g^{cc}_{i0}(\omega) \mid V_{cd} \mid^2 g^{dd}_{00}(\omega)G^{cc}_{0j}(\omega). \tag{2.160}$$

In a quite similar way to the SK problem we first take site i at the origin, obtaining:

$$G^{cc}_{0j}(\omega) = g^{cc}_{0j}(\omega) + g^{cc}_{00}(\omega) \mid V_{cd} \mid^2 g^{dd}_{00}(\omega) G^{cc}_{0j}(\omega), \tag{2.161}$$

or

$$G^{cc}_{0j}(\omega) = \frac{g^{cc}_{0j}(\omega)}{1 - g^{dd}_{00}(\omega) \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)}. \tag{2.162}$$

Then the complete solution for the conduction electron resolvent is:

$$G^{cc}_{ij\sigma}(\omega) = g^{cc}_{ij}(\omega) + g^{cc}_{i0}(\omega) \frac{\mid V_{cd} \mid^2}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} g^{cc}_{0j}(\omega). \tag{2.163}$$

This equation together with the result for $G^{dd}_{ij\sigma}$ are the complete and exact solution within Hartree-Fock approximation of the Friedel-Anderson-Moriya model.

2.6.2 More about Anderson model

In order to obtain a more systematic way to fix the parameters involved in the Anderson model, is is necessary to know in detail the occupation number of the local state and the changes in the conduction bands as induced by the hybridization. The following results can be easily obtained from the resolvent matrix elements:

$$G^{dd}_{00\sigma}(\omega) = \frac{1}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} \tag{2.164}$$

and

$$G^{cc}_{ij\sigma}(\omega) = g^{cc}_{ij}(\omega) + g^{cc}_{i0}(\omega) \frac{\mid V_{cd} \mid^2}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} g^{cc}_{0j}(\omega). \tag{2.165}$$

Firstly we will discuss a sum rule in the same way as in the SK problem. To do this we begin in the above equation with $i = j$:

$$\begin{aligned} \sum_i \left(G^{cc}_{ii\sigma}(\omega) - g^{cc}_{ii}(\omega)\right) &= \frac{\mid V_{cd} \mid^2}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} \sum_i g^{cc}_{i0}(\omega) g^{cc}_{0i}(\omega) \\ &= \frac{- \mid V_{cd} \mid^2 \frac{\partial g^{cc}_{00}}{\partial \omega}}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)} \\ &= \frac{1 - \mid V_{cd} \mid^2 \frac{\partial g^{cc}_{00}}{\partial \omega} - 1}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)}. \end{aligned} \tag{2.166}$$

In this way:

$$\begin{aligned} \sum_i \left(G^{cc}_{ii}(\omega) - g^{cc}_{\mathrm{ii}}(\omega)\right) &= \frac{\partial}{\partial \omega} \log\left(\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)\right) \\ &\quad - \frac{1}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)}. \end{aligned} \tag{2.167}$$

This result combining with (2.164) implies in the first sum rule:

$$G^{dd}_{00\sigma}(\omega) + \sum_i \left(G^{cc}_{\mathrm{ii}\sigma}(\omega) - g^{cc}_{\mathrm{ii}}(\omega)\right) = \frac{\partial}{\partial \omega} \log\left(\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g^{cc}_{00}(\omega)\right). \tag{2.168}$$

The first term describe the density of states associated to the d hump, the second term is the variation of the density of states in the conduction states as a consequence of the hybridization with the d level. Using the imaginary theorem, one gets:

$$\Delta\rho_\sigma(\epsilon) = \frac{\partial}{\partial\epsilon}\delta_\sigma(\epsilon), \tag{2.169}$$

where

$$\delta_\sigma(\epsilon) = \frac{1}{\pi} arctg\left(\frac{\pi \mid V_{cd} \mid^2 \rho^c(\epsilon)}{\epsilon - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 F_{00}(\epsilon)}\right), \tag{2.170}$$

in this case $\Delta\rho(\epsilon)$ is the total variation of the density of states. Remembering that $\epsilon_{d\sigma} = \epsilon_d + \mathbf{V}_{dd} n_{0-\sigma}^{(d)}$ it is possible to fix ϵ_d given the number of d electrons introduced by the impurity and via the self-consistent solution of the problem in the non magnetic or magnetic cases.

2.6.3 The Breit-Wigner approximation in the Anderson model

The discussion above is made for a general density of states and the calculations are necessarily of numerical nature. However a simpler calculation of analytical nature can be made for a constant density of states for the host. Let us first introduce the following hypothesis:

i) The conduction band has constant and wide density of states; this implies in $F_0(\epsilon)$ is approximately equal to zero.

ii) If $F_0(\epsilon) \simeq 0$ then is possible to disregard this function and its derivative. In this conditions ($g_{00}^{cc}(\omega) \simeq -i\pi\rho(\epsilon)$), one gets:

$$G_{00\sigma}^{dd}(\omega) = \frac{1}{\omega - \epsilon_{d\sigma} + i\pi \mid V_{cd} \mid^2 \rho(\epsilon)} \tag{2.171}$$

In this equation $\rho(\epsilon)$ is assumed to be a constant function; we can then introduce the width of the resonance (in the sense of Breit-Wigner)

$$\Delta = \pi |V_{cd}|^2 \rho, \tag{2.172}$$

then

$$G_{00\sigma}^{dd}(\omega) = \frac{1}{\omega - \epsilon_{d\sigma} + i\Delta} = G_{00\sigma}^{dd}(\omega) = \frac{\omega - \epsilon_{d\sigma} - i\Delta}{(\omega - \epsilon_{d\sigma})^2 + \Delta^2}. \tag{2.173}$$

Using the imaginary theorem:

$$\rho_{d\sigma}(\epsilon) = -\frac{1}{\pi} I_m G_{00\sigma}^{dd}(\epsilon) = \frac{1}{\pi}\frac{\Delta}{(\epsilon - \epsilon_{d\sigma})^2 + \Delta^2}. \tag{2.174}$$

Clearly one can verify that

$$\int_{-\infty}^{+\infty} d\epsilon \rho_{d\sigma}(\epsilon) = 1 \tag{2.175}$$

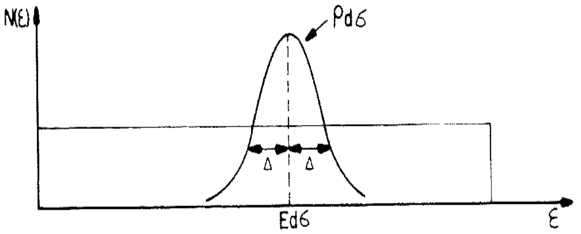


Figure 2.11 The d "hump" density of states.

This simply means that the d hump contains exactly one electron, fig. 2.11. It remains now to compute the change in the conduction band as induced by the hybridization. The result of this calculation is known as the Anderson-Clogston theorem.

Let us start from the expression:

$$\sum_i G_{ii}^{cc}(\omega) - g_{ii}^{cc}(\omega) = \frac{- \mid V_{cd} \mid^2 \frac{\partial g_{00}^{cc}}{\partial \omega}}{\omega - \epsilon_{d\sigma} - \mid V_{cd} \mid^2 g_{00}^{cc}}. \tag{2.176}$$

Within the above hypothesis, that is constant density of states the $\frac{\partial \rho}{\partial \omega} = 0$. Also for large conduction bands again we suppose $F_0(\epsilon) \simeq 0$ and consequently $\frac{\partial F}{\partial \omega} \simeq 0$. In consequence the numerator vanishes and

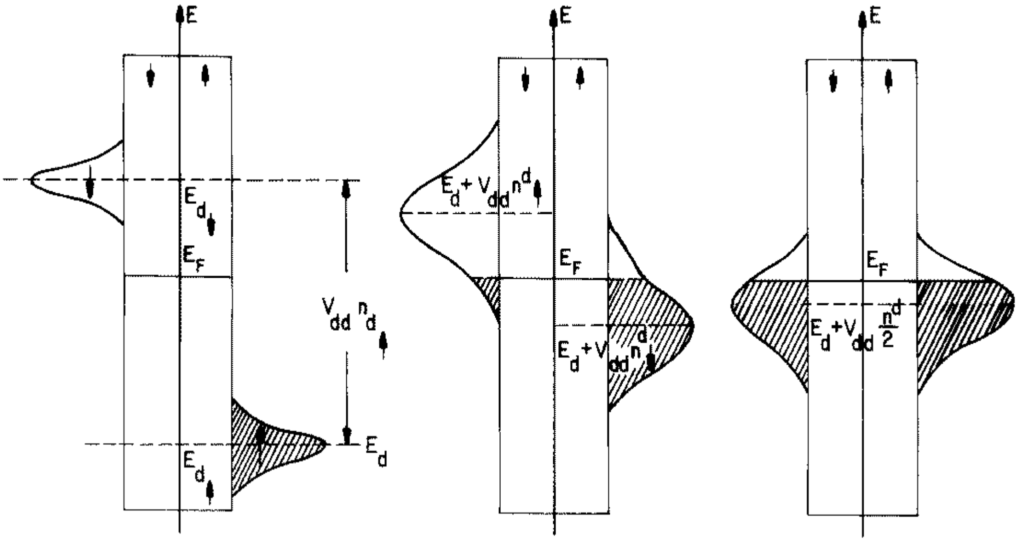
$$\sum_i (G_{ii}^{cc}(\omega) - g_{ii}^{cc}(\omega)) = 0. \tag{2.177}$$

Then the theorem: for a constant density of states the effect of the hybridization in modifying its density of states is zero. It should be emphasized that this theorem in not valid for more complex bands like the Moriya band, the Kanamori model bands or any linear interpolation of first principles bands.

Let us illustrate, for the constant host density of states, some solutions of the Anderson model. We show three possibilities in fig. 2.12: the maximum value for the magnetic moment, intermediate moment and non magnetic solution.

2.7 Example of a simple description of transition impurities in transition hosts

Since we want to study transition impurities in transition hosts, the first step is to adopt a convenient description of the magnetic properties of the hosts. In order to simplify the formulation let us assume that the matrix is not magnetic like *Zr*, *Nb*, *Mo*, *Re*, *Rh* and *Pd*. The difficulty of including electron-electron interaction in the host is that at the impurity site it exists already a perturbation V_0 that breaks translational invariance. We restrict ourselves to that systems where the following



Maximum magnetic moment

Smaller magnetic moment

Non magnetic solution

Figure 2.12 Examples of solutions of the Anderson model

Hamiltonian (the Wolff-Clogston Hamiltonian) applies:

$$H = \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + V_0 \sum_{\sigma} d_{0\sigma}^{+} d_{0\sigma} + \Delta U n_{0_\uparrow} n_{0\downarrow}, \tag{2.178}$$

where ΔU is the local change in Coulomb interaction at the impurity site.

In this Hamiltonian only one band is considered, in other terms: since the host is a transition metal, one has five identical sub bands. Using the Hartree-Fock approximation, as it was done in the case of Anderson model, one gets:

$$H_{HF} \cong \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + V_0 \sum_{\sigma} d_{0\sigma}^{+} d_{0\sigma} + \Delta U \sum_{\sigma} < n_{0-\sigma} > n_{0\sigma}, \tag{2.179}$$

this is the well known Wolff-Clogston model.

The solution of this problem can be trivially obtained using the results of the SK model. Introducing the localized potential at the origin given by:

$$V_0^{\sigma} = V_0 + \Delta U < n_{0-\sigma} >, \tag{2.180}$$

the problem reduces to:

$$H_{HF} \cong \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + \sum_{\sigma} V_0^{\sigma} d_{0\sigma}^{+} d_{0\sigma}. \tag{2.181}$$

The solution is very simple and one gets:

$$G_{ij}^{\sigma}(\omega) = g_{ij}(\omega) + g_{i0}(\omega)\frac{V_0^{\sigma}}{1 - V_0^{\sigma} g_{00}(\omega)} g_{0j}(\omega). \tag{2.182}$$

As before, we calculate now $\sum_i (G_{ii}^{\sigma} - g_{ii})$ and we obtain the Friedel rule generalized to magnetic impurities:

$$\Delta\rho_{\sigma}(\epsilon) = \frac{\partial}{\partial\epsilon}\delta_{\sigma}(\epsilon). \tag{2.183}$$

The generalized spin dependent phase shift is given by:

$$\delta_{\sigma}(\epsilon) = -\frac{1}{\pi}\ arctg\ \frac{\pi V_0^{\sigma} \rho_0(\epsilon)}{1 - V_0^{\sigma} F_0(\epsilon)}, \tag{2.184}$$

or more explicitly:

$$\delta_{\sigma}(\epsilon) = -\frac{1}{\pi} arctg \frac{\pi(V_0 + \Delta U < n_{0-\sigma} >)\rho_0(\epsilon)}{1 - (V_0 + \Delta U < n_{0-\sigma} >)F_0(\epsilon)}. \tag{2.185}$$

If we integrate Friedel rule up to the Fermi level, one obtains:

$$\begin{aligned} \Delta Z &= \delta_{\uparrow}(\epsilon_F) + \delta_{\downarrow}(\epsilon_F) \\ &= -\frac{5}{\pi}\ arctg \frac{\pi(V_0 + \Delta U n_{0\downarrow})\rho_0(\epsilon_F)}{1 - (V_0 + \Delta U n_{0\downarrow})F_0(\epsilon_F)} + \\ &\quad -\frac{5}{\pi} arctg \frac{\pi(V_0 + \Delta U n_{0\uparrow})\rho_0(\epsilon_F)}{1 - (V_0 + \Delta U n_{0_{\uparrow}})F_0(\epsilon_F)}. \end{aligned} \tag{2.186}$$

The factor 5 takes into account the degeneracy of the d band (five identical sub bands). This equation in not enough to completely determine V_0 as a function of ΔZ, since the occupation numbers $n_{0\sigma}$ are explicitly included in the screening sum rule. It is important then to obtain an expression relating the occupation numbers with the potential V_0^{σ}.

Starting from the general solution of the Wolff-Clogston model one calculates:

$$\begin{aligned} G_{00}^{\sigma}(\omega) &= g_{00}(\omega) + g_{00}(\omega)\frac{V_0^{\sigma}}{1 - V_0^{\sigma} g_{00}(\omega)} g_{00}(\omega) \\ &= g_{00}(\omega)\left(1 + \frac{V_0^{\sigma} g_{00}(\omega)}{1 - V_0^{\sigma} g_{00}(\omega)}\right), \end{aligned} \tag{2.187}$$

then

$$G_{00}^{\sigma}(\omega) = \frac{g_{00}(\omega)}{1 - V_0^{\sigma} g_{00}(\omega)}, \tag{2.188}$$

using

$$g_{00}(\epsilon + i\delta) = F_0(\epsilon) - i\pi\rho_0(\epsilon), \tag{2.189}$$

one gets

$$\begin{aligned} G_{00}^{\sigma}(\epsilon + i\delta) &= \frac{F_0(\epsilon) - i\pi\rho_0(\epsilon)}{1 - V_0^{\sigma}F_0(\epsilon) + i\pi V_0^{\sigma}\rho_0(\epsilon)} \\ &= \frac{(1 - V_0^{\sigma}F_0)F_0 - \pi^2 V_0^{\sigma}\rho_0^2 - i\pi\rho_0}{(1 - V_0^{\sigma}F_0)^2 + (\pi V_0^{\sigma}\rho_0)^2}. \end{aligned} \tag{2.190}$$

Consequently (in the limit $\delta \to 0_+$):

$$-\frac{1}{\pi} I_m G_{00}(\epsilon + i\delta) = \frac{\rho_0(\epsilon)}{(\,1 - V_0^{\sigma}F_0(\epsilon)\,)^2 + (\,\pi V_0^{\sigma}\rho_0(\epsilon)\,)^2}. \tag{2.191}$$

The total number of electrons with σ spin at the origin is given by:

$$n_{0\sigma} = 5\int_{\epsilon_b}^{\epsilon_F} \frac{\rho_0(\epsilon)}{(\,1 - V_0^{\sigma}F_0(\epsilon)\,)^2 + (\,\pi V_0^{\sigma}\rho_0(\epsilon)\,)^2} d\epsilon. \tag{2.192}$$

Clearly if one takes $V_0^{\sigma} = 0$ this implies that $n_{0\sigma} = \int_{\epsilon_b}^{\epsilon_F} d\epsilon\rho_0(\epsilon)$. This is the number of electrons of the pure host; given the density of state $\rho_0(\epsilon)$ one can extract the value of the Fermi level. The paramagnetic solution (absence of magnetic moment at the impurity sites) that is $n_{0\uparrow} = n_{0\downarrow} = \bar{n}_0$ is trivially obtained. In fact defining

$$\bar{V}_0 = V_0 + \Delta U \bar{n}_0, \tag{2.193}$$

where $\bar{n}_0$ is not known from the beginning, from Friedel sum rule one gets:

$$\Delta Z = -\frac{10}{\pi}\ arctg\ \frac{\pi\bar{V}_0\rho_0(\epsilon_F)}{1 - \bar{V}_0F_0(\epsilon_F)}. \tag{2.194}$$

Given the charge difference ΔZ and for a given density of states one gets a relation between V_0 and $\bar{n}_0$. Then from the equation for the occupation number at the origin one extracts another relation between V_0 and $\bar{n}_0$ and this solves completely the paramagnetic case.

The self consistent solution for the general case can be also obtained numerically. From equation (2.186) one can obtain, by imposing charge neutrality, $V_{0\uparrow}$ as a function of $V_{0\downarrow}$. We can find a function f such that:

$$V_{0\uparrow} = f(V_{0\downarrow}). \tag{2.195}$$

From the definition of the Hartree-Fock potentials, one has:

$$V_{0\uparrow} = V_0 + \Delta U n_{0\downarrow} \quad \text{and} \quad V_{0\downarrow} = V_0 + \Delta U n_{0\uparrow}. \tag{2.196}$$

Subtracting these equations one obtains:

$$V_{0\uparrow} - V_{0\downarrow} = -\Delta U(n_{0\uparrow} - n_{0\downarrow}). \tag{2.197}$$

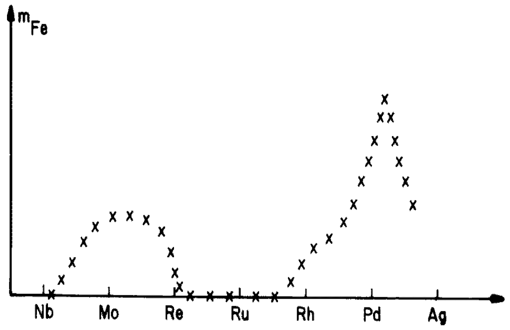


Figure 2.13 Fe magnetic moment in $4d$ hosts

From equation (2.192) one can write in general $n_{0\sigma} = g(V_{0\sigma})$, always with the same function g. Then

$$V_{0\uparrow} - V_{0\downarrow} = -\Delta U \left(g(V_{0\uparrow}) - g(V_{0\downarrow}) \right), \tag{2.198}$$

but using Friedel screening condition(2.195), one can obtain :

$$f(V_{0\downarrow}) - V_{0\downarrow} = -\Delta U \left(g\left(f(V_{0\downarrow})\right) - g(V_{0\downarrow}) \right). \tag{2.199}$$

This equation depends only of the down spin potential and the value that satisfies it is called $V^c_{0\downarrow}$; if this number is known one calculates $V^c_{0\uparrow} = f(V^c_{0\downarrow})$. This last equation defines the self consistent potential for both spins. From that we can calculate the occupation numbers:

$$n_{0\sigma} = g(V^c_{0\sigma}), \tag{2.200}$$

and from the difference of occupation numbers one derives the magnetization. In figure 2.13 we illustrate the situation of Fe impurities in $4d$ metal hosts.

2.8 A two band system (s and d)

In this paragraph we extend the previous one considering the existence, in a transition host, of two sub bands mainly the s and d bands, adopting the simplest model.

The system is described by the following Hamiltonian:

$$H_0 = \sum_{i,j,\sigma} T^{(s)}_{ij} c^+_{i\sigma} c_{j\sigma} + \sum_{i,j,\sigma} T^{(d)}_{ij} d^+_{i\sigma} d_{j\sigma}, \tag{2.201}$$

the impurity induces three different effects: firstly the scattering of d electrons,

$$H^{(d)}_{imp} = V^{dd}_0 \sum_{\sigma} d^+_{0\sigma} d_{0\sigma}; \tag{2.202}$$

secondly, the hybridization introduced by impurity,

$$H_{imp}^{hib} = \sum_{\sigma} \left[V_{sd} c_{0\sigma}^{+} d_{0\sigma} + V_{ds} d_{0\sigma}^{+} c_{0\sigma} \right], \tag{2.203}$$

where V_{sd} is a parameter describing the effective impurity induced hybridization; finally, the Coulomb interaction is treated within the Hartree-Fock approximation,

$$H_{imp}^{Coul} = \Delta U \sum_{\sigma} \left\langle n_{0-\sigma}^{(d)} \right\rangle n_{0\sigma}^{(d)}, \tag{2.204}$$

then:

$$H = H_0 + H_{imp}^{(d)} + H_{imp}^{hib} + H_{imp}^{Coul}, \tag{2.205}$$

explicitly:

$$\begin{aligned} H \;=\; & \sum_{i,j,\sigma} T_{ij}^{(s)} c_{i\sigma}^{+} c_{j\sigma} + \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + \sum_{\sigma} V_{0\sigma}^{dd} d_{0\sigma}^{+} d_{0\sigma} + \\ & + \sum_{\sigma} \left[V_{sd} c_{0\sigma}^{+} d_{0\sigma} + V_{ds} d_{0\sigma}^{+} c_{0\sigma} \right], \end{aligned} \tag{2.206}$$

where the complete potential acting on d-states is:

$$V_{0\sigma}^{dd} = V_{0}^{dd} + \Delta U \left\langle n_{0-\sigma}^{(d)} \right\rangle. \tag{2.207}$$

The solution of the problem follows the habitual way, beginning with the calculation of the $d-d$ propagator and then the $s-s$ propagator.

2.8.1 The $d-d$ propagator

To calculate this propagator we begin with:

$$G_{ij\sigma}^{dd}(\omega) = g_{ij}^{dd}(\omega) + g_{i0}^{dd}(\omega) V_{0\sigma}^{dd} G_{0j\sigma}^{dd}(\omega) + g_{i0}^{dd}(\omega) V_{ds} G_{0j\sigma}^{sd}(\omega). \tag{2.208}$$

For the elements of the $G_{ij\sigma}^{sd}$ matrix we have the equation:

$$G_{ij\sigma}^{sd}(\omega) = g_{i0}^{ss}(\omega) V_{sd} G_{0j\sigma}^{dd}(\omega), \tag{2.209}$$

this equation does not have elements like $g_{ij}^{sd}(\omega)$ since hybridization in the host is neglected. Substituting $G_{0j\sigma}^{sd}(\omega)$ in (2.208) one gets:

$$G_{ij\sigma}^{dd}(\omega) = g_{ij}^{dd}(\omega) + g_{i0}^{dd}(\omega) \left[V_{0\sigma}^{dd} + V_{ds} g_{00}^{ss}(\omega) V_{sd} \right] G_{0j\sigma}^{dd}(\omega). \tag{2.210}$$

This propagator cam be represented in figure 2.14.

Introducing the potential:

$$U_{0\sigma}^{dd} = V_{0\sigma}^{dd} + \left| V_{ds} \right|^{2} g_{00}^{ss}(\omega), \tag{2.211}$$

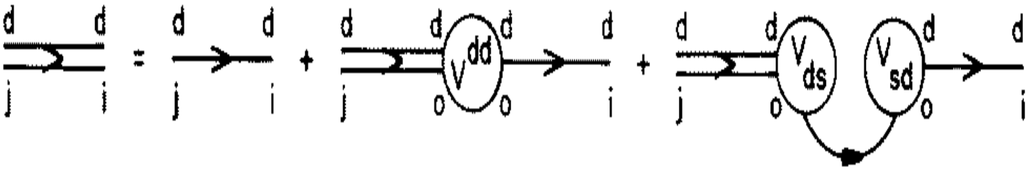


Figure 2.14 Graphic representation of the propagator $G^{dd}_{ij\sigma}$.

one gets:

$$G^{dd}_{ij\sigma}(\omega) = g^{dd}_{ij}(\omega) + g^{dd}_{i0}(\omega)U^{dd}_{0\sigma}G^{dd}_{0j\sigma}(\omega). \tag{2.212}$$

This equation has the simple solution in the form of a pure SK solution:

$$G^{dd}_{ij\sigma}(\omega) = g^{dd}_{ij}(\omega) + g^{dd}_{i0}(\omega)\frac{U^{dd}_{0\sigma}}{1 - U^{dd}_{0\sigma}g^{dd}_{00}(\omega)}g^{dd}_{0j\sigma}(\omega) \tag{2.213}$$

or, in the other way:

$$G^{dd}_{ij\sigma}(\omega) = g^{dd}_{ij}(\omega) + g^{dd}_{i0}(\omega)T^{dd}_{\sigma}(\omega)g^{dd}_{0j}(\omega) \tag{2.214}$$

where

$$T^{dd}_{\sigma}(\omega) = \frac{U^{dd}_{0\sigma}}{1 - U^{dd}_{0\sigma}g^{dd}_{00}(\omega)}. \tag{2.215}$$

This formula determines completely the $d - d$ propagator. The effective potential $V^{dd}_{0\sigma}$ includes the base direct $d - d$ scattering, corrected by impurity induced $s - d$ hybridization.

2.8.2 The $s - s$ propagator

To calculate the $s - s$ propagator we begin with:

$$G^{ss}_{ij\sigma}(\omega) = g^{ss}_{ij}(\omega) + g^{ss}_{i0}(\omega)V_{sd}G^{ds}_{0j\sigma}(\omega) \tag{2.216}$$

and

$$\begin{aligned} G^{ds}_{ij\sigma}(\omega) &= g^{dd}_{i0}(\omega)V^{dd}_{0\sigma}G^{ds}_{0j\sigma} + g^{dd}_{i0}(\omega)V^{ds}(\omega)G^{ss}_{0j\sigma}(\omega) \\ G^{ds}_{0j\sigma}(\omega) &= \frac{1}{1 - V^{dd}_{0\sigma}g^{dd}_{00}(\omega)}g^{dd}_{00}(\omega)V^{ds}G^{ss}_{0j}(\omega). \end{aligned} \tag{2.217}$$

Combining equations (2.216) and (2.217), we get:

$$G^{ss}_{ij\sigma}(\omega) = g^{ss}_{ij}(\omega) + g^{ss}_{i0}(\omega)\frac{\mid V_{sd}\mid^2 g^{dd}_{00}(\omega)}{1 - V^{dd}_{0\sigma}g^{dd}_{00}(\omega)}G^{ss}_{0j\sigma}(\omega), \tag{2.218}$$

or taking $i = 0$:

$$G^{ss}_{0j\sigma}(\omega) = g^{ss}_{0j}(\omega) + \frac{\mid V_{sd} \mid^2 g^{dd}_{00} g^{ss}_{00}}{1 - V^{dd}_{0\sigma} g^{dd}_{00}} G^{ss}_{0j\sigma}(\omega). \tag{2.219}$$

Solving for $G^{ss}_{0j\sigma}(\omega)$ we obtain:

$$G^{ss}_{0j\sigma}(\omega) = \frac{1 - V^{dd}_{0\sigma} g^{dd}_{00}}{1 - V^{dd}_{0\sigma} g^{dd}_{00} - \mid V_{sd} \mid^2 g^{dd}_{00} g^{ss}_{00}} g^{ss}_{0j}, \tag{2.220}$$

therefore

$$G^{ss}_{ij\sigma}(\omega) = g^{ss}_{ij}(\omega) + g^{ss}_{i0}(\omega) \frac{|V_{sd}|^2 g^{dd}_{00}(\omega)}{1 - \left[V^{dd}_{0\sigma} - |V_{sd}|^2 g^{ss}_{00}(\omega)\right] g^{dd}_{00}(\omega)} g^{ss}_{0j}(\omega), \tag{2.221}$$

remembering the definition:

$$U^{dd}_{0\sigma} = V^{dd}_{0\sigma} - \mid V_{sd} \mid^2 g^{ss}_{00}(\omega) \tag{2.222}$$

and defining the $T^{ss}_{\sigma}(\omega)$ matrix:

$$T^{ss}_{\sigma}(\omega) = \frac{\mid V_{sd} \mid^2 g^{dd}_{00}(\omega)}{1 - U^{dd}_{0\sigma} g^{dd}_{00}(\omega)}, \tag{2.223}$$

one gets:

$$G^{ss}_{ij\sigma}(\omega) = g^{ss}_{ij}(\omega) + g^{ss}_{i0}(\omega) T^{ss}_{\sigma}(\omega) g^{ss}_{0j}(\omega). \tag{2.224}$$

To be used later in the calculation of the local susceptibility, let us calculate the off diagonal matrix elements: $G^{ds}_{ij\sigma}(\omega)$ and $G^{sd}_{ij\sigma}(\omega)$.

Calculation of $G^{ds}_{ij\sigma}(\omega)$

$$\begin{aligned} G^{ds}_{ij\sigma}(\omega) &= g^{dd}_{i0}(\omega) V^{dd}_{0\sigma} G^{ds}_{0j\sigma}(\omega) + g^{dd}_{i0}(\omega) V^{ds} G^{ss}_{0j\sigma}(\omega) \\ &= g^{dd}_{i0}(\omega) V^{dd}_{0\sigma} \frac{1}{1 - V^{dd}_{0\sigma} g^{dd}_{00}} g^{dd}_{00}(\omega) V^{ds} G^{ss}_{0j\sigma}(\omega) + g^{dd}_{i0}(\omega) V^{ds} G^{ss}_{0j\sigma}(\omega), \end{aligned} \tag{2.225}$$

where we have used equation (2.217), then:

$$G^{ds}_{ij\sigma}(\omega) = g^{dd}_{i0} \left[1 + \frac{V^{dd}_{0\sigma} g^{dd}_{00}}{1 - V^{dd}_{0\sigma} g^{dd}_{00}}\right] V^{ds} G^{ss}_{0j\sigma} = g^{dd}_{i0} \frac{1}{1 - V^{dd}_{0\sigma} g^{dd}_{00}} V^{ds} G^{ss}_{0j\sigma}, \tag{2.226}$$

finally

$$G^{ds}_{ij\sigma}(\omega) = g^{dd}_{i0}(\omega) \frac{1}{1 - V^{dd}_{0\sigma} g^{dd}_{00}(\omega)} V^{ds} G^{ss}_{0j\sigma}(\omega). \tag{2.227}$$

Substituting the result (2.220) for $G^{ss}_{0j\sigma}(\omega)$, one has:

$$G^{ds}_{ij\sigma}(\omega) = g^{dd}_{i0}(\omega) \frac{1}{1 - V^{dd}_{0\sigma} g^{dd}_{00}(\omega)} V^{ds} \frac{1 - V^{dd}_{0\sigma} g^{dd}_{00}(\omega)}{1 - V^{dd}_{0\sigma} g^{dd}_{00} - \mid V_{sd} \mid^2 g^{dd}_{00} g^{ss}_{00}} g^{ss}_{0j}(\omega) \tag{2.228}$$

Defining the off diagonal T^{ds} matrix:

$$T^{ds}(\omega) = \frac{V_{ds}}{1 - V^{dd}_{0\sigma} g^{dd}_{00} - \mid V_{sd} \mid^2 g^{dd}_{00} g^{ss}_{00}} = \frac{V_{ds}}{1 - U^{dd}_{0\sigma} g^{dd}_{00}(\omega)}, \tag{2.229}$$

therefore:

$$G^{ds}_{ij\sigma}(\omega) = g^{dd}_{i0}(\omega) T^{ds}(\omega) g^{ss}_{0j}(\omega). \tag{2.230}$$

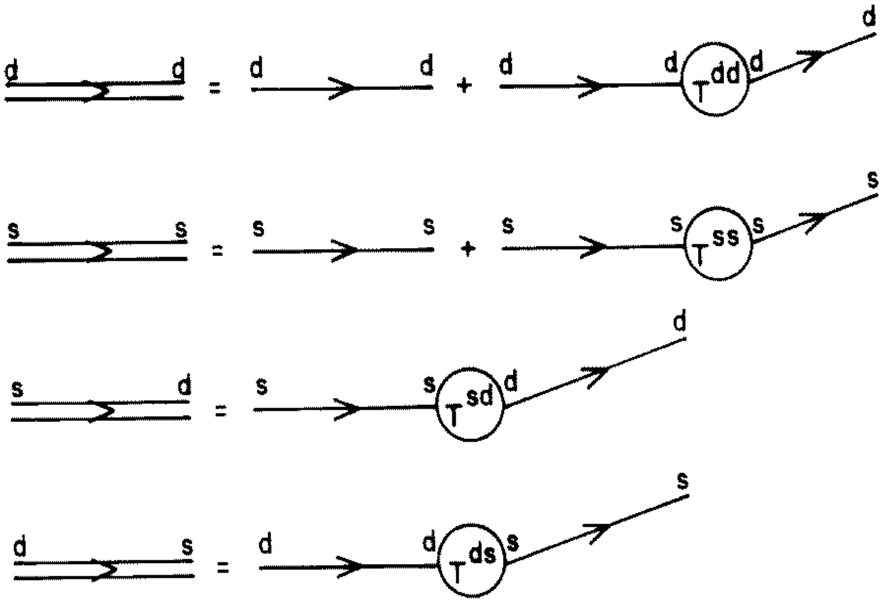


Figure 2.15 Graphic representation of several the propagators

Calculation of $G_{ij\sigma}^{sd}(\omega)$

$$G_{ij\sigma}^{sd}(\omega) = g_{i0}^{ss}(\omega) V_{sd} G_{0j\sigma}^{dd}(\omega) \tag{2.231}$$

From the (2.212), one gets:

$$G_{0j\sigma}^{dd}(\omega) = \frac{1}{1 - U_{0\sigma}^{dd} g_{00}^{dd}(\omega)} g_{0j}^{dd}(\omega) \tag{2.232}$$

Defining:

$$T^{sd}(\omega) = \frac{V_{sd}}{1 - U_{0\sigma}^{dd} g_{00}^{dd}(\omega)} \tag{2.233}$$

finally, one gets:

$$G_{ij\sigma}^{sd}(\omega) = g_{i0}^{ss}(\omega) T^{sd}(\omega) g_{0j}^{dd}(\omega). \tag{2.234}$$

The main advantage of (2.230) and (2.234) is that the incoming and outcoming propagators are the base ones in the corresponding $s-d$ channels, the hybridization effects acting only at the impurity site.

The equations (2.215), (2.224), (2.230) and (2.234) have their graphical representations in the figure 2.15:

2.9 The coherent potential approximation

The coherent potential approximation (CPA) is used as a good approximation to solve the problem of the substitutional alloys. Let us begin with the simplest case of disordered binary alloys where the atoms A and B are distributed randomly in the lattice sites. To describe the system is only necessary to compute averaged physical quantities over the configurations of the alloy.

This averaging process is difficult to perform. It was then suggested to introduce the concept of effective medium σ. To understand the idea behind this, let us begin with the Hamiltonian of the system, written in the TB formalism:

$$H = \sum_i \epsilon_i \mid i >< i \mid + \sum_{i,j} \mid i > t_{ij} < j \mid, \tag{2.235}$$

where $\epsilon_i = \epsilon_A$ or ϵ_B and the t_{ij} is the hopping between the sites i or j. We have used the atomic states $|i>$ as the TB basis to write the Hamiltonian. In the approximation called by diagonal disorder, the hoppings t_{ij} are independent of the occupations of the sites by atoms A or B, the disorder is present only in the diagonal terms of the Hamiltonian. On the other hand, if the hopping term is different from one site to the other, the disorder is called off diagonal.

2.9.1 Diagonal disorder

The effective medium, σ, that is energy dependent $\sigma(\omega)$, with $\omega = \epsilon + i\delta$, replaces the A and B atoms by an effective atom characterized by the effective energy $\sigma(\omega)$, the hopping t_{ij} being independent of the occupation of the site by atoms A or B, that is $t_{ij}^{AA} = t_{ij}^{AB} = t_{ij}^{BA} = t_{ij}^{BB}$. The effective Hamiltonian is then given by:

$$H_{ef} = \sum_i \sigma(\omega) \mid i >< i \mid + \sum_{ij} \mid i > t_{ij} < i \mid . \tag{2.236}$$

The construction of the effective medium is schematically represented by:

$$\left\langle \begin{bmatrix} A & B & B & B \\ B & A & B & A \\ A & B & B & A \end{bmatrix} \right\rangle \equiv \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix},$$

where $\otimes$ are the effective atoms; at this point the translation symmetry is recovered. In conclusion, the effective hamiltoniam H_{ef} preserves all the symmetries of the pure material and the coherent potential approximation is the adopted procedure to determine the effective medium $\sigma(\omega)$.

Let us substitute a given atom placed at origin of the effective medium by an A atom (with probability $1 - x$) or by a B atom (with probability x), where x is the B concentration. The definition of concentration for a lattice of N atoms is

$x = \frac{N_B}{N}$ and $1 - x = \frac{N_A}{N} = \frac{N - N_B}{N}$. Since the alloy is assumed to be completely disordered, the occupation probabilities are given by the concentrations. This procedure is represented by:

$$\left\langle \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & A,B & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix} \right\rangle = (1-x) \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & A & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix} + x \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & B & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix},$$

the left hand side is necessarily equal to:

$$\left\langle \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & A,B & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix} \right\rangle = \begin{bmatrix} \otimes & \otimes & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \\ \otimes & \otimes & \otimes & \otimes \end{bmatrix}.$$

Now let us put the above scheme in mathematical terms. The problem is equivalent to one impurity, A or B embedded in a metal characterized by the effective medium σ. If the resolvents are defined in an adequate way, this problem may be seen to be again a Slater-Koster problem.

The potential of the impurity atom, A or B, dissolved in a effective medium is given by:

$$V_{imp} = \epsilon_i - \sigma, \quad \text{with} \quad \epsilon_i = \epsilon_A \quad \text{or} \quad \epsilon_B \tag{2.237}$$

The resolvent G to the SK problem is then defined by:

$$G = g + gV_{imp}G, \tag{2.238}$$

where g is the resolvent of the effective medium. The potential V_{imp} is localized at the origin and one gets:

$$\begin{aligned} G_{ij}^{Q} &= g_{ij} + g_{i0}\frac{V_{imp}^{Q}}{1 - V_{imp}^{Q}g_{00}}g_{0j} \\ &= g_{ij} + g_{i0}\frac{\epsilon_Q - \sigma}{1 - (\epsilon_Q - \sigma)g_0}g_{0j}, \end{aligned} \tag{2.239}$$

where Q is A or B. The configuration average of the resolvent is necessarily equal to the effective medium resolvent $< G_{ij}^{Q} >= g_{ij}$, then:

$$g_{ij} = g_{ij} + g_{i0}\left\langle \frac{\epsilon_Q - \sigma}{1 - (\epsilon_Q - \sigma)g_{00}} \right\rangle g_{0j}, \tag{2.240}$$

from this equation one has:

$$\left\langle \frac{\epsilon_Q - \sigma}{1 - (\epsilon_Q - \sigma)g_{00}} \right\rangle = 0 \tag{2.241}$$

or in a more explicit way:

$$(1-x)\frac{\epsilon_A-\sigma}{1-(\epsilon_A-\sigma)g_{00}}+x\frac{\epsilon_B-\sigma}{1-(\epsilon_B-\sigma)g_{00}}=0. \tag{2.242}$$

Considering that $g_{00}=g_{00}(\sigma)=F(\omega-\sigma)$, where

$$F(\omega)=\int d\epsilon\frac{\rho(\epsilon)}{\omega-\epsilon}, \tag{2.243}$$

the equation (2.242) fixes the value of $\sigma(\omega)$.

Some classical results like the virtual crystal approximation (VCA) are recovered from equation (2.242). In fact for energies ϵ_A end ϵ_B close together the denominators of (2.242) are almost equal and one obtains:

$$\sigma=(1-x)\epsilon_A+x\epsilon_B. \tag{2.244}$$

2.9.2 Off diagonal disorder

In this case we include both disorder in the energy, which is diagonal, and in the hopping, which is off diagonal. The system is again described by the following Hamiltonian:

$$H=\sum_i|i>\epsilon_i<i|+\sum_{i,j}|i>t_{ij}<j|. \tag{2.245}$$

We include the following hypothesis: a) $\epsilon_i=\epsilon_A$ or ϵ_B; b) Shiba's approximation for the site dependence of the hopping, given by $t_{ij}=\xi_i t\xi_j$. In the last expression t is a reference hopping and $\xi_i=\xi_A$ or ξ_B account for the site dependence of the hopping. In this way:

$$H=\sum_i|i>\epsilon_i<i|+\sum_{i,j}|i>\xi_i t\xi_j<j|, \tag{2.246}$$

or alternativelly

$$\omega-H=\sum_i|i>(\omega-\epsilon_i)<i|-\sum_{i,j}|i>\xi_i t\xi_j<j|. \tag{2.247}$$

To define effective energy levels, let us introduce the useful quantity:

$$[\xi]=\sum_{i'}|i'>\xi_{i'}<i'|.$$

Using this quantity, it is possible to demonstrate the possibility of introducing "effective" diagonal energy levels, having the form:

$$\omega-H=[\xi]\left[\sum_i|i>\frac{\omega-\epsilon_i}{\xi_i^2}<i|-H_0\right][\xi], \tag{2.248}$$

where $H_0 = \sum_{ij} |i > t < j|$. In fact start from (2.248):

$$\begin{aligned}
\omega - H &= \sum_{i',i''} |i' > \xi_{i'} < i'| \left[\sum_i |i > \frac{\omega - \epsilon_i}{\xi_i^2} < i| - H_0 \right] |i'' > \xi_{i''} < i''| \\
&= \sum_{i'i''i} |i' > \xi_{i'} < i'|i > \frac{\omega - \epsilon_i}{\xi_i^2} < i|i'' > \xi_{i''} < i''| - \\
&\quad \sum_{i'i''} |i' > \xi_{i'} < i'|H_0|i'' > \xi_{i''} < i''| \\
&= \sum_i |i > (\omega - \epsilon_i) < i| - \sum_{ij} |i > \xi_i t \xi_j < j|. \qquad (2.249)
\end{aligned}$$

We thus recovered the starting Hamiltonian including both disorders. Following Shiba's approach, let us introduce the locators $\mathcal{L}_i = (\omega - \epsilon_i)/\xi_i^2$ in (2.248), getting:

$$\omega - H = [\xi] \left[\sum_i |i > \mathcal{L}_i < i| - H_0 \right] [\xi]. \qquad (2.250)$$

In this way, the resolvent function:

$$G(\omega) = [\omega - H]^{-1} = [\xi]^{-1} G_S(\omega) [\xi]^{-1}, \qquad (2.251)$$

where

$$G_S(\omega) = \left[\sum_i |i > \mathcal{L}_\rangle < i| - H_0 \right]^{-1}. \qquad (2.252)$$

If the origin is occupied by an atom Q (= A or B):

$$\rho_0^Q(\epsilon) = -\frac{1}{\pi} I_m \left[\xi_Q^{-2} (G_S^Q)_{00}(E) \right], \qquad (2.253)$$

where the resolvent is rewritten:

$$G_S = \left[\sum_{i \neq 0} |i > \mathcal{L}_i < i| + |0 > \mathcal{L}_Q < 0| - H_0 \right]^{-1}. \qquad (2.254)$$

The averaged medium enabling the calculation of $< (G_S^Q)_{00}(E) >$, is defined by:

$$< G_S^Q >= \left[\sum_{i \neq 0} |i >< \mathcal{L} >< i| + |0 > \mathcal{L}_Q < 0| - H_0 \right]^{-1}. \qquad (2.255)$$

The local densities of states are given by:

$$< \rho_0^Q(E) >= -\frac{1}{\pi} Im \left[\xi_Q^{-2} < (G_S^Q)_{00} > \right]. \qquad (2.256)$$

The unknown $< \mathcal{L} >$ is defined by the condition:

$$(1 - x) \left\langle G_S^A \right\rangle + x \left\langle G_S^B \right\rangle = \langle G_S \rangle, \qquad (2.257)$$

where the averaged resolvent is:

$$< G_S >= \left[\sum_i |i >< \mathcal{L} >< i| - H_0 \right]^{-1} . \tag{2.258}$$

In the site representation:

$$(1-x)(G_S^A)_{ij} + x(G_S^B)_{ij} = \langle (G_S)_{ij} \rangle . \tag{2.259}$$

The calculation of $< G_S^Q >$ follows the steps:

$$\begin{aligned} \left\langle G_S^Q \right\rangle &= \left[\sum_i |i >< \mathcal{L} >< i| + \mid 0 > (\mathcal{L}_Q - < \mathcal{L} >< 0 \mid -H_0 \right]^{-1} \\ &= \left[\sum_i |i >< \mathcal{L} >< i| - H_0 + \mid 0 > (\mathcal{L}_Q - < \mathcal{L} >) < 0 \mid \right]^{-1} . \end{aligned} \tag{2.260}$$

Using the inverse of (2.258), one has:

$$\left\langle G_S^Q \right\rangle = \left[< G_S >^{-1} + \mid 0 > (\mathcal{L}_Q - \mathcal{L}) < 0 \mid \right]^{-1} , \tag{2.261}$$

or multiplying to the left by the inverse of the right hand side:

$$\left[< G_S >^{-1} + \mid 0 > (\mathcal{L}_Q - \mathcal{L}) < 0 \mid \right] \left\langle G_S^Q \right\rangle = 1. \tag{2.262}$$

Multiplying on the left by $\langle G_S \rangle$ we get:

$$[1 + < G_S >\mid 0 > (\mathcal{L}_Q - \mathcal{L}) < 0 \mid] \left\langle G_S^Q \right\rangle = \langle G_S \rangle . \tag{2.263}$$

After rearranging the terms:

$$\left\langle G_S^Q \right\rangle = \langle G_S \rangle + \langle G_S \rangle \mid 0 > (\mathcal{L}_Q - \mathcal{L}) < 0 \mid \left\langle G_S^Q \right\rangle . \tag{2.264}$$

In the site representation the above equation may be written in the form:

$$\left\langle (G_S^Q)_{ij} \right\rangle = \langle (G_S)_{ij} \rangle + \langle (G_S)_{i0} \rangle (\mathcal{L} - \mathcal{L}_Q) \left\langle (G_S^Q)_{0j} \right\rangle , \tag{2.265}$$

solving this equation of the SK form:

$$\left\langle (G_S^Q)_{ij} \right\rangle = \langle (G_S)_{ij} \rangle + \left\langle (G_S^Q)_{i0} \right\rangle \frac{\mathcal{L} - \mathcal{L}_Q}{1 - (\mathcal{L} - \mathcal{L}_Q) \langle (G_S)_{00} \rangle} \langle (G_S)_{0j} \rangle \tag{2.266}$$

Performing now the average, the left hand side becomes equal to the first term. Since $< (G_S)_{i0} >$ and $< (G_S)_{0j} >$ depend only on the effective locator, one gets for the self consistent equation:

$$(1-x) \frac{\mathcal{L} - \mathcal{L}_A}{1 - (\mathcal{L} - \mathcal{L}_A) F(\mathcal{L})} + x \frac{\mathcal{L} - \mathcal{L}_B}{1 - (\mathcal{L} - \mathcal{L}_B) F(\mathcal{L})} = 0, \tag{2.267}$$

where

$$F(\mathcal{L}) = \langle G_{00} \rangle (\mathcal{L}), \tag{2.268}$$

and also

$$< (G_S^Q)_{00} >= \frac{F(\mathcal{L})}{1 - (\mathcal{L} - \mathcal{L}_Q)F(\mathcal{L})}. \tag{2.269}$$

Then for the local density of states one obtains:

$$\left\langle \rho^Q(E) \right\rangle = \frac{1}{\pi} Im \left[\epsilon_Q^{-2} \frac{F(\mathcal{L})}{1 - (\mathcal{L} - \mathcal{L}_Q)F(\mathcal{L})} \right] \tag{2.270}$$

and for the averaged density of states,

$$\langle \rho(E) \rangle = (1 - x) \left\langle \rho^{(A)}(E) \right\rangle + x \left\langle \rho^{(B)}(E) \right\rangle. \tag{2.271}$$

This formalism shows that the general case, including both disorders, shows a great similarity to the diagonal disorder case.

Chapter 3

ELEMENTARY DESCRIPTION OF THE MAGNETIC PROPERTIES

The magnetic materials may be classified in three large groups: the first considers the systems with localized spins, for example: the non conductor MnO and rare earths metals like Gd, Tb, Eu, and others; the second contemplates the pure metallic systems like Fe, Co and Ni, and the last one is devoted to the ferromagnetic intermetallics like $ZrZn_2$, $HfFe_2$, $ZrFe_2$, the paramagnetic intermetallics $LuCo_2$, YCo_2, the disordered alloys $Fe_{1-x}Co_x$, $Fe_{1-x}Ni_x$, $Pd_{1-x}Fe_x$, the compounds Pd_3Fe, $FeNi$, the mixed magnetic systems like magnetic Laves phases involving rare earths and transition metals like $GdCo_2$, $GdFe_2$, $HoFe_2$.

3.1 Magnetic susceptibility

The magnetic susceptibility χ is defined as the magnetic response to an applied external magnetic fields H. In the absence of H the magnetization m is zero for a large class of paramagnetic materials. The concept of linear response, in a more simple way, is $m = \chi H$. The generalization to a locally applied magnetic field, using a TB spirit, is given by:

$$m(R_\lambda) = \sum_{\lambda'} \chi(R_\lambda, R_{\lambda'}) H(R_{\lambda'}), \tag{3.1}$$

where $H(R_{\lambda'})$ is the magnetic fields at the site $R_{\lambda'}$. If the system is translation invariant, we have:

$$\chi(R_\lambda, R_{\lambda'}) = \chi(R_\lambda - R_{\lambda'}). \tag{3.2}$$

Examples of the such systems are: the pure metals like Pd and Pt, the intermetallics $LuCo_2$, YCo_2. The coordinate R_λ is the position of the unitary cell and if this cell has more than one atom, the position is described by $R_\lambda + \sigma$, where σ is the position of the different atoms in the cell.

The wave vector dependence of the $H(R_\lambda)$ magnetic fields is determined by the Fourier transform and it is defined by:

$$H(q)=\sum_{\lambda}e^{iqR_{\lambda}}H(R_{\lambda})\qquad\text{and}\qquad H(R_{\lambda})=\sum_{q}e^{-iqR_{\lambda}}H(q).\tag{3.3}$$

To illustrate the definition we calculate three cases:
i. the uniform field $H(R_{\lambda})=H_0$

$$H(q)=H_0\sum_{\lambda}e^{iqR_{\lambda}}=H_0\delta_{q,0},\tag{3.4}$$

where we have used $\sum_{\lambda}e^{iqR_{\lambda}}=\delta_{q,0}$;
ii. field at origin: $H(R_{\lambda})=H_0\delta_{\lambda 0}$ or $H(q)=H_0$;
iii. magnetic field with wave vector q_0:

$$H(R_{\lambda})=H_0e^{-iq_0R_{\lambda}}+c.c..\tag{3.5}$$

The magnetization with a q dependence can be expressed by:

$$\begin{aligned}m(R_{\lambda}) &= \sum_{\lambda'}\chi(R_{\lambda},R_{\lambda'})\sum_{q'}e^{-iq'R_{\lambda'}}H(q')\\ &= \sum_{\lambda' q'}X(R_{\lambda},R_{\lambda'})e^{-iq'R_{\lambda'}}H(q')\end{aligned}\tag{3.6}$$

and

$$\begin{aligned}m(q) &= \sum_{\lambda}e^{iqR_{\lambda}}m(R_{\lambda})\\ &= \sum_{\lambda,\lambda',q'}\chi(R_{\lambda},R_{\lambda'})e^{iqR_{\lambda}}e^{-iq'R_{\lambda'}}H(q').\end{aligned}\tag{3.7}$$

The susceptibility is defined by:

$$\chi(q,q') = \sum_{\lambda',\lambda}\chi(R_{\lambda},R_{\lambda'})e^{iqR_{\lambda}}e^{-iq'R_{\lambda'}}\tag{3.8}$$

$$m(q) = \sum_{q'}\chi(q,q')H(q').\tag{3.9}$$

If the system is translation invariant we may write the susceptibility in the form:

$$\begin{aligned}\chi(q,q') &= \sum_{\lambda',\lambda}\chi(R_{\lambda}-R_{\lambda'})e^{iqR_{\lambda}}e^{-iq'R_{\lambda'}}\\ &= \sum_{\lambda',\lambda}\chi(R_{\lambda}-R_{\lambda'})e^{i(q-q')R_{\lambda}}e^{-iq'(R_{\lambda}-R_{\lambda'})}\\ &= \sum_{\lambda}e^{i(q-q')R_{\lambda}}\sum_{\Delta R}e^{iq'\Delta R}\chi(\Delta R).\end{aligned}\tag{3.10}$$

The last factor gives $\chi(q')$ and the first one introduces $\delta_{qq'}$; then one has:

$$\chi(q,q')=\chi(q)\delta_{qq'}.\tag{3.11}$$

For these systems, an applied field $H(q_0)$ induces:

$$m(q) = \chi(q, q_0)H(q_0) = \delta_{qq_0}\chi(q_0)H(q_0) \tag{3.12}$$

Thus the resulting magnetization contains only the q_0 component, that is the magnetization has the same spatial variation as the field:

$$\begin{aligned} m(R_\lambda) &= \sum_q e^{-iqR_\lambda} m(q) = \sum_q e^{-iqR_\lambda}\chi(q_0)H(q_0)\delta_{qq_0} \\ &= e^{-iq_0R_\lambda}\chi(q_0)H(q_0). \end{aligned} \tag{3.13}$$

The existence of impurities destroy the translational invariance, that is:

$$m(q) = \chi(q, q_0)H(q_0), \qquad \text{with} \qquad q \neq q_0, \tag{3.14}$$

which means that different modulations do appear. The magnetization at the origin induced by a field applied also at the origin is given by:

$$m(R_\lambda) = \sum_q e^{-iqR_\lambda} m(q); \qquad m(0) = \sum_q m(q) = \sum_{qq'} \chi(q, q')H(q'). \tag{3.15}$$

in this case $H(q') = H_0$, then:

$$m(0) = H_0 \sum_{qq'} \chi(q, q') \tag{3.16}$$

or for systems with translation invariance: $m(0) = H_0 \sum_q \chi(q)$.

3.1.1 The Pauli susceptibility

For fermions, the occupation number for particles with dispersion relation ϵ_k, spin σ and applied field H is given by:

$$n_\sigma = \sum_k f^0 \left[\frac{\epsilon_k - \mu - \sigma\mu_0 H}{kT}\right]. \tag{3.17}$$

In terms of the density of states, one has:

$$n_\sigma = \int_{\epsilon_b}^{\infty} \frac{1}{2}\rho(\epsilon) f^0 \left[\frac{\epsilon - \mu - \sigma\mu_0 H}{kT}\right] d\epsilon, \tag{3.18}$$

where $\rho(\epsilon)$ is the density of states for both spins and thus the factor 1/2. The spin dependent energy ϵ, is given by:

$$\epsilon_{k\sigma} = \epsilon_k - \sigma\mu_0 H, \qquad \text{with} \qquad \sigma =\uparrow or \downarrow. \tag{3.19}$$

The magnetic field splitting of the up and down spin bands is illustrated in figure 3.1.

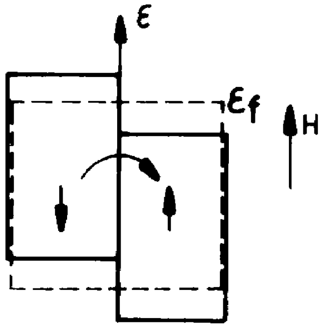


Figure 3.1 Schematic splitting of the up and down spin bands

The Fermi-Dirac distribution function f^0 is defined by:

$$f^0(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT}+1} = f^0\left[\frac{\epsilon-\mu}{kT}\right] = f^0(x), \tag{3.20}$$

μ being the chemical potential. The first order expansion of the f^0 in powers of the magnetic field (remember that $\mu_0 H \ll kT$):

$$f^0\left[\frac{\epsilon-\mu}{kT} - \sigma\frac{\mu_0 H}{kT}\right] = f^0\left[x - \sigma\frac{\mu_0 H}{kT}\right] = f^0(x) - \frac{\sigma\mu_0 H}{kT}\frac{\partial f^0}{\partial x}, \tag{3.21}$$

and

$$\frac{\partial f^0}{\partial \epsilon} = \frac{\partial f^0}{\partial x}\frac{\partial x}{\partial \epsilon} = \frac{1}{kT}\frac{\partial f^0}{\partial x}, \tag{3.22}$$

then:

$$f^0\left[\frac{\epsilon-\mu}{kT} - \sigma\frac{\mu_0 H}{kT}\right] = f^0\left[\frac{\epsilon-\mu}{kT}\right] - \sigma\mu_0 H\frac{\partial f^0}{\partial \epsilon}. \tag{3.23}$$

The occupation number can be written as:

$$n_\sigma = \frac{1}{2}\int_{\epsilon_b}^{\infty} \rho(\epsilon) f^0\left[\frac{\epsilon-\mu}{kT}\right] d\epsilon - \frac{1}{2}\sigma\mu_0 H \int_{\epsilon_b}^{\infty} \rho(\epsilon)\frac{\partial f^0}{\partial \epsilon} d\epsilon. \tag{3.24}$$

The chemical potential ($\mu = \epsilon_F$) is determined via the total number of electrons n,

$$n = n_\uparrow + n_\downarrow = \int_{\epsilon_b}^{\mu} \rho(\epsilon) f^0\left[\frac{\epsilon-\mu}{kT}\right] d\epsilon. \tag{3.25}$$

Given n, this equation defines the chemical potential μ. The magnetic moment is given from (3.24) by:

$$m = \mu_0(n_\uparrow - n_\downarrow) = -\mu_0^2 H \int_{\epsilon_b}^{\infty} \rho(\epsilon)\frac{\partial f^0}{\partial \epsilon} d\epsilon. \tag{3.26}$$

In figure 3.2 we illustrate the Fermi distribution function and its energy derivative for zero and finite temperatures.

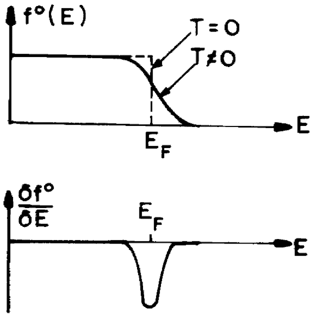


Figure 3.2 Fermi distribution and its energy derivative.

From the definition of the susceptibility we have:

$$m = \chi H, \tag{3.27}$$

then:

$$\chi(T) = -\mu_0^2 \int_{\epsilon_b}^{\infty} \rho(\epsilon) \frac{\partial f^0}{\partial \epsilon} d\epsilon. \tag{3.28}$$

It should be remembered that the derivative of the Fermi function is negative, thus $\chi(T) > 0$ at low temperatures the derivative of the Fermi function reduces to a δ-function centered at $\mu = \epsilon_F$; thus:

$$\chi = \mu_0^2 \rho(\epsilon_F). \tag{3.29}$$

The electronic structure through the density of states completely defines the susceptibility of a paramagnetic metal.

3.2 First approach to itinerant magnetism

In the electron gas Hamiltonian it is included, besides the kinetic energy term, a term that describes the interaction between electrons with opposite spins, the Coulomb repulsion term:

$$H = H_{kinetic} + H_{repulsion} \tag{3.30}$$

where the $H_{repulsion} \simeq \mathbf{U} \sum_i n_{i\uparrow} n_{i\downarrow}$ and $\mathbf{U}$ is the Coulomb interaction parameter.

Let us compare the stability of paramagnetic phase as compared to the formation of magnetic order.

The paramagnetic phase is characterized by $n_{0\uparrow} = n_{0\downarrow} = n/2$. If a charge δn is transferred from the down sub band to the up sub band, the variation of the kinetic energy is:

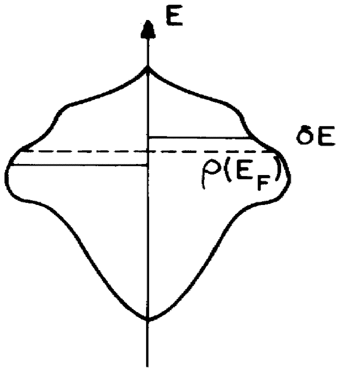


Figure 3.3 Electron transfer between spin sub bands

$$\Delta T = \delta\epsilon \times \delta n = \delta\epsilon \times \rho(\epsilon_F) \times \delta\epsilon = \rho(\epsilon_F)(\delta\epsilon)^2, \tag{3.31}$$

this term is *positive* il all cases, see figure 3.3. The variation of the interaction energy after and before the transfer, is given by:

$$\Delta H_{int} = \mathbf{U}(n_0 + \delta n)(n_0 - \delta n) - \mathbf{U}n_0^2 = -\mathbf{U}\delta n^2 = -\mathbf{U}\rho^2(\epsilon_F)(\delta\epsilon)^2. \tag{3.32}$$

It should be noted that the change in interaction energy is always *negative.* The total variation is:

$$\Delta E_{tot} = \Delta T + \Delta H_{int} = \rho(\epsilon_F)(\delta\epsilon)^2 - \mathbf{U}\rho^2(\epsilon_F)(\delta\epsilon)^2 = \rho(\epsilon_F)(\delta\epsilon)^2[1 - \mathbf{U}\rho(\epsilon_F)]. \tag{3.33}$$

If the $\Delta E_{tot} > 0$ the paramagnetic phase is stable, in the other case, if $\Delta E_{tot} < 0$ the ferromagnetic phase is preferred. The condition to the ferromagnetic stability is then:

$$1 - \mathbf{U}\rho(\epsilon_F) < 0 \qquad \text{or} \qquad \mathbf{U}\rho(\epsilon_F) > 1. \tag{3.34}$$

In conclusion: for a given value of the Coulomb interaction parameter $\mathbf{U}$, the ferromagnetic phase is preferred, if the density of states $\rho(\epsilon_F)$ is large enough.

The molecular fields: an introduction

In systems without interaction between “moments” the magnetization is given by:

$$m = \chi_0 h_{ext}, \tag{3.35}$$

where the χ_0 is the response of an isolated moment to an applied field or of a non interacting electron gas. Examples are: the Curie susceptibility for localized spins and the Pauli susceptibility for a non interacting electron gas. The interaction between "moments" may be described qualitatively introducing effective fields proportional to the magnetization:

$$h_{eff} = \lambda m, \qquad h = h_{ext} + h_{eff} \tag{3.36}$$

$$m = \chi_0(h_{ext} + \lambda m), \qquad m(1 - \lambda\chi_0) = \chi_0 h_{ext} \tag{3.37}$$

or

$$m = \chi h_{ext} \qquad \text{with} \qquad \chi = \frac{\chi_0}{1 - \lambda\chi_0}. \tag{3.38}$$

For example: in the case of insulators or local moments $\chi_0 = \frac{C}{T}$ and $\chi = \frac{C}{T - \lambda C}$; in the case of metallic interacting electrons: $\chi_0 = g_l \mu_B^2 \rho(\epsilon_F)$ and $\chi = g_l \mu_B^2 \rho(\epsilon_F)/\left[1 - g_l \mu_B^2 \lambda \rho(\epsilon_F)\right]$.

In this case defining λ as:

$$\lambda = \frac{\mathbf{U}}{g_l \mu_B^2}, \tag{3.39}$$

one obtains

$$\chi = \frac{g_l \mu_B^2 \rho(\epsilon_F)}{1 - \mathbf{U}\rho(\epsilon_F)}. \tag{3.40}$$

We finally have for the magnetization:

$$m = \frac{g_l \mu_B^2 \rho(\epsilon_F)}{1 - \mathbf{U}\rho(\epsilon_F)} h_{ext}. \tag{3.41}$$

If $\mathbf{U}\rho(\epsilon_F) = 1$, it is possible to have finite m even for $h_{ext} \to 0$.

Thus the study of the ferromagnetic instability is reduced, given a reliable estimate of the electron-electron interaction parameter $\mathbf{U}$, to the analysis of the density of states near the Fermi level. The present simplified discussion, holds not only for pure transition metals, but it applies also to intermetallic compounds. Thus the difference in magnetic behavior of YCo_2 and YFe_2 can be understood in terms of (3.34); YCo_2 is paramagnetic since near the Fermi level $\mathbf{U}\rho(\epsilon_F) < 1$, in contrast to YFe_2 where the opposite occurs.

3.3 A simple application of the molecular field approach

It is considered the effect of dilute isoeletronic impurities, which present different local Coulomb interaction, like Ni in Pd, $PdNi$ and Co in YRh_2, $Y(Rh_{1-x}Co_x)_2$. In these cases one has a high susceptibility host, doped with isoeletronic impurities.

The susceptibility of pure metal is $\chi_0(R, R') = \chi_0(R - R')$. The externally applied magnetic field is $H_{ext}(R')$; including now the molecular field corrections $\Delta\lambda$ due to the impurity, the total field acting on the system, is:

$$H(R') = H_{ext}(R') + \Delta\lambda m(0)\delta_{R'0}. \tag{3.42}$$

The magnetization at the R site is:

$$\begin{aligned} m(R) &= \sum_{R'} \chi_0(R,R')H(R') \\ &= \sum_{R'} \chi_0(R,R')H_{ext}(R') + \sum_{R'} \chi_0(R,R')\Delta\lambda m(0)\delta_{R'0} \\ &= \sum_{R'} \chi_0(R,R')H_{ext}(R') + \chi_0(R,0)\Delta\lambda m(0), \end{aligned} \tag{3.43}$$

to $R = 0$ one has:

$$m(0) = \sum_{R'} \chi_0(0,R')H_{ext}(R') + \chi_0(0,0)\Delta\lambda m(0). \tag{3.44}$$

Solving for $m(0)$, one gets:

$$m(0) = \frac{1}{1-\Delta\lambda\chi_0(0,0)} \sum_{R'} \chi_0(0,R')H_{ext}(R'), \tag{3.45}$$

then:

$$\begin{aligned} m(R) &= \sum_{R'} \chi_0(R,R')H_{ext}(R') + \chi_0(R,0)\frac{\Delta\lambda}{1-\Delta\lambda\chi_0(0,0)} \sum_{R'} \chi_0(0,R')H_{ext}(R') \\ &= \sum_{R'} \left[\chi_0(R,R') + \chi_0(R,0)\frac{\Delta\lambda}{1-\Delta\lambda\chi_0(0,0)}\chi_0(0,R')\right] H_{ext}(R'). \end{aligned} \tag{3.46}$$

By definition of the susceptibility of the perturbed system:

$$m(R) = \sum_{R'} \chi(R,R')H_{ext}(R'). \tag{3.47}$$

In this way:

$$\chi(R,R') = \chi_0(R,R') + \chi_0(R,0)\frac{\Delta\lambda}{1-\Delta\lambda\chi_0(0,0)}\chi_0(0,R'). \tag{3.48}$$

Equation (3.48) in Fourier transform version reads:

$$\chi(q,q') = \chi_0(q,q') + \sum_{q_1}\sum_{q_2} \chi_0(q,q_1)\frac{\Delta\lambda}{1-\Delta\lambda\sum_{q_1q_2}\chi(q_1,q_2)}\chi_0(q_2,q'). \tag{3.49}$$

If the $\Delta\lambda$ is the only perturbation acting on the system and we approximately assume that besides the $\Delta\lambda$ term the system is translational invariant, one gets:

$$\begin{aligned} \chi(q,q') &= \chi_0(q)\delta_{qq'} + \sum_{q_1q_2} \chi_0(q)\delta_{qq_1}\frac{\Delta\lambda}{1-\Delta\lambda\sum_{q_1,q_2}\chi_0(q_1)\delta_{q_1q_2}}\chi_0(q')\delta_{q_2q'} \\ &= \chi_0(q)\delta_{qq'} + \chi_0(q)\frac{\Delta\lambda}{1-\Delta\lambda\sum_{q_1}\chi(q_1)}\chi_0(q'). \end{aligned} \tag{3.50}$$

This formula has a direct application on the *NiPd* Knight shift (see later) and the T^2 term in the resistivity of these strongly exchange enhanced materials.

3.4 The localized spins: origin of the Zener interaction

The interaction between the localized ($\vec{S}_{R_\lambda}$) and itinerant spin ($\vec{s}$) is given by the Zener model,

$$H_{int} = -J\vec{s}.\vec{S}_{R_\lambda}, \tag{3.51}$$

where J is the exchange interaction.

To obtain this Hamiltonian we will follow the Casper method. Beginning with the conduction ($\psi_k(r)$) and the localized states ($\varphi_\beta(r)$),

$$(T+V)\psi_k(r) = E_k\psi_k(r), \qquad (T+V)\varphi_\beta(r) = E_\beta\varphi_\beta(r). \tag{3.52}$$

Since the localized states lie outside the conduction band the states are orthogonal: $< \varphi_\beta \mid \psi_k >= 0$.

The wave function of this pair of electrons (localized and itinerant) is given by:

$$\Psi^{(\pm)}_{k,\beta,M}(r_1,r_2) = \frac{1}{2^{1/2}}\left[\psi_k(r_1)\varphi_\beta(r_2) \pm \psi_k(r_2)\varphi_\beta(r_1)\right]\left|S^\pm, M\right\rangle \tag{3.53}$$

where ± correspond to singlet and triplet states, the normalized function $\mid S^\pm, M >$ are the spin functions correspondent to $+$, $M=0$ and $-$ with $M=-1,0,1$.

The electron pair Hamiltonian is given by:

$$H = T(r_1)+V(r_1)+T(r_2)+V(r_2)+H'_{12}, \qquad H'_{12} = \frac{e^2}{\mid r_1 - r_2 \mid}. \tag{3.54}$$

The idea is using the wave functions $\Psi^\pm_{k,\beta,M}$ to calculate the matrix elements and to find the approximate solution of the problem. However using these symmetrized functions the calculations become very complicated. The idea is then to find an effective Hamiltonian $\tilde{H}$ such that the matrix elements of $\tilde{H}$ between non-symmetrized functions is *identical* to that of H between symmetrized functions. Then the Pauli principle is automatically included.

The non-symmetrized wave function are given by:

$$\tilde{\Psi}^{(\pm)}_{k,\beta,M}(r_1,r_2) = \psi_k(r_1)\varphi_\beta(r_2) \mid S^{(\pm)}, M > . \tag{3.55}$$

The effective Hamiltonian $\tilde{H}$ is defined by:

$$\left\langle \Psi^{(\pm)}_{k'\beta'M'}\right| H \left|\Psi^{(\pm)}_{k\beta M}\right\rangle = \left\langle \tilde{\Psi}^{(\pm)}_{k'\beta'M'}\right| \tilde{H} \left|\tilde{\Psi}^{(\pm)}_{k\beta M}\right\rangle . \tag{3.56}$$

To use in the proof we define the operators P^r_{12} and $P^{S'}_{12}$, acting respectively is space variables and in spin variables, one has:

$$\begin{aligned} P^{(r)}_{12}\psi(r_1,r_2) &= \psi(r_2,r_1) && (3.57)\\ P^{(S)}_{12}\left|S^{(\pm)},M\right\rangle &= \pm\left|S^{(\pm)},M\right\rangle, && (3.58)\end{aligned}$$

where

$$P_{12}^{(S)} = \frac{1}{2} + 2\vec{s}_1.\vec{s}_2 = \frac{1}{2} + (\vec{s}_1 + \vec{s}_2)^2 - (\vec{s})_1^2 - (\vec{s})_2^2 \tag{3.59}$$

and the $\psi(r_1, r_2)$ is a general function of space variables. Therefore for our specific case:

$$\Psi_{k,\beta,M}^{(\pm)} = \frac{1}{2^{1/2}} \left(1 - P_{12}^{(r)} P_{12}^{(S)}\right) \tilde{\Psi}_{k\beta M}^{(\pm)}(r_1, r_2). \tag{3.60}$$

In conclusion: An equivalent formulation to the above problem is:

$$\Psi_\lambda(r_1, r_2) = \left(1 - P_{12}^{(r)} P_{12}^{(S)}\right) \tilde{\Psi}_\lambda(r_1, r_2) \tag{3.61}$$

where Ψ_λ is the linear combination of the $\Psi_{k\beta M}^{(\pm)}$ and $\tilde{\Psi}_\lambda$ is a linear combination of the $\tilde{\Psi}_{k,\beta M}^{(\pm)}$. Thus the diagonalization of the Hamiltonian can be made.

To do the explicit calculation of the matrix elements of $\tilde{H}$ we proceed as follows:

$$H = H_0 + H_{12} \qquad \text{and} \qquad H_0 = T(r_1) + V(r_1) + T(r_2) + V(r_2) \tag{3.62}$$

$$H_0 \Psi_{k,\beta,M}^{(\pm)} = (E_k + E_\beta) \Psi_{k,\beta,M}^{(\pm)} \tag{3.63}$$

$$H \Psi_{k\beta M}^{(\pm)} = \left[(E_k + E_\beta)\left(1 - P_{12}^{(r)} P_{12}^{(S)}\right) + H'_{12}\left(1 - P_{12}^{(r)} P_{12}^{(S)}\right)\right] \frac{1}{2^{1/2}} \tilde{\Psi}_{k\beta M}^{(\pm)} \tag{3.64}$$

Now it is necessary to calculate:

$$\begin{aligned} < \Psi_{k',\beta' M'}^{(\pm)} \mid H \mid \Psi_{k,\beta,M}^{(\pm)} > \; = \; & \delta_{MM'} \Big[(E_k + E_\beta) \delta_{kk'} \delta_{\beta\beta'} + \\ & + \int \psi_{k'}^*(r_1) \psi_k(r_1) \frac{e^2}{\mid r_1 - r_2 \mid} \varphi_{\beta'}^*(r_2) \varphi_\beta(r_2) dr_1 dr_2 \pm \\ & \pm \int \psi_{k'}^*(r_1) \varphi_{\beta'}^*(r_2) \frac{e^2}{\mid r_1 - r_2 \mid} \psi_k(r_2) \varphi_\beta(r_1) dr_1 dr_2 \Big] \end{aligned} \tag{3.65}$$

the last two terms may be written as:

$$\begin{aligned} & \int \psi_{k'}^*(r_1) \varphi_{\beta'}^*(r_2) \frac{e^2}{\mid r_1 - r_2 \mid} \psi_k(r_1) \varphi_\beta(r_2) dr_1 dr_2 \pm \\ \pm & \int \psi_{k'}^*(r_1) \varphi_{\beta'}^*(r_2) \frac{e^2}{\mid r_1 - r_2 \mid} P_{12}^{(r)} \psi_k(r_1) \varphi_\beta(r_2) dr_1 dr_2 = \\ = & < \tilde{\Psi}_{k'\beta' M}^{(\pm)} \mid H'_{12} \mid \tilde{\Psi}_{k,\beta,M}^{(\pm)} > - < \tilde{\Psi}_{k'\beta' M}^{(\pm)} \mid H'_{12} P_{12}^{(r)} P_{12}^{(S)} \mid \tilde{\Psi}_{k\beta M}^{(\pm)} > = \\ & = \left\langle \tilde{\Psi}_{k'\beta' M}^{(\pm)} \middle| H'_{12} \left(1 - P_{12}^{(r)} P_{12}^{(S)}\right) \middle| \tilde{\Psi}_{k\beta M}^{(\pm)} \right\rangle . \end{aligned} \tag{3.66}$$

Finally:

$$\left\langle \Psi_{k'\beta' M}^{(\pm)} \middle| H \middle| \Psi_{k\beta M}^{(\pm)} \right\rangle = \left\langle \tilde{\Psi}_{k'\beta' M}^{(\pm)} \middle| H_0 + H'_{12} \left(1 - P_{12}^{(r)} P_{12}^{(s)}\right) \middle| \tilde{\Psi}_{k\beta M}^{(\pm)} \right\rangle , \tag{3.67}$$

then using the definition of the effective Hamiltonian:

$$\begin{aligned}\tilde{H} &= H_0 + H'_{12}\left(1 - P^{(r)}_{12}P^{(S)}_{12}\right)\\ &= H_0 + H'_{12}\left[1 - P^{(r)}_{12}\left(\frac{1}{2} + 2\vec{s}_1.\vec{s}_2\right)\right]\\ &= H_0 + H'_{12}\left[1 - \frac{1}{2}P^{(r)}_{12}\right] - 2H'_{12}P^{(r)}_{12}\vec{s}_1.\vec{s}_2. \end{aligned} \tag{3.68}$$

The effective Hamiltonian has then two terms: the last one is of the Zener form and couples itinerant and local spins, respectively $\vec{s}_1$ and $\vec{s}_2$. Note that in this simplified approach, $\vec{s}_2$ is the spin of a localized state. The first term of (3.68) introduces correction to the *spin independent* part of the problem. This term is not important for the magnetic properties, which involve differences in up and down spin occupations numbers. Finally let us recall that for actual situations this simplified approach has to be generalized to include total localized spin large that 1/2, orbital effects and total spins J. Some comments about that will be made in Chapter 5.

3.4.1 Aplication of the linear response theory

Indirect spin-spin interaction

Let us start from the Zener Hamiltonian, involving a local spin at the site R_λ:

$$H_{int} = -J\vec{s}.\vec{S}_{R_\lambda} \tag{3.69}$$

and then define the following effective magnetic field:

$$H_{int} = -g_l\mu_B\vec{s}.\vec{H}_{R_\lambda}, \tag{3.70}$$

equating these interaction energies one derives the effective field

$$\vec{H}_{R_\lambda} = \frac{J}{g_l\mu_B}\vec{S}_{R_\lambda}. \tag{3.71}$$

The magnetic response to the application of this field is:

$$\vec{m}_{R_{\lambda'}} = \chi(R_{\lambda'}, R_\lambda)\vec{H}_{R_\lambda} = \frac{J}{g_l\mu_B}\chi(R_{\lambda'}, R_\lambda)\vec{S}_{R_\lambda}. \tag{3.72}$$

The induced polarization of the electron gas can be written:

$$\vec{m}_{R_{\lambda'}} = g_l\mu_B\vec{s}(R_{\lambda'}) \qquad \text{with} \qquad \vec{s}_{R_{\lambda'}} = \frac{\vec{m}_{R_{\lambda'}}}{g_l\mu_B}. \tag{3.73}$$

Calculating the Zener energy associated to the site R_λ, gives:

$$\begin{aligned} E^{\lambda\lambda'}_{int} &= -J\frac{\vec{m}_{R_{\lambda'}}}{g_l\mu_B}.\vec{S}(R_{\lambda'}) = -\frac{J^2}{g_l^2\mu_B^2}\chi(R_{\lambda'}, R_\lambda)\vec{S}_{R_{\lambda'}}.\vec{S}_{R_\lambda}\\ &= j(R_{\lambda'}, R_\lambda)\vec{S}_{R_{\lambda'}}.\vec{S}_{R_\lambda}, \end{aligned} \tag{3.74}$$

where the effective interaction $j(R_{\lambda'}, R_\lambda)$ is given in a general case by:

$$\begin{aligned} j(R_{\lambda'}, R_\lambda) &= -\frac{J^2}{g_l^2 \mu_B^2} \chi(R_{\lambda'}, R_\lambda) \\ &= -\frac{J^2}{g_l^2 \mu_B^2} \sum_{qq'} e^{-i\vec{q}.\vec{R}_{\lambda'}} e^{i\vec{q}'.\vec{R}_\lambda} \chi(q, q'). \end{aligned} \tag{3.75}$$

For pure metals , for example: Gd, Ho or Eu, the relation is:

$$\chi(q, q') = \chi(q)\delta_{qq'}, \tag{3.76}$$

and consequently:

$$j(R_{\lambda'}, R_\lambda) = -\frac{J^2}{g_l^2 \mu_B^2} \sum_q e^{i\vec{q}.(\vec{R}_\lambda - \vec{R}_{\lambda'})} \chi(q). \tag{3.77}$$

This is the Ruderman, Kittel, Kasuya and Yoshida (RKKY) interaction and the original derivation of (3.77) is due to Doniach.

In terms of the calculation of the total energy (summing over all sites), a simple estimate of the ordering temperature in a system of localized spins is given by $kT_c \simeq E_{int}^{total}$. In this calculation we fix fix λ and sum over all the other λ'.

The induced magnetization by localized magnetic moments

For example: in *LuGd* alloys, the *Lu* do not exhibits local magnetic moment; the magnetization at the *Lu* site is given by:

$$\vec{m}_{transf}(0) = \frac{J}{g_l \mu_B} \sum_\lambda \chi(0, R_\lambda) \vec{S}_{R_\lambda}. \tag{3.78}$$

If the magnetic order is the ferromagnetic, then:

$$\begin{aligned} \vec{m}_{transf}(0) &= \frac{J}{g_l \mu_B} \vec{S} \sum_{\lambda \neq 0} \chi(0, R_\lambda) \qquad \text{whit} \qquad \chi(0, R_\lambda) = \sum_{q,q'} e^{i\vec{q}'.\vec{R}_\lambda} \chi(q, q') \\ &= \frac{J}{g_l \mu_B} \vec{S} \sum_{\lambda \neq 0} \sum_{q,q'} e^{i\vec{q}'.\vec{R}_\lambda} \chi(q, q'). \end{aligned} \tag{3.79}$$

We illustrate this situation considering *Lu* impurities diluted in *Gd*, in figure 3.4.

Self polarization

If at the origin one put a local localized spin and then calculate the electron gas magnetization induced by this spin at its own site, one gets:

$$\vec{m}_{self}(0) = \frac{J}{g_l \mu_B} \vec{S}_{R_{\lambda=0}} \chi(0, 0) = \frac{J}{g_l \mu_B} \vec{S}_{R_{\lambda=0}} \sum_{q,q'} \chi(q, q'). \tag{3.80}$$

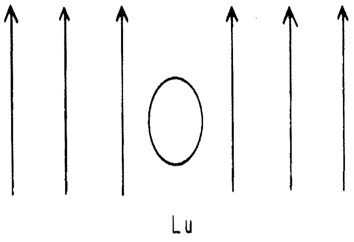


Figure 3.4 Lu impurity in Gd

Two examples:

i. $GdLu$, is this case $\chi(q,q') \cong \chi(q)\delta_{qq'}$, because both are trivalent rare hearths; then:

$$\vec{m}_{self} = \frac{J}{g_l \mu_B} \vec{S}_{R_\lambda = 0} \sum_q \chi(q) \tag{3.81}$$

ii. $GdPd$, is this case $\chi(q,q') \neq \chi(q)\delta_{qq'}$, then:

$$\vec{m}_{self} = \frac{J}{g_l \mu_B} \vec{S}_{R_\lambda = 0} \sum_{qq'} \chi(q.q') \tag{3.82}$$

The Knight shift

A nucleus with magnetic moment $\vec{\mu}_I$ in an uniform magnetic field, in the vacuum, has the energy $E = \vec{\mu}_I.\vec{H}$. In the material, one has an additional hyperfine interaction given by:

$$E_{int} = A\vec{\mu}_I.\vec{m}_e, \tag{3.83}$$

where $\vec{m}_e$ is the electronic magnetization. In this way, the total energy is:

$$E_{tot} = \vec{\mu}_I.\vec{H} + A\vec{\mu}_I.\vec{m}_e. \tag{3.84}$$

The nucleus is at the origin, then:

$$\vec{m}_e(0) = \sum_{qq'} \chi(q,q')\vec{H}_{q'}. \tag{3.85}$$

In the uniform field case $\vec{H}_{q'} = \delta_{q'0}\vec{H}$, and:

$$\vec{m}_e(0) = \vec{H} \sum_q \chi(q,0), \tag{3.86}$$

therefore

$$E_{tot} = \vec{\mu}_I.\vec{H} + A\sum_q \chi(q,0)\vec{\mu}_I.\vec{H} = \vec{\mu}_I.\vec{H}\left[1 + A\sum_q \chi(q,0)\right]. \tag{3.87}$$

Figure 3.5 Induced energy shift

The energy may be written as $E = \hbar\omega$, then:

$$\omega = \omega_0 \left[1 + A \sum_q \chi(q,0) \right], \tag{3.88}$$

where we have defined $\omega_0 = 2 g_N \vec{\mu}_N^I I H$ is the energy in vacuum. Introduce the change in the resonance frequency:

$$\frac{\Delta\omega}{\omega_0} = \frac{\omega - \omega_0}{\omega_0} = A \sum_q \chi(q,0). \tag{3.89}$$

The $\Delta\omega/\omega_0$ is defined as the Knight shift. It should be remembered that the material is paramagnetic; this contrasts with hyperfine field results in ferromagnetic materials, since in the second case no externally applied magnetic field is necessary in ferromagnetic pure metals. Schematic magnetic field induced energy shift, figure 3.5.

Two cases are considered separately: a pure metal and a dilute alloy. Consider firstly a pure metals. Then:

$$\sum_q \chi(q,0) = \sum_q \delta_{q0} \chi_{Pauli} = \chi_{Pauli} \quad \text{then} \quad \frac{\Delta\omega}{\omega_0} = A \chi_{Pauli}. \tag{3.90}$$

Consider now the $NiPd$ alloy. In this compound it is necessary to include the different Coulomb interaction ($\Delta\mathbf{U} = \mathbf{U}_{Ni} - \mathbf{U}_{Pd} > 0$). Using the previously obtained results for the susceptibility:

$$\chi(q,q') = \chi(q')\delta_{qq'} + \chi(q) \frac{\Delta\mathbf{U}}{1 - \Delta\mathbf{U} \sum_{q''} \chi(q'')} \chi(q') \tag{3.91}$$

$$\chi(q,0) = \chi(0)\delta_{q,0} + \chi(q) \frac{\Delta\mathbf{U}}{1 - \Delta\mathbf{U} \sum_{q''} \chi(q'')} \chi(0). \tag{3.92}$$

For the Knight shift one needs to sum over the q vectors getting:

$$\begin{aligned} \sum_q \chi(q,0) &= \chi_{Pauli} + \sum_q \chi(q) \frac{\Delta\mathbf{U}}{1 - \Delta\mathbf{U} \sum_{q'} \chi(q')} \chi_{Pauli} \\ &= \chi_{Pauli} \left[1 + \frac{\Delta\mathbf{U}\ddot{\chi}}{1 - \Delta\mathbf{U}\ddot{\chi}} \right] = \frac{\chi_{Pauli}}{1 - \Delta\mathbf{U}\ddot{\chi}}, \end{aligned} \tag{3.93}$$

where $\tilde{\chi} = \sum_q \chi(q)$. The Knight Shift is, then:

$$\frac{\Delta\omega}{\omega_0} = \frac{A\chi_{Pauli}}{1 - \Delta\mathbf{U}\tilde{\chi}(q)}; \qquad \left(\frac{\Delta\omega}{\omega_0}\right)_{PdNi} = \frac{\left(\frac{\Delta\omega}{\omega_0}\right)_{Pd-pure}}{1 - \Delta\mathbf{U}\tilde{\chi}(q)}. \tag{3.94}$$

3.5 The Hubbard Hamiltonian

Let us start with a system of non interacting electrons. The complete set of Bloch functions $\varphi_k(\vec{r})$ satisfy:

$$H_0\varphi_k(\vec{r}) = \epsilon_k\varphi_k(\vec{r}), \tag{3.95}$$

where

$$H_0 = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]. \tag{3.96}$$

Considering the operators $c^+_{k\sigma}$ and $c_{k\sigma}$, that are the creation and annihilation operators of an electron in an one electron state with spin σ and wave vector k, and the states $\varphi_k(\vec{r})$ it is possible to obtain the creation and annihilation operators of a particle at the position $\vec{r}$:

$$\psi^+_\sigma(\vec{r}) = \sum_k \varphi^*_k(\vec{r})c^+_{k\sigma} \qquad \psi_\sigma(\vec{r}) = \sum_k \varphi_k(\vec{r})c_{k\sigma}. \tag{3.97}$$

The Hamiltonian for a particle system interacting with an external potential and pair interaction, may be written in the second quantization formalism as:

$$H = \sum_\sigma \int d\vec{r}\psi^+_\sigma(\vec{r})H_0\psi_\sigma(\vec{r}) + \frac{1}{2}\sum_{\sigma,\sigma'}\int d\vec{r}d\vec{r'}\psi^+_\sigma(\vec{r'})\psi^+_{\sigma'}(\vec{r})V(\vec{r},\vec{r'})\psi_{\sigma'}(\vec{r})\psi_\sigma(\vec{r'}), \tag{3.98}$$

where $V(\vec{r},\vec{r'})$ is the pair interaction between particles. Using the Bloch representation, in the first part of the Hamiltonian, we called A, one gets:

$$\begin{aligned} A &= \sum_\sigma \int d\vec{r}\psi^+_\sigma(\vec{r})H_0\psi_\sigma(r) = \sum_\sigma\sum_{kk'} c^+_{k\sigma}c_{k'\sigma}\int d\vec{r}\varphi^*_k(\vec{r})H_0\varphi_{k'}(\vec{r}) \\ &= \sum_\sigma\sum_{kk'} c^+_{k\sigma}c_{k'\sigma}\epsilon_{k'}\int d\vec{r}\varphi^*_k(\vec{r})\varphi_{k'}(\vec{r}) = \sum_{k\sigma}\epsilon_k c^+_{k\sigma}c_{k\sigma}, \end{aligned} \tag{3.99}$$

since the Bloch functions are supposed to be orthonormal.

The second part, are called B, is:

$$B = \frac{1}{2}\sum_{\sigma\sigma'}\sum_{k_1k_2}\sum_{k_3k_4} c^+_{k_1\sigma}c^+_{k_2\sigma'}c_{k_3\sigma'}c_{k_4\sigma}\int \varphi^*_{k_1}(\vec{r'})\varphi^*_{k_2}(\vec{r})V(\vec{r},\vec{r'})\varphi_{k_3}(\vec{r})\varphi_{k_4}(\vec{r'})d\vec{r}d\vec{r'}. \tag{3.100}$$

For systems that can be described within the TB approximation and assuming the non degenerate case, one gets:

$$\varphi_k(\vec{r}) = \sum_i e^{i\vec{k}.\vec{R}_i}\phi(\vec{r} - \vec{R}_i). \tag{3.101}$$

In this case it is possible to define the creation and annihilation operators for electrons of spin σ at site i:

$$c_{k\sigma} = \sum_i e^{-i\vec{k}.\vec{R}_i} c_{i\sigma} \quad \text{or} \quad c_{i\sigma} = \sum_k e^{i\vec{k}.\vec{R}_i} c_{k\sigma}, \qquad c^+_{i\sigma} = \sum_k e^{-i\vec{k}.\vec{R}_i} c^+_{k\sigma}. \tag{3.102}$$

Using this definition, one gets for the part A:

$$\sum_{k\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} = \sum_{ij\sigma} c^+_{i\sigma} c_{j\sigma} \sum_k e^{i\vec{k}.\vec{R}_i} e^{-i\vec{k}.\vec{R}_j} \epsilon_k. \tag{3.103}$$

Defining $T_{ij} = \sum_k \epsilon_k e^{i\vec{k}(\vec{R}_i - |vecR_j)}$, one obtains:

$$A = \sum_{k\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} = \sum_{ij\sigma} T_{ij} c^+_{i\sigma} c_{j\sigma}. \tag{3.104}$$

In the case of $\epsilon_k = constant$, there is no possibility of hopping between sites i and j. The T_{ij} is then defined as the hopping energies (T_{ij} are band width dependent).

To calculate the part B, we begin with the integral:

$$\int \varphi^*_{k_1}(\vec{r}')\varphi^*_{k_2}(\vec{r})V(\vec{r},\vec{r}')\varphi_{k_3}(\vec{r})\varphi_{k_4}(\vec{r}')d\vec{r}d\vec{r}' = \sum_{ijlm} e^{-i\vec{k}_1.\vec{R}_i} e^{-i\vec{k}_2.\vec{R}_j} e^{i\vec{k}_3.\vec{R}_l} e^{i\vec{k}_4.\vec{R}_m} U_{ijlm} \tag{3.105}$$

where

$$U_{ijlm} = \int d\vec{r}d\vec{r}'\phi^*(\vec{r}' - \vec{R}_i)\phi^*(\vec{r} - \vec{R}_j)V(\vec{r},\vec{r}')\phi(\vec{r} - \vec{R}_l)\phi(\vec{r}' - \vec{R}_m). \tag{3.106}$$

In this way:

$$\begin{aligned} B &= \frac{1}{2}\sum_{\sigma,\sigma'} \sum_{k_1k_2k_3k_4} c^+_{k_1\sigma} c^+_{k_2\sigma'} c_{k_3\sigma'} c_{k_4\sigma} \sum_{ijlm} U_{ijlm} e^{-ik_1.R_i} e^{-ik_2.R_j} e^{ik_3.R_l} e^{ik_4.R_m} \\ &= \frac{1}{2}\sum_{\sigma,\sigma'} \sum_{ijlm} U_{ijlm} \sum_{k_1k_2k_3k_4} e^{-ik_1R_i} c^+_{k_1\sigma} e^{-ik_2R_j} c^+_{k_2\sigma'} e^{ik_3R_l} c_{k_3\sigma'} e^{ik_4R_m} c_{k_4\sigma} \\ &= \frac{1}{2}\sum_{\sigma,\sigma'} \sum_{ijlm} U_{ijlm} c^+_{i\sigma} c^+_{j\sigma'} c_{l\sigma'} c_{m\sigma}. \end{aligned} \tag{3.107}$$

After this transformation the Hamiltonian $A + B$ reads:

$$H = \sum_{ij\sigma} T_{ij} c^+_{i\sigma} c_{j\sigma} + \frac{1}{2}\sum_{\sigma,\sigma'} \sum_{ijlm} U_{ijlm} c^+_{i\sigma} c^+_{j\sigma'} c_{l\sigma'} c_{m\sigma}. \tag{3.108}$$

Within the TB spirit, in the definition of U_{ijlm} we retain only the largest possible overlap of atomic like functions; this occurs when all the wave functions are centered at the same site. Then:

$$\begin{aligned} U_{ijlm} &= \int d\vec{r}d\vec{r}'\phi^*(r' - R_i)\phi^*(r - R_j)V(\vec{r},\vec{r}')\phi(r - R_l)\phi(r' - R_m) \\ &= \delta_{im}\delta_{jl}\delta_{ij}U \end{aligned} \tag{3.109}$$

where

$$U = \int \phi^*(\vec{r}')\phi^*(\vec{r})V(\vec{r},\vec{r}')\phi(\vec{r})\phi(\vec{r}') = \int \mid \phi(\vec{r}') \mid^2 \mid \phi(\vec{r}) \mid^2 V(\vec{r},\vec{r}')d\vec{r}d\vec{r}'. \tag{3.110}$$

Now, the Hamiltonian becomes:

$$H = \sum_{ij\sigma} T_{ij} c^+_{i\sigma} c_{j\sigma} + \frac{1}{2} U \sum_{\sigma,\sigma',i} c^+_{i\sigma} c^+_{i\sigma'} c_{i\sigma'} c_{i\sigma}, \tag{3.111}$$

Since $c_{i\sigma} c_{i\sigma} = 0$, the only term that survives is:

$$H = \sum_{ij\sigma} T_{ij} c^+_{i\sigma} c_{j\sigma} + \frac{1}{2} U \sum_{\sigma,i} c^+_{i\sigma} c^+_{i-\sigma} c_{i-\sigma} c_{i\sigma}. \tag{3.112}$$

Using the anti-commutation relations:

$$\begin{aligned} \sum_{\sigma} c^+_{i\sigma} c^+_{i-\sigma} c_{i-\sigma} c_{i\sigma} &= \sum_{\sigma} c^+_{i\sigma} c_{i\sigma} c^+_{i-\sigma} c_{i-\sigma} = \sum_{\sigma} n_{i\sigma} n_{i-\sigma} \\ &= n_{i\uparrow} n_{i\downarrow} + n_{i\downarrow} n_{i\uparrow} = 2 n_{i\uparrow} n_{i\downarrow}. \end{aligned} \tag{3.113}$$

The Hubbard Hamiltonian is finally:

$$H = \sum_{ij\sigma} T_{ij} c^+_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}. \tag{3.114}$$

This is the Hamiltonian to be used in the description of pure transition metals, alloys or intermetallics. Although its simple form, many qualitative results can be extracted from its solution, even approximate.

3.5.1 The Hartree-Fock approximation

In the Hartree-Fock approximation, the second term of the Hubbard Hamiltonian is linearized in the following way:

$$\begin{aligned} \sum_{i} n_{i\uparrow} n_{i\downarrow} &\simeq \sum_{i} (< n_{i\uparrow} > n_{i\downarrow} + < n_{i\downarrow} > n_{i\uparrow}) \\ &\simeq \sum_{ij} < n_{i\uparrow} > c^+_{i_\downarrow} c_{j\downarrow} \delta_{ij} + \sum_{ij} < n_{i_\downarrow} > c^+_{i\uparrow} c_{j\uparrow} \delta_{ij} \\ &\simeq \sum_{ij\sigma} < n_{i-\sigma} > \delta_{ij} c^+_{i\sigma} c_{j\sigma}. \end{aligned} \tag{3.115}$$

The Hamiltonian is rewritten as:

$$H \cong \sum_{ij\sigma} \left[T_{ij} + U < n_{i-\sigma} > \delta_{ij} \right] c^+_{i\sigma} c_{j\sigma} = \sum_{ij\sigma} T_{ij\sigma} c^+_{i\sigma} c_{j\sigma}. \tag{3.116}$$

For ferromagnetic and paramagnetic solutions it is possible to assume site independence, that is, $< n_{i\sigma} > = < n_{\sigma} >$. The Fourier transform of the Hamiltonian is:

$$H = \sum_{k\sigma} \left(\epsilon_k + U < n_{-\sigma} > \right) c^+_{k\sigma} c_{k\sigma}. \tag{3.117}$$

The resolvent associated to this Hamiltonian is diagonal; using the imaginary theorem:

$$\begin{aligned}\rho_\sigma(\epsilon) &= -\frac{1}{\pi} I_m Tr_k \frac{1}{\epsilon - U < n_{-\sigma} > - \epsilon_k} \\ &= \sum_k \delta(\epsilon - \epsilon_k - U < n_{-\sigma} >). \end{aligned} \tag{3.118}$$

The number of electrons of spin σ, $< n_\sigma >$, at $T = 0$, is given by:

$$< n_\sigma > = \int^{\epsilon_F} \rho_\sigma(\epsilon) d\epsilon = \int^{\epsilon_F} N(\epsilon - U < n_{-\sigma} >) d\epsilon, \tag{3.119}$$

where $N(\epsilon) = \sum_k \delta(\epsilon - \epsilon_k)$ is the density of states associated to the band structure.

This problems is transformed into a self-consistent one, through the equations:

$$n = \langle n_\uparrow \rangle + \langle n_\downarrow \rangle , \tag{3.120}$$

where

$$\langle n_\uparrow \rangle = \int^{\epsilon_F} N(\epsilon - U n_\downarrow) d\epsilon \tag{3.121}$$

$$\langle n_\downarrow \rangle = \int^{\epsilon_F} N(\epsilon - U n_\uparrow) d\epsilon. \tag{3.122}$$

3.5.2 A dilute transition impurity in a transition host

Examples of this situations are $NiPd$ and $FePd$. In this case the Coulomb interaction $\sum_i \mathbf{U}^i n_{i\uparrow} n_{i\downarrow}$ with $\mathbf{U}^i$ site dependent: $\mathbf{U}^0 = \mathbf{U}^{Ni,Fe}$ and $\mathbf{U}^i = \mathbf{U}^{Pd}$, $i \neq 0$. Therefore:

$$\begin{aligned}\sum_i \mathbf{U}_i n_{i\uparrow} n_{i\downarrow} &= \sum_{i \neq 0} \mathbf{U}^{Pd} n_{i\uparrow} n_{i\downarrow} + \mathbf{U}^{Ni} n_{0\uparrow} n_{0\downarrow} \\ &= \mathbf{U}^{Pd} \sum_i n_{i\uparrow} n_{i\downarrow} + (\mathbf{U}^{Ni} - \mathbf{U}^{Pd}) n_{0\uparrow} n_{0\downarrow}. \end{aligned} \tag{3.123}$$

It is possible to write the Coulomb terms as:

$$\sum_i \mathbf{U}_i n_{i\uparrow} n_{i\downarrow} = \mathbf{U}^{Pd} \sum_i n_{i\uparrow} n_{i\downarrow} + \Delta\mathbf{U} n_{0\uparrow} n_{0\downarrow}, \tag{3.124}$$

where $\Delta\mathbf{U} = \mathbf{U}^{Ni} - \mathbf{U}^{Pd} > 0$, since the Ni wave functions are less extended than those of Pd.

The hopping terms, involving the overlap dependence ($< \phi_i | V | \phi_j >$), may be rewritten for the impurity located at the origin:

$$H_{kin} = \sum_{i,j \neq 0, \sigma} T_{ij}^{(0)} c_{i\sigma}^{+} c_{j\sigma} + \sum_{j(neighbor),\sigma} \left[\tilde{T}_{0j} c_{0\sigma}^{+} c_{j\sigma} + \tilde{T}_{j0} c_{j\sigma}^{+} c_{0\sigma} \right], \tag{3.125}$$

where $\tilde{T}_{j0} = (1+\gamma)T_{0j}^{(0)}$ and γ is greater than or less than zero if the impurity wave function is larger or narrower than the host one, respectively, then:

$$H = \sum_{i,j\neq 0,\sigma} T_{ij}^{(0)} c_{i\sigma}^{+} c_{j\sigma} + (1+\gamma) \sum_{j\neq 0,\sigma} T_{0j}^{0} \left[c_{0\sigma}^{+} c_{j\sigma} + c_{j\sigma}^{+} c_{0\sigma} \right] + \mathbf{U} \sum_{i} n_{i\uparrow} n_{i\downarrow} + \Delta \mathbf{U} n_{0\uparrow} n_{0\downarrow}. \tag{3.126}$$

Including the local atomic levels ϵ^{i}, not considered in the hopping terms:

$$\begin{aligned} \sum_{i\sigma} \epsilon^{i} c_{i\sigma}^{+} c_{i\sigma} &= \sum_{i\neq 0,\sigma} \epsilon^{(h)} c_{i\sigma}^{+} c_{i\sigma} + \epsilon^{0} \sum_{\sigma} c_{0\sigma}^{+} c_{0\sigma} \\ &= \epsilon^{(h)} \sum_{i\sigma} c_{i\sigma}^{+} c_{i\sigma} + (\epsilon^{(h)} - \epsilon^{0}) \sum_{\sigma} c_{0\sigma}^{+} c_{0\sigma}, \end{aligned} \tag{3.127}$$

where ϵ^{0} and $\epsilon^{(h)}$ are the impurity and host atom levels respectively.

Therefore the complete Hamiltonian is:

$$\begin{aligned} H_{tot} &= \epsilon^{(h)} \sum_{i\sigma} c_{i\sigma}^{+} c_{i\sigma} + (\epsilon^{(h)} - \epsilon^{0}) \sum_{\sigma} c_{0\sigma}^{+} c_{0\sigma} + \sum_{ij\neq 0,\sigma} T_{ij}^{(0)} c_{i\sigma}^{+} c_{i\sigma} \\ &+ (1-\gamma) \sum_{j\neq 0,\sigma} T_{0j}^{(0)} \left[c_{0\sigma}^{+} c_{j\sigma} + c_{j\sigma}^{+} c_{o\sigma} \right] + \mathbf{U}^{(h)} \sum_{i} n_{i\uparrow} n_{i\downarrow} + \Delta \mathbf{U} n_{0\uparrow} n_{0\downarrow} \end{aligned} \tag{3.128}$$

3.5.3 Numerical method for Hartree-Fock solution

The usual models for the density of states are shown in figure 3.6: a constant function, the Moriya model ($\rho = A[1 - (\epsilon/\Delta)^{2}]$, a model for FCC metals (with a peak in the high energy side), a model to BCC metals (superposition of two Moriya's bands) and finally and closed to the reality an interpolation of a calculated density of states. Start assuming a value for the Coulomb interaction parameter, smaller than the band width. The number of electrons per atom is specified as $\bar{n}$, if the bands are normalized to 1, $\bar{n}/2$ varies of 0 to 1 per spin direction.

Remembering the self-consistence conditions:

$$n = n_{\uparrow} + n_{\downarrow} \tag{3.129}$$

$$n_{\uparrow} = \int^{\epsilon_F} N(\epsilon - U n_{\downarrow}) d\epsilon \tag{3.130}$$

$$n_{\downarrow} = \int^{\epsilon_F} N(\epsilon - U n_{\uparrow}) d\epsilon. \tag{3.131}$$

Combining (3.129) and (3.130) we get's:

$$n_{\uparrow} = \int^{\epsilon_F} \rho \left(\epsilon - \mathbf{U}(n - n_{\uparrow}) \right). \tag{3.132}$$

For a given $\bar{n}$ and a value for $n_{\uparrow}$, the Fermi level ϵ_F is determined by equation (3.132). With this value of ϵ_F and $n_{\uparrow}$, from (3.131) one gets the corresponding value of $n_{\downarrow}$. Plotting the values of $n_{\uparrow} \times n_{downarrow}$ one obtains the figure 3.7. Using symmetry

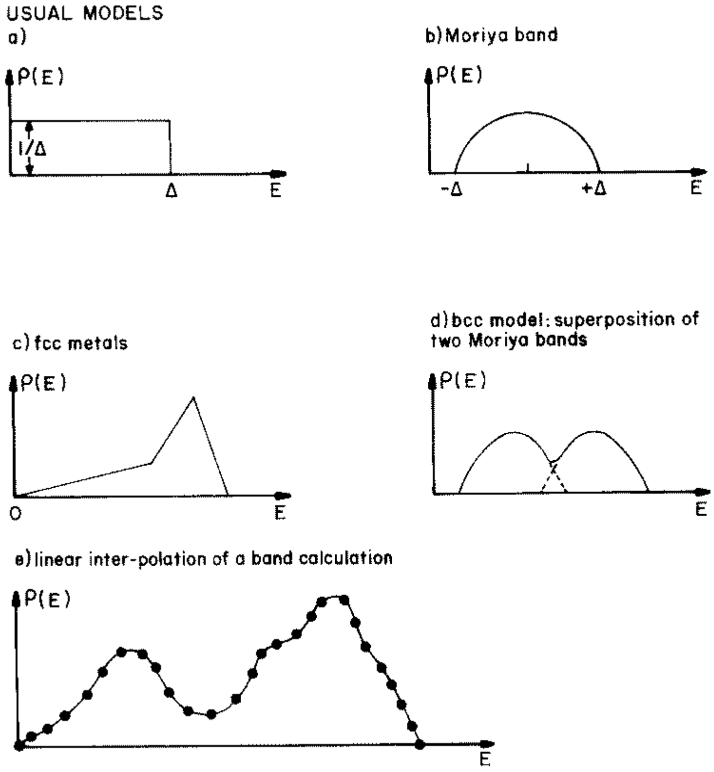


Figure 3.6 Models for the density of states.

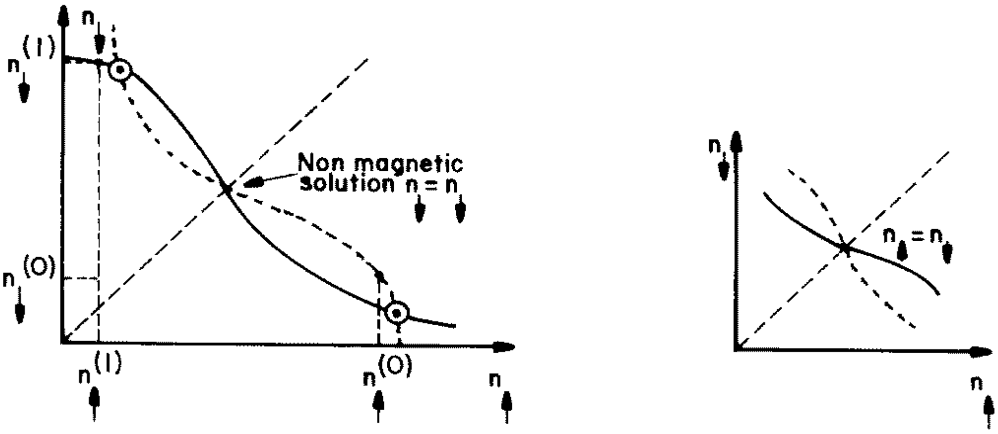


Figure 3.7 Numerial solutions of the Hartree-Fock problem.

arguments the dot dashed is obtained; the crossing points are the self-consistence solutions.

With the obtained solutions, it is necessary to calculate the energy of ferromagnetic solution and compare with that paramagnetic one. In this way it is possible to obtain ferromagnetic solution as a function of the number of electrons, band width and band shape.

3.5.4 The mixed magnetic systems

There is in the systems like $GdFe_2$, $GdCo_2$, $GdRh_2$ and $GdIr_2$, the localized spins $\vec{S}_{TR}$, associated to the rare earth and, consequently, its exchange interaction with the conductions electrons is given by $J_{df}\vec{s}_d.\vec{S}_{TR}$. The d electrons can exhibit magnetic properties independently of the presence of the rare earths.

The relevant experimental test to know if the magnetic properties are associated to the d band are the compounds $LuCo_2$ (paramagnetic) and $LuFe_2$ (ferromagnetic). In the first case the Stoner condition is not satisfied. The expected value for $\mathbf{U}\rho(\epsilon_F) < 1$, but $\mathbf{U}\rho(\epsilon_F)$ can be quite close to 1. This implies that $X = X_0(1 - \mathbf{U}\rho(\epsilon_F))^{-1}$ is very large.

Experimentally $X_{LuCo_2} \cong 3X_{Pd}$. The compound $LuFe_2$ is ferromagnetic with saturation magnetic moment about 1.5 u_B, therefore close to Fe metallic value.

Chapter 4

ELECTRONIC STRUCTURE: REVISITED

4.1 Electronic structure calculation: a brief overview

4.1.1 Self consistent procedure

Let us start from the one electron approximation. The first step consists in solving the Schrödinger equation for the electronic states $\psi_j(\vec{k},\vec{r})$:

$$\left[-\nabla^2 + V_S(r)\right]\psi_j(\vec{k},\vec{r}) = E_j(\vec{k})\psi_j(\vec{k},\vec{r}), \tag{4.1}$$

where the quantum number $\vec{k}$ and j correspond to the wave vector and the sub band respectively. Using the solution of equation (4.1) it is possible to derive the electronic density $\rho(\vec{r})$, starting from :

$$\rho(\vec{r}) = \sum_j \sum_k^{occup} \left|\psi_j(\vec{k},\vec{r})\right|^2. \tag{4.2}$$

The effective one body potential (spherically symmetric) can be written in terms of the radial part of the electronic density:

$$V_S(r) = -\frac{2Z}{r} + V_H(r) + V_{XC}(\rho(r)), \tag{4.3}$$

in the potentials is included the Hartree and the exchange-correlation potential, they are is defined by:

$$V_H(r) = \int_S d\vec{r}' \frac{2\rho(r')}{|\vec{r}-\vec{r}'|} \tag{4.4}$$

and

$$V_{XC}(r) = \mu_{XC}(\rho(r)) = \mu_{XC}\left(\rho(r), \alpha_1, \alpha_2, \ldots, \alpha_P\right), \tag{4.5}$$

the adopted potential model is defined by α.

Equations (4.1 -4.5) define the self consistent program for the electronic structure. This problem is usually solved within the rigid core approximation. In this approximation only the more external electrons s, p and d are considered; the charge density of the remaining electrons is kept fixed. The core density is obtained from an atomic calculation, taking only account of a renormalization, consistent with the adequate atomic volume. It should be noted however, that this procedure fails in presence of high pressures, since the inner levels overlap with the neighbors, transformed in internal bands. In the case of hyperfine interactions, it is also necessary to introduce modifications of these internal states.

In general, a computer program to solve these equations (4.1- 4.5) should have the following structure:

i. the atomic charge densities are obtained from any method of the Hartree-Fock type;

ii. the projected densities of states and the number of occupied states per atom and per angular momentum l, should be derived from the diagonalization of the Hamiltonian;

iii. the main output of the self consistent program should be the parameters defining the potential.

One of the results extracted from this calculations is for instance the electronic pressure, from which the equilibrium lattice parameter can be derived.

4.1.2 Steps of the self consistent program

First of all let us recall that the radius S of the Wigner-Seitz cell, for a monoatomic material, is given by:

$$\Omega = \vec{a_1}.\,(\vec{a_2} \times \vec{a_3}) = \frac{4\pi}{3} S^3. \tag{4.6}$$

In order to get a trial charge density $\rho_0(r)$ one uses an atomic charge density, renormalised to the volume given by the radius S.

Then one solves the Poisson's equation:

$$\nabla^2 V_H(r) = -8\pi\rho(r) \tag{4.7}$$

using for that, the so obtained charge density. From the solution of Poisson's equation, one obtains the Hartree potential $V_H(r)$. Given this solution, one should add the potential $2Z/r$ associated to the nuclei. The exchange-correlation potential, for a given approximation, is calculated using the charge density $\rho(r)$. Once this part is finished, the potential $V_S(r)$, for a given step of the self consistence is defined.

The third step consists in obtaining the radial wave functions, and with that calculating the corresponding potential parameters. One proceeds through the following steps: i. to solve Dirac's equations, without spin-orbit coupling, using the potential function obtained in the preceding step; ii. using the so obtained solution, one calculates the following potential parameters defined by:

$$\begin{aligned} mS^2 &= \left(S\phi_\nu^2\right)^{-1} && (4.8)\\ a &= -S\phi_\nu\dot{\phi}_\nu && (4.9)\\ b &= S^{-1}\phi_\nu^2\left\langle\dot{\phi_\nu}^2\right\rangle. && (4.10) \end{aligned}$$

Equation(4.8) involves only the wave function, whereas in (4.9) and (4.10) the energy derivative of the solution of the Dirac's equation is required. This derivative is obtained calculating the wave function in two energies $E_\nu + \epsilon$ and $E_\nu - \epsilon$, where ϵ is a convenient and small fraction of the band width.

The fourth step involves the construction of a new charge density, using the obtained solutions $\phi_{\nu l}(r)$ and their first and second energy derivatives; it can be shown that:

$$\begin{aligned} 4\pi\rho(r) &= \sum_l \Bigg[n_l \phi_{\nu l}^2(r) + 2\phi_{\nu l}(r)\dot{\phi}_{\nu l}(r) \int^{E_F} 2N_l(E)\,(E - E_{\nu l})\,dE \\ &\quad + \left(\dot{\phi}_{\nu l}^2(r) + \ddot{\phi}_{\nu l}(r)\phi_{\nu l}(r)\right) \int^{E_F} 2N_l(E)\,(E - E_\nu)^2\,dE + \ldots \Bigg] \end{aligned} \tag{4.11}$$

where $N_l(E)$ is the state density with orbital momentum l and

$$n_l = \int^{E_F} 2N_l(E)dE, \tag{4.12}$$

the factor 2 occurs for spin.

The program should then at this step, to be able of calculating this density of states, the Fermi level and the moments of the density of states.

It remains to know if self consistency is obtained. It should be noted that energy E_ν was introduced in a not very precise way; this energy being chosen by imposing $E\nu$ around the center of the band. The self consistency is made, starting from the moments of the occupation number $N(E)$, since these give an idea of the occupied part of the band.

Self consistence: the first order moment, if imposed to be zero, defines the center of gravity of the band.

4.2 The recursive method: general formulation

4.2.1 Notation

Let us start with some general considerations. First of all a technical detail: in order to get a programmable theory, one should have a finite basis. The computer is a discrete and finite machine.

A discrete basis is defined by a set of wave functions not necessarily orthogonal; if $\vec{r}$ are the coordinates of the system:

$$\{\phi_0(\vec{r}), \phi_1(\vec{r}), \phi_2(\vec{r}), \ldots, \phi_N(\vec{r}), \ldots\}\,, \qquad N finite. \tag{4.13}$$

The states of the system are represented by column vectors. A given arbitrary u state of the system is represented by a column vector with the elements $u_0, u_1, u_2, \ldots u_N, \ldots$

in the form:

$$u = \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \vdots \\ u_N \end{bmatrix}. \tag{4.14}$$

Using the basis, as defined in (4.13) we can construct the wave function associated to the state u:

$$u(\vec{r}) = \sum_{n=0}^{N} u_n \phi_n(\vec{r}). \tag{4.15}$$

Linear operators A are represented by matrices. Using the basis (4.13) to represent any operator A, the matrix is given by:

$$a_{mn} = \int d\vec{r} \phi_m^*(\vec{r}) \mathbf{A} \phi_n(\vec{r}), \tag{4.16}$$

where the integration is performed in all coordinate space. If **A** is the Hamiltonian we introduce:

$$H u_\alpha = E_\alpha u_\alpha, \tag{4.17}$$

where α is an index defining the quantum numbers associated to the problem.

Definition of the adjoint operator, of state, in this context (superscript $\dagger$).

The state u has an adjoint $u^\dagger$ defined by the line vector with the elements u_i^*:

$$u^\dagger = \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \vdots \\ u_N \end{bmatrix}^\dagger \equiv [u_0^*, u_1^*, u_2^*, \ldots] \tag{4.18}$$

Note that line and column vectors can be interchanged (the adjoint of a line vector is a column vector); consequently $\left(u^\dagger\right)^\dagger = u$.

The operator **A** has an adjoint $\mathbf{A}^\dagger$, such that the corresponding matrix is the transpose, complex conjugate of the matrix associated to **A**; then again $\left(A^\dagger\right)^\dagger = A$.

Definition of the overlap: starting from two states u and v we can define the scalar s:

$$s = v^\dagger u = [v_0^*, v_1^*, v_2^*, \ldots] \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \vdots \end{bmatrix}. \tag{4.19}$$

This correspond to multiply a line vector by a column vector. The adjoint of a product is the product of the adjoints in the inverse order $(v^\dagger u)^\dagger = u^\dagger v$.

4.2.2 Hamiltonian and orthogonality

In general, the basis constituted by the $\phi_n(\vec{r})$ is not necessarily orthogonal,

$$\int \phi_m^*(\vec{r})\phi_n(\vec{r})d\vec{r} \neq 0. \tag{4.20}$$

It should be noted that, to construct an orthogonal basis is not very useful since the orthogonalization process destroy the simple idea of orbitals located at each atom, chemical neighborhood and other simple concepts.

Thus we introduce the overlap matrix S, in the chosen basis via:

$$(S)_{mn} = \int d\vec{r}\phi_m^*(\vec{r})\phi_n(\vec{r}). \tag{4.21}$$

We then define the internal product of physical overlap of two states by $v^\dagger Su$. This is connected to overlap between wave functions as written in the chosen basis:

$$\int d\vec{r}v^*(\vec{r})u(\vec{r}) = \sum_{m,n} v_m^* u_n \int d\vec{r}\phi_m^*(\vec{r})\phi_n(\vec{r}) = \sum_{m,n} v_m^* S_{mn} u_n = v^\dagger Su \tag{4.22}$$

This expression relates the overlap of two states with the overlaps of the basis orbitals. Note that $v^\dagger u$ is not a physical overlap; this is just a formal sum. Two states are orthogonal if they are physically orthogonal:

$$v^\dagger Su = 0 \tag{4.23}$$

Matrix representation for the Hamiltonian operator. Let H be the Hamiltonian operator. If H acts in an orbital of the $\phi_n(\vec{r})$ basis, then the result is a linear combination of the elements of that basis. One has then:

$$H\phi_n(\vec{r}) = \sum_{m=0}^{\infty} H_{mn}\phi_m(\vec{r}), \tag{4.24}$$

where H_{mn} is the Hamiltonian matrix. Note that the Hamiltonian matrix or the parameters H_{mn}, should not be identified in general with the matrix elements of the Hamiltonian H defined by:

$$\mathbf{H}_{mn} = \int d\vec{r}\phi_m^*(\vec{r})H\phi_n(\vec{r}). \tag{4.25}$$

The overlap matrix S relates H_{mn} through:

$$\mathbf{H}_{mn} = [SH]_{mn}. \tag{4.26}$$

The proof is made following the usual way, combining (4.24) and (4.25):

$$\begin{aligned} \mathbf{H}_{mn} &= \int d\vec{r}\phi_m^*(\vec{r})H\phi_n(\vec{r}) = \int d\vec{r}\phi_m^*(\vec{r})\left[H\phi_n(\vec{r})\right] \\ &= \int d\vec{r}\phi_m^*(\vec{r})\left[\sum_l H_{ln}\phi_l(\vec{r})\right] = \sum_l \left[\int d\vec{r}\phi_m^*(\vec{r})\phi_l(\vec{r})\right] H_{ln} \\ &= \sum_l S_{ml}H_{ln} = [SH]_{mn}. \end{aligned} \tag{4.27}$$

Then:

$$\mathbf{H}_{mn} = [SH]_{mn} \tag{4.28}$$

Note that in the case of orthogonal basis there is no difference because $S_{mn} = \int \phi^*_m \phi_n d\vec{r} = \delta_{mn} = [I]_{mn}$ and one has $\mathbf{H}_{mn} = H_{mn}$.

It remains to make some comments about the overlap matrix S: this matrix is self adjoint, since:

$$S^\dagger_{nm} = S^*_{mn} = \left[\int \phi^*_m(\vec{r})\phi_n(\vec{r})d\vec{r}\right]^* = \int \phi^*_n(\vec{r})\phi_m(\vec{r})d\vec{r} = S_{nm} \tag{4.29}$$

Consequently $S^\dagger = S$. Also one has $H^*_{mn} = H_{mn}$.

4.2.3 The chain model

Theorem: any quantum system can be transformed in *one or several* one dimensional pseudo chains and then solved. The reason for that is based in the fact that any matrix can be transformed into a tri-diagonal matrix (also called the Jacobi matrix). To perform this program, let us introduce two definitions.

Definition 1 A quantum model is defined by An Hamiltonian and a set of orbitals over which the Hamiltonian acts and a physical interpretation of these orbitals. The Hamiltonian describes the motion of the system through the tunneling between orbitals, it is always assumed to be hermitian and the overlaps are defined by an hermitian matrix.

Definition 2 The chain model is defined in the following way: a sequence of orthonormal orbitals: $[u_0, u_1, \ldots, u_n, \ldots]$. Two sequences of real parameters: $[a_0, a_1, a_2, \ldots][b_1, b_2, b_3,$ The orbitals and the parameters describe the action of the Hamiltonian through the recursive formula:

$$Hu_n = a_n u_n + b_{n+1}u_{n+1} + b_n u_{n-1}. \tag{4.30}$$

Since the u_n are orthonormal, one can deduce the component of the u_{n+1} in the recursion formula through $b_{n+1} = u^\dagger_{n+1}Hu_n$. The recursion relation gives also:

$$Hu_{n+1} = a_{n+1}u_{n+1} + b_{n+2}u_{n+2} + b_{n+1}u_n. \tag{4.31}$$

The component of u_n in Hu_{n+1} is b_{n+1}; then $b_{n+1} = u^\dagger_n Hu_{n+1}$.

In conclusion: the chain is symmetric, namely $u^\dagger_{n+1}Hu_n = u^\dagger_n Hu_{n+1}$.

This result presents a certain similarity with the hermiticity property. Another result is:

$$u^\dagger_n S u_m = \delta_{nm}. \tag{4.32}$$

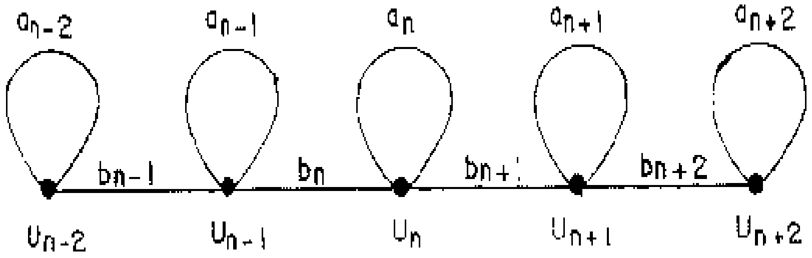


Figure 4.1 Pictorical representaion of the action of the Hamiltonian

A sequence of orbitals $u_0, u_1, \ldots, u_N, \ldots$ may be finite or infinite. In the case of finite sequence the orbitals u_{-1} and u_{N+1} are taken equal to zero.

A graphical representation of the chain is the following: the orbitals are represented by the vertices and the Hamiltonian is represented by the connections between vertices. The loop corresponds the a component associated to the vertex, due to the application of Hamiltonian, figure 4.1.

Formally one has:

$$\begin{aligned} Hu_0 &= a_0u_0 + b_1u_1; \qquad u_{-1} = 0 && (4.33)\\ Hu_1 &= a_1u_1 + b_2u_2 + b_1u_0 && (4.34)\\ Hu_2 &= a_2u_2 + b_3u_3 + b_2u_1, && (4.35)\end{aligned}$$

and so on.

Equivalence between the chain model and the Jacobi matrix

To demonstrate that, let us introduce a representation for the state u_n: this is a column vector with all the components equal to zero except the n-th:

$$u_n = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix}. \tag{4.36}$$

We use the formal definitions (4.35) to calculate the matrix elements:

$$u_m^{\dagger}Hu_0 = a_0u_m^{\dagger}u_0 + b_1u_m^{\dagger}u_1. \tag{4.37}$$

Two non vanishing elements are $H_{00} = a_0$ and $H_{10} = b_1$. The terms of the second line of the matrix are given bay:

$$u_m^{\dagger}Hu_1 = a_1u_m^{\dagger}u_1 + b_2u_m^{\dagger}u_2 + b_1u_m^{\dagger}u_0, \tag{4.38}$$

there are three non vanishing elements: $H_{01} = b_1$, $H_{11} = a_1$ and $H_{21} = b_2$. The third line is given by:

$$u_m^\dagger H u_2 = a_2 u_m^\dagger u_2 + b_3 u_m^\dagger u_3 + b_2 u_m^\dagger u_1. \tag{4.39}$$

There are also three non vanishing elements: $H_{22} = a_2$, $H_{12} = b_2$ and $H_{32} = b_3$. Then:

$$[H] = \begin{bmatrix} a_0 & b_1 & 0 & 0 & \dots \\ b_1 & a_1 & b_2 & 0 & \dots \\ 0 & b_2 & a_2 & b_3 & \dots \\ 0 & 0 & b_3 & a_3 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \tag{4.40}$$

4.2.4 Physical interpretation of the chain model

Let us start from equations (4.33 - (4.35); let u_0 be the initial state of the system, for example: one electron in the orbital of the central atom. This electron makes a transition to another orbital u_1. The orbital u_1 may be a linear combination of orbitals in neighboring atoms. Once the electron lies in orbitals u_1, two possibilities may occur: or the electron hops to the orbital u_2, more extended, or can back to the first one.

4.2.5 Formal aspects of the tranformation of the chain model

First of all let us choose the initial state u_0; this choice determines the physics of the problem. To each choice for u_0 it corresponds a different chain. We take then the u_0 that contains the relevant information for the problem of interest. Secondly we recall the definition of the internal product:

$$(v, u) = v^\dagger S u, \tag{4.41}$$

where S is the overlap matrix of the considered basis. Thirdly, the starting state u_0 should satisfy the following requirement:

$$u_0^\dagger \left(SH\right)^n u_0 < \infty, \tag{4.42}$$

for any finite value of n. The physical interpretation of this equation is that the high energy components of u_0 should quickly decrease by applying H. Let us suppose that the starting state is normalized:

$$u_0^\dagger S u_0 = 1. \tag{4.43}$$

We now build up a vector u_1, as closed as possible to u_0, using the recursion (4.30) and imposing $u_{-1} = 0$.

$$H u_0 = a_0 u_0 + b_1 u_1 \tag{4.44}$$

If we impose the orthonormality condition we determine a_0:

$$u_0^\dagger SHu_0 = a_0 u_0^\dagger Su_0 + b_1 u_0^\dagger Su_1, \tag{4.45}$$

the first term is one and the second is zero, both by orthonormality. In conclusion:

$$a_0 = u_0^\dagger SHu_0 \tag{4.46}$$

and from (4.44):

$$b_1 u_1 = (H - a_0 I)u_0. \tag{4.47}$$

In order to determine the value of b_1, let us impose the u_1 state is normalized ($u_1^\dagger Su_1 = 1$). Multiplying equation (4.47) on the left by $b_1 u_1^\dagger S$, one gets:

$$b_1 u_1^\dagger S b_1 u_1 = b_1^2 u_1^\dagger Su_1 = \left[(H - a_0 I)\, u_0\right]^\dagger S \left[(H - a_0 I)\, u_0\right], \tag{4.48}$$

then by the normalization condition:

$$b_1^2 = \left[(H - a_0 I)\, u_0\right]^\dagger S \left[(H - a_0 I)\, u_0\right]. \tag{4.49}$$

One should note b_1^2 is larger or equal to zero, since the scalar product is positively defined. If b_1 is different from zero, we take the positive root of (4.49), and we get from (4.47):

$$u_1 = (H - a_0 I)u_0 / b_1. \tag{4.50}$$

In conclusion u_1 is normalized and we can verify using (4.50) that u_1 is orthogonal to u_0. In fact:

$$u_0^\dagger Su_1 = \frac{1}{b_1} u_0^\dagger S(H - a_0 I)u_0 = \frac{1}{b_1}\left[u_0^\dagger SHu_0 - a_0 u_0^\dagger Su_0\right] = 0, \tag{4.51}$$

where we have used equation (4.46).

In this way we have constructed the first recurrence of the chain.

Let us suppose we have constructed the orthonormal states $[u_0, u_1, \ldots, u_n]$ and obtained the corresponding parameters $[a_0, a_1, \ldots, a_{n-1}]$ and $[b_1, b_2, \ldots, b_n]$. Let us make the assumption that any one of the b_j is zero. Now we intend to construct u_{n+1}, a_n and b_{n+1} using the recursion:

$$Hu_n = a_n u_n + b_{n+1} u_{n+1} + b_n u_{n-1}. \tag{4.52}$$

Introducing the overlap matrix S:

$$SHu_n = a_n Su_n + b_{n+1} Su_{n+1} + b_n Su_{n-1}. \tag{4.53}$$

Now we perform the internal product with $u_{n-1}^{\dagger}$; we impose orthogonality and using the *previous construction* $u_{n-1}^{\dagger}Su_{n-1}=1$, then:

$$u_{n-1}^{\dagger}SHu_n = a_n u_{n-1}^{\dagger}Su_n + b_{n+1}u_{n-1}^{\dagger}Su_{n+1} + b_n. \tag{4.54}$$

Using orthogonality condition, one gets:

$$b_n = u_{n-1}^{\dagger}SHu_n. \tag{4.55}$$

It should be noted that this b_n was obtained starting from (4.52); alternatively we can use the preceding recurrence:

$$Hu_{n-1} = a_{n-1}u_{n-1} + b_n u_n + b_{n-1}u_{n-2}, \tag{4.56}$$

in this case:

$$b_n = u_n^{\dagger}SHu_{n-1}. \tag{4.57}$$

It remains to show that the two b_n are identical. To do that we start from (4.55) and use the fact SH is self adjoint: $[SH]^{\dagger} = SH = H^{\dagger}S$. The qualitative proof is the following:

$$\begin{aligned} u_{n-1}^{\dagger}SHu_n &= u_{n-1}^{\dagger}H^{\dagger}Su_n = \left[Hu_{n-1}\right]^{\dagger}Su_n \\ &= \left[Hu_{n-1}\right]^{\dagger}\left[u_n^{\dagger}S\right]^{\dagger} = \left[u_n^{\dagger}SHu_{n-1}\right]^{\dagger}. \end{aligned} \tag{4.58}$$

The first term on the left was calculated in the new recurrence and the last one is calculated in the previous recurrence.

Then in expression (4.52) we have the term b_n as constructed from the previous recurrence; it remains only to calculate a_n and b_{n+1} to obtain the new state. The calculation of a_n goes has follows:

$$u_n^{\dagger}SHu_n = a_n u_n^{\dagger}Su_n + b_{n+1}u_n^{\dagger}Su_{n+1} + b_n u_n^{\dagger}Su_{n-1}, \tag{4.59}$$

since the last two terms are zero due to orthogonality and the first one is a_n one gets:

$$a_n = u_n^{\dagger}SHu_n. \tag{4.60}$$

Remember that u_n was obtained in the preceding recurrence. Now we construct the new state u_{n+1} starting from (4.52)

$$b_{n+1}u_{n+1} = (H - a_n I)u_n - b_n u_{n-1}. \tag{4.61}$$

Again if we impose that u_{n+1} is normalized, one gets then:

$$b_{n+1}^2 u_{n+1}^{\dagger}Su_{n+1} = b_{n+1}^2 = \left[(H-a_nI)u_n - b_nu_{n-1}\right]^{\dagger} S \left[(H-a_nI)u_n - b_nu_{n-1}\right], \tag{4.62}$$

this defines the quantity b_{n+1}, because the quantities on the right side have been calculated in the preceding recurrence.

4.2.6 Expansion in continuous fractions

Using the Jacobi form for the matrix H we write the matrix:

$$E - H = \begin{bmatrix} E-a_0 & -b_1 & 0 & \dots \\ -b_1 & E-a_1 & -b_2 & \dots \\ 0 & -b_2 & E-a_2 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{matrix} D_0 \\ D_1 \\ D_2 \\ \vdots \end{matrix} \tag{4.63}$$

Since we need the resolvent to obtain the density of states, let us calculate:

$$G =< \mu_0 \mid [E-H]^{-1} \mid \mu_0 >= \frac{\det \mid D_1 \mid}{\det \mid D_0 \mid} = \frac{1}{\frac{\det|D_0|}{\det|D_1|}}, \tag{4.64}$$

considering that the determinant D_0 as a functions of minor determinants id given by:

$$\det \mid D_0 \mid = (E-a_0) \det \mid D_1 \mid - b_1^2 \det \mid D_2 \mid, \tag{4.65}$$

then the Green functions is:

$$G = \frac{1}{E - a_0 - b_1^2 \frac{\det|D_2|}{\det|D_1|}} = \frac{1}{E - a_0 - b_1^2 \frac{1}{\frac{\det|D_1|}{\det|D_2|}}}. \tag{4.66}$$

In general one has:

$$\frac{\det \mid D_n \mid}{\det \mid D_{n+1} \mid} = E - a_n - \frac{b_{n+1}^2}{\frac{\det|D_{n+1}|}{\det|D_{n+2}|}}. \tag{4.67}$$

This equation furnishes naturally the expansion in continuous fractions as:

$$G = \cfrac{1}{E - a_0 - \cfrac{b_1^2}{E - a_1 - \cfrac{b_2^2}{E - a_2 - \cfrac{b_3^2}{\dots}}}}. \tag{4.68}$$

4.3 Theoretical basis of the LMTO method

4.3.1 The concept of muffin tin orbitals

Let us start defining the energy independent muffin tin orbitals (MTO) $\chi^\alpha_{RL}(\vec{r}_R)$, these orbitals are characterized by angular momentum with indices $L = (l, m)$. They are centered in sites R of the lattice of the material. In the general α representation, the *MTO* are defined by:

$$\chi^\alpha_{RL}(\vec{r}_R) = \varphi_{RL}(\vec{r}_R) + \sum_{R'L'} \dot{\varphi}^\alpha_{RL}(\vec{r}_{R'}) h^\alpha_{R'L',RL} + K^{\alpha,i}_{RL}(\vec{r}_R), \tag{4.69}$$

with

$$\dot{\varphi}^{\alpha}_{RL}(\vec{r}_{R'}) = \dot{\varphi}_{RL}(\vec{r}_{R'}) + \varphi_{RL}(\vec{r}_{R'})o^{\alpha}_{RL}, . \tag{4.70}$$

In this definition $\varphi_{RL}(\vec{r}_R) = \varphi_{RL}(r_R)Y(\hat{r}_R)$, where $Y(\hat{r}_R)$ are the spherical harmonics and the vector $\vec{r}_R$ is $\vec{r} - \vec{R}$, $r_R =\mid \vec{r}_R \mid$ with $\hat{r}_R = \vec{r}_R / \mid \vec{r}_R \mid$. The other quantities in (4.69)will be now systematically defined. The function $\varphi_{RL}(\vec{r}_R)$ is the solution of the scalar relativistic Schrödinger radial equation for a given potential $V_R(\vec{r}_R)$; usually this potential is determined within the local density formalism. A very traditional approximation used in most cases is the von Barth-Hedin. The adopted value of the energy $E_{\gamma RL}$ is usually taken as the center of the energy interval of interest.

The function $\varphi_{RL}(\vec{r}_R)$ is normalized to unity within a sphere centered at $\vec{R}$ and with radius s_R,

$$\int_0^{s_R} |\varphi_{RL}(\vec{r}_R)|^2 r_R^2 dr_R = 1. \tag{4.71}$$

The function $\dot{\varphi}_{RL}(\vec{r}_R)$ is the energy derivative of the wave function ($\dot{\varphi} = \frac{\partial\varphi}{\partial E}$), again calculated at the energy $E_{\gamma RL}$. The quantity o^{α}_{RL} in equation (4.70) is the mixing amplitude of the wave function φ_{RL} with its derivative $\dot{\varphi}_{RL}$, ($o^{\alpha}_{RL} = \langle\varphi_{RL}|\dot{\varphi}_{RL}\rangle$). The amplitude of the energy derivative of the wave function is defined by $p_{RL} = \langle\dot{\varphi}_{RL}|\dot{\varphi}_{RL}\rangle$. The function $K^{\alpha,i}_{RL}(\vec{r}_R)$ in (4.69) is the contribution to the MTO arising from the interstitial region. Finally, the matrix $h^{\alpha}_{R'L',RL}$, connects functions centered at different sites; this function is determined in such a way that the wave function (4.69) is continuous with continuous derivative at the surface of radius s_R. The explicit form will be demonstrated at the end of these general considerations and it turns out to be:

$$h^{\alpha}_{RL,R'L'} = \left(C^{\alpha}_{RL} - E_{\gamma RL}\right)\delta_{RR'}\delta_{LL'} + \left(\Delta^{\alpha}_{RL}\right)^{1/2} S^{\alpha}_{RL,R'L'} \left(\Delta^{\alpha}_{R'L'}\right)^{1/2}, \tag{4.72}$$

In the expression (4.72) $S^{\alpha}_{RL,R'L'}$ are the site and angular momentum matrix elements of the structure matrix S^{α} in the representation MTO-α. Δ^{α} and C^{α} are the potential parameters which, together with the mixing amplitude o^{α}_{RL}, can be expressed by the potential function P^{α}_{RL} and their energy derivatives $\dot{P}^{\alpha}_{RL}$ e $\ddot{P}^{\alpha}_{RL}$, always calculated at the energy $E_{\gamma RL}$. These relations are made explicit at the and of these general considerations. These relations are:

$$\begin{aligned}
(\Delta^{\alpha}_{RL}) &= \left[\dot{P_{RL}}^{\alpha}(E_{\gamma RL})\right]^{-1}, \\
C^{\alpha}_{RL} - E_{\gamma RL} &= -\frac{P^{\alpha}_{RL}(E_{\gamma RL})}{\dot{P_{RL}}^{\alpha}(E_{\gamma RL})}, \\
o^{\alpha}_{RL} &= \frac{\ddot{P_{RL}}^{\alpha}(E_{\gamma RL})}{2\dot{P_{RL}}^{\alpha}(E_{\gamma RL})}.
\end{aligned} \tag{4.73}$$

The potential function in the α representation $P^{\alpha}_{RL}(E)$ are expressed in terms of the conventional potential function $P^{0}_{RL}(E)$ and of the elements α_{RL} of the matrix defining the representation MTO-α. Such a relation is obtained and discussed in more detail also at the end of these considerations. One has:

$$P^{\alpha}_{RL}(E) = \frac{P^{0}_{RL}(E)}{1 - \alpha_{RL} P^{0}_{RL}(E)}. \tag{4.74}$$

The quantities $P^{0}_{RL}(E)$ have a direct physical interpretation. They are proportional to the cotangents of the phase shifts associated to the potentials $V_R(\vec{r}_R)$ of the sphere centered at R. An interesting point is that a parametrization of the functions $P^{0}_{RL}(E)$, can be made in a broad spectrum of energies. This is made in terms of the centers C_{RL}, in terms of the width Δ_{RL} and of the form γ_{RL} of the bands. As shown at the end of these considerations the parametrized form of the potential function is:

$$P^{0}_{RL}(E) = \frac{E - C_{RL}}{\Delta_{RL} + \gamma_{RL}(E - C_{RL})}. \tag{4.75}$$

The quantities C_{RL}, Δ_{RL} and γ_{RL} are often called potential parameters, and are characteristic of the atom occupying site R with orbital L. These potential parameters can be understood as the diagonal elements of the diagonal matrices C, Δ and γ.

These potential functions can be written in another general representations β using the transformation formula:

$$P^{\beta}_{RL}(E) = \frac{P^{0}_{RL}(E)}{1 - \beta_{RL} P^{0}_{RL}(E)}, \tag{4.76}$$

The connection between the potential functions in representations α and β, that is the transformation rule, enables to obtain a given function in terms of the corresponding in another representation. This is done by eliminating $P^{0}_{RL}(E)$ in equations (4.74) and (4.76); the result is:

$$P^{\alpha}_{RL}(E) = \frac{P^{\beta}_{RL}(E)}{1 - (\alpha_{RL} - \beta_{RL}) P^{\beta}_{RL}(E)}. \tag{4.77}$$

The crystal lattice enters the theory through the structure constant S^{α}, defined in terms of the canonical structure constant S^{0}:

$$S^{\alpha}_{RL,R'L'} = \left[S^{0} \left(1 - \alpha S^{0} \right)^{-1} \right]_{RL,R'L'}. \tag{4.78}$$

The matrix elements $S^{\alpha}_{RL,R'L'}$, depend only on R/ω and R'/ω, where R and R' are the atomic positions and ω is the averaged Wigner-Seitz (WS) radius of the solid. The structure constant S^{0} depends only on the geometry of the lattice, independent of the atomic occupation of the several sites by different atoms. The matrix $S^{0}_{RL,R'L'}$ is given in general form by Slater and Koster. Taking the z axes in the $\vec{R}-\vec{R}'$ directions, this matrix is given by

$$S^0_{l,l'm} = (-1)^{l+m+1}(l'+l)!2\left[\frac{(2l'+1)(2l+1)}{(l'+m)!(l'-m)!(l+m)!(l-m)!}\right]^{1/2}\left(\frac{w}{d}\right)^{l'+l+1}. \quad (4.79)$$

As the equation (4.79) indicates, $S^0_{RL,R'L'}$ behaves as a power law of the type $(\frac{\omega}{d})^{l+l'+1}$, where $d = |R-R'|$. For small values of the angular momentum ($l = 0$ or 1) , S^0 has a long range on real space. Considering the $l = 0$, s band, the canonical structure matrix S^0 is $S^0(d) = -2w/d$; in reciprocal space the matrix in this case is $S^0(k) = -6/(wk)^2$. The same matrix element in other representation defined by (4.78), is given by:

$$S^\alpha(k) = \frac{-\frac{6}{(wk)^2}}{1+\alpha\frac{6}{(wk)^2}} = \frac{-6}{(wk)^2+6\alpha}, \quad (4.80)$$

The inverse Fourier transform implies in:

$$S^\alpha(d) = (-2w/d)e^{-\sqrt{6\alpha}d/w}. \quad (4.81)$$

This result shows that the quantities, $S^\alpha_{RL,R'L'}$ behaves like $e^{-(\lambda^\alpha_{ll'})d/\omega}$, where $\lambda^\alpha_{ll'}$ depends on the representation. Numerical studies have shown that for compact lattices, a representation exists in which S has rapid monotonic decay in real space. This representation, called the MTO-β or localized representation, is site independent, but angular momentum dependent and is defined by:

$$\beta_s = 0,3485; \quad \beta_p = 0,05303; \quad \beta_d = 0,010714 \quad and \quad \beta_l = 0 \quad for \quad l > 2. \quad (4.82)$$

For compact crystal structures S^β vanishes for distances larger than the second neighbors, and consequently the values wave function χ^β_{RL} is localized in real space. On the contrary the conventional function χ^0_{RL} is long ranged.

For the structure constant, in a way similar to the potential function, a transformation rule can be shown to exist between different representation. The proof is quite similar to that used in the proof of (4.77) and one gets the result:

$$S^\alpha = S^\beta\left[1-(\alpha-\beta)\,S^\beta\right]^{-1}. \quad (4.83)$$

This equation connects the structure matrix S^α with the β representation S^β.

4.3.2 Hamiltonian of the system

The scalar relativistic Schrödinger equation for the solid is solved taking for $\psi^\alpha(\vec{r})$ a linear combination of MTO wave functions,

$$\psi^\alpha(\vec{r}) = \sum_{\vec{R},L}\xi^\alpha_{RL}\chi^\alpha_{RL}(\vec{r}_R). \quad (4.84)$$

The variational or Ritz method furnishes the eigenvectors ξ^{α}_{RL} and the energy eigenvalues from the equation:

$$\sum_{R,L}\left(H^{\alpha}_{RL,R'L'} - EO^{\alpha}_{RL,R'L'}\right)\xi^{\alpha}_{RL} = 0. \tag{4.85}$$

Note that the matrix elements of H^{α} and O^{α} are energy independent. Equation (4.85) is a classical equation of eigenvalues for the energy E, and (4.85) is main equation for the linear muffin tin orbital method (LMTO). In this method the basis set is composed by the MTO and the energy E appears only explicitly.

The overlap matrix $O^{\alpha}_{RL,R'L'} = \langle\chi^{\alpha}_{RL}|\chi^{\alpha}_{R'L'}\rangle$ is easily obtained substituting the wave functions (4.69) and assuming $\langle\dot{\chi}^{\alpha}_{RL}|\dot{\chi}^{\alpha}_{R'L'}\rangle = 0$, one gets the result:

$$O^{\alpha} = (1 + o^{\alpha}h^{\alpha})(h^{\alpha}o^{\alpha} + 1) + h^{\alpha}ph^{\alpha} + \langle k^{\alpha,i}|k^{\alpha,i}\rangle. \tag{4.86}$$

The Hamiltonian matrix is defined by:

$$H^{\alpha}_{RL,R'L'} = \langle\chi^{\alpha}_{RL}| - \nabla^2 + V(r)\,|\chi^{\alpha}_{R'L'}\rangle\,, \tag{4.87}$$

and, using again the wave function (4.69), one obtains:

$$H = h^{\alpha}+h^{\alpha}o^{\alpha}h^{\alpha}+(1+h^{\alpha}o^{\alpha})E_{\gamma}(o^{\alpha}h^{\alpha}+1)+h^{\alpha}E_{\gamma}ph^{\alpha}+\langle k^{\alpha,i}|-\nabla^2+V(r)|k^{\alpha,i}\rangle. \tag{4.88}$$

In (4.88) h^{α} is the matrix defined in (4.72), o^{α} and E_{γ} are diagonal matrices with elements defined in (4.73) and p is the diagonal matrix of elements $p_{RL} = \langle\dot{\varphi}_{RL}|\dot{\varphi}_{RL}\rangle$. The last term in (4.86) and in (4.87) arise from the interstitial region.

Within the muffin tin (MT) approximation the interstitial region is well described since the potential is constant and spherically symmetric. The simples way to introduce the interstitial region is via the atomic sphere approximation (ASA). This simplifies also the solution of the eigenvalue equation (4.85). The ASA approximation consists in replacing the MT spheres by Wigner-Seitz spheres, consequently introducing superpositions. The ASA furnishes a good description of the electronic structure if the WS spheres superpose in such a way that its overlap contains almost all electrons of the interstitial region. The validity of the approximation is given for an intersection less than 30%,

$$\frac{|s_R + s_{R'} - d|}{d} < 0,3, \tag{4.89}$$

where d $(= |R - R'|)$ is the distance between the centers of WS spheres which are next neighbors. For compact structures this condition is normally satisfied.

Using the atomic sphere approximation in equations (4.86) and (4.88) the last term vanishes in both equations, and considering also that the P_{RL} quantity is a small parameter in LMTO theory, one gets:

$$\begin{aligned} O^{\alpha} &= (1+o^{\alpha}h^{\alpha})(h^{\alpha}o^{\alpha}+1) && (4.90)\\ H &= h^{\alpha}(1+o^{\alpha}h^{\alpha})+(1+h^{\alpha}o^{\alpha})E_{\gamma}(o^{\alpha}h^{\alpha}+1). && (4.91)\end{aligned}$$

A very simple representation for these equations is obtained when α_{RL} is given by the potential parameter γ_{RL}; in this representation the potential function is given by:

$$P^{\gamma}_{RL}=\frac{(E-C_{RL})}{\Delta_{RL}}. \tag{4.92}$$

Given this function and using (4.73), one gets $C^{\gamma}_{RL}=C_{RL}$, $\Delta^{\gamma}_{RL}=\Delta_{RL}$ and $o^{\gamma}_{RL}=0$. In this case the function H^{γ} and O^{γ} have the form:

$$H^{\gamma}=h^{\gamma}+E_{\gamma}, \qquad O^{\gamma}=1. \tag{4.93}$$

Since the overlap vanishes, this particular representation is called the orthogonal representation. In this case one obtains finally:

$$\begin{aligned} H^{\gamma}_{RL,R'L'} &= C_{RL}\delta_{RR'}\delta_{LL'}+\Delta^{1/2}_{RL}S^{\gamma}_{RL,R'L'}\Delta^{1/2}_{R'L'} && (4.94)\\ O^{\gamma}_{RL,R'L'} &= \delta_{RR'}\delta_{LL'} && (4.95)\\ S^{\gamma}_{RL,R'L'} &= \left[S^{0}\left(1-\gamma S^{0}\right)^{-1}\right]_{RL,R'L'}. && (4.96)\end{aligned}$$

In the first principles Hamiltonian (4.94), hopping is associated to the structural terms (S^{γ}) and on the potential parameters characteristic of the WS spheres. These in turns are obtained from the solution of the scalar relativistic equation. The possibility of separation the structural part from that depending on the particular site occupation enables the application of this method in the description of disordered systems using the classical approximation of the coherent potential approximation (CPA).

4.3.3 The Green's function

In the determination of the electronic structure the adequate technique is the one-electron Green's function (or resolvent). The Green's function (GF) associated to a given Hamiltonian is defined as:

$$G_{RL,R'L'}(z)=\left[(z-H^{\gamma})^{-1}\right]_{RL.R'L'}, \tag{4.97}$$

where z is the complex energy. If in (4.97) we introduce the Hamiltonian (4.94) and consider the orthogonal representation of the potential function given in (4.92), one gets:

$$G_{RL,R'L'}(z)=\Delta^{-1/2}_{RL}\left[(P^{\gamma}(z)-S^{\gamma})^{-1}\right]_{RL,R'L'}\Delta^{-1/2}_{R'L'}, \tag{4.98}$$

when the notation $P^{\gamma}(z)$ corresponds in (4.92) to replace E by z.

It is possible to express $G(z)$ in other representation. Due to the importance in passing, from one representation for $G(z)$ to another, let us present the proof in some detail.

Let us start from (4.98) in the matrix notation:

$$G = \Delta^{-1/2} \left[P^{\gamma} - S^{\gamma}\right]^{-1} \Delta^{-1/2}, \tag{4.99}$$

Using the relation (4.83)between S^{γ} and S^{α} one gets:

$$G = \Delta^{-1/2} \left[P^{\gamma} - S^{\alpha} \left[1 - (\gamma - \alpha) S^{\alpha}\right]^{-1}\right]^{-1} \Delta^{-1/2}. \tag{4.100}$$

After some algebraic transformations and again using the representations transform $\frac{P^{\alpha}}{P^{\gamma}} = [1 + (\gamma - \alpha) P^{\gamma}]^{-1}$, one has:

$$G = \Delta^{-1/2} \left[1 - (\gamma - \alpha) S^{\alpha}\right] \left[P^{\alpha} - S^{\alpha}\right]^{-1} \frac{P^{\alpha}}{P^{\gamma}} \Delta^{-1/2}. \tag{4.101}$$

Introduce the auxiliary GF:

$$g^{\alpha}(z) = \left[P^{\alpha}(z) - S^{\alpha}\right]^{-1}, \tag{4.102}$$

one obtains the following scaling law between G and g:

$$G = \Delta^{-1/2} (\gamma - \alpha) \frac{P^{\alpha}}{P^{\gamma}} \Delta^{-1/2} + \Delta^{-1/2} \frac{P^{\alpha}}{P^{\gamma}} g^{\alpha} \frac{P^{\alpha}}{P^{\gamma}} \Delta^{-1/2}. \tag{4.103}$$

In terms of matrix elements of G, one has:

$$\begin{aligned} G_{RL,R'L'} \quad = \quad & \Delta_{RL}^{-1/2} \left(\gamma_{RL} - \alpha_{RL}\right) \left(\frac{P^{\alpha}}{P^{\gamma}}\right)_{RL} \Delta_{RL}^{-1/2} \delta_{RR'} \delta_{LL'} + \\ & + \Delta_{RL}^{-1/2} \left(\frac{P^{\alpha}}{P^{\gamma}}\right)_{RL} g^{\alpha}_{RL,R'L'} \left(\frac{P^{\alpha}}{P^{\gamma}}\right)_{R'L'} \Delta_{R'L'}^{-1/2}. \end{aligned} \tag{4.104}$$

Introduce now the auxiliary variable:

$$D = \Delta_{RL}^{-1/2} \left(\frac{P^{\alpha}}{P^{\gamma}}\right)_{RL}, \tag{4.105}$$

combining the relation (4.77) and the orthogonal representation of the potential:

$$\left(\frac{P^{\alpha}}{P^{\gamma}}\right)_{RL} = \frac{\Delta_{RL}}{\Delta_{RL} - (\alpha_{RL} - \gamma_{RL})(z - C_{RL})}, \tag{4.106}$$

then:

$$D = \frac{\Delta_{RL}^{1/2}}{\Delta_{RL} + (\gamma_{RL} - \alpha_{RL})(z - C_{RL})}. \tag{4.107}$$

In a similar way one gets the first term of (4.104) as $D/\Delta^{1/2}$. Introducing in the above equation, one finally gets:

$$G_{RL,R'L'}(z) = \lambda^{\alpha}_{RL}(z)\delta_{RR'}\delta_{LL'} + \mu^{\alpha}_{RL}(z)g^{\alpha}_{RL,R'L'}(z)\mu^{\alpha}_{R'L'}(z), \tag{4.108}$$

where

$$\lambda^{\alpha}_{RL} = (\gamma_{RL} - \alpha_{RL})\,\frac{\mu^{\alpha}_{RL}(z)}{\Delta^{1/2}_{RL}} \tag{4.109}$$

and

$$\mu^{\alpha}_{RL}(z) \equiv \left(\dot{P}^{\alpha}_{RL}(z)\right)^{1/2} = \frac{\Delta^{1/2}_{RL}}{\Delta_{RL} + (\gamma_{RL} - \alpha_{RL})(z - C_{RL})}. \tag{4.110}$$

The structure constant $S^{\alpha} = S^{0}(1 - \alpha S^{0})^{-1}$ in equation (4.102), defining the auxiliary resolvent, may be random in a disordered system, since it depends on the occupation through the values of α_{RL}. In the MTO-β, however the structure constant is site independent.

4.3.4 Derivation of the hopping term

In the approximation of neglecting the interstitial part, the α representation of the MTO orbital is given by:

$$|\chi^{\alpha}>= |\phi> +|\dot{\phi}^{\alpha}> h^{\alpha}, \tag{4.111}$$

and

$$|\dot{\phi}^{\alpha}>= |\dot{\phi}> +|\phi> o^{\alpha}, \tag{4.112}$$

where o^{α} introduces a small mixing of ϕ with $\dot{\phi}$. We have also used the simplified notation where $|\chi^{\alpha}>\equiv \chi^{\alpha}_{RL}(\vec{r}_R)$.

The matrix h^{α} is build up through the imposition of the *continuity* of the function and its derivatives in the inner and outer parts of the sphere.

The functions outside the sphere are the regular and irregular solution of the Laplace equation:

$$\begin{aligned} |K^{\alpha}> &= |K> -|J^{\alpha}> S^{\alpha} && (4.113)\\ |J^{\alpha}> &= |J> -\alpha|K> . && (4.114) \end{aligned}$$

Thus in the surface of the sphere, one should ensure continuity between these functions and linear combination of ϕ and $\dot{\phi}$, the latter being the solution of Schrödinger equation and its derivative inside the sphere.

In general, given a general junction $f(r)$, there is continuity between a linear combination of the functions $a(r)$ and $b(r)$ in a given surface s when:

$$f(r) \rightarrow \left[a(r)W\{f,b\} - b(r)W\{f,a\}\right]\left(W\{a,b\}\right)^{-1}, \tag{4.115}$$

where $W\{a, b\}$ is the Wronskian of the functions a and b, defined by:

$$W\{a, b\} \equiv s^2 \begin{vmatrix} a(s) & b(s) \\ a'(s) & b'(s) \end{vmatrix}. \tag{4.116}$$

Introducing the general criterion to one particular case one gets:

$$|\chi^\alpha >= |\phi > +|\dot{\phi}^\alpha > \left[-\frac{W\{K, \phi\}}{W\{K, \dot{\phi}^\alpha\}} + \sqrt{\frac{2}{s}} W\{J^\alpha, \phi\} S^\alpha W\{J^\alpha, \phi\} \sqrt{\frac{2}{s}} \right]. \tag{4.117}$$

Comparing this result with (4.111), we have:

$$h^\alpha = \left[-\frac{W\{K, \phi\}}{W\{K, \dot{\phi}^\alpha\}} + \sqrt{\frac{2}{s}} W\{J^\alpha, \phi\} S^\alpha W\{J^\alpha, \phi\} \sqrt{\frac{2}{s}} \right]. \tag{4.118}$$

Since the Wronskian are diagonal matrices, depending only on the site occupation, we define the following parameters:

$$C = \epsilon_\nu - \frac{W\{K, \phi\}}{W\{K, \dot{\phi}^\alpha\}} \tag{4.119}$$

$$\Delta^{1/2} = \sqrt{\frac{2}{s}} W\{J^\alpha, \phi\}. \tag{4.120}$$

Thus finally one has:

$$h^\alpha = C - \epsilon_\nu + \Delta^{1/2} S^\alpha \Delta^{1/2}. \tag{4.121}$$

4.3.5 Derivation of the potential function

The potential function P_ν is defined as:

$$P_\nu = -\frac{1}{\pi} arctg(D_\nu) + 0,5, \tag{4.122}$$

where:

$$D_\nu = s \frac{\frac{\partial}{\partial r} \Psi(s)}{\Psi(s)} \equiv s \frac{\Psi'(s)}{\Psi(s)}, \tag{4.123}$$

is the logarithmic derivative of the wave function at he surface of the sphere.

The function P_ν is limited between 0 and -1, due to the constants π and $0,5$. Its major property is to be a function which has a better behavior than D_ν, since when $D_\nu \to \infty$, $P_\nu \to 0$.

In order to obtain P_ν it is enough to know D_ν as a function of the potential parameters C, Δ and γ. To obtain this proof let us start from the functions Φ^+ and Φ^-, related to the potential parameters by:

$$\Delta^{1/2} = \left(\frac{a}{s}\right) \left(\frac{a}{2}\right)^{1/2} \Phi^-(s) \tag{4.124}$$

$$\frac{\Delta^{1/2}}{\gamma} = 2(2\mathrm{l} + 1) \left(\frac{a}{s}\right) \left(\frac{a}{2}\right)^{1/2} \Phi^+(s), \tag{4.125}$$

where a is a scale parameter and s is the radius of the muffin tin sphere. These functions are defined by:

$$\Phi^{+} = \phi + \omega_{+}\dot{\phi}, \quad \Phi^{-} = \phi + \omega_{-}\dot{\phi}, \tag{4.126}$$

where ω_{+} and ω_{-} are taken in such a way that Φ^{+} and Φ^{-} have logarithmic derivatives respectively equal to $\mathbf{l}$ and $-(\mathbf{l}+1)$. As usually ϕ and $\dot{\phi}$ are the wave function and its derivative respect to the muffin tin sphere.

In general, the functions Φ^{+} and Φ^{-} can be written as:

$$\Phi(D,r) = \phi(r) + \omega(D)\dot{\phi}(r), \tag{4.127}$$

where $\omega(D)$ is such that $\Phi(D,r)$ has a logarithmic derivative equal to D in the sphere surface. Starting from the definition $D = s\frac{\Phi'}{\Phi}$, one obtains:

$$D = \frac{D_{\nu} + \omega(D) D_{\dot{\nu}} \frac{\dot{\phi}}{\phi}}{1 + \omega(D)\frac{\dot{\phi}}{\phi}}, \tag{4.128}$$

where we used the definitions $D_{\dot{\nu}} = s\frac{\dot{\phi}'}{\dot{\phi}}$ and $D_{\nu} = s\frac{\phi'}{\phi}$.

Defining

$$\omega(D) = -\frac{\phi}{\dot{\phi}}\frac{D - D_{\nu}}{D - D_{\dot{\nu}}} \tag{4.129}$$

and introducing it in (4.127), for $r = s$, one obtains:

$$\Phi(D,s) = \phi\frac{D_{\nu} - D_{\dot{\nu}}}{D - D_{\dot{\nu}}}. \tag{4.130}$$

Replacing D by its value in the surface of the sphere:

$$\begin{aligned} \Phi^{+} &= \phi\frac{D_{\nu} - D_{\dot{\nu}}}{\mathbf{l} - D_{\dot{\nu}}}, & (4.131) \\ \Phi^{-} &= \phi\frac{D_{\nu} - D_{\dot{\nu}}}{-\mathbf{l} - 1 - D_{\dot{\nu}}}, & (4.132) \end{aligned}$$

one gets to the ratio of these equations:

$$\frac{\Phi^{+}}{\Phi^{-}} = \frac{-\mathbf{l} - 1 - D_{\dot{\nu}}}{\mathbf{l} - D_{\dot{\nu}}}. \tag{4.133}$$

From that relation one gets:

$$D_{\dot{\nu}} = \mathbf{l} + (2\mathbf{l}+1)\left[\frac{\Phi^{+}}{\Phi^{-}} - 1\right]^{-1}. \tag{4.134}$$

Introducing the value of $D_{\dot{\nu}}$ in (4.131) and using the relation extracted from (4.126):

$$\frac{\omega_{-}}{\omega_{+}} = \frac{\Phi^{+} - \phi}{\Phi^{-} - \phi}, \tag{4.135}$$

one finally gets:

$$D_\nu = \mathbf{l} + (2\mathbf{l}+1)\left(\frac{\Phi^+}{\Phi^-}\frac{\omega_-}{\omega_+} - 1\right)^{-1}. \tag{4.136}$$

Using the relation between the functions Φ^+ an Φ_- with the potential parameters as given in (4.124) and (4.125), one has:

$$\frac{\Phi^+}{\Phi^-} = \frac{\gamma^{-1}}{2(2\mathbf{l}+1)}. \tag{4.137}$$

Imposing the continuity of the wave functions, using the Wronskians, between the functions inside and outside the spheres, one has:

$$\omega_- = C - \epsilon_\nu, \quad \omega_+ = \omega_- - \Delta\gamma^{-1}. \tag{4.138}$$

Replacing these values of ω_+, ω_- in (4.136), one has:

$$D_\nu = \mathbf{l} + (2\mathbf{l}+1)\left(\frac{1}{2(2\mathbf{l}+1)}\frac{\epsilon_\nu - C}{\Delta + \gamma(\epsilon_\nu - C)} - 1\right)^{-1}. \tag{4.139}$$

Finally introducing D_ν in the definition of P_ν given in (4.122), one has:

$$P_\nu = -\frac{1}{\pi}arctg\left[\mathbf{l} + (2\mathbf{l}+1)\left(\frac{1}{2(2\mathbf{l}+1)}\frac{\epsilon_\nu - C}{\Delta + \gamma(\epsilon_\nu - C)} - 1\right)^{-1}\right] + 0,5. \tag{4.140}$$

This is the exact definition of the potential function for numerical self consistent calculation. This function may be approximately represented in an energy range defined by $\tilde{\epsilon}_\nu$, by:

$$P_\nu = \frac{\tilde{\epsilon}_\nu - C}{\Delta + \gamma(\tilde{\epsilon}_\nu - C)}. \tag{4.141}$$

It can be shown that the above function approximates quite well the above general expression.

Chapter 5

RARE EARTH METALS AND COMPOUNDS

5.1 Introduction

We present here a brief discussion of stable compounds, intermediate valence, Kondo and heavy fermion compounds. Contrary to the previous Chapters, this is mostly devoted to the discussion of materials including elements of two specific series of the Periodic Table, namely the $4f$ and the $5f$. The first one, called the lantanide series, is divided in two distinct groups: materials including the stable Rare Earths and those with the anomalous ones, constituted by Ce, Yb, Eu, Sm, Tm.

These materials are in general intermetallic compounds, exhibiting structures like the cubic, hexagonal, tetragonal, orthorombic, modified cubic, Laves phase and Heusler. These compounds may contain or not, in their composition, transition metal elements.

The **stability** of these rare earths is understood here in terms of the existence of *localized* $4f$ *states* **well separated** from the extended conduction states, as discussed in Chapter 3. On the contrary, unstable rare earths present $4f$ levels which, in the absence of interaction with the conduction states, lie close to the Fermi level of the metallic material.

A first attempt to discuss these stable rare earths was made in Chapter 3, in the presentation of the exchange interaction between a localized spin and the conduction electrons (Zener interaction). In that Chapter a very simplified picture was presented, in order to exhibit the main ingredients of this problem, namely the Pauli principle and the electron- electron Coulomb interaction.

Using the linear response theory, formally developed in the Appendix, it was possible, following Doniach's formulation, to derive the classical RKKY interaction between localized f-moments (cf. Chapter 3). In that case, the problem of describing the coupling between the magnetic moments of stable rare earths was transformed into an electronic structure calculation and a statistical mechanics problem for the localized and coupled moments. The first part corresponds to estimate the independent electron susceptibility for the itinerant $sp-d$ electrons of a pure rare earth metal or a compound. The second part is a statistical mechanics problem for obtaining the thermal average of the coupled localized spins, made via a simple molecular field or a Monte Carlo procedure.

Clearly, a suitable generalization of the description of the Zener Hamiltonian, presented in Chapter 3, is necessary in order to include a better description of the rare earth trivalent ion. In the present Chapter we introduce more details, like the more realistic "atomic" description of the isolated rare earth ion, the existence or not of crystal field effects, comments about the effect of the spin orbit coupling, the possibility of J as a good quantum number.

This theory applies equally well to pure rare earth metals and compounds, the difference lying in the computation of the susceptibility. The existence of sublattices and also the possibility of other magnetic orders like ferrimagnetism, associated in certain cases, to the magnetic order in the sublattice of transition metal atoms, makes the description these compounds more complex.

In the case of unstable rare earths, the phenomenon of intermediate valence may occur. By unstable rare earths we understand those cases, where the energy levels of the rare earth ions lie close to the Fermi level of the material , thus enabling a mixing of the local states to the extended ones. A first picture of a $4f$ ion in a metal was proposed by Hirst. Such a picture was developed, having unstable atoms like Ce in mind and more generally $4f$ atoms like Eu and Yb. We must then, first of all, introduce some energy scales involved in the description of these $4f$ states.

We insist that the picture for actinide pure metals and compounds, although some times described using a similar approach, is more adequately described by a multiband (sp, d, f) itinerant electron structure. This stems from the fact that $5f$ states are more spatially extended as compared to $4f$ ones, thus introducing strong tunneling effects to neighbouring atoms, as in usual pure transition metals or intermetallics.

Coming back to the Ce ion case, let us remember that for this atom two distinct valences may be considered: the trivalent f^1 and tetravalent f^0 valence states. In general for cerium compounds, due to the neighborhood of the $4f$ level with the Fermi level, a more sophisticated description than the Zener model is required.

As described in Chapter 2, the adequate way to start is the Anderson Hamiltonian, since a localized level, here the $4f$ level, hybridizes with the sp, d band of the pure unstable rare earth metal or compound. Unfortunately, the simplified Hartree-Fock description of the Anderson Hamiltonian, presented in Chapter 2, is not adequate in these cases due to the existence of a ratio $U_{ff}/\Delta >> 1$, Δ being the one electron Friedel virtual bound state width. Then a rather extensive "collection of approaches" has been set up to discuss this particular situation.

Around the years of 1969, a very interesting approach to describe Ce compounds was provided by the derivation of the Coqblin-Schrieffer (CS) Hamiltonian. In a quite similar way as in the Hubbard Hamiltonian, the difficulties with the Anderson Hamiltonian arise from the competition between Coulomb interactions and the band kinetic energy, via the hybridization term. The idea behind the CS Hamiltonian was to use the canonical transformation method to eliminate, to a certain order in perturbation, the hybridization term. This generates an effective Hamiltonian of the Zener type, but including scattering processes where the detailed ionic structure is involved. Thus, the Hamiltonian including the "ionic" details, via the M components of J, defines an "effective exchange interaction" $J_{MM'}$ generalizing for these cases, the Zener interaction.

We introduce now a series of concepts and definitions to construct an adequate exchange interaction Hamiltonian extending the Zener Hamiltonian discussed in Chapter 3. To do that, we make several remarks concerning the ionic description of the $4f^1$ and $4f^{13}$ configurations. For that we consider the involved energy scales.

Consider first the Coulomb interaction U, the most important energy term, whose estimate is $10eV$. If the energy of one electron is E_M, to add another electron costs $E_M + U$. This is a very high energy. Secondly, we neglect multiplet splitting due to exchange interactions, when there are two or more electrons in the $4f$ shell.

The second contribution in energy is the large spin-orbit coupling: in the case of Ce, this amounts to $0.1eV$. This coupling splits levels with different j values, and leads to a given value j for the ground state; examples are $j = 5/2$ for Ce impurities and $j = 7/2$ for Yb impurities.

In this energy scale, the third term is the crystal field splitting. This interaction splits the levels inside the ground state multiplet. We introduce the notation E_M for the energies of the different crystal field split levels. The order of magnitude of this interaction is $0.01eV$ again for Ce and Yb.

It remains to consider other energy scales, the conduction electron band-width and the hybridization strength. Some comments however are necessary, to justify the CS procedure in deriving the effective Hamiltonian. The general idea is to start from Anderson's Hamiltonian including the "ionic" description and then to eliminate the hybridization between conduction and localized states, via the canonical transformation. We present this formalism following Kittel approach described in his book Quantum Theory of Solids.

5.2 Canonical transformation

Let us start from a general Hamiltonian H and let us define a new transformed Hamiltonian $\tilde{H}$ through :

$$\tilde{H} = e^{-S} H e^{S} \tag{5.1}$$

where S should be determined with an adequate receipt. Before defining the procedure, expanding the exponentials in (5.1) one gets:

$$\begin{aligned} \tilde{H} &= \left\{1 - S + \frac{1}{2!}S^2 + \ldots\right\} H \left\{1 + S + \frac{1}{2!}S^2 + \ldots\right\} \\ &= H + [H, S] + \frac{1}{2}\left[[H, S], S\right] + \ldots \end{aligned} \tag{5.2}$$

The interest of applying such transformation occurs in cases where the Hamiltonian can be *naturally* split in two terms :

$$H = H_0 + \lambda H'. \tag{5.3}$$

From (5.2) one sees that:

$$\tilde{H} = H_0 + \lambda H' + [H_0, S] + \lambda[H', S] + \ldots \tag{5.4}$$

If one decides that S is to be chosen in such a way that:

$$\lambda H' + [H_0, S] = 0, \tag{5.5}$$

then, the Hamiltonian $\tilde{H}$ of (5.4) contains only terms of higher order than the first in λ. A very interesting way to do that to derive the CS Hamiltonian is the following: suppose that H' and consequently S are time independent in the Schrödinger picture. One introduces the interaction representation for S, we call S_I , defined by:

$$S_I = e^{iH_0 t} S e^{-iH_0 t} \tag{5.6}$$

Then:

$$i\dot{S}_I = [S_I, H_0] \tag{5.7}$$

as it follows from the differentiation of (5.6). Transforming equation (5.5) to the interaction representation, it implies that :

$$[S_I, H_0] = \lambda H'_I. \tag{5.8}$$

Thus the equation of motion for the S_I operator reads:

$$i\dot{S}_I = \lambda H'_I \tag{5.9}$$

Assuming that $S_I(-\infty) = 0$, equation (5.9) can be integrated to give:

$$S_I(t) = -i\lambda \int_{-\infty}^{t} dt' H_I'(t') \tag{5.10}$$

The next step in the determination of the transformed Hamiltonian, to second order in the coupling strength λ, starts from (5.2) including the complete Hamiltonian:

$$\begin{aligned} \tilde{H} &= H_0 + \lambda[H', S] + \frac{1}{2}\left[[H_0, S], S\right] + O(3) \\ &= H_0 + \lambda[H', S] - \frac{1}{2}\left[\lambda H', S\right] + O(3) \end{aligned} \tag{5.11}$$

Then, combining with (5.10) one obtains:

$$\tilde{H} = H_0 + \frac{1}{2}\lambda[H', S] = H_0 - \frac{1}{2}i\lambda^2 \int_{-\infty}^{t} dt' \left[H', H_I'(t')\right]. \tag{5.12}$$

Recalling that $H' = H_I'(0)$, as it follows from (5.6), one finally obtains for the second order correction in λ:

$$\tilde{H} = H_0 + \frac{1}{2}i\lambda^2 \int_{-\infty}^{t} dt' \left[H_I'(t'), H_I'(0)\right]. \tag{5.13}$$

This is the starting point for the Wolf-Schriefer transformation as applied to Anderson's Hamiltonian.

5.3 Transformation of the Anderson Hamiltonian: Coqblin-Schrieffer version

Let us start from the following simple version of the Anderson Hamiltonian:

$$H = \sum_{kM} \epsilon_k n_{kM} + \sum_M E_0 n_M + \frac{1}{2}U \sum_{\substack{M,M' \\ M\neq M'}} n_M n_{M'} + \sum_{kM}\left(V_k c_{kM}^{+} c_M + V_k^* c_M^{+} c_{kM}\right) \tag{5.14}$$

In (5.14) and without crystal field effects, the quantum number M correspond to the z-component of the total angular momentum J. Introducing *crystal field effects* for an hexagonal symmetry, the multiplet of value J is split in doublets of the same J_z^2 value. In the case of Ce impurities, one has *three* doublets, with z-component :

$$J_z = \pm 1/2, \pm 3/2, \pm 5/2 \quad \text{for Ce} \tag{5.15}$$

In the case of Yb we have *four* doublets,

$$J_z = \pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2 \tag{5.16}$$

In this case we can keep the J_z representation of the Hamiltonian (5.14), introducing only minor corrections, replacing the energy level term $E_0 n_M$ above by $E_M n_M$ for each J value, and introducing the new values for E_M, the new energy of each doublet.

A different situation is provided by cubic symmetry. The existence of a crystal field splits the multiplet into doublets and quartets. Contrary to the hexagonal symmetry, *no half integer eigenvalues exist* in this case. Then, the eigenfunctions are *linear combinations* of functions which have M eigenvalues. Examples are the following: in the case of $J = 5/2$ for the Ce case, the multiplet is split into a doublet Γ_7 and a quartet Γ_8. The corresponding eigen functions are:

$$\begin{aligned}
\Gamma_7 &: |J_z = \mp 0.83 >= 0.4083| \pm 5/2 > -0.9129| \pm 3/2 > \\
\Gamma_8 &: |J_z = \pm 1.83 >= 0.9129| \pm 5/2 > +0.4083| \mp 3/2 > \\
&: |J_z = \pm 0.5 >= | \pm 1/2 >
\end{aligned} \tag{5.17}$$

For the case of Yb impurities, the multiplet is slitted into two doublets and a quartet, which wave functions are given by:

$$\begin{aligned}
\Gamma_6 &: |J_z = \pm 1.17 >= 0.6455| \pm 7/2 > +0.7638| \mp 1/2 > \\
\Gamma_7 &: |J_z = \pm 1.50 >= 0.8660| \pm 5/2 > -0.5000| \mp 3/2 > \\
\Gamma_8 &: |J_z = \pm 1.83 >= 0.7638| \pm 7/2 > -0.6455| \mp 1/2 > \\
&: |J_z = \mp 1.50 >= 0.5000| \pm 5/2 > +0.8669| \mp 3/2 >
\end{aligned} \tag{5.18}$$

The Hamiltonian then should be rewritten in the basis of the new functions as defined in (5.17) and (5.18). The *transformation operation* passing from the operators c_M^+ to the new ones c_μ^+ is an *unitary transformation*, which conserve the commutation relations and the fermion character:

$$\left[c_M, c_{M'}^+\right] = \delta_{MM'}, \qquad [c_\mu, c_{\mu'}^+] = \delta_{\mu\mu'} \tag{5.19}$$

The same transformation can be introduced for the creation operators $c_{k\mu}^+$ of the conduction electrons, starting from c_{kM}^+.

The *general Hamiltonian* using the above discussion is then:

$$\begin{aligned}
H &= H_0 + H_1 \\
H_0 &= \sum_{kM} \epsilon_k n_{kM} + \sum_M E_M n_M + \frac{1}{2} U \sum_{\substack{M,M' \\ M \neq M'}} n_M n_{M'} \\
H_1 &= \sum_{kM} \left(V_k c_{kM}^+ c_M + V_k^* c_M^+ c_{kM} \right).
\end{aligned} \tag{5.20}$$

Now we follow the receipt described in (5.10) above to perform the canonical transformation; after the commutations of H_1 and the exponential $\exp(-iH_0 t)$, one obtains for the transformation operator S:

$$\begin{aligned}
S &= -i \int_{-\infty}^{0} dt \sum_{kM} V_k c_{kM}^+ c_M e^{it(\epsilon_k - E_M)} \prod_{M" \neq M} \left[(1 - n_{M'}) + e^{-iUt_{MM'}} \right] \\
&\quad + V_k^* c_M^+ c_{kM} e^{it(E_M - \epsilon_k)} \prod_{M" \neq M} \left[(1 - n_{M'}) + e^{+iUt_{MM'}} \right]
\end{aligned} \tag{5.21}$$

Introducing the definitions:

$$\prod_{M"\neq M}\left[(1-n_{M'})+e^{+iUt_{MM'}}\right]=\sum_{p=0}^{2j}e^{ipUt}A_p(M) \tag{5.22}$$

$$A_p(M)=\sum_{M\neq M'}\left[\ldots n_{M'}\ldots\right]\left[\ldots(1-n_{M'})\ldots\right] \tag{5.23}$$

the S operator reads:

$$S=\sum_{kM}\left(V_k^* c_M^+ c_{kM}-V_k c_{kM}^+ c_M\right)\sum_p\frac{A_p(M)}{\epsilon_K-E_M-pU} \tag{5.24}$$

Introduce now the auxiliary quantities:

$$\begin{aligned} J_p^{MM'}(k,k') &= W_{p+1}^{MM'}(k,k')-W_p^{MM'}(k,k') && (5.25)\\ W_p^{MM'}(k,k') &= \frac{V_k^* V_{k'}}{2}\left[\frac{1}{\epsilon_k-E_M-pU}+\frac{1}{\epsilon_{k'}-E_{M'}-pU}\right] && (5.26)\end{aligned}$$

The transformed Hamiltonian H will finally be:

$$H=H_0+H_0'+H_{exch}+H_{dir}+H_{dd} \tag{5.27}$$

To get the final form of (5.27) we introduce the quantity $B_p(M,M')$, obtained from the expansion of $A_p(M)$ as:

$$A_p(M)=(1-n_{M'})B_p(M,M')+n_{M'}B_{p-1}(M,M') \tag{5.28}$$

Besides the H_0, the remaining of (5.27) are given by:

$$\begin{aligned} H_0' &= \sum_{k,p,M}W_p^{MM'}(k,k)A_p(M)n_M && (5.29)\\ H_{exch} &= -\sum_{\substack{k,k',M,M',p\\ M\neq M'}}J_p^{MM'}(k,k')B_p(M,M')c_{k'M'}^+ c_{kM} c_M^+ c_{M'} && (5.30)\\ H_{dir} &= \sum_{k,k',M,p}W_p^{MM}(k,k')A_p(M)c_{k'M}^+ c_{kM} && (5.31)\\ H_{dd} &= -\frac{1}{2}\sum_{\substack{k,k',M,M'\\ M\neq M'}}J_p^{MM'}(k,k')B_p(M,M')\left[c_{k'M}^+ c_{kM}^+ c_M c_{M'}+c_{k'M'}c_{kM}c_M^+ c_{M'}^+\right] && (5.32)\end{aligned}$$

Up to this point, the Hamiltonian (5.27 is quite general; simplifications can be introduced in some specific cases: supposing that one has N electrons, the previous terms acquire a simpler form. First of all, the term H_{dd} is very small since this term creates or destroys two $4f$ electrons, and this is highly improbable. The first term

H_0' only incorporates a shift in the energy E_M. For the given configuration some of the auxiliary quantities can be written as:

$$\begin{aligned} A_p(M) &= \left(\delta_{p,N} - \delta_{p,(N-1)}\right)\left(\sum_{M'\neq M} n_{M'} - N\right) + \delta_{p,N} && (5.33)\\ B_p(M,M') &= \delta_{p,N-1} && (5.34) \end{aligned}$$

Finally the remaining terms, H_{ex} and H_{dir} can be incorporated in H_{eff} in such a way that:

$$\begin{aligned} H_{eff} &= H_{exch} + H_{dir}\\ &= -\sum_{k,k',M,M'} J_{N-1}^{MM'}(k,k')c^{+}_{k'M'}c_{kM}c^{+}_{M}c_{M'} + \sum_{k,k',M} W_N^{MM}(k,k')c^{\dagger}_{k'M}c_{kM} && (5.35) \end{aligned}$$

Expression (5.35) is applied to the case of Ce ($N = 1$) and Yb for which N is the number of $4f$ holes. To introduce a further simplification, instead of W_1^{MM} we introduce a semi-phenomenological direct potential $V_{M,M'}(k,k')$. Then the complete Hamiltonian becomes:

$$H = \sum_{k,M} \epsilon_k n_{kM} - \sum_{k,k',M,M'} J_{MM'}c^{+}_{k'M'}c_{kM}c^{+}_{M}c_{M'} + \sum_{k,k',M} V_{MM}c^{+}_{k'M}c_{kM}. \qquad (5.36)$$

Also we neglect the k dependence of $J_{MM'}$ through the energies ϵ_k and $\epsilon_{k'}$ We take a cutoff D , independent of M and M' in such a way that $J_{MM'} = 0$ if $|\epsilon_k|$ or $|\epsilon_k'|$ are larger than D. The cutoff value is taken to be of the order of the average value of E_M.

In the case of Ce, since U is much larger than E_M , the effective exchange coupling reads:

$$J_{MM'} = \frac{V^*V}{2}\left[\frac{1}{E_M} + \frac{1}{E_{M'}}\right] \qquad (5.37)$$

Finally some comments about the Hamiltonian (5.36): for $M = M'$ the average value of the second term is not zero, thus implying that this term contains both exchange and direct scattering terms. If one wants to separate these terms one rewrites the Hamiltonian as :

$$\begin{aligned} H &= \sum_{k,M} \epsilon_k n_{kM} - \sum_{k,k',M,M'} J_{MM'}c^{+}_{kM'}c_{kM}\left(c^{+}_{M}c_{M'} - \delta_{M,M'} < n_M >\right)\\ &\quad + \sum_{k,k',M}\left[V_{MM} - J_{MM} < n_M >\right]c^{+}_{k'M}c_{kM} && (5.38) \end{aligned}$$

where we have added and subtracted the direct term $J_{MM'} < n_M >$. Then in (5.38) the second term is pure exchange scattering, and the last one is pure direct scattering. The relative relevance of these terms should be established from the application of these calculations to specific cases.

This interaction $J_{MM'}$ is negative and connected to the "ionic" energies E_M and $E_{M'}$ (relative to the Fermi level) and also to the hybridization matrix elements $\mid V_{kf} \mid^2$. The result obtained by CS is the following :

$$J_{MM'} = \frac{1}{2} \mid V_{kf} \mid^2 \left[\frac{1}{E_M} + \frac{1}{E_{M'}} \right] \tag{5.39}$$

and the "generalized" Zener Hamiltonian G^Z_{gen} describing the scattering between ionic states and the conduction electrons is:

$$H^Z_{gen} = - \sum_{kk'MM'} J_{MM'} c^+_{k'M'} c_{kM} \left(c^+_M c_{M'} - \delta_{M,M'} < n_M > \right) + \sum_{kk'MM'} V_{MM'} c^+_{k'M'} c_{kM}. \tag{5.40}$$

In the Hamiltonian above, c^+_M creates an electron in the $4f$ state with $l = 3, s = 1/2, J = 5/2$ and $M = J_z$. Contrary to Chapter 3, the internal degrees of freedom of the ion are explicitly included in the "exchange" scattering term. For the conduction electrons, an adequate representation, projected in these states is used. This ends with the derivation of a generalized Zener Hamiltonian, adequate to describe these rare earth impurities in anomalous situations. Also we recall that at high temperature respect to a characteristic one, the calculation of some transport properties has been performed using third order perturbation theory.

5.4 Qualitative remarks about Ce compounds

Let us describe here some general ideas discussed by Coqblin and collaborators. From the experimental point of view, many cerium compounds have been studied. It is well established that a single Kondo impurity, described by the Hamiltonian above, behaves like a free ion at high temperatures as compared to a characteristic temperature T_K. This temperature is called the Kondo temperature, and defines an specific regime: for temperatures very low as compared with T_K, a regime characterized by high effective masses sets in. Experimentally, this situation corresponds to huge values for the electronic specific heat, γ, and simultaneously high values for the susceptibility χ.

Before discussing compounds, let us briefly recall the low temperature properties of an isolated Kondo impurity. At $T = 0K$, the properties correspond to those of a nonmagnetic singlet state. The magnetic susceptibility and the electronic specific heat are enhanced respect to the normal magnetic behaviour. The Wilson ratio, defined by $R = \chi/\gamma$ and using appropriate units (those adequate to the density of states) is constant and ranging between 1 and 2. This corresponds to strongly correlated electron gas. An interesting behaviour is shown by the de Haas-van Alphen measurement. For example in CeCu$_6$ one observes a cyclotron mass of the order of

$80m_0$ where m_0 is the bare electron mass; this should be compared to the result for $LaCu_6$, which is $2.5m_0$. Such difference indicates the role of electron correlations in "dressing" the electrons.

At very low temperatures, the transport properties in particular, are well described by the Fermi liquid approach. In the compound $CeCu_6$, the resistivity at low temperatures varies like $\rho = AT^2$, where the coefficient A is very large. To be more explicit, if T_K is the Kondo temperature as defined below, separating two resistivity regimes, one notes that χ and γ behave as $1/T_K$ at $T = 0$. The dependence of A however is $1/T_K^2$. Several values of the constant A are observed, varying like 0.5, 6., 10, 30, 120 for different cerium compounds.

Again let us emphasize that the characteristic Kondo temperature defines a smooth "crossover" between a Fermi liquid behaviour at low temperatures to free ion like behaviour, at high temperatures compared to T_K.

A very interesting behaviour concerns the density of states for a single Kondo impurity at $T = 0$K. This density of states shows two peaks, contrary to the most naive treatments of the Anderson picture. In fact, the broad peak centered at the position of the $4f$ level is associated to the Hartree-Fock treatment of the Anderson model. The other peak is associated to a more adequate treatment of the electron correlations, outside the scope of the HF treatment. This *extremely narrow peak* is located near the Fermi level and is thus responsible for the important values of χ and γ. The width of this peak is given by T_K/N, where N is the degeneracy; thus increasing N, or decreasing the Kondo temperature or both decreases its value. In the slave boson approach, these results will become more apparent.

A very important point in *compounds* is the competition between the Kondo effect itself, implying in the screening of the magnetic moment by the antiferromagnetically polarized electron gas, and the RKKY interaction, inducing long range magnetic order of the local moments. Experimental examples of these opposite situations are the following: $CeAl_2$, $CeCu_2$, CeB_6, that show low temperature magnetic order. These compounds show specific heats of the order of $100mJ/molK$. On the contrary, $CeAl_3$, $CeCu_6$, $CePd_3B$ show a very high specific heat of the order of $1000mJ/molK$, but at the same time complex magnetic behaviour, short range magnetic correlations or even non magnetic behaviour. The description of these situations needs a long and complex discussion. Firstly we intend to present, although not rigorous, the main lines of the simplest approach. The first main lines of an attempt to describe this situation of Kondo lattices was proposed by Doniach, and we describe now this simple picture. Consider a lattice of rare earth Kondo atoms. The Kondo effect tends to suppress the magnetic moment with decreasing temperature, by condensing the electron gas antiferromagnetically around the ionic moment. Introduce T_{K_0}, as the Kondo temperature for an isolated rare earth impurity. For the classical Zener Hamiltonian, $H = -\Gamma s.S$, this

Kondo temperature depends on Γ and on the density of states of the conduction band near the Fermi level $\rho(E_f)$, in the following way:

$$T_{K_0} \simeq \exp\left[-1/\mid \Gamma\rho \mid\right] \tag{5.41}$$

This result shows that for small values of the product $\mid \Gamma\rho \mid$ one has a small value of T_{K_0}. On the other hand, as shown in Chapter 3, the RKKY coupling between local moments may introduce an antiferromagnetic Néel temperature T_{N0}, which varies with the product $\mid \Gamma\rho \mid$ as:

$$T_{N_0} \simeq \mid \Gamma\rho \mid^2 \tag{5.42}$$

This quadratic dependence again implies in T_{N_0} tending to zero for small values of the product $\mid \Gamma\rho \mid$. The origin of the competition becomes now very clear, since both temperatures, the Kondo and the ordering, depend on the same quantity $\mid \Gamma\rho \mid$, but with different functional forms.

The competition is then clearly associated to the **functional** form of the $\mid \Gamma\rho \mid$ dependence of the corresponding temperatures. It is clear that the power law dependence of T_{N0} *overcomes* that of T_{K0} at *low values* of $\mid \Gamma\rho \mid$. However, it exists a critical value of $\mid \Gamma\rho \mid, \mid \Gamma\rho \mid_c$ such that the exponential dependence of T_{K0} *overcomes* the power law behaviour of T_{N0} and a crossing exists of the two curves as a function of $\mid \Gamma\rho \mid$. This means that a two regime behaviour occurs: firstly the ordering temperature increases with the strength of $\mid \Gamma\rho \mid$, passes through a maximum (the competition between RKKY and Kondo effect start to set in importantly), then decreases to zero indicating the Kondo like dominance.

This proof however is quite oversimplified, and more rigorous attempts have been tried. Among these, we quote firstly the slave boson method, discussed later in general grounds. Secondly, the case of two magnetic Kondo impurities, discussed using the numerical renormalization group approach. This last method was originally devised by Wilson to treat an isolated Kondo impurity, and its application to the two impurity case can improve the above discussion of the competition between the RKKY and the Kondo screening.

Finally let us mention that the perturbation theory treatment of the Coqblin-Schriefer Hamiltonian has enabled the description of many experimental data. Quite recently, the possibility of producing *single crystals* of these materials, introduced new theoretical problems. The transport properties at temperatures higher than T_K, well described up to this moment within the third order perturbation approach on the effective coupling, required an adequate treatment to take explicitly into account the anisotropy of these single crystal compounds. The perturbation theory scheme however fails at low temperatures $(T < T_K)$, where a different temperature dependence is observed.

5.5 The Read and Newns approach

Let us first introduce the simplest version of the slave boson approach to the Kondo lattice. This model applies to Ce and Yb and may be approximately used for Sm and Eu cases. Using a formulation suggested by Coleman to describe strongly correlate f-electrons, let us start from the Hamiltonian:

$$H = \sum_k \epsilon_k c_k^+ c_k + E_0 \sum_{i,m} f_{im}^+ f_{im} + V \sum_{i,m} \left[c_{im}^+ f_{im} b_i^+ + f_{im}^+ c_{im} b_i \right]. \tag{5.43}$$

In this expression i stands for the sites, k corresponds to the wave vector of the conduction states and m is the magnetic quantum number, $-l < m < l$. Note that in this first approach we neglect spin, which is a $1/N$ effect, taking $N = 2j + 1$. In (5.43), f_{im} and c_k are respectively, fermion operators for the rare earth site and for conduction states of wave vector k; these states correspond to energies E_0 and ϵ_k respectively. Finally, following a truck introduces by Coleman, let us introduce the operator c_{im}^+ which projects a conduction states characterized by l, m at the site i, and such state is constructed from the band states. The definition of these operators is:

$$c_{im}^+ = (4\pi)^{1/2} \sum_k \left[Y_l^m(\Omega_k) \right]^* e^{-kR_i} c_k^+. \tag{5.44}$$

In the Hamiltonian (5.43), the hybridization or "local hopping" V, describes the passage from the local $4f$ state f_{im} to the localized state c_{im}^+ and vice-versa.

Finally and more importantly, the boson creation and destruction operators b_i and b_i^+, introduced originally by Coleman, act in the following way: start from a state with zero f-electrons and one boson; successive applications of the Hamiltonian reproduce the original state or create a state with one electron and no bosons. This is true provided that the following condition is satisfied for all sites i:

$$Q_i = N_{fi} + b_i^+ b_i = 1, \tag{5.45}$$

where $N_{fi} = \sum_m f_{im}^+ f_{im}$ for all sites i. This shows that no excited states, like $f^2, f^3 \ldots$, very high in energy, can be created, via this constraint.

We include this constraint in the partition function Z using a representation of the δ function. The result is:

$$Z = \int_{-\pi/\beta}^{\pi/\beta} \prod_i \frac{\beta d\lambda_i}{2\pi} Tr \left[e^{-\beta H - i\beta \sum_i \lambda_i (Q_i - 1)} \right]. \tag{5.46}$$

It should be noted that the integral over λ reproduces the constraint (5.45), in the expression for Z, projecting out deviations from this equality. Now using Feyman's method, the partition function is written as a functional integral, in terms of the imaginary time lagrangian $L(\tau)$. The result is:

$$Z = \int_{-\pi/\beta}^{\pi/\beta} \prod_i \frac{\beta d\lambda_i}{2\pi} \int DbDb^+ D_f D_f^+ D_c D_c^+ e^{-\int_0^\beta d\tau L(\tau)} \tag{5.47}$$

where the lagrangian is defined by:

$$\begin{aligned} L &= \sum_i b_i^+ \frac{d}{d\tau} b_i + \sum_{im} f_{im}^+ \left[\frac{d}{d\tau} + E_0\right] f_{im} + \sum_k c_k^+ \left[\frac{d}{d\tau} + \epsilon_k\right] c_k + \\ &\quad V \sum_{im} \left[c_{im}^+ f_{im} b_i^+ + f_{im}^+ c_{im} b_i\right] + i \sum_i \lambda_i \left[N_{fi} + b_i^+ b_i - 1\right] \end{aligned} \tag{5.48}$$

In (5.47) we have used D to mean $\prod_{im} Df_{im}$ in the functional integral. In (5.47) and (5.48), the c_k and f_{im} are anticommuting Grassman numbers, as it follows from the general Feyman's theorem for the expression of the partition function. In view of future calculations, it is useful to make a gauge transformation in the action defined above. For that we introduce the following transformation for the imaginary time dependent boson operators:

$$b(\tau) = r(\tau) e^{i\theta(\tau)}, \text{ with } \quad dbdb^+ = rdrd\theta \tag{5.49}$$

This transformation introduces new quantities defined as :

$$f_{im}'(\tau) = f_{im}(\tau) e^{-i\theta(\tau)} \quad \text{and} \quad c_k'(\tau) = c_k(\tau) \tag{5.50}$$

obtaining for the λ parameter, ensuring the constraint, a new value

$$\lambda_i'(\tau) = \lambda_i + \dot{\theta}(\tau) \tag{5.51}$$

Introducing the transformation in the functional integral one gets:

$$Z = \int D\lambda \left[\prod_\tau r(\tau) DrDfDf^+ DcDc^+ e^{-\int_0^\beta L'(\tau) d\tau}\right] \tag{5.52}$$

$$\begin{aligned} L' &= \sum_{im} f_{im}^+ \left[\frac{d}{d\tau} + E_0 + i\lambda_i\right] f_{im} + \sum_k c_k^+ \left[\frac{d}{d\tau} + \epsilon_k\right] c_k + \\ &\quad V \sum_{im} r_i \left[c_{im}^+ f_{im} + f_{im}^+ c_{im}\right] + i \sum_i \lambda_i \left[r_i^2 - 1\right] \end{aligned} \tag{5.53}$$

It is to be noted that the variable $\theta(\tau)$ has disappeared from L: that means we have "real bosons", because, due to the periodicity of r on the interval 0 to β, the integral in this interval of $r\dot{r}$ vanishes. The interesting feature of this transformation is that "new parameters" appear in the lagrangian, renormalizing the "hybridization V", as compared to (5.43).

The main points of these transformations have been presented above. The next and more important step is to find an approximate way to deal with it; we will present evidence that the "static approximation" which is simply treated, is valid in the large N limit, for low temperatures T and magnetic fields H. A good approximation is obtained when $N = 7$, which corresponds in our spinless case to $j = 6/2 = 3$. First of all let us assume *translation invariance*, and define a new time independent parameter ϵ_f by :

$$i\lambda_i(\tau) = \epsilon_f - E_0 \tag{5.54}$$

and a new time independent hybridization strength $r_0 = r(\tau)$. Once defined these constants, the next step is to minimize the free energy, and to extract the corresponding values of the parameters. For that let us present the proof of a simple result.

Starting from the definition of the free energy in terms of the *parameter dependent Hamiltonian* $H_{eff}(\alpha)$, where α stands for a series of parameters, the free energy is:

$$F(\alpha) = -\frac{1}{\beta} log Z(\alpha), \tag{5.55}$$

with

$$Z(\alpha) = Tre^{-\beta H_{eff}(\alpha)}. \tag{5.56}$$

Performing the derivative of $F(\alpha)$ respect to any α one has:

$$\frac{\partial F(\alpha)}{\partial \alpha} = -\frac{1}{\beta}\frac{\partial Z(\alpha)/\partial\alpha}{Z(\alpha)}; \quad \frac{\partial Z(\alpha)}{\partial\alpha} = -\beta Tr\left[\frac{\partial H_{eff}(\alpha)}{\partial\alpha}e^{-\beta H_{eff}(\alpha)}\right] \tag{5.57}$$

Imposing the partial derivative is zero, one obtains that the thermodynamic average of the partial derivative of the Hamiltonian is also zero. The theorem is then:

$$\frac{1}{Z(\alpha)}Tr\left[\frac{\partial H_{eff}(\alpha)}{\partial\alpha}e^{-\beta H_{eff}(\alpha)}\right] = \left\langle\frac{\partial H_{eff}(\alpha)}{\partial\alpha}\right\rangle = 0. \tag{5.58}$$

The result of these considerations is called the Hellman-Feyman theorem.

The effective Hamiltonian with the above transformations bacomes:

$$H_{eff} = \sum_k \epsilon_k c_k^+ c_k + \epsilon_f \sum_{im} f_{im}^+ f_{im} + r_0 V \sum_{im}\left[c_{im}^+ f_{im} + H.C.\right] + \sum_i (\epsilon_f - E_0)(r_0^2 - 1) \tag{5.59}$$

The result is that the Hamiltonian (5.43), which is complex, has been replaced by a *quasi particle one*, containing however a renormalized f level ϵ_f *to be determined and a renormalized hybridization strength*, r_0V.

The final result is that the solution of (5.59) leads directly to renormalized band structure, since one has a one particle Hamiltonian. The ground state corresponds to a normal Fermi liquid. Again, if the chemical potential lies in a gap of the effective electronic structure, the system is an insulator. Recently, Fulde et al. have extended this effective Hamiltonian in order to get a more first principles electronic structure. This was obtained by introducing, as parameters, the "potential parameters" of a LMTO calculation. In these notes we follow the simplest approach, and introduce simplifications for the one electron propagators.

Let us first compute the propagator going from site i state m to the same site and state. We intend to calculate this propagator in powers of the hybridization strength r_0V; this procedure holds for energies far enough from ϵ_f. Since one needs the f-state occupation numbers, let us calculate the *trace* over the degenerate states m, getting:

$$ImTr_mG_{fim,im} = \frac{r_0^2V^2}{(\epsilon-\epsilon_f)^2}NImg_{m,m}(0,\epsilon) + Im\sum_{mm'} g_{m,m'}(-R_{ij},\epsilon)\frac{r_0^2V^2}{\epsilon-\epsilon_f}g_{m,m'}(R_{ij},\epsilon). \tag{5.60}$$

In expression (5.60), $g_{mm'}(R,\epsilon)$ is the non hybridized propagator from a conduction state defined in (5.44) at the site $0, m'$ to a state R, m. The result is:

$$g_{m,m'}(R,\epsilon) = 4\pi\sum_R Y_l^m(\Omega_k)\left(\epsilon-\epsilon_k+i\delta\right)^{-1}\left(Y_l^{m'}(\Omega_k)\right)^* e^{ik.R} \tag{5.61}$$

A simplified form for the conduction electron propagator can be obtained in the limit of large N (in the present case large l). The idea is to take the quantization axis as the vector R, making g_{mm} diagonal, and using the Darboux formula for the spherical harmonics in the large l limit one finally gets:

$$g_{m,m}(R,\epsilon) = \int\frac{\rho(k)kdk}{\epsilon-\epsilon_k+i\delta}J_0(kR); \quad m\le l \tag{5.62}$$

In this expression $\rho(k)$ is the number of states in the free electron band with vector k and J_0 is the Bessel function of order zero. Equation (5.62) is N independent and this is an essential point for the following considerations.

Then, keeping only the first term of (5.60), and introducing the renormalized width by:

$$\Delta = \pi r_0^2V^2\rho \tag{5.63}$$

one can calculate:

$$\rho_f = -\pi^{-1}TrG_{fimim} = \pi^{-1}N\Delta/(\epsilon-\epsilon_f)^2 \tag{5.64}$$

This corresponds to a gaussian line width, centered around the effective level ϵ_f. The density of states at the Fermi level μ can be extracted from (5.64), provided that the level ϵ_f is self consistently determined. This procedure is based in the Helmann-Feyman theorem shown in (5.57) and (5.55). Taking the thermal average of equation (5.59) and performing the partial derivative of the average energy respect to ϵ_f one gets:

$$1 - < n_f >= r_0^2. \tag{5.65}$$

Introducing the "unrenormalized width" by the natural formula of Chapter 3, one has:

$$\Delta_0 = \pi V^2 \rho. \tag{5.66}$$

one obtains for the ratio of widths:

$$\Delta / \Delta_0 = r_0^2. \tag{5.67}$$

Then the first self consistency relation reads:

$$1 - < n_f >= \Delta / \Delta_0. \tag{5.68}$$

From equation (5.64) one calculates the occupation number of the f resonance. For zero temperature, integrating (5.64) up to the Fermi level μ, one gets the equivalent of the Friedel sum rule; the result is:

$$< n_f >= \pi^{-1} N \Delta / (\epsilon_f - \mu). \tag{5.69}$$

As a final remark let us note that the renormalized width Δ is determined by the occupation number of f-electrons or the valence, as it follows from (5.65). Note that near occupation number equal to 1, the width tends to zero (r_0^2 tends to zero) as expected for a situation close to a local and stable state.

It remains to determine the effective f-level ϵ_f to have the problem entirely solved. This corresponds to establish the *energy scale* of the problem. To do that, one needs to estimate the average value of the mixing matrix element $< c_{im}^{+} f_{im} >$, since $r_0 V$ appears multiplying it.

The thermal average of the effective Hamiltonian (5.59) as derived respect to the renormalized hybridization parameter r_0 reads:

$$V \sum \left[< c_{im}^{+} f_{im} > + < HC > \right] + 2 r_0 (\epsilon_f - E_0) = 0 \tag{5.70}$$

The next step is to calculate the averaged values in the above equation; symmetry considerations make equal the two terms in the parenthesis. The equation becomes then:

$$2V \sum < c_{\mathrm{im}}^{+} f_{\mathrm{im}} > + 2 r_0 (\epsilon_f - E_0) = 0 \tag{5.71}$$

In order to calculate the average value one needs the propagator G_{cf}, which can be written in terms of the G_{ff} and the conduction band propagator g_{cc}, as:

$$G_{cf} = r_0 V g_{cc} G_{ff} \tag{5.72}$$

Then the averaged value is given by:

$$< c^+_{im} f_{im} >= -\frac{1}{\pi} r_0 V Im \int d\epsilon g_{cc} G_{ff}. \tag{5.73}$$

For a flat conduction band of width D we can neglect the real part of the propagator g_{cc} and replace g_{cc} by $-i\pi\rho$. Using the explicit form of the G_{ff} one finally gets:

$$\begin{aligned} < c^+_{im} f_{im} > &= \frac{1}{\pi} r_0 V Im \int d\epsilon \frac{i\pi\rho}{\epsilon - \epsilon_f - i\Delta} \\ &= r_0 V \rho \int d\epsilon \frac{\epsilon - \epsilon_f}{(\epsilon - \epsilon_f)^2 + \Delta^2}. \end{aligned} \tag{5.74}$$

The integral is performed between 0 and $-D$ and this integration makes a log to appear. Including this result in the equation obtained using the minimization respect to r_0, one gets:

$$V^2 \rho \int d\epsilon \frac{\epsilon - \epsilon_f}{(\epsilon - \epsilon_f)^2 + \Delta^2} + (\epsilon_f - E_0) = 0. \tag{5.75}$$

Performing the calculations one gets:

$$\epsilon_f - E_0 = -\frac{1}{\pi} N \Delta_o \log[(\epsilon_f - \mu)/D]. \tag{5.76}$$

Let us introduce some applications of the theory developed above. Consider the susceptibility associated to the resonance above:

$$\chi_0 = \frac{1}{3} \mu^2_{eff} \rho(\mu) = \frac{1}{3\pi} \mu^2_{eff} \frac{N\Delta}{(\mu - \epsilon_f)^2}. \tag{5.77}$$

We can use now the Friedel's sum rule connecting the occupation number or valence in terms of the same parameters:

$$< n_f >= 1/\pi \frac{N\Delta}{(\mu - \epsilon_f)}. \tag{5.78}$$

From this result one obtains a relation between the local density of states and the above parameters:

$$\frac{1}{\pi} \frac{N\Delta}{(\mu - \epsilon_f)^2} = \frac{\pi < n_f >^2}{N\Delta} = \rho(\mu) \tag{5.79}$$

Combining with the expression for the susceptibility one gets:

$$\chi_0 = \frac{1}{3} \mu^2_{eff} \frac{\pi < n_f >^2}{N\Delta} \tag{5.80}$$

Introducing the unrenormalized width Δ_0, one gets:

$$\chi_0 = \frac{1}{3}\mu_{eff}^2 \frac{\pi < n_f >^2}{N\Delta} = \frac{1}{3}\mu_{eff}^2 \frac{\pi < n_f >^2}{N\Delta_0(\Delta/\Delta_0)} \tag{5.81}$$

Using the relation between the occupation number and the renormalized width (5.68), one gets:

$$\chi_0 = \frac{1}{3}\mu_{eff}^2 \frac{\pi < n_f >^2}{N\Delta_0(1- < n_f >)} \tag{5.82}$$

It should be remembered that if we reintroduce the existence of the quantum number j, one would get, $\mu_{eff}^2 = g^2 j(j+1)\mu_B^2$. Quite similarly, for the specific heat one obtains from the local density of f-states:

$$\gamma = \frac{1}{3}\pi^2 k_B^2 \rho(\mu) \tag{5.83}$$

Expressions (5.82) and (5.83) correspond to the local Fermi liquid theory. There is however another quantity that can be estimated using the same procedures: this is the *charge susceptibility*, defined by the change in occupation number with the position of the bare f-level. Taking the change in the stationary value of (ϵ_f, Δ) one gets for χ_c defined as

$$\chi_c = -\frac{d < n_f >}{dE_0} = \pi N^{-1}\Delta_0^{-1} < n_f >^2 (1- < n_f >) \tag{5.84}$$

These remarks conclude this simplified description of the slave boson method.

Chapter

APPENDIX - LINEAR RESPONSE THEORY

In this Appendix we focus our interest in describing how an external perturbation can modify the dynamics of a given system. In Chapter 3 we have defined and applied the concept of susceptibility which corresponds to induce a change in magnetic properties of a system upon the application of a magnetic field. This concept has been very useful in describing magnetic instabilities and the RKKY interaction. Here we intend to present, for a general system and using the formulations introduced by Kubo, the response to a general externally applied perturbation. We will try to be the most general possible in the calculated responses and in the order of the perturbation.

First of all consider a system described by an Hamiltonian H_0 and let us apply an external time dependent perturbation, we call $H^{ext}(t)$. External perturbations couple to the system via the corresponding operators. For example in the susceptibility case, the operator is the magnetic moment of the system.

Returning to the general case, the complete Hamiltonian is then:

$$H = H_0 + H^{ext}(t), \tag{A.1}$$

where

$$H^{ext}(t) = -\sum_j B_j F_j(t), \tag{A.2}$$

in this equation B_j are operators of the system and $F_j(t)$ is the form and intensity of the external perturbation. Usually the external perturbations are adiabatically switched. This induces the absence of transients associated to the quick switching of an external perturbation. In order to mathematically define the adiabatic process, let us present (A.2) in Fourier transformed form and including the adiabatic switching term proportional to $e^{\epsilon t}$. One sees that for large negative times the perturbation vanishes, and for $t = 0$ the full strength occurs. In mathematical terms:

$$H^{ext}(t) = \sum_j \sum_\omega e^{\epsilon t - i\omega t} B_j F_j(\omega), \qquad \epsilon \to 0. \tag{A.3}$$

Note that all the time dependence is included in the exponential and the B_j operators are time independent.

The physically interesting quantities involve both the averages, in the quantum mechanical and statistical mechanics senses, of the operators associated to the system in consideration. In order to obtain these averages the density matrix operator ρ is required, since $< A >= trace[\rho A]$.

The time evolution of the density matrix operator is given by Liouville's equation:

$$i\frac{\partial \rho}{\partial t} = \left[H_0 + H^{ext}(t), \rho(t)\right]. \tag{A.4}$$

where we use, for practical purposes, $\hbar = 1$. Since we intend to separate the effects of internal dynamics of the system from the external perturbation, let us introduce the *interaction representation* for the operator density matrix. This is defined by:

$$\rho_1 = e^{iH_0t}\rho(t)e^{-iH_0t}. \tag{A.5}$$

The derivation of the above equation is given by:

$$\begin{aligned} \frac{\partial \rho_1}{\partial t} &= iH_0e^{iH_0t}\rho(t)e^{-iH_0t} + e^{iH_0t}\frac{\partial \rho(t)}{\partial t}e^{-iH_0t} - ie^{iH_0t}\rho(t)H_0e^{-iH_0t}. \\ &= i\left[H_0, \rho_1(t)\right] + +e^{iH_0t}\frac{\partial \rho(t)}{\partial t}e^{-iH_0t}. \end{aligned} \tag{A.6}$$

Using the definition (A.5) and the identity operator $e^{-iH_0t}e^{iH_0t}$, we get:

$$i\frac{\partial \rho_1}{\partial t} = \left[H_1^{ext}(t), \rho_1(t)\right], \tag{A.7}$$

where $H_1^{ext}(t) = e^{iH_0t}H^{ext}(t)e^{-iH_0t}$ is the interaction representation form of the external interaction.

Writing in $H_1^{ext}(t)$ in such a way that the operators B_j are written in the interaction representation leads to:

$$H_1^{ext}(t) = -\sum_j B_j(t)F_j(t) \tag{A.8}$$

Combining equation (A.7) and (A.8) one finally gets:

$$i\frac{\partial \rho_1}{\partial t} = \sum_j \left[\rho_1(t), B_j(t)\right] F_j(t). \tag{A.9}$$

This differential equation can be easily transformed in an integral equation, including the boundary condition $\rho_1(t) = \rho_0$ to for large negative times. ρ_0 is the density operator in the absence of external perturbations, namely:

$$\rho_0 = \frac{e^{-\beta H_0}}{Tre^{-\beta H_0}} \tag{A.10}$$

The integral form is given by:

$$\rho_1(t) = \rho_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j \left[\rho_1(t'), B_j(t')\right] F_j(t')dt'. \tag{A.11}$$

This is the general integral form of equation (A.9). Formally its solution in terms of ρ_0, $B_j(t')$ and $F_j(t')$ is obtained by an interaction procedure increasing powers of the perturbation $B_j(t')$

However usually the strength of the external perturbation is small as compared to the internal energies of the system. An example of this situation was presented in Chapter 3 for the derivation of the Pauli susceptibility.

We then retain our calculations only to first order in the external perturbation. This corresponds to retains in the right hand side only the term $\rho_1(t') = \rho_0$, getting:

$$\rho_1(t) = \rho_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j \left[\rho_0, B_j(t')\right] F_j(t')dt' \tag{A.12}$$

Multiplying (A.12) on the left by $e^{-iH_0(t)}$ and on the right by $e^{iH_0(t)}$ one finally gets:

$$\rho(t) = \rho_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j \left[\rho_0, B_j(t'-t)\right] F_j(t')dt'. \tag{A.13}$$

This equation enables the calculation of the averaged value of any operator in terms of the unperturbed density matrix, and this is the central result for the linear response theory.

Next step is to obtain a closed expression for the change in average value of an observable upon application of the perturbation. From equation (A.13) one gets:

$$< A >= Tr(\rho_0 A) + \int_{-\infty}^{t} \frac{1}{i} \sum_j Tr\left(\left[\rho_0, B_j(t'-t)\right] A\right) F_j(t')dt'. \tag{A.14}$$

Using the trace invariance under interchange of operators, it is possible to transform equation (A.14) in to the following:

$$< A >=< A >_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j trace\left[\left[A, B_j(t'-t)\right] \rho_0\right] F_j(t')dt' \tag{A.15}$$

Performing the averaged using the density matrix ρ_0 one gets:

$$< A >=< A >_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j \left\langle\left[A, B_j(t'-t)\right]\right\rangle F_j(t')dt'. \tag{A.16}$$

In words, the change in average value of the observable A is given by the average value of commutator of the observable A with the time dependent operator coupling to the external perturbation.

In order to get a more adequate expression including the causality principle let us introduce some transformations explicitating the t and t' dependence of the operator $e^{iH_0 t}$ and $e^{H_0 t'}$. The final result is:

$$< A >=< A >_0 + \int_{-\infty}^{t} \frac{1}{i} \sum_j \langle [A(t), B_j(t')] \rangle \, F_j(t') dt'. \tag{A.17}$$

This means that the change in averaged value is connected to commutator of the observable A and perturbation B_j, in the system Heisenberg representation.

Chapter

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