

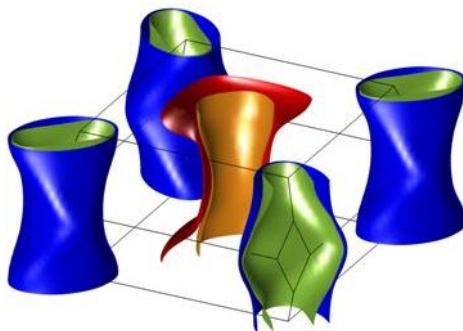


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THESIS SUBMITTED FOR THE DEGREE OF MASTER IN PHYSICS

Bogoliubov-de Gennes studies of Fe-based superconductors

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ABSTRACT

The recent discovery of superconductivity in the Fe-based compounds has led to thousands of publications on this subject over the last four years. These compounds are the second-highest-temperature superconducting material family known to date. In this work, we built a real-space five-orbital Hubbard model relevant to the Fe-based superconductors. A correct stripe-type antiferromagnetic order is found for the parent compound. Moreover, the model reproduces a reasonable phase diagram of the mean fields against doping. In the single-impurity problem, local orbital ordering, in-gap bound states and magnetization are induced around the potential. Finally, we include the effective pairing couplings calculated within the spin fluctuation theory, and find realistic gap structures and impurity bound states than can be directly compared to STM measurements.

LABURPENA

Fe-oinarritutako konposatueta supereroankortasuna aurkitu zenetik, milaka argitalpen agertu dira gai honen inguruan azken lau urteotan. Konposatu hauek bigarren tenperatura-altueneko material familia osatzen dute. Lan honetan, espazio errealeko bost-orbital Hubbard eredu bat eraiki dugu, Fe-konposatuetaarako aproposa. Lerromota antiferromagnetiko zuzena aurkitua izan da “guraso” konposatuan. Gainera, ereduak batez besteko eremuen zentzuzko fase diagrama erreproduzitzen du. Ezpurutasunbazarreko probleman, orbital-ordena, egoera propioak tarte debekatuan, eta magnetizazio lokalak indutitzen dira potentzialaren inguruan. Azkenik, spin fluktuazio teoriatik lortutako parekatze lotura efektiboak erabiliz, STM neurketekin zuzenean aldera daitezkeen tarte debekatuaren egitura eta ezpurutasun egoera propio errealistak lortu dira.

RESUME

Den nylige opdagelse af superledning i de Fe-baserede materialer har allerede ført til tusindvis af publikationer indenfor dette felt i de seneste fire år. Disse systemer har vakt opsigt fordi de har den anden-højeste kritiske temperatur kendt til dato. I dette speciale anvender vi en real-space fem-orbital Hubbard model hvilket er relevant for disse Fe-baserede superledere. For de udoterede systemer forudsiger modellen den korrekte stribe-formede antiferromagnetisme. Desuden reproducerer modellen de selv-konsistente middelfelter det korrekte fasediagram. I tilfældet med en enkelt urenhed finder vi at der naturligt induceres lokal orbital og magnetisk orden, samt bundne tilstande inden i det superledende gap. Vi har også inkluderet de effektive par-koblinger udregnet indenfor spin-fluktuations teorien, og finder en resulterende realistisk superledende gap-struktur, samt medførende urenheds bundne tilstande som kan blive direkte sammenlignet med fremtidige STM målinger.

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Chapter 1

Introduction to the Fe-based superconductors

1.1 Fe-based SC

The discovery of superconductivity at 26 K in LaFeAsO by Kamihara *et al.* [1] in 2008 opened a new route to high-temperature superconductivity. Within two months, the critical temperature T_c of Fe-based materials was risen to 56 K, becoming the second-highest-temperature superconducting material family known to date. The highest-temperature superconducting material family are cuprates, with T_c beyond 150 K. Historically, the typically antagonistic relationship between superconductivity and magnetism has led researchers to avoid using magnetic elements as potential blocks of new superconducting materials. Fe metal is a ferromagnet so the discovery of this new *high- T_c* class was a big surprise. In the past few years, there have been efforts to understand these new compounds, including the normal state properties, the pairing mechanism, and the symmetry and structure of the superconducting gap. Their conceptual importance is agreed to be the following: however unique cuprates may be, their features are not prerequisites for non-phonon, high-temperature superconductivity.

Looking at the crystallographic structure of Fe-based superconductors (FeSC), one finds a common chemical building block: a quasi-two-dimensional layer FeX. The X = As, P, S, Se or Te element, lies in nearly tetrahedral positions above and below a square array of Fe as shown in figures 1.1(a) (FeX highlighted in yellow) and (b). It is widely believed that the interaction that leads to superconductivity originates within these common FeX trilayers. In some of the compounds these FeX layers are separated by other “bridging layers” along the crystallographic c-axis (perpendicular to FeX) such as Ba layers in BaFe₂As₂, or LaO layers in LaOFeAs.

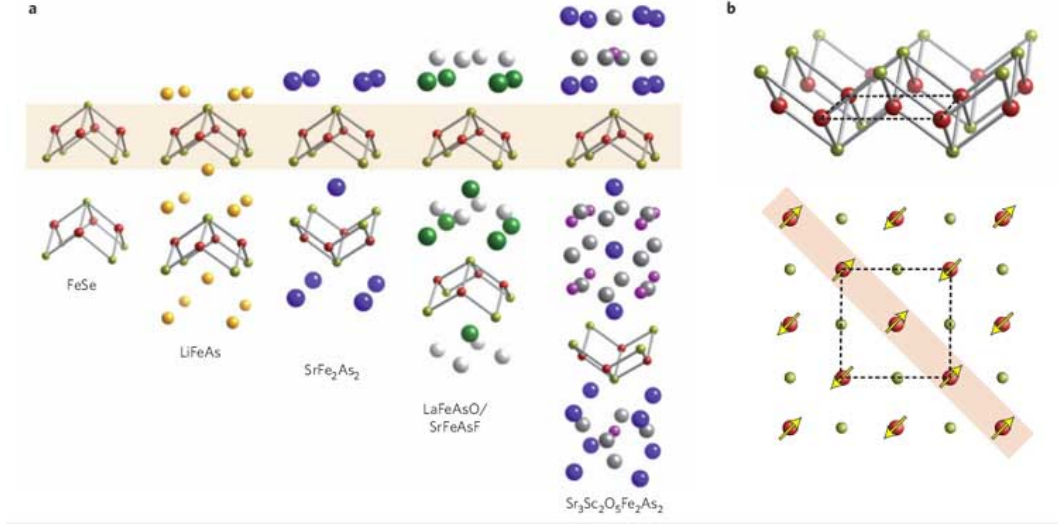


Figure 1.1: Crystallographic and magnetic structures of the Fe-based superconductors. (a) Five subfamilies. From left to right 11, 111, 122, 1111 and 32522. This naming is chosen from their elements chemical ratio. (b) Top: FeX building common block. Red spheres represent Fe and yellow spheres the element X. Bottom: Striped antiferromagnetic order. Spins are ferromagnetically aligned along one chain and antiferromagnetically along the perpendicular direction (see section 1.3 for more details). From [2].

FeSC come in many different chemical compositions forming a quite large family (see figure 1.1(a)). Some of them include 1111-type compounds such as LaOFeAs (for its 1:1:1:1 ratio of the four elements), 122-type in BaFe_2As_2 , 111-type LiFeAs , and 11-type FeSe , with critical temperatures of 28 K, 38 K, 18 K and 8 K respectively. These have been the most extensively studied Fe based compounds so far.

In the next sections of this chapter, a brief overview of selected FeSC topics relevant for the following chapters, will be discussed: the normal state properties, the phase diagram, and the superconducting state.

1.2 Electronic structure and multiorbital physics

The nature of the ground state of the “parent” (undoped) compounds is an important issue. In the normal state the band structure is semimetallic, with equal density of negative and positive charge carriers. Figure 1.2(a) shows a schematic band structure of a semiconductor and a semimetal. The lower band is the valence band and the upper band is the conduction band. In a semimetal, those

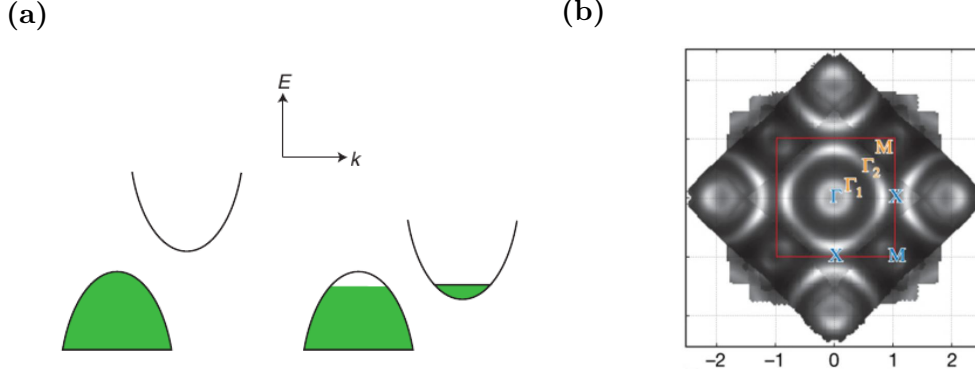


Figure 1.2: (a) Sketch of the band structure of a semiconductor (left) and a semimetal (right). The energy E of an electron is plotted versus the momentum k . The parts of each band filled by electrons are shown as solid green. The semiconductor has a filled lower band and a empty upper conduction band separated by a band gap so that at $T = 0$ the material is an insulator. The semimetal on the contrary has a slight overlap in energy of both bands so that at $T = 0$ the material behaves as a metal, with a finite conductivity. (b) ARPES measurements of the 1111-type compound LaOFeP. Fermi surface map in a 2-Fe BZ (see text) with the three sheets: Γ_1 and Γ_2 are two hole-like pockets centered at Γ , and M is the electron pocket centered at M . The axis are the momentum in units of π/a . From [3].

two bands are horizontally displaced and overlap slightly in energy. Therefore, some electrons from the valence band spill over to the conduction band, until the energies of the highest occupied electron states in each band become the same. The current carriers in the valence bands are “holes”, because they arise from holes in the electron population at the top of the band, and are “electrons” at the bottom of the conduction band. Thus one speaks of hole and electron pockets. These disconnected pockets are directly observed in angle-resolved photoemission spectroscopy (ARPES) measurements [3] of the Fermi surface of FeSC: two hole bands near the centre of the Brillouin zone (BZ) and two electron bands near the corners (see figure 1.2(b)).

Let us go back to the crystallographic structure of the FeX trilayer. The element X is located above and below the Fe plane in tetrahedral positions, as shown in figure 1.3(a). The correct crystallographic unit cell includes then two Fe atoms, and is known as the 2-Fe unit cell. However, in some cases the low-energy part (measured from the Fermi level and compared to the bandwidth) can be “unfolded” into one containing just one Fe, which is half as large as the correct one. This is known as the 1-Fe unit cell. Both unit cells are schematically shown in figure 1.3(a) as a blue square (2-Fe) and a green square (1-Fe). (b) and (c)

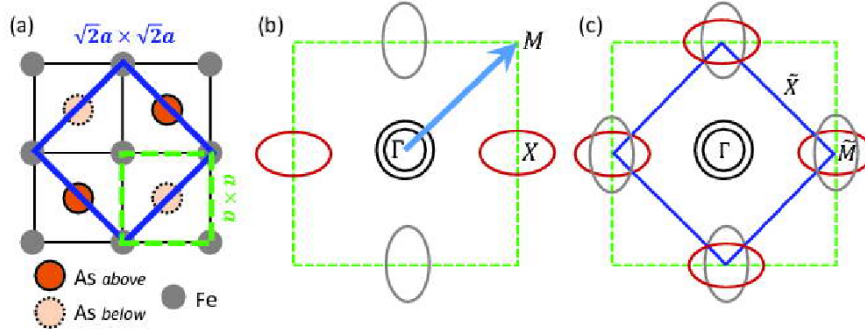


Figure 1.3: (a) FeX trilayer where $X=\text{As}$. Solid blue square indicates the 2-Fe correct crystallographic unit cell and dashed green the 1-Fe unit cell. (b) Sketch of the FS in the 1-Fe unit cell. (c) Sketch of the FS in the 2-Fe unit cell. The mapping would be such that $\tilde{M} = (\pi/\tilde{a}, \pi/\tilde{a})$ in the correct crystallographic cell unfolds to $X = (0, \pi/a)$ and $Y = (\pi/a, 0)$ in the 1-Fe unit cell. From [4].

in the same figure show the Fermi surface in the 1-Fe and 2-Fe BZs, respectively. The hole-pockets are the black rings in the center of the BZ, and the gray and red ellipses in the corners, the electron pockets. The blue arrow indicates the folding wave vector that connects both BZs. Theoretically, the 1-Fe unit cell simplifies the model, since the number of bands is smaller by a factor of two. Throughout this work, we will assume that the system can be unfolded, and work in the simplified 1-Fe crystallographic unit cell.

What do we know about the electronic states that lie around this Fermi surface? Fe^{2+} is a 3d transition metal ion with five d-states: d_{xz} , d_{yz} , d_{xy} , $d_{x^2-y^2}$ and d_{3z^2} . Electronic structure properties have been studied from a theoretical point of view within density functional theory (DFT) calculations, a quantum mechanical modeling method. These calculations successfully predicted the right Fermi surface and reasonable band structures compared to, for example, ARPES measurements (see figure 1.4(a)). It was found that:

1. All five d orbitals have weight at the FS.
2. The density of states (DOS) near the FS is due almost entirely to these 5 d-states, with the states of the other elements some eV below the Fermi level (see figure 1.4(b)). In principle this would allow to make a simplified low-energy model which includes just Fe d-states.
3. In addition, there is substantial overlap between the orbitals, making the minimal model (the simplest model that describes the main features of FeSC) be essentially *multiband*, i.e., one should include both hole and electron

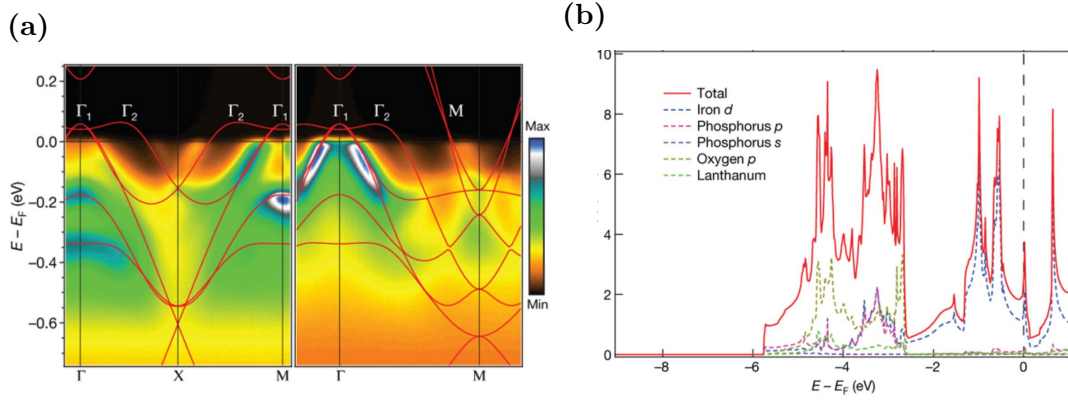


Figure 1.4: (a) ARPES data of the LaOFeP parent compound. Comparison between measured spectra and local density approximation (LDA) band structures (red curves). Along the Γ -X direction, two bands crossing E_F can be identified: Γ_1 and Γ_2 associated with the two hole-like pockets centered at Γ . Along the Γ -M direction, an additional crossing near the M point can be observed, related to the electron pocket centered at M. (b) LDA DOS calculation for LaOFeP. The full red curve represents the total DOS. The Fe d-states (dashed blue line) dominate around E_F , whereas the rest of the states (the other dashed curves) lie several eV below. Both figures were taken from [3].

bands. This has the complication of harder calculations including several orbitals, but also brings new interesting multiband physics to the scene.

1.3 Magnetic order and the phase diagram

Crudely the phase diagrams of all FeBS are quite similar. Schematic of different possibilities are shown in figure 1.5. A generic phase diagram can be produced either by manipulating the chemical properties (using chemical doping), or by applying pressure.

In all these systems of parent compounds, the high temperature structures are tetragonal and the low temperature structures are distorted variants. As temperature is lowered, a structural transition happens at T_s from tetragonal to orthorhombic phase for most materials. The distance between iron atoms in one of the directions shortens by approximately 1% as compared with the perpendicular direction. In most of the undoped compounds, this structural transition is followed by (or happens simultaneously with) a magnetic transition at the Néel temperature $T_N \lesssim T_s$, where an antiferromagnetic order of spins appears. This long-range magnetic order couples intimately with the structural distortion and also shares a

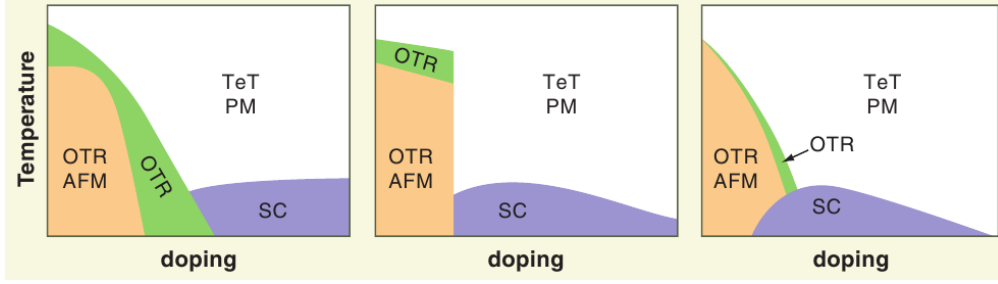


Figure 1.5: Schematic possible phase diagrams for FeBS. Different colors stand for different phases. The main difference is how superconductivity (solid purple) emerges. OTR, orthorhombic; Tet, tetragonal; AFM, antiferromagnetic; SC, superconducting; PM, paramagnetic phase. From F. Wang *et al.* [5].

similar pattern in all of the Fe-based systems. With the exception of the 11 subfamily, the spatial arrangement of the magnetic moments is striped AFM, with the ordering vector $Q = (1, 0)_o$, where o stands for orthorhombic basis. In real space this means that spins are ferromagnetically arranged along one chain of nearest neighbors within the iron lattice plane, and antiferromagnetically arranged along the perpendicular direction (see figure 1.1(b)). The 11 subfamily has a distinct structural transition to monoclinic structure and a different $Q = (1/2, 0)_o$ magnetic ordering.

The nature of the ordered state in these materials has been a topic of considerable study. It has been explained from both the itinerant (weak correlations) and the localized (strong correlations) electron point of view.

For the itinerant electron magnetism, it was shown [6] that a spin-density-wave (SDW) state develops due to Fermi surface nesting. Nested Fermi surfaces are such that different sections of it coincide when shifted by a certain wavevector $\mathbf{q}$. Mathematically, the energy spectrum satisfies the condition $\xi(\mathbf{k} + \mathbf{q}) = -\xi(\mathbf{k})$ at the Fermi surface, at a particular $\mathbf{q}$ for all (perfect nesting) or several (quasi-nesting) $\mathbf{k}$ vectors. Then the system is said to be nested, and it is unstable with respect to a wave formation with the corresponding wavevector $\mathbf{q}$. If the electron-electron interaction is repulsive, the instability develops in the spin channel and a SDW appears (see D. Khomskii [7]). In FeSC, the Fermi surface is quasi-nested by the commensurate vector $\mathbf{q} = (\pi, 0)$ (and the C_4 symmetric $(0, \pi)$), which connects the hole and electron pockets (see figure 1.3(b)). With the appearance of the stripe-like ordering pattern (see figure 1.1(b)) at the nesting vector, partial gaps open at different locations of the Fermi surface (because the nesting is not perfect) and the system remains semimetallic. This reconstruction of the FS has been measured by ARPES [8]. Recently, the SDW gap was directly observed for the first time by STM measurements on the 122-type NaFeAs compound [9]. Moreover, the

typically measured small ordering moment by neutrons [10] has been also invoked as evidence for the itinerant character of the magnetism.

A drastically different viewpoint of antiferromagnetic ordering arising from local moments (Heisenberg model) has also been proposed. To reconcile the apparent conflict, another theoretical model proposes that the local moments and itinerant electrons may coexist. In this last scenario, part of the Fe d bands are delocalized and contribute to the itineracy, whereas the others are localized due to strong correlation effect and provide the source for local moments. Finally, it has been also proposed that both the magnetic and structural transitions are driven by orbital-physics. At this writing, there is no clear consensus about the nature of magnetism in these compounds.

Going back to the phase diagram, when doping the system, antiferromagnetism vanishes. At some nonzero doping superconductivity appears and then disappears, such that T_c forms a “dome”. Therefore, like cuprates, the superconducting regime in these Fe-based materials occurs in close proximity to a long-range-ordered antiferromagnetic ground state. The main difference among different materials is how superconductivity emerges, as illustrated in figure 1.5. It may appear either abruptly or continuously, but it may also coexist with antiferromagnetism over a finite range.

The next section focuses on the superconducting state in these materials.

1.4 The superconducting state

The fundamental mechanism that causes the high-temperature superconductivity in these materials is still a debated issue. Early after their discovery, it was realized that the mechanism involving exchange of phonons, as in the BCS theory, was not enough to produce the observed high T_c [11] (as it happened also with cuprates). Once superconductivity is settled down however, the BCS theory of conventional superconductors still suffices to explain quite accurately the physics of these materials. We begin then this section by reviewing the BCS theory, and focus the rest of the chapter on the superconducting state of the FeSC.

1.4.1 Microscopic BCS theory

Cooper’s analysis from 1956 of the instability of the electron gas shows that below a certain critical temperature T_c a new ground state is formed involving bound electron pairs in time-reversed states. These quasiparticles, called Cooper pairs, are formed near the Fermi level and form the superconducting condensate. After this result, the Bardeen-Cooper-Schrieffer (BCS) microscopic theory of superconductivity was developed in 1957. The reduced mean field BCS Hamiltonian is

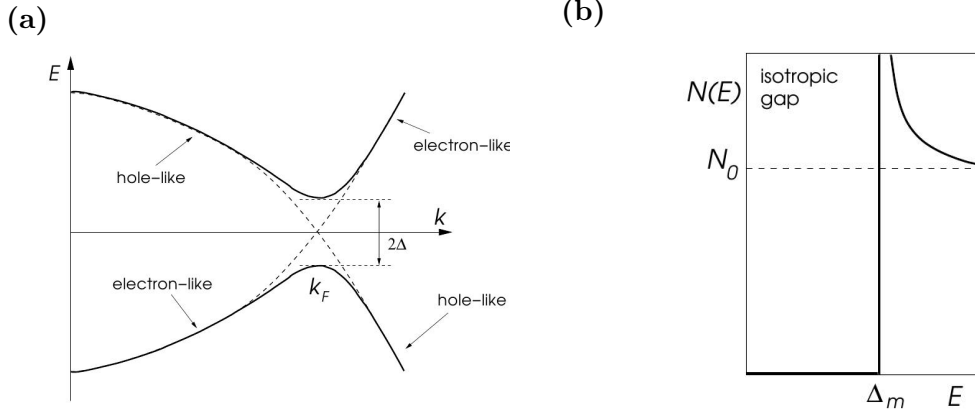


Figure 1.6: (a) Schematic BCS quasiparticle spectrum. The solid line shows the spectrum with a finite energy gap and the dashed line corresponds to the spectrum for $\Delta = 0$. (b) Density of states. There are no quasiparticles with an excitation energy between $-|\Delta|$ and $|\Delta|$, and outside this interval there are spikes in the density of states.

given by

$$H_{BCS}^{MF} = \sum_{k\sigma} \xi_k \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} - \sum_k (\Delta_k \hat{c}_{k\uparrow}^\dagger \hat{c}_{-k\downarrow}^\dagger + H.c.) \quad (1.1)$$

where the operators $\hat{c}_{k\sigma}^\dagger$ ($\hat{c}_{k\sigma}$) create (annihilate) an electron with momentum k and with spin projection σ . Here ξ_k is the energy spectrum of the free electrons and $\Delta_k = -\sum_{k'} V_{kk'} \langle \hat{c}_{-k'\downarrow} \hat{c}_{k'\uparrow} \rangle$ the mean field parameter or superconducting order parameter (OP). An attractive coupling strength $V_{kk'} < 0$ is assumed, which in conventional superconductors is due to the phonon-mediated electron-electron interaction. Solving this Hamiltonian by the unitary Bogoliubov transformation we obtain

$$H_{BCS}^{MF} = \sum_k E_k (\gamma_{k\uparrow}^\dagger \gamma_{k\uparrow} + \gamma_{k\downarrow}^\dagger \gamma_{k\downarrow}) + GS. \quad (1.2)$$

The Bogoliubov quasiparticle excitation spectrum is given by $E_k = \sqrt{\xi_k^2 + |\Delta_k|^2}$, which implies that there are no fermion excitations with energies less than $|\Delta_k|$. The mean-field parameter Δ_k thus provides an energy gap denoted the superconducting gap. In a uniform superconductor the interaction depends only on the relative position of the electrons $V(\rho)$, with $V(\rho) \equiv r - r'$ in real space. Therefore in the absence of impurities the structure of the OP in real space depends on the symmetry properties of $V(\rho)$. If the attraction is local, $V(\rho) = V_0 \delta(\rho)$, the Fourier transform of the interaction is featureless and $\Delta_k = \Delta_0$, the conventional isotropic s-wave superconductor. Figure 1.6(a) shows the Bogoliubov spectrum with a gap of size $2|\Delta|$ opening around the Fermi energy, and the lack of quasiparticles in the

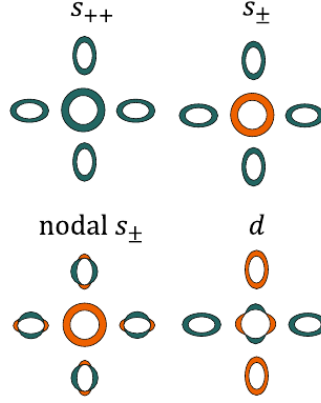


Figure 1.7: Cartoon of order parameters under discussion in FeSC superconductors represented in the 1-Fe Brillouin zone. Different colors stand for different signs of the gap.

energy range $-|\Delta| < E < |\Delta|$ in the DOS is shown in the same figure (b).

BCS derived several theoretical predictions that have been confirmed in numerous experiments.

1.4.2 Gap symmetry and structure

Let us now turn to the superconductivity in the FeSC materials. The superconducting order parameter Δ or “gap function”, is a complex function with both amplitude and phase that describes the macroscopic quantum state of Cooper pairs. Details of the pairing interaction, can induce a variation in momentum space of this amplitude, or a variation of phase that could imply a change of sign of the OP. Understanding both the symmetry character of the superconducting ground states and the detailed structure should then provide clues to the microscopic pairing mechanism in the FeSC .

The first question to be asked regarding the pairing state in these novel superconductors is, what is the *symmetry* of the order parameter? Electrons being fermions the full wave function is always antisymmetric under particle exchange of the Cooper pair. The pair wave function $\Psi_{\sigma\sigma'}(k) = g(k)\chi_{\sigma\sigma'}$ has a spin part $\chi_{\sigma\sigma'}$ and a spatial part $g(k)$. Therefore, the spatial part of $\Psi_{\sigma\sigma'}(k)$ is even for spin singlet superconductors and odd in the spin-triplet case. Expanding in eigenfunctions of orbital momentum, it follows that spin singlet pairing corresponds to *even* orbital function of momentum $\mathbf{k}$ and hence we call it s-wave (for $l = 0$), d-wave (for $l = 2$), etc. superconductor in analogy with the notation of atomic states. In the same way, for a spin triplet superconductor, the orbital part is an *odd* function of $\mathbf{k}$ and it can be p-wave ($l = 1$), f-wave ($l = 3$) etc. Characterization in

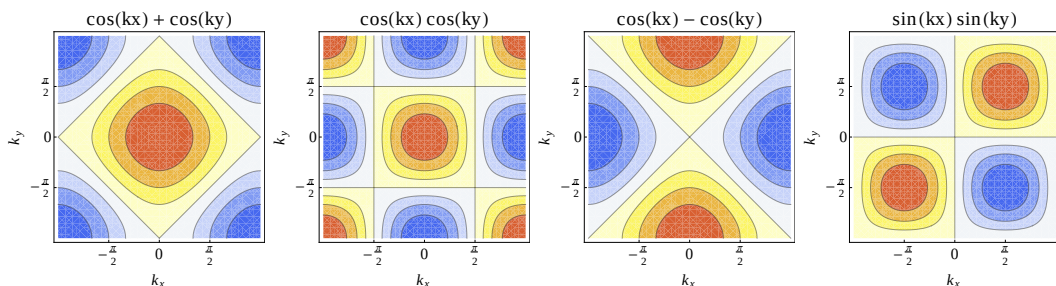


Figure 1.8: Representative gap functions for the tetragonal lattice (red=+, blue=-). From left to right: Δ_k^{s*} , $\Delta_k^{s\pm}$, $\Delta_k^{d_{x^2-y^2}}$ and $\Delta_k^{d_{xy}}$. Note where nodal lines lay for the different cases. Nodes in the hole pockets are unavoidable for d-wave symmetry.

terms of orbital moments is an oversimplification, and this terminology has to be used understanding that the correct symmetries are implied for a given crystal structure (tetragonal, hexagonal etc.). Experiments in FeSC appear to rule out spin triplet states, so the orbital part has to be *even*. We are left then with the following singlet pairing possibilities: s-wave, d-wave, g-wave etc. according to how the order parameter transforms under rotations by $\pi/2$ and other operations of the tetragonal group. For example, s-wave order parameter does not change sign under a $\pi/2$ rotation; on the contrary, d-wave does change its sign.

Within a given symmetry class, the order parameter can have a k-dependent variation, i.e. a gap *structure*. Gaps with the same symmetry may have different structures which include anisotropy of the amplitude, nodes, changes of sign etc. These are driven by the details of the pairing interaction and are not dictated by symmetry. Given the complexity of the FS in these materials there are multiple ways in which superconducting gaps may open in each band, even in the simple s-wave symmetry. The simplest option is the isotropic and fully gapped s_{++} state, in which all pockets develop a gap with the same amplitude and phase. But one could also have a case in which there is a relative phase of π (sign change) between the hole and electron pockets. This is the so called extended s-wave or $s_{\pm}$ state. Note that this state is still invariant under a $\pi/2$ rotation. Another possibility is one for which apart from this sign change between pockets, nodes develop in the electron pockets, what is called nodal $s_{\pm}$ state. These three examples have the same gap symmetry but different gap structure and are shown in figure 1.7 for a model FS with a hole and an electron pocket.

Representative basis gap functions in a tetragonal lattice for both s- and d-wave symmetries are discussed below and showed in figure 1.8. We consider here pairing until next-nearest neighbor on a simple square lattice. Note that the gap of an s-wave state must conserve the sign under a $\pi/2$ rotation, whereas a d-

wave state must change its sign. For the s-wave symmetry, linear combinations of singlets between the l^{th} site and its four next-nearest neighbors, leads to the $s_{\pm}$ gap function,

$$\Delta_k^{s_{\pm}} = 4\Delta_0 \cos k_x \cos k_y. \quad (1.3)$$

If the pairing is with the four nearest neighbors instead, we then get the nodal $s_{\pm}$

$$\Delta_k^{s_{\pm}^*} = 2\Delta_0(\cos k_x + \cos k_y). \quad (1.4)$$

In the d-wave symmetry case (sign changing now) pairing of nearest neighbor sites gives the $d_{x^2-y^2}$ -wave,

$$\Delta_k^{d_{x^2-y^2}} = 2\Delta_0(\cos k_x - \cos k_y) \quad (1.5)$$

and finally with the next-nearest neighbors the d_{xy} -wave

$$\Delta_k^{d_{xy}} = 4\Delta_0 \sin k_x \sin k_y. \quad (1.6)$$

Among all those possibilities the leading candidate is the $s_{\pm}$ state. To understand why, let us examine the finite-temperature BCS gap equation,

$$\Delta_k = - \sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \tanh \frac{E_{k'}}{2T}. \quad (1.7)$$

One sees that the sign of $V_{kk'}$ constraints the possible solutions for Δ_k . For the conventional phonon-exchange mechanism, the effective interaction between electrons is attractive, $V_{kk'} < 0$. The gap equation (1.7) allows then an isotropic full gap solution $\Delta_k = \Delta_0$. In the FeSC, the exchange of phonons is not enough to overcome the repulsion, and therefore $V_{kk'} > 0$. The only way of satisfying equation (1.7) is then if the state changes sign,

$$\Delta_k = -\Delta_{k+Q}. \quad (1.8)$$

Therefore, repulsive interactions can cause pairing when, and only when, the wave vector of such a fluctuation spans parts of the Fermi surface(s) with opposite signs of the OP. Let us assume now, within a weak-coupling approach, that the pairing interaction in FeSC arises from the exchange of spin fluctuations (for more details see chapter 5). The quasi-nesting of the hole and electron pockets suggests a peak in the spin susceptibility at $Q = (\pi, 0)$, implying that the effective interaction mediated by the exchange of spin fluctuations $V_{kk'}$ is peaked at this nesting vector. The gap equation admits then a solution if there is a sign change between hole and electron pockets. This led in the very beginning to theorists to suggest the isotropic $s_{\pm}$ state [11] (see figure 1.12(a)), right after the discovery of the first Fe based compounds.

1.4.3 Experiments

Generally speaking, three types of experimental results have been reported: full-gap like, nodal-gap like, and multi-gap superconducting states. Surface probes such as Scanning tunneling microscopy (STM) and ARPES show full gaps with no nodes for a large variety of materials. Since in the d-wave symmetric state nodes on the hole pockets are mandated by symmetry (figure 1.8 and the FS in 1.3), a d-wave state seems in general unlikely. Even though it is more or less agreed that the symmetry is for most, if not for all compounds, s-wave, it does not tell us much about the structure of the order parameter. After few years of intensive research on the FeSC, no consensus on any universal gap structure has been reached, and there is strong evidence that small differences in electronic structure can lead to strong diversity of superconducting gap structures, including nodal gaps in some and full gaps in other materials.

In the following, some experimental results are presented:

1. *STM*. A scanning tunneling microscope consists of a sharp metallic tip which is rastered several Å above an electrically conducting sample. When a voltage V is applied between the tip and the sample, a current will flow. This current can be measured as a function of location (x, y) and V . STM can measure the sample DOS as a function of energy, up to several eV from the Fermi level in both occupied and unoccupied states. This is accomplished by sweeping the bias voltage V and measuring the tunneling current I while maintaining constant tip-sample separation d . By differentiating $I(V)$, the conductance dI/dV is found to be proportional to the sample DOS. This gives us a direct information about the energy spectrum, and then about the superconducting gap features. Figure 5.13 shows STM measurements of two different compounds, with different nodeless and nodal multiple-gaps. More examples will be shown in the next chapters.
2. *Quasiparticle interference (QPI)*. When materials are inhomogeneous, quasiparticles scatter off defects within the crystal, and energy-dependent standing waves form. The resulting interference patterns in the quasiparticle DOS can be imaged with STM. The Fourier transform of the real space interference highlights the dominant sets of quasiparticle momenta. This information can be used to distinguish between candidate superconducting OPs. Figure 1.10 shows two examples of QPI measurements in FeSC. In (a) the magnetic field-induced change in the QPI intensities was analyzed on the 11-type compound $\text{FeTe}_{1-x}\text{Se}_x$. Red (blue) areas represent decreasing (increasing) intensity at those momenta. From the opposite behaviors of vectors q_2 (connecting hole and electron pockets) and q_3 (connecting electron pockets), which indicate two different scattering characters, the authors conclude a sign change

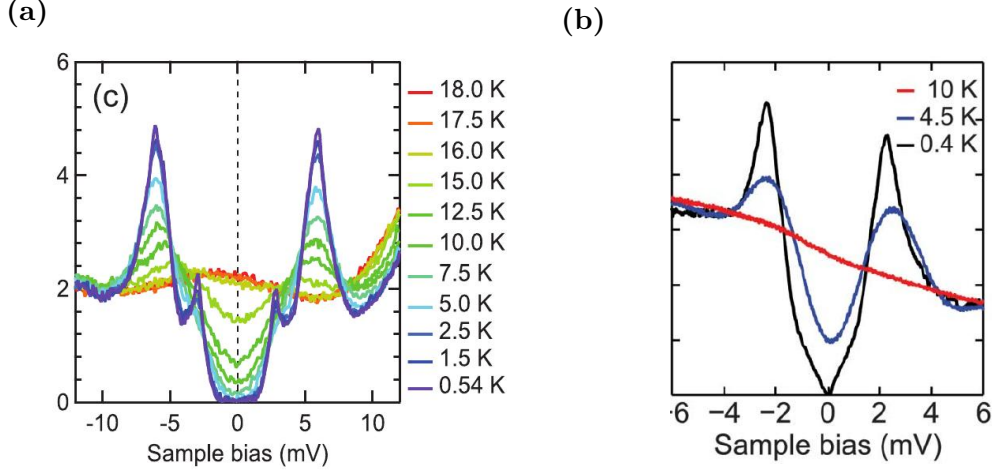


Figure 1.9: STM measurements of the conductance dI/dV for different FeSC compounds. (a) Low energy tunneling spectra of the 111-type material LiFeAs at different temperatures. Two gaps are identified at $\Delta_1 \sim 3$ meV and $\Delta_2 \sim 6$ meV. From [12]. (b) Temperature dependence of differential conductance spectra of the 11-type material FeSe. The superconducting gap presents clear nodes. From [13].

of the superconducting gap. They also observed a fully gapped superconducting spectra, which supports the $s_{\pm}$ scenario. In figure 1.10(b), multiple anisotropic energy gaps were found in the hole-like bands of LiFeAs. They were able to determine the magnitude and relative orientations of the gaps by the QPI technique.

3. *ARPES*. Is a direct experimental technique to observe the distribution of the electrons (more precisely, the density of single-particle electronic excitations) in the reciprocal space of solids. ARPES is one of the most direct methods of studying the electronic structure of the surface of solids, and then one of the most direct probes of superconducting gap structure. Until the beginning of 2012 no ARPES experiment had reported gap nodes or even significant anisotropy [16], [17], in disagreement with several other probes. Figures 1.11(a) and (b) show full isotropic superconducting gaps in the 122-type compounds. Nodes by ARPES were reported for the first time in an FeSC compound earlier this year by Y. Zhang *et al.* [18]. They found a horizontal ring node around Z point, $(0, 0, \pi)$.

4. *Inelastic neutron scattering*. Neutron scattering is a powerful tool to measure dynamical spin susceptibility $\chi_s(q, \omega)$. Within the RPA approach the spin susceptibility can be obtained from the bare electron-hole bubble $\chi_0(q, \omega)$

$$\chi_s(q, \omega)^{RPA} = \chi_0(q, \omega)[1 - U\chi_0(q, \omega)]^{-1}. \quad (1.9)$$

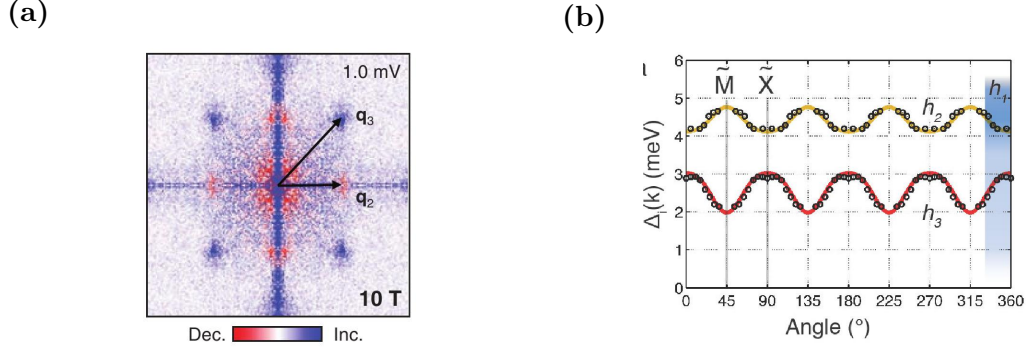


Figure 1.10: Measurements by QPI technique on FeSC materials. (a) Magnetic-field induced change in QPI intensities on $\text{FeTe}_{1-x}\text{Se}_x$, supports the sign changing $s_{\pm}$ scenario. From [14]. (b) Anisotropic energy gap structure Δ_i measured using QPI on the hole-bands of LiFeAs . From [15].

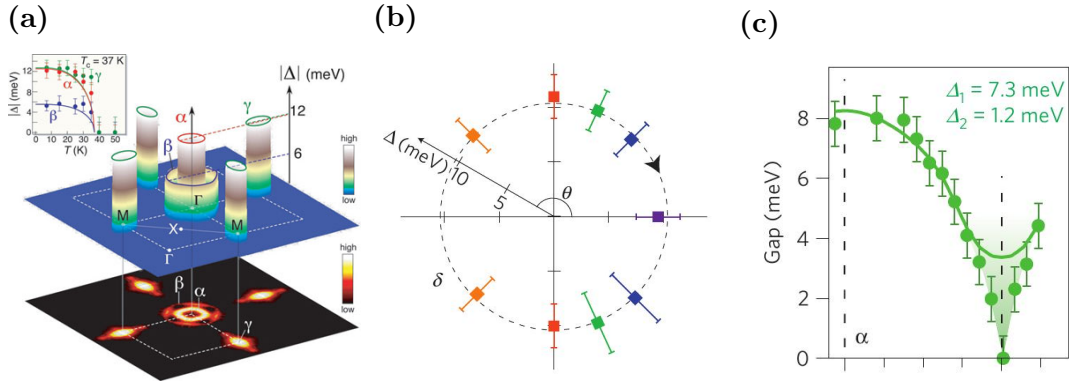


Figure 1.11: ARPES measurements on FeSC compounds. (a) Schematic Fermi sheets and superconducting gaps of hole-doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. From [16] (b) Nodeless superconducting gap in $\text{A}_x\text{Fe}_2\text{Se}_2$. The gap distribution in polar coordinates (the radius represents the gap) shows isotropic features. From [17]. (c) Nodal superconducting gap structure in $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$. Gaps of the electron FSs as function of k_z , closing at $k_z = \pi$. From [18].

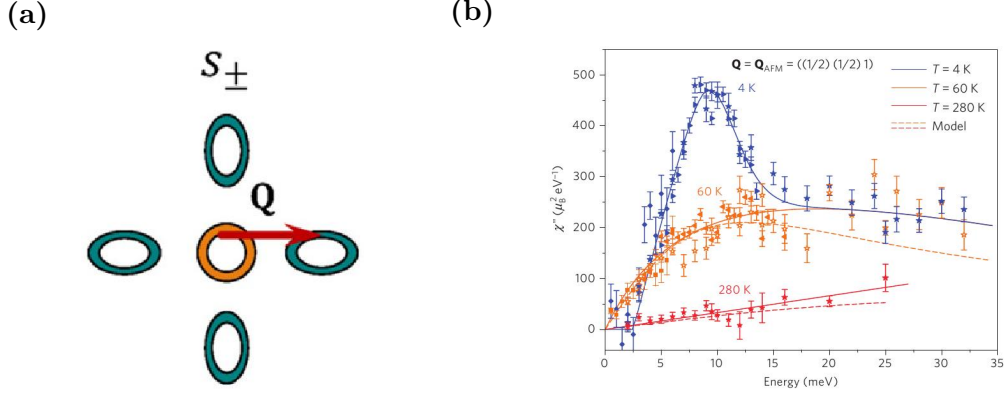


Figure 1.12: (a) Cartoon of the order parameter of the $s_{\pm}$ state with the nesting wave vector Q connecting the hole and electron fermi sheets. (b) Experimental neutron data showing the appearance of the spin resonance in $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$ below T_c [19]. The resonance is at the stripe-like antiferromagnetic vector, which connect the hole and electron pockets.

If one looks at the bare bubble $\chi_0(q, \omega)$ in the superconducting state, the term arising from the anomalous Green's function ($F_{\uparrow\downarrow}(k, \tau)$, which is nonzero when there are Cooper-pairs) is proportional to

$$\sum_k \left[1 - \frac{\Delta_k \Delta_{k+q}}{E_k E_{k+q}} \right] \dots \quad (1.10)$$

At the Fermi level, $E_k = \sqrt{\xi_k^2 + |\Delta_k|^2} = |\Delta_k|$. It is clear from expression (1.10) that if Δ_k and Δ_{k+q} have the same sign, the expression above vanishes. If there is a sign change, however, this coherence factor is nonzero, which results in an enhancement of the spin susceptibility (1.9). This spin resonance was observed experimentally [19] at the vector that connected the hole and electron pockets, consistent with the sign changing $s_{\pm}$.

We conclude that experiments show in general lack of universality, with a rather diversified superconducting gap distribution. The same materials appear to have isotropic, fully gapped states, that develop anisotropy with doping and eventually nodes. However, the general hypothesis is that in the “typical” FeSC has a sign changing s-wave isotropic superconducting state, and details of the band structure (change of the FS with doping etc.) can frustrate the isotropic $s_{\pm}$ creating anisotropy and eventually evolving into a nodal $s_{\pm}$.

Chapter 2

Five-orbital model

Density functional theory (DFT) is a modeling method used to investigate the electronic structures of many-body systems, where correlation effects are treated in a mean field level. They have been successful in predicting the right Fermi surface and the correct band structure. Calculations based on this approach concluded that the density of states near the Fermi surface of FeSC is almost entirely due to Fe states, and that the states of the rest of the elements of the compound are located approximately 2 eV below the Fermi level (figure 1.4(b)). We will use an effective model based entirely on Fe states working with a square 2D lattice with sites corresponding to Fe atoms. We also assume that the 1-Fe unit cell (section 1.2) captures the essential physics of these compounds, simplifying the problem from ten to five orbitals.

Since the Fermi surface consists of hole and electron pockets, a minimal model that describes the low-energy physics of these materials must include both hole and electron bands. In previous works, further assumptions have been done, reducing the number of orbitals in the model from five to two [20]-[22]. This approximation takes only the Fe d_{xz} and d_{yz} degenerate orbitals into account, which gives rise to the Fermi surface shown in figure 2.1 (a). The two-orbital model has several disadvantages however. It reproduces the wrong Fermi surface, with the larger hole pocket located at (π, π) , contradicting the symmetry of the DFT wavefunctions. In addition, the d_{xy} contribution along Fermi surface is missing (see figure 2.1 (b)) which appears to be important for the structure and modulation of the superconducting gap [23].

We will work with a more realistic model including all five Fe orbitals: d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{xy} and $d_{3z^2-r^2}$.

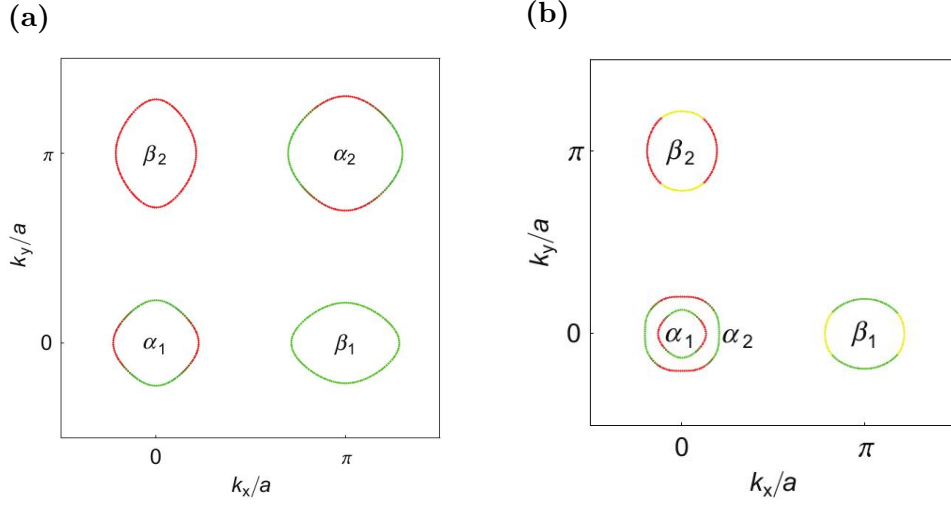


Figure 2.1: Fermi surface with the main orbital contributions in the 1-Fe unit cell of a (a) two-orbital model and (b) five-orbital model. α_1 and α_2 represent the hole pockets and β_1 and β_2 the electron pockets. Note the position of the larger hole pocket α_2 at (π, π) in (a). After folding back to the 2-Fe zone, it is centered at $(0, 0)$, but the fact that α_1 and α_2 are not degenerated at $(0, 0)$ in the 1-Fe zone contradicts the symmetry of the DFT wavefunctions. In addition, the two-orbital model is missing the small d_{xy} patches at the tips of the electron pockets that exist in the five-orbital model. [red = d_{xz} , green = d_{yz} and yellow = d_{xy}]. From [24].

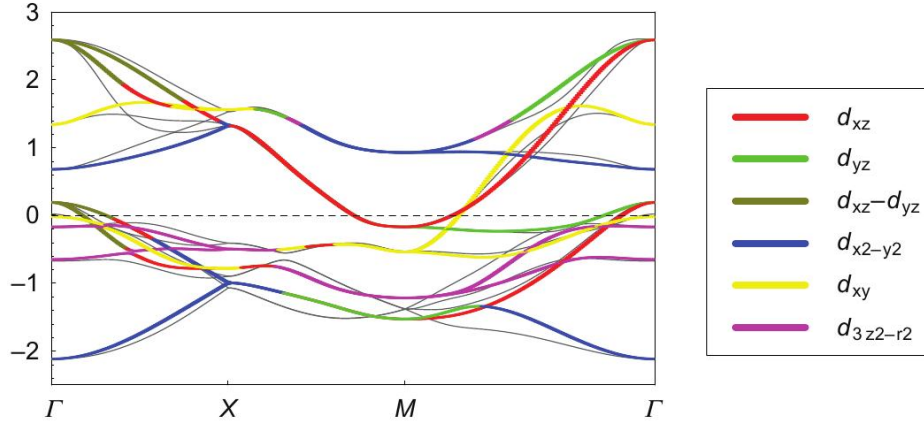


Figure 2.2: The band structure for the five-orbital model backfolded to the 2-Fe zone. The main orbital contributions are shown by different colors. A substantial overlap between the orbitals can be seen. The gray lines show the DFT band structure to which the five-orbital model is fitted. From [24].

2.1 Hamiltonian

Our real-space Hubbard model Hamiltonian consists of a kinetic energy H_0 for the effective Fe bands, a Coulomb interaction term H_{int} containing the two-body *onsite* interactions between electrons, a BCS term H_{BCS} that accounts for superconductivity, and an impurity term H_{imp} which includes disorder effects,

$$H = H_0 + H_{int} + H_{BCS} + H_{imp}. \quad (2.1)$$

The rest of the section is devoted to explaining term by term this microscopic Hamiltonian.

2.1.1 Tight-binding Hamiltonian

The kinetic energy is given by a tight-binding model term

$$H_0 = \sum_{ij, \mu\nu, \sigma} t_{ij}^{\mu\nu} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma} - \mu_0 \sum_{i\mu\sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}. \quad (2.2)$$

Here the operators $\hat{c}_{i\mu\sigma}^\dagger$ ($\hat{c}_{i\mu\sigma}$) create (annihilate) an electron at the i -th site in the orbital μ and with spin projection σ . Orbital indexes μ and ν run from 1 to 5 for d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{xy} and $d_{3z^2-r^2}$ respectively. We allow the electrons to jump from site i and orbital μ to site j and orbital ν in the square lattice by the hopping amplitude $t_{ij}^{\mu\nu}$. The hoppings $t_{ij}^{\mu\nu}$ are the same as those in Graser *et al.* [24], and included up to fifth nearest neighbours. They are calculated from a fit to a DFT band structure determined by Cao *et al.* [25] (figure 2.2). Here, as elsewhere in this work, the energy units are in electron volt (eV).

By tuning the chemical potential μ_0 we can fix the number of electrons $\hat{n} = \sum_{i\mu} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}$ of the system. This adjustment is built into the self-consistent loop of our algorithm once the desired average electron density is specified.

2.1.2 Interactions

Since the 3d electrons are generally tightly bound, the crystallographic effects on the interaction between them should be rather small. We neglect these effects, so that the interaction on site i is rotationally invariant and has the form $V(\mathbf{r}, \mathbf{r}') = V(|\mathbf{r} - \mathbf{r}'|)$. Moreover, because of this “localization”, inter-site interactions will be much weaker than the ones taking place at the same site, so we only consider the *onsite* Coulomb interactions. With $\Psi_{i\sigma}(\mathbf{r}) = \sum_{\mu} \phi_{i\mu}(\mathbf{r}) \hat{c}_{i\mu\sigma}$ the quantum field operator for an electron at lattice site i with spin σ , the general Coulomb interaction term of the Hamiltonian is

$$H_{int} = \frac{1}{2} \sum_i \sum_{\sigma\sigma'} \int d\mathbf{r} d\mathbf{r}' \Psi_{i\sigma}^\dagger(\mathbf{r}) \Psi_{i\sigma'}^\dagger(\mathbf{r}') \frac{e_0^2}{|\mathbf{r} - \mathbf{r}'|} \Psi_{i\sigma'}(\mathbf{r}') \Psi_{i\sigma}(\mathbf{r}). \quad (2.3)$$

We assume the first quantization wave function to be a Hydrogen-like atomic orbital $\phi_{i\mu}(\mathbf{r}) = R_{32}(r)Y_{2\mu}(\Omega)$, where it has been used that the quantum numbers are $n = 3$ and $l = 2$ from the electronic configuration of Fe. The Coulomb interaction will then have the form

$$H_{int} = \frac{1}{2} \sum_i \sum_{\mu\nu\mu'\nu'} \sum_{\sigma\sigma'} V(\mu, \nu; \mu', \nu') \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\nu\sigma'}^\dagger \hat{c}_{i\nu'\sigma'} \hat{c}_{i\mu'\sigma}, \quad (2.4)$$

with the matrix elements

$$V(\mu, \nu; \mu', \nu') = \int d\mathbf{r} d\mathbf{r}' \phi_{i\mu}^*(\mathbf{r}) \phi_{i\nu}^*(\mathbf{r}') \frac{e_0^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{i\nu'}(\mathbf{r}') \phi_{i\mu'}(\mathbf{r}). \quad (2.5)$$

In this expression μ, ν, μ' and ν' refer to azimuthal quantum numbers of $l = 2$ spherical harmonics for Fe d-states. The main contribution arises from elements involving just two different orbitals. Those matrix elements give rise to four different kind of terms:

$$\begin{aligned} H_{int}^{(1)} &= U \sum_{i\mu} \hat{n}_{i\mu\uparrow} \hat{n}_{i\mu\downarrow} \\ H_{int}^{(2)} &= U' \sum_{i, \mu < \nu, \sigma} (\hat{n}_{i\mu\sigma} \hat{n}_{i\nu\bar{\sigma}} + \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma}) \\ H_{int}^{(3)} &= -J \sum_{i, \mu < \nu, \sigma} (\hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma} + \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}} \hat{c}_{i\nu\bar{\sigma}}^\dagger \hat{c}_{i\nu\sigma}) \\ H_{int}^{(4)} &= J' \sum_{i, \mu < \nu, \sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}}^\dagger \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\nu\sigma}. \end{aligned} \quad (2.6)$$

The first two are direct integrals, $U = V(\mu, \mu; \mu, \mu)$ and $U' = V(\mu, \nu; \mu, \nu)$, and the last two are exchange integrals, $J = V(\mu, \nu; \nu, \mu)$ and $J' = V(\mu, \mu; \nu, \nu)$. A physical explanation for each term will be given later in this section. Rearranging the terms, we arrive to the multi-orbital Hubbard-type model:

$$\begin{aligned} H_{int} &= U \sum_{i\mu} \hat{n}_{i\mu\uparrow} \hat{n}_{i\mu\downarrow} + U' \sum_{i, \mu < \nu, \sigma} \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\bar{\sigma}} + (U' - J) \sum_{i, \mu < \nu, \sigma} \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma} \\ &+ J \sum_{i, \mu < \nu, \sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\nu\bar{\sigma}}^\dagger \hat{c}_{i\mu\bar{\sigma}} \hat{c}_{i\nu\sigma} + J' \sum_{i, \mu < \nu, \sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}}^\dagger \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\nu\sigma}. \end{aligned} \quad (2.7)$$

From the symmetry of spherical harmonics in the Coulomb matrix elements (2.5), the relations $U' = U - 2J$ and $J = J'$ hold [26]. These relations have also been explained as a spin and orbital rotational invariance [27]. One can rewrite the interaction Hamiltonian in terms of the orbital angular momentum and spin operators L^2 and S^2 , except one term which is proportional to $(U - U' - 2J)$. The invariance condition then requires that $U - U' - 2J = 0$.

In order to have a physical idea of each term, we rearrange (2.7) in an alternative way:

$$\begin{aligned}
H_{int} = & U \sum_{i\mu} \hat{n}_{i\mu\uparrow} \hat{n}_{i\mu\downarrow} + (U' - \frac{J}{2}) \sum_{i,\mu<\nu,\sigma} (\hat{n}_{i\mu\sigma} \hat{n}_{i\nu\bar{\sigma}} + \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma}) \\
& - 2J \sum_{i,\mu<\nu} \vec{S}_{i\mu} \cdot \vec{S}_{i\nu} + J' \sum_{i,\mu<\nu,\sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}}^\dagger \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\nu\sigma}.
\end{aligned} \tag{2.8}$$

In the first two terms, we distinguish between an intraorbital Coulomb interaction of electrons in the same orbital, and an interorbital interaction of electrons in different orbitals. The third term is a Hund's coupling interaction which, since $J > 0$, favours the parallel alignment of electron spins on the same site, and the last interaction term is the pair hopping energy J' . Remember that all these terms were generated from a multiorbital Coulomb interaction between electrons on the same site.

2.1.3 BCS Hamiltonian

The next term in the Hamiltonian is the one accounting for superconductivity. It was mentioned earlier in chapter 1 that the pairing glue for unconventional superconductors is unknown to date. Even if the BCS theory does not explain the origin of the pairing mechanism in FeSC (is not driven by the exchange of phonons), it works quite well once the superconducting state is settled down. We take the view that at low energies, superconductivity is adequately described by the BCS theory in FeSC, and include a BCS term in our Hamiltonian of the form,

$$H_{BCS} = -V_{ij}^{\mu\nu} \sum_{i \neq j, \mu\nu} \hat{n}_{i\mu\uparrow} \hat{n}_{j\nu\downarrow}. \tag{2.9}$$

Here $V_{ij}^{\mu\nu}$ is the strength of an effective attraction between site i (orbital μ) and site j (orbital ν). In the beginning of this study, we do not worry about the microscopic origin of this effective attraction and the pairing is chosen as next-nearest-neighbour (nearest-neighbour) intra-orbital pairing (see 2.3), in order to reproduce the $s_{\pm}$ (nodal $s_{\pm}$) state (see equation 1.3 (1.4)) as shown in figure 2.3. However, later in the text (chapter 5) we will assume that the driving force for attraction comes from a spin-fluctuation mechanism and introduce the real-space effective pairings calculated within the fluctuation-exchange approximation [28].

2.1.4 Impurity

Impurities influence local electronic states in their vicinity. The pattern of impurity-induced states in a superconducting state, is closely connected to the symmetry

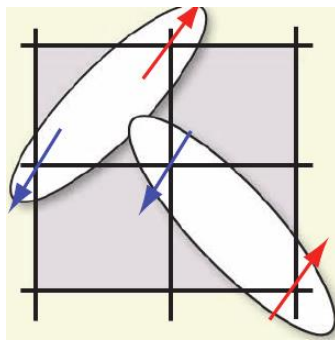


Figure 2.3: Singlet pairing of electrons in next-nearest neighbors sites which gives rise to the isotropic $s_{\pm}$ state.

and structure of the superconducting gap. Disorder studies can then help us in determining some properties of the superconducting state.

We will focus on one type of imperfection: impurity atoms. An impurity atom has a different electronic configuration than the host solid, and therefore interacts with the density of conduction electrons via a Coulomb potential. If the Coulomb interaction is screened at the length scales comparable to the lattice spacing, a local scattering potential can be assumed, $V_{imp}(\mathbf{r}) = V_{imp}\delta(\mathbf{r} - \mathbf{r}')$ with the impurity at $\mathbf{r}^*$. So the last term in our Hamiltonian is of the form,

$$H_{imp} = V_{imp} \sum_{i^* \mu \sigma} \hat{c}_{i^* \mu \sigma}^{\dagger} \hat{c}_{i^* \mu \sigma}, \quad (2.10)$$

which adds a finite potential V_{imp} at site i^* . In a real system each orbital will probably couple differently to the impurity [29][30] but here we assume V_{imp} is the same for all five orbitals for simplicity. The sign of the potential is given by the new electronic configuration of the impurity atom. If the electrons are attracted to the impurity site, it is negative, $V_{imp} < 0$. An attractive potential will then rise the electronic occupation at the impurity site. The opposite is true for a repulsive potential, $V_{imp} > 0$, where electrons are repelled from the impurity site and the occupation is lowered. An example of this local density modulation is shown in figure 2.4.

2.2 Mean Field Treatment

Now that the microscopic Hamiltonian is defined, we can study it by numerical methods. First, we want our Hamiltonian to be quadratic in the electron operators, in order to diagonalize it. So we make use of mean field theory to simplify the expressions (2.7) and (2.9). Mean field approximation consists of decoupling

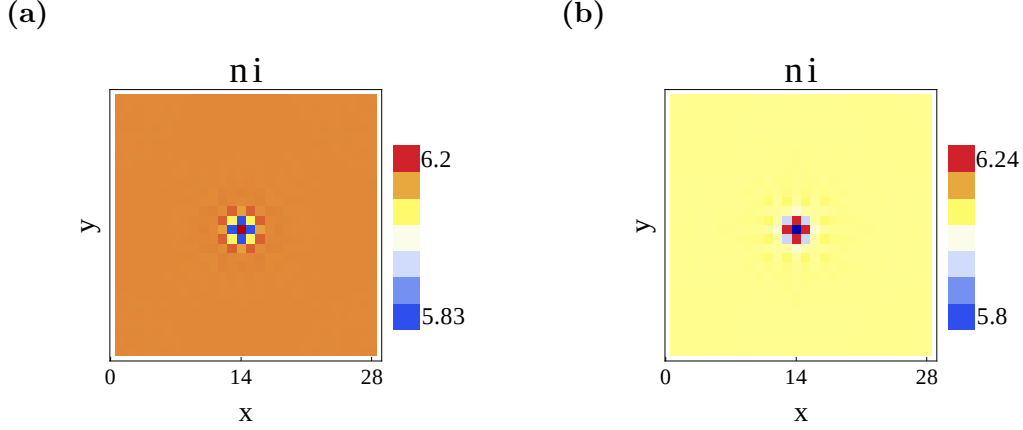


Figure 2.4: An example of the electronic density modulation in the vicinity of (a) an attractive potential and (b) a repulsive potential. In the first case the occupation is raised at the impurity site, then suppressed around it and after a few lattice sites the bulk value is recovered. This coherence length is given by the Fermi wavevector k_F , $\xi \sim 1/k_F$. In the repulsive potential on the contrary, the density oscillates in the opposite way, i.e. it is suppressed at the impurity site, enhanced around it, and the bulk value is recovered again at the coherence length.

the four-fermion interaction into a sum of all possible bilinear terms, by including correlations “on the average”. We assume on the onsite interaction term (2.7) non-vanishing mean field quantities in both the “density” and the “Cooper” channels, allowing for the usual Hartree-Fock terms and an onsite pairing term. The BCS term (2.9) is decoupled in the “Cooper” channel introducing a pairing field between different sites i (orbital μ) and j (orbital ν). After doing some algebra (see Appendix A) we arrive at the following quadratic mean-field Hamiltonian,

$$\begin{aligned}
H^{MF} = & \sum_{ij, \mu\nu, \sigma} t_{ij}^{\mu\nu} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma} \\
& + \sum_{i, \mu \neq \nu, \sigma} (-\mu_0 + U n_{i\mu\bar{\sigma}} + U' n_{i\nu\bar{\sigma}} + (U' - J) n_{i\nu\sigma} + \delta_{i*} V_{imp}) \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma} \\
& + \sum_{i, \mu \neq \nu} [(\Delta_i^{\mu(U)} + 2\Delta_i^{\nu(J')}) \hat{c}_{i\mu\uparrow}^\dagger \hat{c}_{i\mu\downarrow}^\dagger + h.c.] \\
& + \sum_{i, \mu \neq \nu} [(2\Delta_i^{\mu\nu(U')} + 2\Delta_i^{\nu\mu(J)}) \hat{c}_{i\mu\uparrow}^\dagger \hat{c}_{i\nu\downarrow}^\dagger + h.c.] \\
& - \sum_{i \neq j, \mu\nu} [\Delta_{ij}^{\mu\nu} \hat{c}_{i\mu\uparrow}^\dagger \hat{c}_{j\nu\downarrow}^\dagger + h.c.],
\end{aligned} \tag{2.11}$$

where the self-consistent mean field quantities are:

$$\begin{aligned} n_{i\mu\sigma} &= \langle \hat{n}_{i\mu\sigma} \rangle, \\ \Delta_i^{\mu\nu(X)} &= X \langle \hat{c}_{i\mu\downarrow} \hat{c}_{i\nu\uparrow} \rangle, \\ \Delta_{ij}^{\mu\nu} &= V_{ij} \langle \hat{c}_{j\nu\downarrow} \hat{c}_{i\mu\uparrow} \rangle. \end{aligned} \quad (2.12)$$

The first quantity in (2.12) is a density field and the other two are onsite and general pairing fields respectively. Here, $X = U, U', J$ or J' for the onsite pairing order parameters.

2.3 The Bogoliubov-de Gennes equations

This mean-field Hamiltonian is quadratic in the electron operators and should be readily solvable. Because terms like $\hat{c}^\dagger \hat{c}^\dagger$ and $\hat{c} \hat{c}$ appear we use the spin generalized Bogoliubov transformation defined by the following unitary transformation of the electron operators,

$$\begin{aligned} \hat{c}_{i\mu\sigma} &= \sum_n (u_{i\mu\sigma}^n \hat{\gamma}_{n\sigma} + v_{i\mu\sigma}^{n*} \hat{\gamma}_{n\bar{\sigma}}^\dagger) \\ \hat{c}_{i\mu\sigma}^\dagger &= \sum_n (u_{i\mu\sigma}^{*n} \hat{\gamma}_{n\sigma}^\dagger + v_{i\mu\sigma}^n \hat{\gamma}_{n\bar{\sigma}}) \end{aligned} \quad (2.13)$$

to diagonalize the Hamiltonian. Here, n is the index of the new eigenstates and eigenvalues. The diagonalized Hamiltonian is $H = GS + \sum_{n\sigma} E_{n\sigma} \hat{\gamma}_{n\sigma}^\dagger \hat{\gamma}_{n\sigma}$ and hence it runs only for those n states with the associated eigenvalue $E_{n\sigma} > 0$.

Comparing $[H, \hat{c}_{i\mu\sigma}]$ calculated by explicitly commuting (2.1), to the one calculated using Bogoliubov transformation (2.13), we arrive at the multiband BdG equations (see Appendix B),

$$\begin{pmatrix} \hat{\xi}_\uparrow & \hat{\Delta}_{ij} \\ \hat{\Delta}_{ji}^* & -\hat{\xi}_\downarrow^* \end{pmatrix} \begin{pmatrix} u^n \\ v^n \end{pmatrix} = E_n \begin{pmatrix} u^n \\ v^n \end{pmatrix}. \quad (2.14)$$

Here the matrix operators are defined as:

$$\begin{aligned} \hat{\xi}_\sigma u_{i\mu} &= \sum_{j\nu} t_{ij}^{\mu\nu} u_{j\nu} + \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\bar{\sigma}} + U' n_{i\nu\bar{\sigma}} + (U' - J) n_{i\nu\sigma} + \delta_{\mathbf{ii}^*} V_{imp}) u_{i\mu}, \\ \hat{\Delta} u_{i\mu} &= \sum_{\mu \neq \nu} (\Delta_i^{\mu(U)} + 2\Delta_i^{\nu(J')}) u_{i\mu} + \sum_{\mu \neq \nu} (2\Delta_i^{\mu\nu(U')} + 2\Delta_i^{\nu\mu(J)}) u_{i\nu} - \sum_{j\nu} \Delta_{ij}^{\mu\nu} u_{j\nu}. \end{aligned} \quad (2.15)$$

The mean field quantities can be expressed in terms of the eigenvalues and eigenvectors as (Appendix B):

$$\begin{aligned}
n_{i\mu\uparrow} &= \sum_n |u_{i\mu}^n|^2 f(E_n), \\
n_{i\mu\downarrow} &= \sum_n |v_{i\mu}^n|^2 (1 - f(E_n)), \\
\Delta_i^{\mu\nu(X)} &= X \sum_n u_{i\mu}^n v_{i\nu}^{n*} f(E_n), \\
\Delta_{ij}^{\mu\nu} &= V_{ij}^{\mu\nu} \sum_n u_{i\mu}^n v_{j\nu}^{n*} f(E_n),
\end{aligned} \tag{2.16}$$

where $f(E_n)$ is the Fermi function for particles with energy E_n . Therefore, the matrix (2.14) contains mean field terms that depend upon its own eigenvalues and eigenvectors: $n_{i\mu\sigma}$, $\Delta_i^{\mu\nu(X)}$ and $\Delta_{ij}^{\mu\nu}$. These are the self-consistent quantities of the problem and we find them iteratively. Some initial guess is chosen, the matrix is diagonalized, and the parameters are computed self-consistently.

Once we have solved the BdG equations self-consistently, we can build the single-particle Greens function, $G_{i\sigma j\sigma',\mu}^R(t) = -i\theta(-t)\langle[\hat{c}_{i\mu\sigma}(0), \hat{c}_{j\mu\sigma'}^\dagger(t)]\rangle$, from the eigenstates (u^n, v^n) and associated eigenvalues E_n ,

$$G_{ij,\mu}^R(\omega) = \sum_{n\sigma} \left(\frac{u_{i\mu}^n u_{j\mu}^{n*}}{\omega - E_n + i\eta} + \frac{v_{i\mu}^n v_{j\mu}^{n*}}{\omega + E_n + i\eta} \right). \tag{2.17}$$

From the Greens function one can calculate several quantities, such as the orbitally resolved local density of states (LDOS), $n_{i\mu}(\omega) = -\frac{1}{\pi N} \text{Im} G_{ii,\mu}^R(\omega)$,

$$n_{i\mu}(\omega) = -\frac{1}{\pi} \text{Im} \sum_n \left(\frac{|u_{i\mu}^n|^2}{\omega - E_n + i\eta} + \frac{|v_{i\mu}^n|^2}{\omega + E_n + i\eta} \right) \tag{2.18}$$

from where we can compute the local density of states by summing over all the orbitals $n_i(\omega) = \sum_\mu n_{i\mu}(\omega)$. This quantity will be very useful when analyzing the impurity-induced local effects, and can be directly compared to STM measurements.

One can also map out the Fermi surface by Fourier transforming the spectral function at zero energy, $A_{ij,\mu}(\omega = 0) = -\frac{1}{\pi} \text{Im} G_{ii,\mu}^R(\omega = 0)$.

For some calculations, especially in DOS computations, we will use the so called supercell method. The model provides for a $N \times N$ system with 5 orbitals in each site, $2 \times 5^2 \times N^2$ energy levels, and the spectral resolution is often not sufficient for getting smooth curves (without system size effects). Thus, we will use a technique known as “replicas” or “supercells”. In this method, the original $N \times N$ system is

pictured as lying within a larger $M \times M$ lattice of identical systems. The periodic boundary conditions of each replica are replaced by Bloch boundary conditions, so that the eigenvectors elements are given by:

$$\begin{aligned} u_{i \pm N\mu} &= u_{i\mu} e^{\pm i k N}, \\ v_{i \pm N\mu} &= v_{i\mu} e^{\pm i k N}. \end{aligned} \tag{2.19}$$

The replica systems, which have the same self-consistent parameters as the original system, now depend on the Bloch momentum k . They are averaged over the first BZ, $0 \leq k_x < 2\pi/N$ and $0 < k_y < 2\pi/N$. This averaging tends to smooth out the energy spectrum.

The results for the homogenous system and the single-impurity problem will be presented in the following two chapters.

Chapter 3

Homogeneous system

In this chapter we will study the simplest case one can consider, a clean system without impurities ($V_{imp} = 0$). By doing so, we will verify whether the model

$$H^{MF} = H_0 + H_{int}^{MF} + H_{BCS}^{MF} \quad (3.1)$$

can reproduce the main features of the FeSC. We will focus on the following questions to investigate those features:

- First, for the kinetic term of the Hamiltonian H_0 (which would correspond to the system above the magnetic transition), do we get the correct Fermi surface? From ARPES measurements we know it should have two hole pockets around Γ and two electron pockets at X and Y.
- Second, when including interactions at the mean field level, $H_0 + H_{int}^{MF}$, the system goes through a magnetic transition. So does the resulting state have the striped AFM order reported by the experiments? And once the system is in this ordered phase, how does the electronic structure change from the non-magnetic case?
- Finally, in the electron doped regime of the FeSC, magnetism is suppressed and superconductivity appears. As we saw in chapter 1, this can happen in several ways. Can the model (3.1) reproduce any of the possible experimental phase diagrams? What kind of superconducting gap has the resulting state?

After one has understood the physics of the homogeneous system, the next most simple case to study is the single-impurity problem (chapter 4).

3.1 Tight-binding Hamiltonian

In this section, we discuss the results for the electronic structure of the kinetic energy term of the Hamiltonian, H_0 . We work with a square lattice where each site corresponds to an Fe ion. Fe^{2+} ion's electronic configuration is $[\text{Ar}]3d^6$, which means that six electrons have to be distributed in the five d orbitals. The average electron density, $n = \frac{1}{N} \sum_{i\mu} (n_{i\mu\uparrow} + n_{i\mu\downarrow})$, is then $n = 6.0 + x$. Here, N is the total number of sites of the lattice, and x refers to the doping. $x = 0$ corresponds to the undoped system and as the value of x is increased (decreased), the total number of electrons in the system increases (decreases), and one speaks about electron (hole) doping.

Figure 3.1 shows the orbitally resolved and total density of states (DOS) versus energy of the undoped system. When looking at the orbital projections of the DOS (colored curves), it can be seen that all five orbitals have weight around the Fermi level but the contributions of d_{xz} , d_{yz} and d_{xy} are dominant. The other two orbitals, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, also contribute at low energies but their weight at the Fermi energy is minimal. d_{xz} and d_{yz} are degenerate in H_0 , and hence their DOS projection is the same. The peaks in the curves are van Hove singularities arising from extremums of the energy spectrum, $\nabla_k E = 0$. See again figure 2.2 where a similar spectrum (the same but backfolded to the 2-Fe zone) with the different orbital contributions is shown.

In the single-band Hubbard model

$$H = t \sum_{ij\sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \quad (3.2)$$

the interaction U describes the repulsion between electrons on the same site, and hence U/t is a dimensionless parameter which gives a measure of the interaction strength. It can describe two limits: that of weakly interacting electrons, $U \ll t$; and the strongly interacting electrons, $U \gg t$, in which the physics is described mainly by the interacting term. If one starts from the itinerant-electron or weakly interacting point of view, the kinetic energy term dominates and the main characteristics of the bands will be described by it. The interacting term will just slightly modify it, bringing new features to the energy spectrum. For a 2 dimensional nearest neighbors tight-binding Hamiltonian, the bandwidth is given by $W = 8t$. In this case, one can define the $U > 8t$ limit, in which the itinerant-electron regime breaks down; the system enters the strong interacting regime, and the resulting state is the famous Mott insulator. FeSC remain metallic after the magnetic transition has happened, and hence the correlations should be smaller than the kinetic energy. Therefore, an itinerant point of view seems reasonable and that is also why it made sense to make use of the mean field theory in chapter 2. Following the same reasoning, the width of the total DOS (black curve in figure 3.1), $W \sim 5$

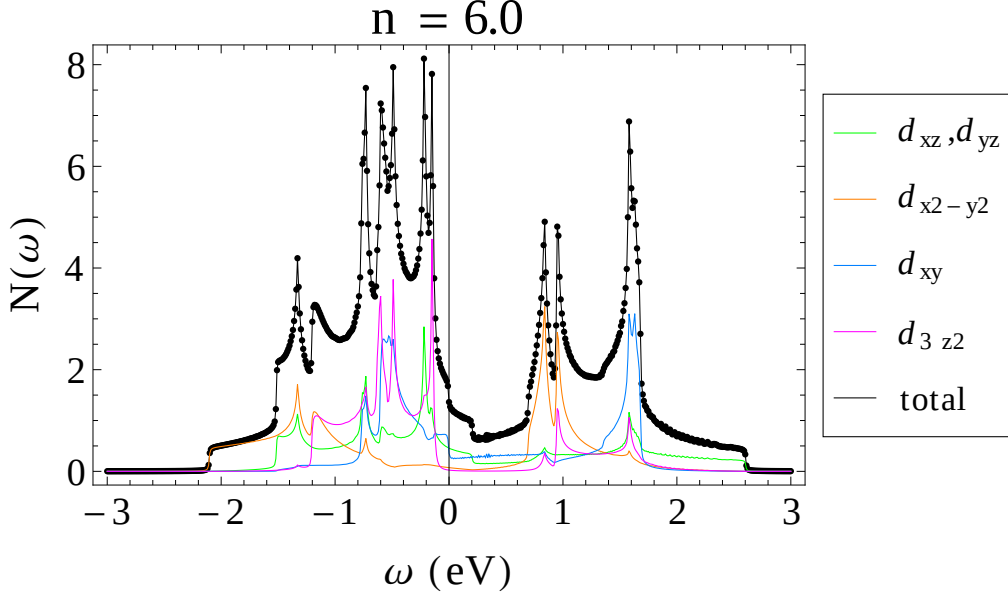


Figure 3.1: Orbitally resolved and total density of states of the undoped H_0 . All five orbitals are present at the Fermi level ($\omega = 0$) but d_{xz} , d_{yz} and d_{xy} (green and blue lines) have considerably more weight than $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. The orbitals d_{xz} and d_{yz} are degenerate and therefore have the same density of states. The calculation was made in a 20×20 lattice with 20×20 supercells.

eV, constraints on the range of values that can be considered “realistic” for the interacting parameters U , U' , J and J' in our model.

In order to map out the Fermi surface, we fix the energy at zero and Fourier transform the spectral function $A_{ij,\mu}(\omega = 0) = -\frac{1}{\pi} \text{Im} G_{ii,\mu}^R(\omega = 0)$. The resulting first quadrant of the Brillouin zone is shown in figure 3.2 (a). There are two hole pockets centered at Γ (0, 0) and two electron pockets centered at X (π , 0) and Y (0, π). The main contribution comes from the three orbitals d_{xz} , d_{yz} and d_{xy} and their spectral weight in k space can be seen in top of figure 3.5. These results agree with Graser *et al.* [24] (figure 2.1 (b)).

3.2 Magnetic order

As explained in section 1.3, it is well established that the undoped or “parent” compounds exhibit some form of antiferromagnetic long range order. The term H_0 in our Hamiltonian is a fit to a DFT of a 1111 compound. The compounds belonging to the 1111 subfamily develop a stripe-type antiferromagnetic order below $T_N \sim 140$ K. They have the lowest measured moments of all FeSC, between

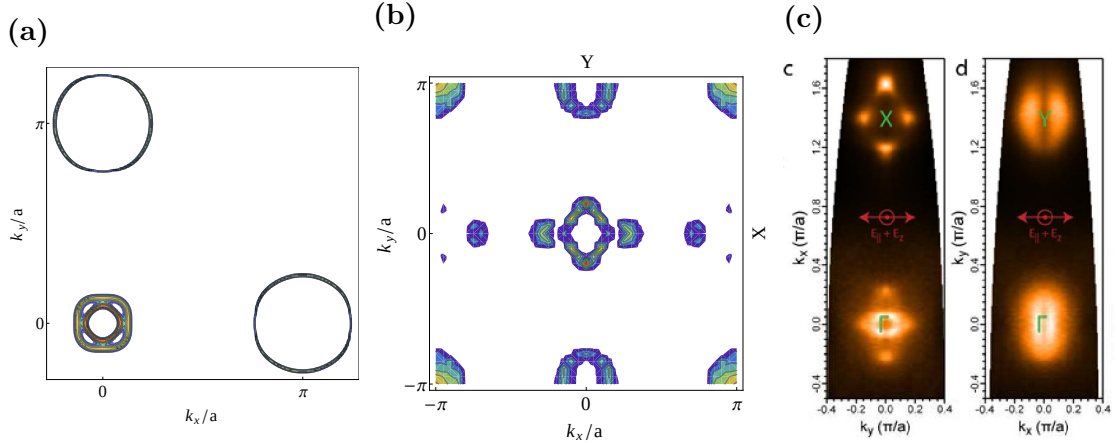


Figure 3.2: (a) The Fermi surface of the non-interacting undoped system in the first quadrant of the Brillouin zone. (b) Fermi surface reconstruction in the whole Brillouin zone when including the interacting parameters $U = 1.35$ and $J = U/4$ in the undoped system. (c) Electronic reconstruction through the magnetic transition observed by ARPES in NaFeAs. Fermi surface measured along Γ -X and Γ -Y directions. The same polarized light is used in two different domains $(\pi, 0)$ and $(0, \pi)$, in order to sort out the electronic reconstruction of a single domain. From [34].

$0.25 \mu_B$ and $0.8 \mu_B$ per Fe [31], much smaller than the $2.2 \mu_B$ moment observed in metallic Fe. In real-space the spins align antiferromagnetically along the elongated a -axis and ferromagnetically along the b -axis.

In this section, the interactions are included at the mean field, and the term $H_0 + H_{int}^{MF}$ will be studied. Allowing some non-zero value for the interacting parameters U , U' , J and J' , the resulting state is a $Q = (\pi, 0)$ striped anti-ferromagnetic state. Figure 3.3 (a) shows the typical lattice spin distribution $S_{zi} = \frac{1}{2} \sum_{i\mu} (n_{i\mu\uparrow} - n_{i\mu\downarrow})$. Since our model is tetragonal (a square lattice) instead of orthorhombic, the resulting magnetic ordering depends on our initial guess. For another initial input parameters, the degenerate configuration with $Q = (0, \pi)$ can be obtained (figure 3.3 (a) right).

We assume in all of our numerical calculations spin and orbital rotational invariance so that the relations $U' = U - 2J$ and $J' = J$ hold. By doing so, we only need to assign values for the on-site intra-orbital Coulomb repulsion U and Hund's coupling J .

So what is the origin of magnetism in our system? The spin-spin response function or spin susceptibility in the random phase approximation (RPA) for a

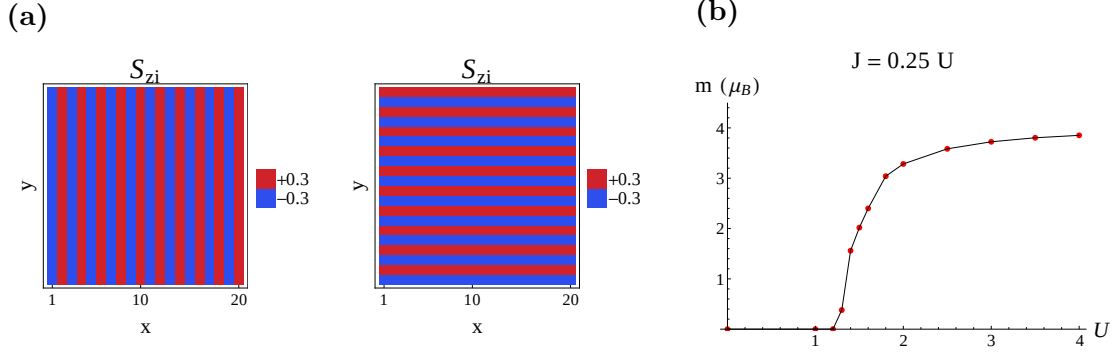


Figure 3.3: Spin distribution in a lattice for $U = 1.35$ and $J = U/4$ in the (a) $Q = (\pi, 0)$ antiferromagnetic state and the $Q = (0, \pi)$ degenerate state. (b) Magnetic moment versus U for the rate $J = U/4$. At high U values, the curve saturates at $m = 4 \mu_B$, when the system reaches its maximum spin $S_z = 2$.

single-band system is given by

$$\chi_s^{RPA}(k, \omega) = \frac{\chi_0(k, \omega)}{1 - U\chi_0(k, \omega)}. \quad (3.3)$$

The divergence of this function leads to an instability in the spin channel and the system goes through a magnetic transition. When the interaction strength U exceeds a certain critical value so that the condition $U\text{Re}\chi_0(k) \rightarrow 1$ is satisfied, (3.3) diverges. This is known as the Stoner criterion, and the instability will in general appear for the wavevector $\mathbf{k}$ at which the function is peaked. Special shapes of the Fermi surface or nesting, can also lead to an instability in the spin channel. A Fermi surface is nested if the condition $\xi(\mathbf{k} + \mathbf{q}) = -\xi(\mathbf{k})$ is satisfied for a given wavevector $\mathbf{q}$ and all (perfect nesting) or several (incomplete nesting) $\mathbf{k}$ vectors of the Fermi surface. In other words, a nested Fermi surface is one for which different sections of it coincide when shifted by a certain wavevector $\mathbf{q}$. If the nesting is perfect, the non-interacting response function χ_0 itself diverges and the magnetic transition will happen for arbitrarily small repulsion U . If the nesting is incomplete, χ_0 will be peaked at the nesting vector $\mathbf{q}$. The Stoner criterion will then be satisfied for a certain critical U at this nesting wavevector, and the system will develop a spin-density wave (SDW) with the corresponding ordering vector $\mathbf{q}$. The role that the interaction U and the nesting play in the SDW formation in one-band systems will be used below to explain the origin and structure of magnetism in our multi-band mean field model.

3.2.1 Role of U and J

In the single-band Hubbard model (3.2), the interaction U describes the repulsion between electrons on the same site. In a multi-orbital model however, in addition to the repulsion U , there is another interacting parameter to be fixed, the Hund's coupling J , which favours the parallel alignment of the spins (see equation (2.8)).

We explore the $\{U, J\}$ parameter space, in order to find the role of the two interacting parameters. We find that for a given rate J/U , there exists a critical U_c (Stoner criterion) above which the system develops a stripe-type antiferromagnetic order. A curve showing the development of the magnetic order parameter for the rate $J/U = 1/4$ versus U is plotted in figure 3.3 (b). In general, we will stay in this J/U rate and vary U throughout this work. Lowering the J/U rate implies a larger critical U_c for the magnetic ordered phase to appear, which would shift the magnetic curve to the right. This is a consequence of decreasing the strength of the Hund's coupling J , which favors the parallel alignment of spins. For all U/J rates, these curves saturate at the same value at high U . To understand this behavior, one can consider possible ways to arrange six electronic spins in five orbitals. The maximum total spin projection is $S_z = 2$, for the case of four parallel unpaired spins in four of the orbitals (half filled orbitals), and the remaining orbital fully occupied by the other two spins. That is why for all U/J rates, the magnetic moment $m = gS_z\mu_B = 2S_z\mu_B$ saturates at the maximum value, $m = 4\mu_B$. These results are in agreement with several other studies of the couplings of the multi-orbital Hubbard model [32],[33].

3.2.2 Reconstruction of the Fermi surface and orbital ordering

The spin structure formed upon the magnetic transition breaks the translational symmetry. We present now the consequences of this new ordered state in the electronic structure, and go back to the origin of the magnetic state in order to understand them.

The first thing to be noted is new features appearing in the Fermi surface of the interacting system, shown in figure 3.2 (b). Around the Γ point there is now an elongated pocket and two new “satellite” pockets sitting next to it. The electron pocket at X (mainly d_{yz} character) has almost disappeared, with some weight left at the tips of the ellipse. On the contrary, the other electron pocket located at Y (mainly d_{xz} character) is almost unchanged from the non-magnetic state (compare to figure 3.2 (a)). An explanation for these results will be given below. This reconstruction of the Fermi surface has been reported by several ARPES experiments [34]. We can directly compare our results with recent ARPES measurements in figure 3.2 (c). We also see signatures of electronic reconstruction

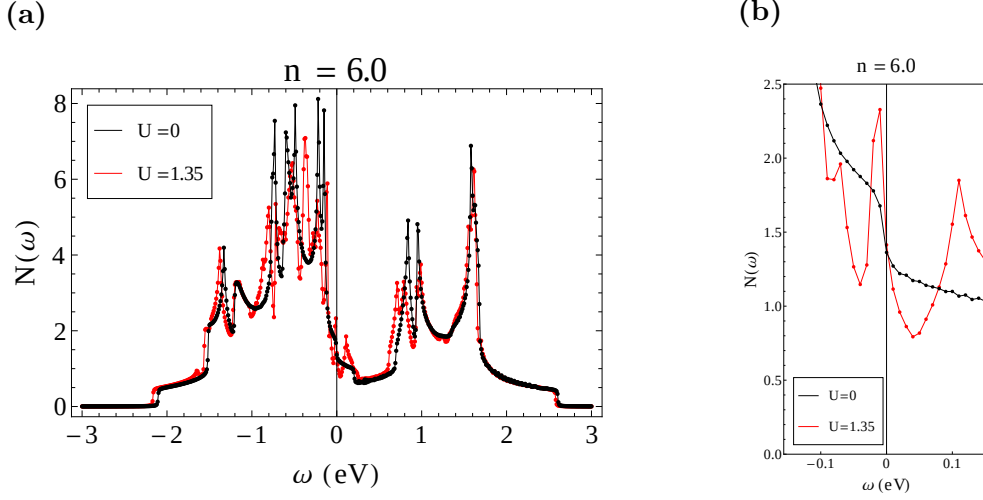


Figure 3.4: (a) Total DOS for the non-magnetic (black line) and magnetic (red line) phases. (b) Zooming into the Fermi level ($\omega = 0$) one can see the SDW gap that has developed in the magnetic state. It is particle-hole asymmetric, tilted toward positive bias with the gap bottom located at ~ 0.4 eV. The residual DOS at the Fermi level indicates that the FS is only partially gapped by the SDW order. The DOS were calculated in a 20×20 lattice and 20×20 supercells.

in the total density of states, plotted in figure 3.4. There is a gap opening slightly above the Fermi level ($\omega=0$) in the magnetic state (red curve) that was not there in the non-magnetic case (black curve).

This results (FS reconstruction and a gap in the DOS) can be understood within the development of a SDW instability caused by a nested Fermi surface, as explained in the beginning of this section. We start from the one-band Hubbard model in momentum representation, and allow a periodic modulation in the density of spins (SDW) at the characteristic wavevector $\mathbf{q}$. The mean field Hamiltonian has the form,

$$H = \sum_{k\sigma} (\epsilon_k - \mu_0) \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + \sum_{k\sigma} (\Delta_q \hat{c}_{k\sigma}^\dagger \hat{c}_{k+q\sigma} + H.c.) \quad (3.4)$$

where $\Delta_q = U \langle S_z \rangle = U \sum_{k'} (\langle \hat{c}_{k'\uparrow}^\dagger \hat{c}_{k'-q\uparrow} - \hat{c}_{k'\downarrow}^\dagger \hat{c}_{k'-q\downarrow} \rangle)$ is the SDW order parameter. Diagonalizing (3.4) we obtain the new energy spectrum,

$$E(k) = \pm \sqrt{\epsilon_k^2 + |\Delta_q|^2} - \mu_0. \quad (3.5)$$

This new dispersion has an energy gap Δ_q , which is also going to appear in the density of states $N(\omega)$ at $\omega = \mu_0$. If the nesting is perfect, a gap will open along

the whole Fermi surface, i.e. the system will become insulating, for an arbitrarily small repulsion U . If the Fermi surface is quasi-nested instead, partial gaps develop (just in those nested areas) at that $\mathbf{q}$ for values of U that satisfy Stoner criterion, and the system remains metallic.

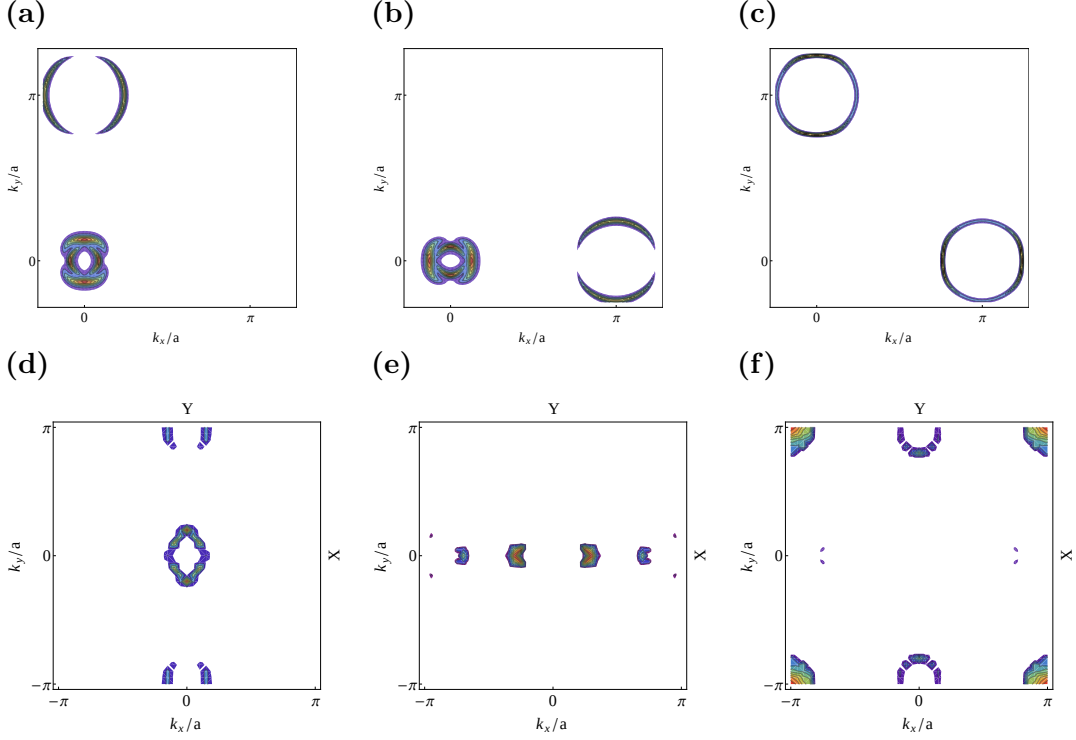


Figure 3.5: Orbital contributions to the Fermi surface from the orbitals d_{xz} (left), d_{yz} (middle) and d_{xy} (right). (a)-(c) The non-magnetic case in the first quadrant of the BZ. The total FS is shown in figure 3.2(a). The features of d_{yz} in (b) are exactly the same as the features of d_{xz} in (a) but with a $\pi/2$ rotation. Both hole pockets at Γ are a mixture of the degenerate d_{xz} and d_{yz} . The electron pocket located at X, has d_{yz} character, and the one at Y, d_{xz} character. (c) The d_{xy} orbital's Fermi surface is C_4 symmetric. The contribution of this orbital to the total FS is located mainly at the tips of the electron pockets. (d)-(f) The magnetic $Q = (\pi, 0)$ state in the whole BZ. The total FS is shown in figure 3.2(b). When the SDW develops at $Q = \mathbf{q}_Y = (\pi, 0)$, the orbitals d_{yz} (e) and d_{xy} (f) are much more affected than d_{xz} (d). The C_4 symmetry of the spectral weight of d_{xy} is broken by the new magnetically ordered state.

Going back to our multi-orbital model, we find quasi-nested Fermi surfaces. Therefore, for those $\{U, J\}$ values that satisfy the Stoner criterion, a SDW order parameter develops at the nesting vector, and the corresponding gaps open in the

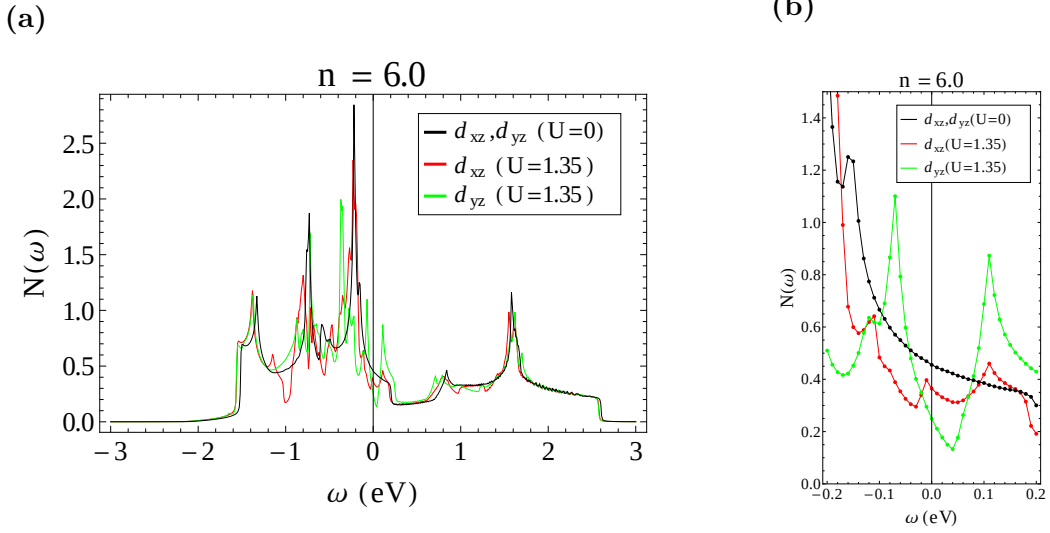


Figure 3.6: (a) DOS of d_{xz} and d_{yz} orbitals for the non-interacting (black line) and interacting (red and green) cases. Orbital ordering can be seen from the splitting of both orbitals that were degenerate in the $U = 0$ case. (b) Zooming into the Fermi level is clear that the gap is more pronounced in d_{yz} . The same results were reported in [35]. Correspondingly, $m_{yz} > m_{xz}$. For this magnetic state the Fermi level has d_{xz} character.

Fermi surface and the DOS.

Let us analyze first the Fermi surface of the non-magnetic state. In the tight-binding Hamiltonian H_0 , the orbitals d_{xz} and d_{yz} are degenerate (see green line in figure 3.1). However, if we focus on the orbital composition of the Fermi surface in k -space, we can see from the top of figure 3.5 that the d_{yz} spectral weight is rotated by $\pi/2$ with respect to d_{xz} spectral weight. d_{xz} has a $\mathbf{q}_x = (0, \pi)$ nesting wave vector, while d_{yz} orbital's nesting vector is $\mathbf{q}_y = (\pi, 0)$. We have then two nesting wavevectors $\mathbf{q}_x$ and $\mathbf{q}_y$ which peak the non-interacting susceptibility χ_0 .

When the system is in the $Q = (\pi, 0) = \mathbf{q}_y$ magnetic state, the opening of the gap affects mainly d_{yz} , and leaves d_{xz} almost unchanged. This reconstruction of the orbitally resolved Fermi surface is shown in the bottom of figure 3.5. The magnetic state has broken the degeneracy of the orbitals d_{xz} and d_{yz} . Figure 3.6 (a) shows the d_{xz} and d_{yz} contributions to the density of states in the non-magnetic ($U < U_c$) and magnetic ($U > U_c$) cases. We see that the two orbitals' DOS is no longer the same after the magnetic transition; most of the weight at the FS arises from the d_{xz} orbital, while a more pronounced SDW gap is developed in d_{yz} (figure 3.6 (b)). This agrees with what was found in a previous two-band model study [35].

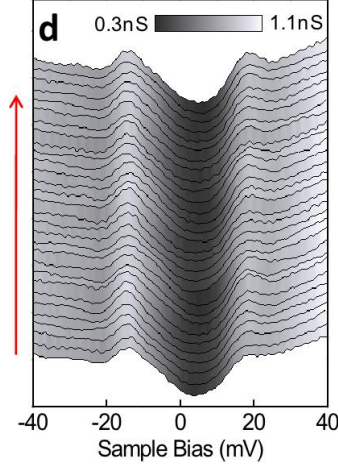


Figure 3.7: STM measurements of the SDW gap in the parent compound NaFeAs for several locations in the sample along a straight line (red line). From [36].

The densities of each orbital are now no longer the same, $n_{xz} > n_{yz}$, so there is a spontaneous *orbital ordering* as a consequence of the magnetic order. Since this difference is the same in all lattice sites, it is called ferro-orbital ordering. The magnetic moment of each orbital is not the same either. The most affected d_{yz} orbital has a higher magnetic moment, $m_{yz} > m_{xz}$, as expected.

So far we have only considered the $(\pi, 0)$ magnetic state, but if one starts with the degenerate $Q = (0, \pi) = \mathbf{q}_x$ state instead, all the results remain the same. One just has to interchange the roles of d_{xz} and d_{yz} , and rotate all the features by $\pi/2$.

These results are in agreement with laser-ARPES measurements, which find that each feature of the FS in the magnetic phase has mainly d_{xz} or d_{yz} character [8],[34]. In real systems one can find different domains of magnetic states (arising from different orthorhombic domains). It is then found that for the $(\pi, 0)$ state the main contribution comes from d_{xz} , and for the $(0, \pi)$ state from d_{yz} by using polarized lasers.

Recently, the SDW gap was directly observed for the first time by STM measurements in the 122-type NaFeAs parent compound [9],[36]. Figure 3.7 shows the dI/dV spectroscopy taken along several points in the sample below T_{SDW} . Is clear that the parent compound exhibits a uniform particle-hole asymmetric SDW gap. The residual DOS at FS indicates that the FS is only partially gapped by the SDW order. All these features are consistent with our results (cf figures 3.4(b) and 3.2(b)).

3.3 Model phase diagram

A quite intriguing question is how the magnetic order competes with superconductivity in the FeSC. From experimental phase diagrams we know that at some non-zero doping a superconducting dome develops, sometimes before the magnetic order has vanished, forming a coexistence region of both orders. In the previous section, we have studied the magnetic order in the undoped system, when superconductivity was not present. In this section, we want to examine this competing issue between magnetism and superconductivity for the electron-doped samples, and see if our model can reproduce a reasonable phase diagram. We will now work with the full homogeneous model (3.1)

$$H^{MF} = H_0 + H_{int}^{MF} + H_{BCS}^{MF}.$$

First, the interacting parameters U and J are chosen so that the undoped system has a reasonable magnetic moment, i.e. in the range of the experimentally reported moments for the 1111 subfamily ($0.25 < m < 0.8 \mu_B$). For $U = 1.35$ and $J = 0.25U$ we get $m = 0.58 \mu_B$. Second, we switch on the superconducting term H_{BCS} by setting the pairing potentials $V_{ij}^{\mu\nu} \neq 0$. We do not care about the microscopic origin of the superconducting pairings for now, and assume a non-zero attractive pairing that we introduce “by hand”. In order to get the $s_{\pm}$ state, this pairing is chosen between the next-nearest neighbors sites. We remind the reader about this state, which is characterized by a sign change between the hole and electron pockets that would result from a pure $\cos(k_x)\cos(k_y)$ gap function (see equation (1.3)). We choose them to be intra-orbital, based on previous microscopic studies which find that the inter-orbital amplitudes of the gap are negligible [24], and that the intra-orbital pairings are the ones tending to stabilize an isotropic $s_{\pm}$ state [37]. Then, the BdG equations are self-consistently solved for different electron dopings $x > 0$ at zero temperature. Finally, we obtain the magnetic moment of the system m , and the singlet and triplet components of the superconducting OP of the five orbitals Δ_{μ}^S and Δ_{μ}^T for each doping,

$$\begin{aligned} m &= \sum_{\mu} (n_{i'\mu\uparrow} - n_{i'\mu\downarrow}), \\ \Delta_{\mu}^S &= \frac{1}{2} \sum_j (\Delta_{i'j}^{\mu\mu} - \Delta_{ji'}^{\mu\mu}), \\ \Delta_{\mu}^T &= \frac{1}{2} \sum_j (\Delta_{i'j}^{\mu\mu} + \Delta_{ji'}^{\mu\mu}). \end{aligned} \tag{3.6}$$

Here we have used the fact that translational invariance is only broken by the sign of the magnetic order (it is a homogeneous system), so we can read all the

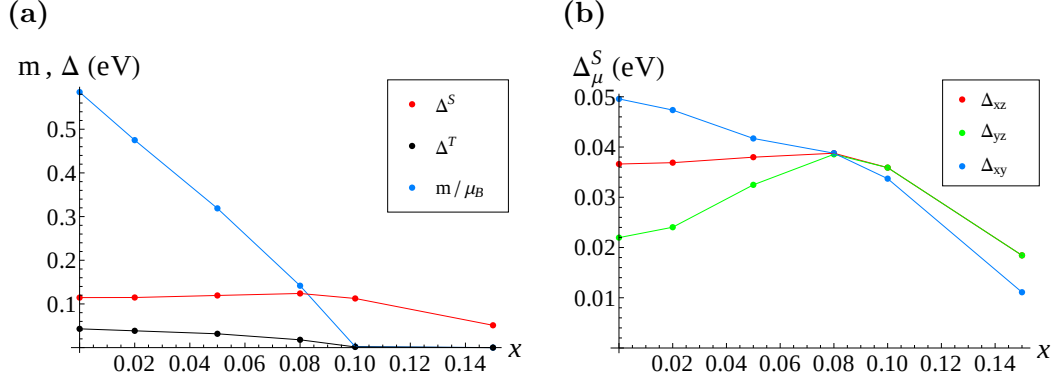


Figure 3.8: (a) Model phase diagram for $V_{ij}^{\mu\mu} = 0.5$ in all five orbitals. The magnetic order parameter is gradually suppressed with doping because the nesting gets deteriorated when increasing the average electron occupation of the system. The representative singlet component does not vanish at low dopings, it remains constant. The triplet component has the same behavior as the magnetic OP; it peaks when the system has the maximum magnetic moment and vanishes when the moment has disappeared. (b) The singlet component of the superconducting OP for the main orbitals d_{xz} , d_{yz} and d_{xy} . d_{yz} decreases as magnetization increases and d_{xz} has a really small decrease. d_{xy} on the contrary, increases showing a non-competing effect with magnetism.

order parameters of expression (3.6) from a given site i' . A correct tuning of $V_{ij}^{\mu\mu}$ would be one for which all Δ_μ vanish at zero doping, and form a dome at higher dopings. We can not find such a pairing. For all the values we tried, the dome does not vanish at $x = 0$. An example is shown in figure 3.8 (a) for the $V_{ij}^{\mu\mu} = 0.5$ case. The magnetic order (blue curve) peaks at zero doping, and as the system is electron doped, magnetism is suppressed. This is because when one dopes the system (shift of the chemical potential upwards), the hole pockets shrink and the electron pockets expand, making the nesting less and less perfect. At $x = 0.1$ doping, for the chosen U and J interacting parameters, the deteriorated nesting of the Fermi surface is not enough to cause the development of the SDW instability, and the system evolves into a non-magnetic state. The other two curves in the same figure show a representative superconducting singlet (red) and triplet (black) components,

$$\begin{aligned}\Delta^S &= \sum_{\mu} \Delta_{\mu}^S, \\ \Delta^T &= \sum_{\mu} \Delta_{\mu}^T,\end{aligned}\tag{3.7}$$

where we have simply summed for all the orbitals. One can see in figure 3.8 (a) that the triplet component (black) is non-zero just if the system is in the magnetic state. This agrees with its definition in expression (3.6). If the translational invariance is broken by an ordering of spins (stripes), then $\Delta_{ij}^{\mu\mu}$ will also have the same order (stripes). That means that for a given pair of sites i and j , in general $\Delta_{ij}^{\mu\mu} \neq -\Delta_{ji}^{\mu\mu}$, and then the triplet component is non-zero. In the non-magnetic state on the contrary, there is translational invariance and then $\Delta_{ij}^{\mu\mu}$ will be constant everywhere. In this case the condition $\Delta_{ij}^{\mu\mu} = -\Delta_{ji}^{\mu\mu}$ is trivially fulfilled and the triplet component vanishes.

The last curve (red) in figure 3.8 (a) shows that the singlet component does not vanish at zero doping. A possible reason is that due to the multi-orbital character of the system, a direct competition between magnetism and superconductivity can be avoided by some of the orbitals. This is not possible in a one-band model at which, when magnetism grows, superconductivity is suppressed, and vice versa. The singlet component for three representative orbitals is plotted in figure 3.8 (b). This behavior of skipping the competition is especially clear in the case of the orbital d_{xy} . Below certain doping, when the magnetic moment starts to grow, Δ_{xy} even grows as the system gets closer to the zero doping. The other OP Δ_{xz} and Δ_{yz} show a more usual competing behavior, especially the last orbital (where the magnetic order is the largest). The conclusion is that for the parameters chosen, superconductivity can survive in some of the orbitals even in the high magnetic moment zone. The case of Δ_{xy} growing as the system gets closer to the undoped regime, may have to do with the fact that there is a step in the DOS of d_{xy} at the Fermi level ($\omega = 0$) (cf figure 3.1). Doping the system results in a rigid band-shift, so as one approaches $n = 6.0$ from higher dopings, there is a sudden increase of the DOS of orbital d_{xy} at the Fermi level. In BCS theory, the superconducting OP is proportional to the DOS at the Fermi level, and that may be the reason why superconductivity manages to survive in d_{xy} avoiding to compete with magnetism. These band effects will be discussed in greater detail in chapter 5.

In order to check whether this results are $V_{ij}^{\mu\mu}$ parameter dependent, we reduce the amount of orbitals by including only the pairings in d_{xz} and d_{yz} and set the rest to zero. Figure 3.9 shows the model phase diagram for $V_{ij}^{11} = V_{ij}^{22} = 0.55$ and $V_{ij}^{33} = V_{ij}^{44} = V_{ij}^{55} = 0$. The blue data represents the magnetic order and the red and green data the singlet components of the superconducting order parameters of orbitals d_{xz} and d_{yz} respectively. The undoped system has now no superconductivity and the maximum magnetic moment. As the doping is increased, magnetization is gradually suppressed and superconductivity starts setting in. There is a coexistence region of both orders at $0 < x < 0.1$, after which magnetism vanishes. The superconducting order parameters peak at this point, and for higher dopings start decreasing, until they disappear at around $x \sim 0.2$, in the end of the

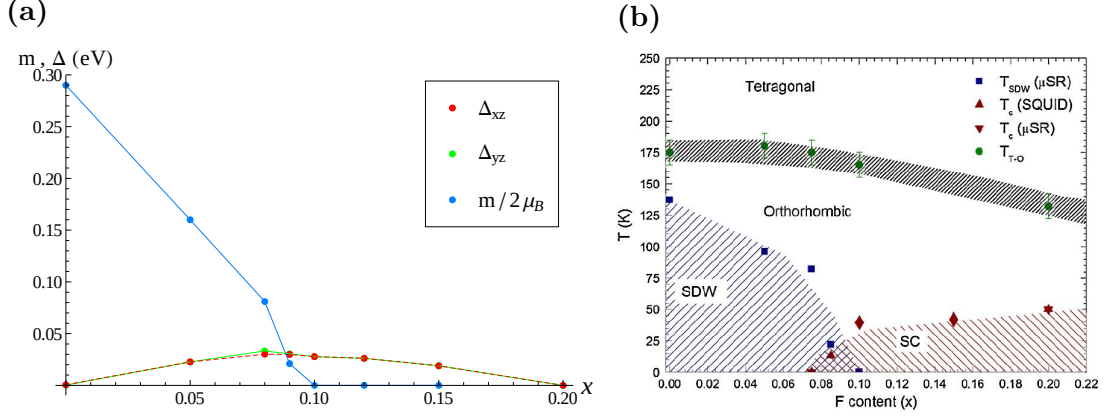


Figure 3.9: (a) Model phase diagram for $V_{ij}^{11} = V_{ij}^{22} = 0.55$ and $V_{ij}^{33} = V_{ij}^{44} = V_{ij}^{55} = 0$. It can be divided into three zones: a magnetic zone ($x = 0$), a mixed zone ($0 < x < 0.1$) in which both magnetism and superconductivity coexist, and a superconducting zone ($0.1 < x < 0.2$). (b) Experimental phase diagram of $\text{SmFeAs}(\text{O}_{1-x}\text{F}_x)$. The three regions mentioned in (a) are also present in this compound. From [38].

superconducting dome. Figure 3.9 (b) shows an experimental phase diagram for comparison.

One can see in the model phase diagram (and also in figure 3.8 (b) for the previous phase diagram), that when the system is in the magnetic state, Δ_{xz} and Δ_{yz} split apart. When magnetism vanishes at around $x = 0.1$ doping, they come together. This is a consequence of the orbital ordering developing in the $Q = (\pi, 0)$ antiferromagnetic state that was discussed in section 3.2. The electronic densities are different for both orbitals, and that is reflected in the superconducting order parameters. The splitting of the densities and the superconducting order parameters are plotted in figures 3.10 (a) and (b), respectively. The black data refers to the non-magnetic system ($U = J = 0$). In this case, as the density (the same for both orbitals because they are degenerate) increases with doping, the superconducting OP decreases. Red and green data refer as usual to the d_{xz} and d_{yz} orbitals respectively, in the magnetic case. The splitting of Δ_{xz} and Δ_{yz} is more pronounced at $x = 0.08$. At this doping, n_{yz} has decreased with respect to its value in the non-magnetic state. It gets closer to half-filling, $n = 1$, that could be interpreted as getting closer to the localized picture, since d_{yz} is strongly affected by the SDW. As we pointed out, in the non-interacting case lower density corresponds to higher superconducting OP. n_{yz} has decreased and therefore Δ_{yz} has increased (both with respect to the non-magnetic case). Following the same reasoning, the opposite is true for the orbital d_{xz} ; it has a higher density, (away from half-filling,

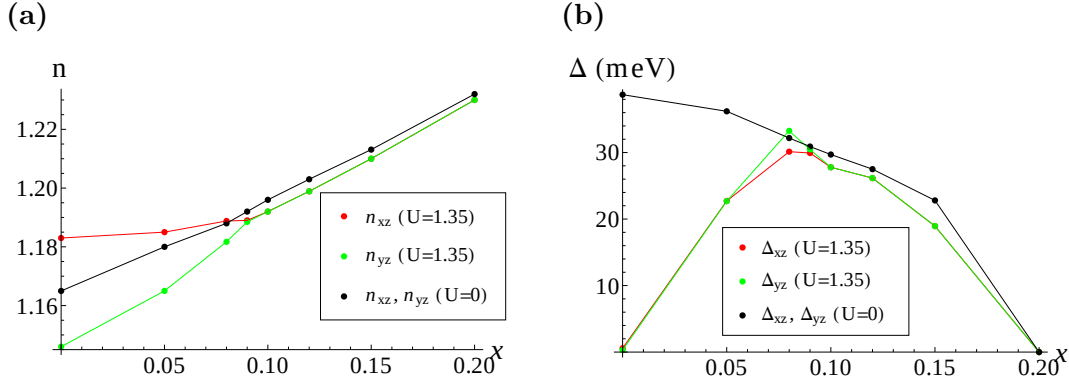


Figure 3.10: (a) The densities and (b) superconducting order parameters versus electron doping of the orbitals d_{xz} (red) and d_{yz} (green) in the interacting system and both orbitals again in the non-interacting system (black). There is a splitting of the order parameters of both orbitals in the magnetic regime. This is another effect of the orbital ordering.

closer to the itinerant picture), and consequently a lower Δ_{xz} . At lower dopings however, the magnetic moment gets so big that both of the superconducting order parameters are suppressed, independently of their densities.

The last thing to be noted in these two plots (figure 3.10 (a) and (b)) is the difference between the non-interacting and interacting cases once magnetism has vanished. The interacting data is shifted downwards and does not coincide with the non-magnetic data. This is the effect of the on-site pairing terms arising from the mean field decoupling of H_{int} in the Cooper channel (see equations (2.11) and (2.12)). They are typically an order of magnitude smaller than the rest of the superconducting OP, and their effect is in general small.

To close this section, we show the superconducting gap of the model phase diagram (figure 3.9) in the non-magnetic regime ($x = 0.1$), by plotting the density of states in figure 3.11. Both d_{xz} and d_{yz} have U-shaped full gaps. The same kind of gap is induced in the orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, even if their superconducting order parameter is zero ($V_{ij}^{33} = V_{ij}^{55} = 0$). This is a characteristic of multi-band systems, because the energy spectrum does not trivially decouple in independent BCS spectrums in a general case. Finally, a gap is also induced in d_{xy} , but it is a V-shaped nodal gap. The total superconducting gap of the system, after summing all the orbital contributions, is then *nodal*. Figure 3.9(b) shows STM measurements on the 1111-type material SmFeAsO [39] for comparison. When doping the compound, it becomes superconducting, and the spectra shows a V-shaped nodal gap.

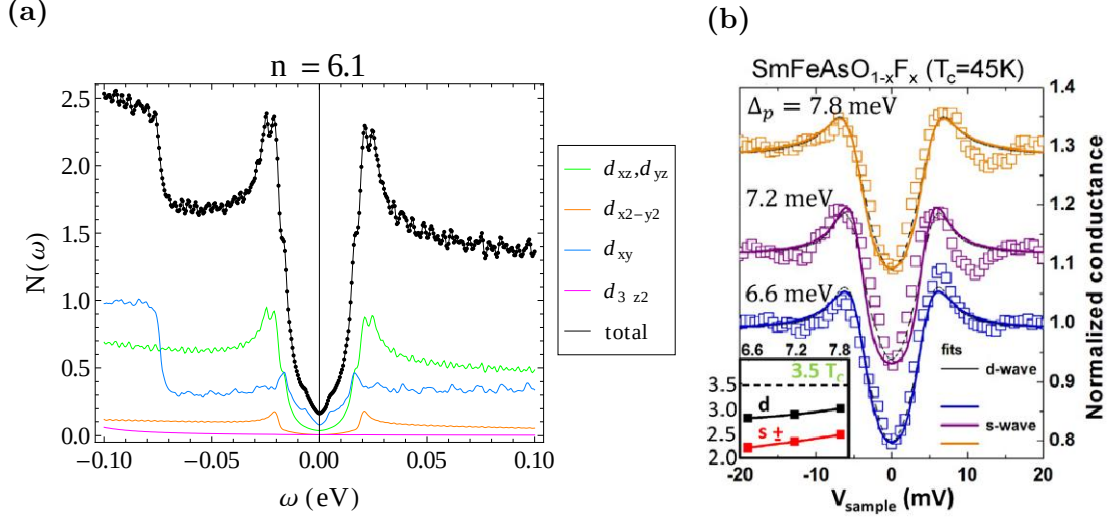


Figure 3.11: (a) Superconducting gap of the phase diagram at $n = 6.1$, when magnetism has vanished. Both d_{xz} and d_{yz} have U-shaped full gaps. The same kind of gap is induced in the orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. A V-shaped nodal gap is induced in d_{xy} . As a result, when summing them all, the total superconducting gap is nodal. The coherence peaks are located at $\omega \sim \pm 20$ meV. The DOS was calculated in a 20×20 lattice and 35×35 supercells. (b). STM measurements on the superconducting $\text{SmFeAsO}_{1-x}\text{F}_x$ with nominal $x = 0.2$. The spectra shows a V-shaped nodal gap. The open symbols are data and the full lines fits. From [39].

3.4 Conclusion

In this chapter the microscopic model (2.11) was tested and studied in a homogeneous system.

For the kinetic energy term H_0 , we get the correct Fermi surface composed of two hole pockets at Γ and two electron pockets at X and Y. The main contribution around the Fermi level comes from the orbitals d_{xz} , d_{yz} and d_{xy} , and the first two are degenerate.

When including interactions at the mean field level, $H_0 + H_{int}$, the system develops a SDW instability at the nesting wavevector, and a stripe-like antiferromagnetic ordering appears, in agreement with neutron experiments. This order of spins leads to a reconstructed Fermi surface with orbital order as a result of the broken degeneracy of d_{xz} and d_{yz} . These features have been reported by ARPES experiments and other similar theoretical models.

Finally, a reasonable phase diagram of the magnetic and superconducting order parameters versus electron doping was reproduced. The phase diagram can be divided into three different zones: the magnetic zone, the mixed zone with

coexistence of magnetism and superconductivity, and the superconducting zone. For the chosen parameters the resulting superconducting gap is nodal. However, this result seems in a way unsatisfactory, because it depends strongly on how one chooses the superconducting pairings $V_{ij}^{\mu\nu}$. Later in chapter 5, we get rid of this dependence by assuming that the driving force for superconductivity comes from a spin-fluctuation mechanism and include the $V_{ij}^{\mu\nu}$ effective pairings calculated within the fluctuation-exchange approximation.

Chapter 4

Single-impurity problem

4.1 Introduction

The parent compounds of FeSC become superconducting by chemical doping, for example, by partial random-site substitution of transition-metal atoms such as Co, Ni or Cu, for Fe. The study of disorder effects is then an important topic in these materials.

An individual impurity influences *local* electronic states in its immediate vicinity, and the corresponding change in physical quantities occurs locally. These impurity-induced electronic states are closely connected to the underlying electronic band structure. Impurity effects can then be a useful tool to probe the symmetry of the superconducting gap [40]. For example, in the case of cuprates, STM measurements near isolated Ni impurities showed clear evidence for d-wave pairing symmetry[41].

Several theoretical studies of the single-impurity problem have been reported both in the two-orbital model [20]-[22],[42]-[44] and the five-orbital model [45] for FeSC. These reports put main emphasis on the impurity effect as a probe for the gap symmetry and structure, i.e. they propose particular patterns for distinguishing between $s_{\pm}$, $d_{x^2-y^2}$ and conventional s_{++} states. The entangled nature of the multiple bands in these systems seems important, and the results were different for the simplified two-orbital and the five-orbital models.

We will extend the single-impurity problem study by including the effect of correlations at the mean field level within a five-orbital model.

4.2 Effect of disorder in FeSC

So far we have assumed that when the system is doped, there is simply a band shift which one can get by readjusting the chemical potential. In this chapter,

the single-impurity problem will be studied by placing the impurity in a system which has the Fermi surface of the shifted undoped band. But one could ask if this situation is reasonable or even realistic at all. In fact, when the doping is made in real compounds by substitution of other atoms, these impurity atoms are likely to influence the electronic structure of the whole system, and the spectrum and the total density of states could be different from the undoped system. The so called rigid-band-like scenario would then not be applicable. This issue has been studied by ARPES experiments [46]. They estimated the deviation from the rigid-band model for different transition-metal atoms in the FeSC. They find that for Co doping, the FSs evolve following the rigid-band model with electron doping, i.e. the volumes of the FSs change according to the number of extra electrons and the chemical potential is shifted accordingly. For other atoms such as Ni or Cu the rigid-band model works qualitatively, but the electron FS volumes are smaller than expected. This suggests that part of the electrons doped are trapped around the impurities, and do not behave like mobile carriers. There has been also theoretical DFT studies [29],[30] which find that impurity substitution indeed works as effective doping, with a rigid band shift around the Fermi level. We conclude then that since the rigid-band model works for some doped FeSC, it is “realistic” to study impurity effects within our model.

4.3 Single-impurity results

As mentioned in chapter 2, an impurity atom has a different electronic configuration than the host solid and it interacts with the conduction electrons via a Coulomb potential. We assume for simplicity that this *potential scattering* is completely local, constrained to the impurity site. In addition to the electrostatic potential, if the impurity atom has a magnetic moment, there is a local interaction between the spin of the impurity and the conduction electrons. However, a previous DFT study of Co substitution found that while the scattering potential is an intermediate-strength scatterer, the *magnetic scattering* is considerably smaller [29]. We will then focus on nonmagnetic impurities, neglecting the magnetic part of the scattering.

The chemical potential is fixed so that the total density is $n = 6.1$, where the system is in the superconducting state but close to the SDW (cf figures 3.8 and 3.9), and a non-magnetic impurity is placed at $(x_{imp}, y_{imp}) = (14, 14)$ in a 28×28 lattice. We focus on signatures associated with the $s_{\pm}$ state, including by hand an intra-orbital superconducting pairing $V_{ij}^{\mu\mu} = 0.65$ in next-nearest neighbors. Using the self-consistent BdG equations, we analyze below the resulting properties of the single-impurity problem.

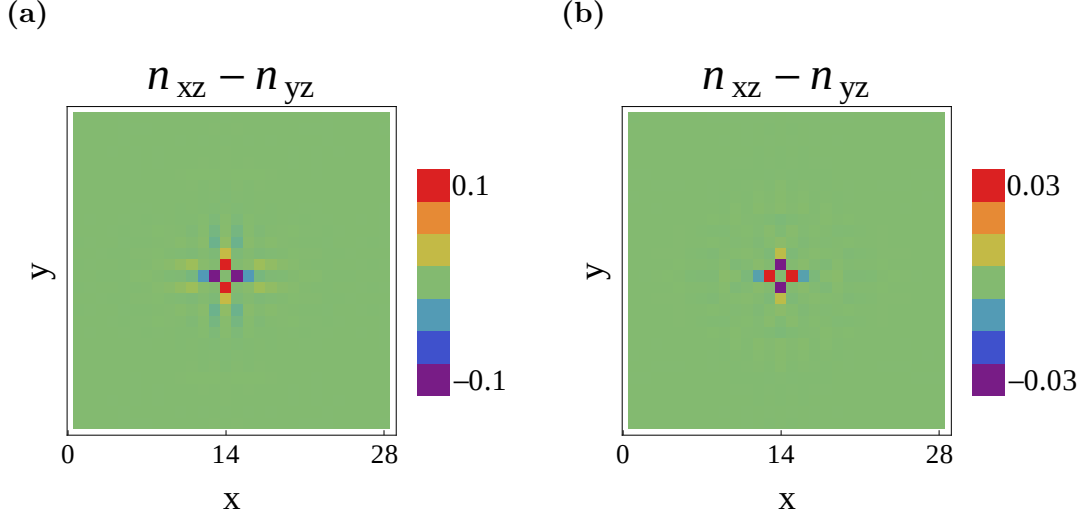


Figure 4.1: Orbital ordering for a (a) repulsive potential, $V_{imp} = 1$ and (b) attractive potential, $V_{imp} = -1$. In both cases the interacting parameters are set to zero ($U = J = 0$).

4.3.1 Induced local orbital ordering

For repulsive potentials ($V_{imp} > 0$), there is an energy penalty for the electrons to jump into the impurity site. From the orientations of the orbitals d_{xz} and d_{yz} in each Fe site, their hopping amplitudes along x and y directions are the same but rotated by $\pi/2$ with respect to each other. Therefore the effective “forbidden hopping” effect of the impurity is going to be reflected in orbital d_{yz} with a $\pi/2$ rotation with respect to the same effect in orbital d_{xz} , and a local twofold orbital ordering is induced around the impurity. Figure 4.1 (a) shows the orbital ordering around a repulsive impurity for the $U = 0$ case.

For attractive potentials, following the same argument, it is energetically advantageous now for the electrons to jump into the impurity site. The orbital ordering will then be qualitatively the same as for the repulsive potentials, but with the extremums rotated by $\pi/2$, as shown in figure 4.1 (b).

4.3.2 Induced local magnetization and in-gap bound states

Now we include correlations at the mean field level, by allowing non-zero interacting parameters U and $J = U/4$. Above a Stoner critical value U_c , a local magnetization is induced around the repulsive impurities ($V_{imp} > 0$). An example of the real space distribution of the magnetic order parameter $m_i = \sum_{\mu} (n_{i\mu\uparrow} - n_{i\mu\downarrow})$ is plotted in figure 4.2 (a). The new magnetic ordering is a checkerboard-like anti-

ferromagnet (not the homogeneous system's stripe-like antiferromagnet), with the ordering vector $Q = (\pi, \pi)$. This result does not depend on the impurity strength, i.e. the same magnetic ordering is induced for strong scatterers ($V_{imp} = 8$). For attractive potentials on the contrary, no induced magnetization was found, as shown in figure 4.2 (c).

Let us analyze why this effect depends on the type of impurity. The superconducting state results from pairing of fermionic quasiparticles, and these Cooper pairs may be broken by interaction with impurities. They can be then classified as pair-breaking and non pair-breaking impurities. When the impurity is pair-breaking, the Greens function has new poles and quasiparticle states are created inside the superconducting gap (in-gap bound states) in the vicinity of the impurity. This is an old subject from back in the 60's, when it was theoretically found by Shiba that there are quasiparticle states inside the energy gap of conventional superconductors, localized in the vicinity of a magnetic impurity.

Figures 4.2 (b) and (d) show the local density of states (LDOS) for both types of impurities in the uncorrelated $s_{\pm}$ superconducting state. States are generated inside the superconducting gap around the repulsive impurity; on the contrary, the gap is almost unchanged and clean around the attractive impurity. It can be then concluded that when the system is in the $s_{\pm}$ state, attractive potentials are non pair-breaking (clean gaps) and repulsive potentials are pair-breaking with the resulting local in-gap bound states. In the simplest static, long-wave limit ($\omega = 0, k \rightarrow 0$), the real part of the bare spin susceptibility $\chi_0(k \rightarrow 0, 0)$ is proportional to the density of states at the Fermi level, and the Stoner criterion becomes $UN(E_F) \rightarrow 1$. Because of the presence of these bound states, the density of states is higher around the Fermi level. The Stoner instability can then be crossed around a repulsive potential, inducing local magnetization in the vicinity of the impurity site. The presence of local in-gap bound states only around repulsive impurities when the system is in the $s_{\pm}$ state agrees with a previous single-impurity study [45], within a five-band model and no Hartree-Fock mean field correlations (our $U = J = 0$ case).

The magnetic ordering of the homogeneous system was found to be a stripe-like antiferromagnetic $(\pi, 0)$ state. Around nonmagnetic impurities however, a different (π, π) magnetic ordering is induced. Why is there a change of the magnetic order? Local enhancement of $U\chi_0(q)$ around a nonmagnetic impurity in the normal state (without superconductivity) of a one-band system has been recently reported [47] for cuprates. Figure 4.3(a) shows this enhancement for different values of the interaction parameter U . Due to local variations in the bare spin susceptibility $\chi_0(\mathbf{k})$, the sites around the impurity are closer to the Stoner instability $U\chi_0(\mathbf{Q}) \rightarrow 1$. Here, $\mathbf{Q}$ is the nesting vector (cuprate Fermi surface) at which the function $\chi_0(\mathbf{k})$ is peaked in the normal state, and then the ordering vector of spins in

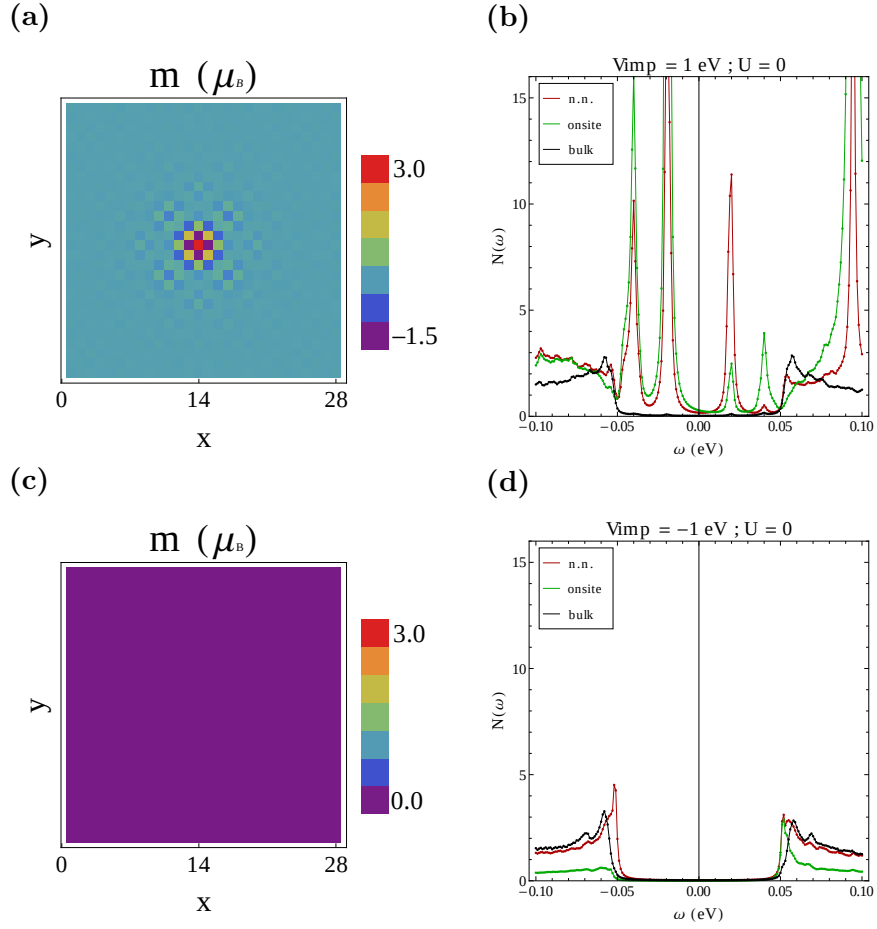


Figure 4.2: Magnetization of the lattice for (a) a repulsive impurity ($V_{imp} = 1$) and (c) an attractive impurity ($V_{imp} = -1$). In both cases $U = 1.35$. (b) and (d) show the local density of states for the two previous kind of impurities (a) and (b) respectively, without correlations $U = 0$. The black curve is the DOS far away from the impurity site and the red and green curves the DOS at the nearest neighbor and impurity site respectively. In-gap bound states can be seen for the repulsive scatterer. For higher impurity strength, the states are pushed away from the Fermi level, but they are still generated inside the gap. Clean superconducting gaps are found for attractive scatterers; in fact, the DOS around the impurity is almost unchanged from the bulk DOS. When the correlations are switched on, $U = 1.35$, local magnetization is induced only for the repulsive potential (a), the one for which bound states were found in the $U = 0$ case. The LDOS in this chapter are calculated in a 28×28 lattice with 35×35 supercells.

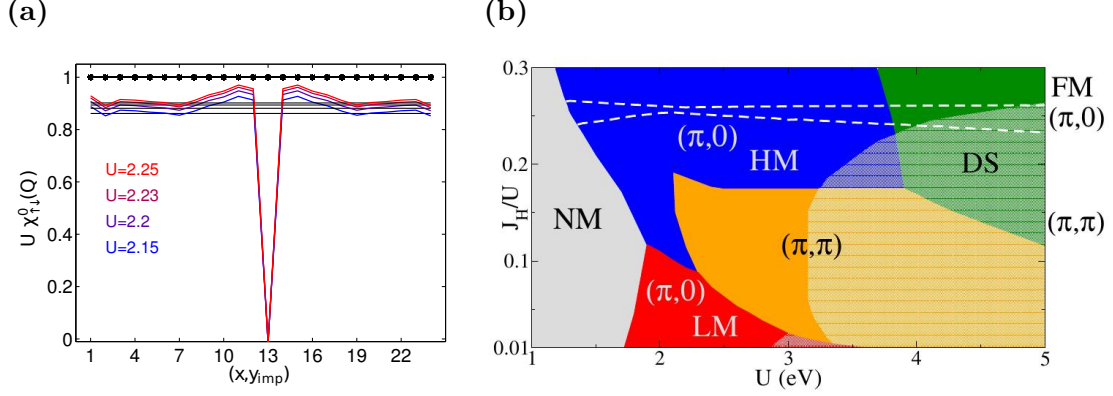


Figure 4.3: (a) Average of $U\chi_0(\mathbf{Q})$ around $\mathbf{Q} = (\pi, \pi)$ for different values of U as a function of site $\mathbf{r}_i = (x, y_{imp})$. Black lines are $U\chi_0(\mathbf{Q})$ for a homogeneous system, and colored lines are for systems with a nonmagnetic impurity $(x_{imp}, y_{imp}) = (13, 13)$. Due to local variations in the bare spin susceptibility, the sites around the impurity are closer to the Stoner instability $U\chi_0(\mathbf{Q}) \rightarrow 1$. From [47]. (b) Theoretical magnetic phase diagram of the homogeneous undoped system as a function of U and J/U . From [48].

the magnetic state. If a similar enhancement in the real part of $\chi_0(\mathbf{k})$ would happen around an impurity when the system is in the superconducting state, it would be easier to cross the Stoner instability around the impurity and induce local magnetization. This argument could explain why magnetization is induced around a nonmagnetic impurity in our system. However, the enhancement happens for a different $Q = (\pi, \pi)$ vector than the normal state's ordering vector $Q = (\pi, 0)$ (or the degenerate $(0, \pi)$). As we will discuss in detail in chapter 5, the bare susceptibility of the homogeneous system evolves with doping, and the peaked structure at the stripe SDW vector $(\pi, 0)$ is gradually suppressed. When the system is at $x = 0.1$ filling, the modified response function is starting to be dominated by a plateau around (π, π) instead. This could explain why at this filling the impurity “chooses” the checkerboard ordering, the leading magnetic instability of the homogeneous system at that doping.

In figure 4.3(b) a magnetic phase diagram of the undoped compound is shown. The (π, π) ordering (orange region) is “around the corner”, for lower J/U rates. It is not surprising a change of this diagram with doping, with a new scenario in which the orange region is moved to lower U values.

Magnetically polarized dopant atoms have been measured by x-ray resonant magnetic scattering earlier this year [49]. They isolate the magnetic behavior of the dopant's d states, by tuning the incident x-ray energy, and find that they are magnetically polarized with stripe-like antiferromagnetic order.

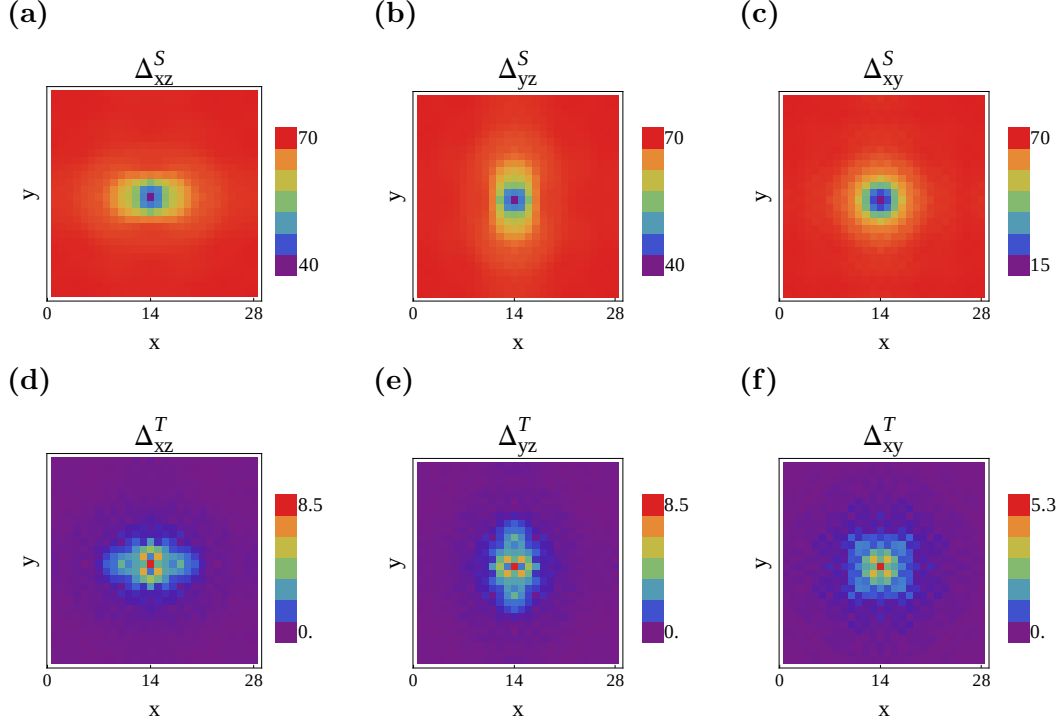


Figure 4.4: Superconducting singlet (a)-(c) and triplet (d)-(f) components of the orbitals d_{xz} , d_{yz} and d_{xy} . The same parameters as in figure 4.2 (b), $V_{imp} = 1$ and $U = 1.35$. The order parameters modulation around the impurity follow the symmetry of their corresponding orbitals; twofold symmetry for Δ_{xz} and Δ_{yz} , and C_4 for Δ_{xy} . There is local induced magnetization in the system and therefore the triplet components are non-zero around the magnetic area, as expected from its definition in expression (4.1).

4.3.3 Superconducting order parameters

We present here the real space distribution of the superconducting order parameters in the presence of the impurity. Representative singlet and triplet components of the superconducting OP for each orbital μ at each site i are given by,

$$\begin{aligned}\Delta_{i\mu}^S &= \frac{1}{2} \sum_j (\Delta_{ij}^{\mu\mu} - \Delta_{ji}^{\mu\mu}), \\ \Delta_{i\mu}^T &= \frac{1}{2} \sum_j (\Delta_{ij}^{\mu\mu} + \Delta_{ji}^{\mu\mu}),\end{aligned}\tag{4.1}$$

where S stands for the singlet component and T for the triplet component.

For the simplest non-correlated $U = 0$ case, there is a suppression of the singlet component around the impurity for all five orbitals. The singlet component is then

suppressed near the impurity site due to the presence of the impurity itself ($U = 0$). This is a general result, and happens for both repulsive and attractive impurities and different potential strengths.

For $U > U_c$ values, in the case of repulsive impurities, magnetization is locally induced and a triplet component develops in the magnetic region, as expected from their definition (see again section 3.3). The singlet components are again suppressed around the potential, but their structure is slightly different, with a broadening induced by the competing magnetic order. An example is shown in figure 4.4 for the orbitals d_{xz} , d_{yz} and d_{xy} , in a case where magnetization is locally induced ($U = 1.35$). Correlation effects in the order parameters will be extensively studied in the next subsection.

4.3.4 The role of correlations

Several theoretical studies of the single-impurity problem have been reported. Here, we extend this study by analyzing the correlations strength effects in the inhomogeneous state. We focus on repulsive potentials, where local in-gap bound states are generated and magnetization can be induced around the impurity. So far, two extreme cases have been considered: the non-correlated $U = 0$ case, and the $U = 1.35 > U_c$ case, for which magnetization is locally induced. But how are the results affected for intermediate values of the interaction strength U and J ? We will be discussing two repulsive potential limits: the *weak* impurity ($V_{imp} = 1$), where the electron density is finite at the impurity site; and the *strong* impurity ($V_{imp} = 8$), where there is no electrons left at the impurity site $n_{i*} \rightarrow 0$.

Weak impurity

Figure 4.5 shows the triplet and singlet superconducting order parameters of the orbital d_{xz} for various correlation strengths. (a)-(b) show both components in the uncorrelated $U = 0$ case. The singlet component is suppressed around the impurity, and the triplet component is zero. Increasing slightly the correlations, $U = 0.4$ in (c)-(d), changes drastically the structure of the singlet component. It is enhanced around the impurity site. The triplet component is still zero everywhere because $U < U_c = 1.1$ is not high enough to cross the Stoner instability. At higher correlations, $U = 1.2 \gtrsim U_c$ in (e)-(f), the singlet is still peaked around the impurity site, but the maximum value has decreased. Magnetization is locally induced, and a nonzero triplet component appears in the magnetic region. Finally, when correlations are high, $U > U_c$ in (g)-(h), a strong magnetization sets in, and the singlet component is suppressed again, showing the competing effect with the magnetic order. These results are just shown for one of the orbitals, but the evolution with correlations is the same in the other four. The five orbitals share

a range of U values for which their singlet component is enhanced around the impurity. In a single-band system, this would be reflected in the size of the gap around the impurity site, it would appear bigger than the bulk.

Let us now take a look at the local density of states around the impurity in figure 4.6. In the uncorrelated system (a) there are four in-gap bound states at the nearest-neighbor and impurity sites. When the correlations are increased, these states are pushed away from the Fermi level as shown in (b)-(c). At $U = 1.0 \lesssim U_c$ in (d), they are generated at the gap edges, and no in-gap state is left. For higher values of $U \gtrsim U_c$ (e) they start getting inside the gap again and is possible for the system to locally cross the Stoner instability. Finally, for high correlations, $U > U_c$ (f), strong magnetization sets in and new local in-gap magnetic features appear in the LDOS around the Fermi level. To check that they are induced by magnetization, we did a non self-consistent run with a magnetic impurity at $U = 0$ and calculated the LDOS. The same magnetic features appeared inside the gap around the impurity.

The superconducting gap size has not increased for any of the calculated LDOS. We conclude then, that even if there was a superconducting order parameter enhancement around the impurity for a range of U values, this is not reflected in the energy gap of the LDOS (as it would in the one-band system).

Strong impurity

In the high impurity potential limit, no low correlation effects can be seen, as shown in figures 4.7 (a)-(d) and 4.8 (a)-(c). There is no electrons left at the impurity site so the singlet components remain suppressed. No change is appreciable in the LDOS for values of U smaller than the critical Stoner interaction $U_c \sim 1.2$. At higher correlations, when the strength of $U \sim U_c$ is enough to cross the Stoner instability, magnetization is induced, and the corresponding nonzero triplet component appears in the magnetic region (cf figure 4.7 (f)). The singlet component however, remains qualitatively the same as for lower correlations. At high correlations, $U = 1.35 > U_c$, when strong magnetization is induced, the singlet and triplet components spread into a bigger area around the impurity (figures 4.7 (g)-(h)), and the same magnetic features that appeared in the weak impurity develop around the Fermi level (see figure 4.8 (f)).

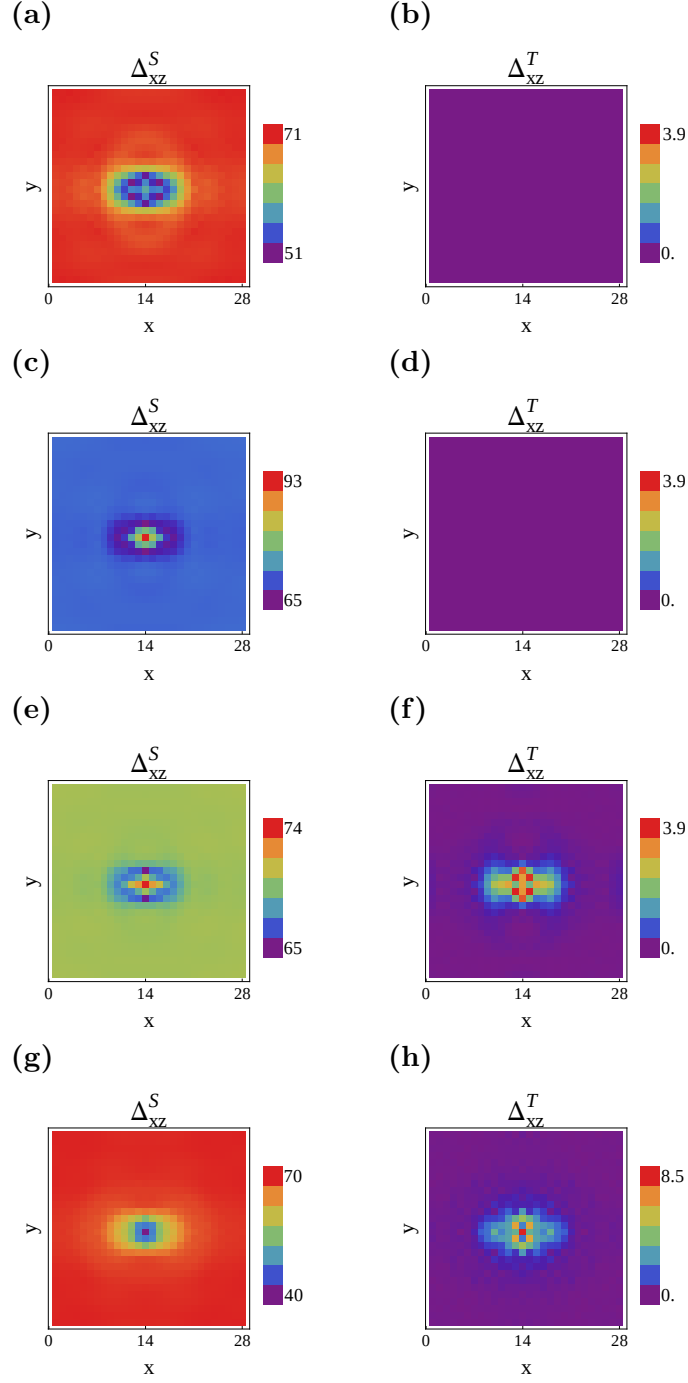


Figure 4.5: *Weak impurity* ($V_{imp} = 1$). Effect of correlations for the singlet (left) and triplet (right) components of the orbital d_{xz} . Correlation strength: (a)-(b) $U = 0$, (c)-(d) $U = 0.4$, (e)-(f) $U = 1.2$ and (g)-(h) $U = 1.35$.

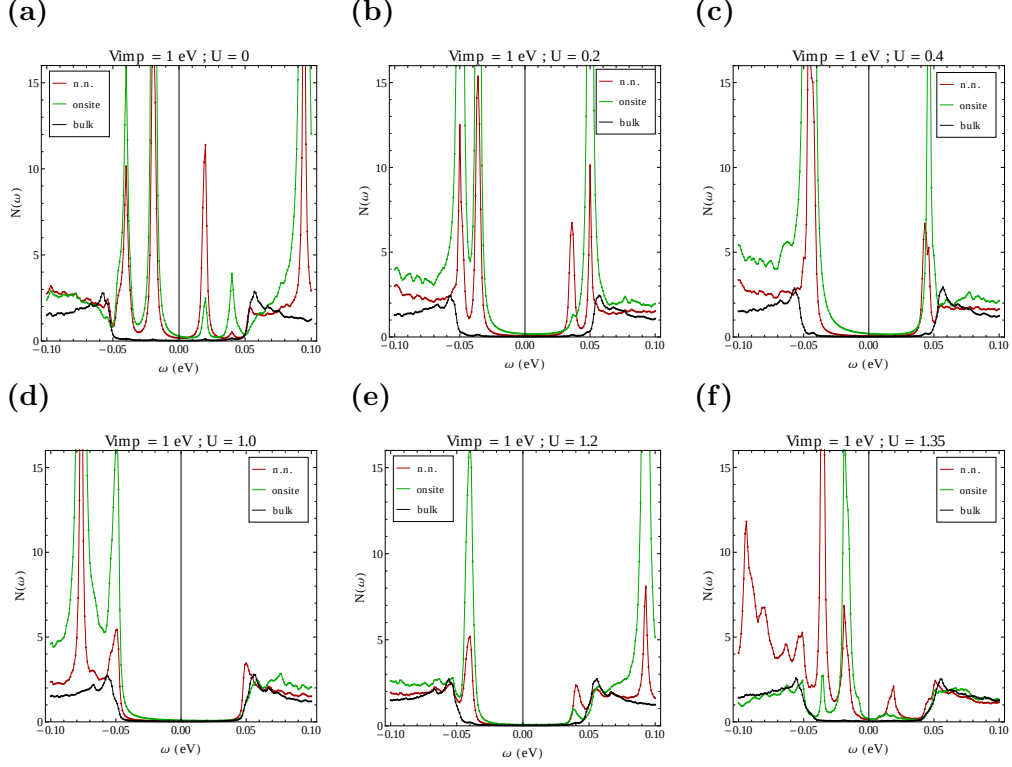


Figure 4.6: LDOS around a *weak impurity* ($V_{imp} = 1$), for various correlation strengths. The black curve is the DOS far away from the impurity, and red and green curves the nearest neighbor and impurity sites respectively. (a) $U = 0$, four local in-gap bound states (red and green curves). (b)-(c) $U = 0.2$ and $U = 0.4$, these states are pushed away from the Fermi level. (d) $U = 1.0 \lesssim U_c = 1.1$, there is no in-gap bound state left, they are generated at the gap edges. (e) $U = 1.2 \gtrsim U_c$, the states are pushed back again into the gap and Stoner instability is locally crossed. (f) $U = 1.35 > U_c$ magnetization is settled down and new magnetic features appear inside the gap in the vicinity of the impurity.

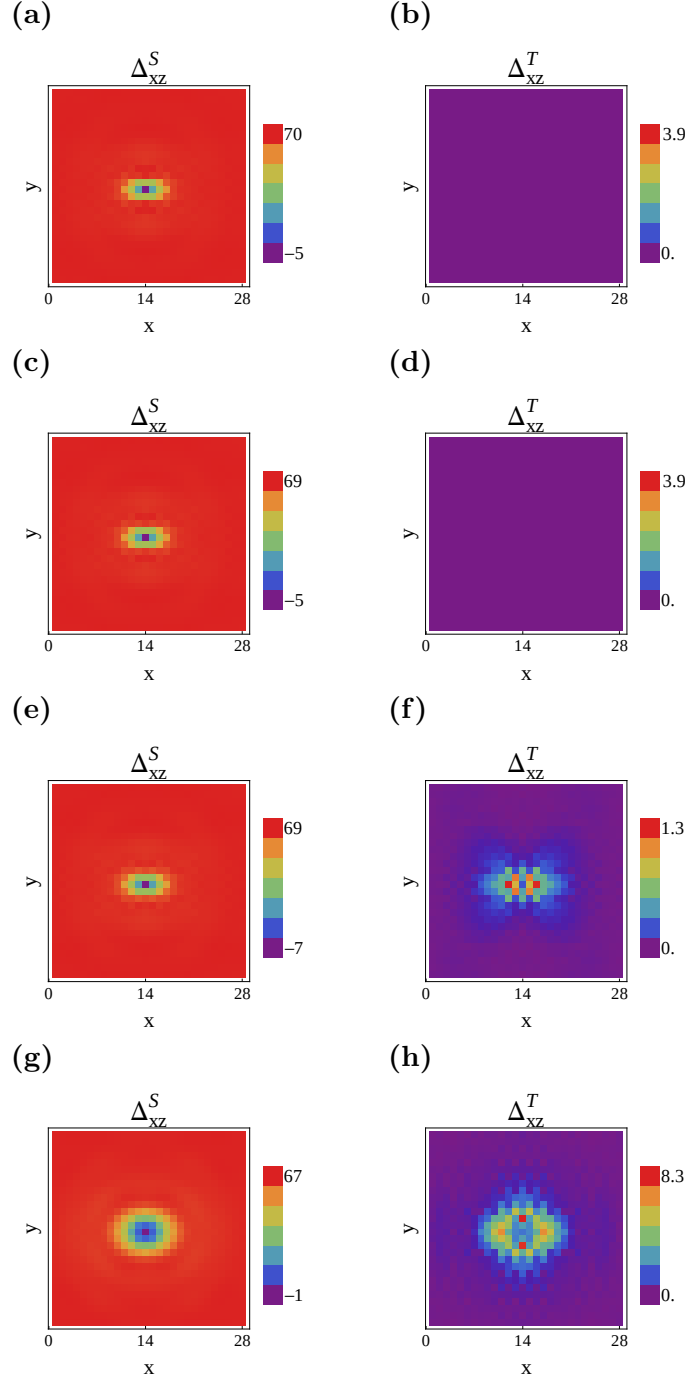


Figure 4.7: *Strong impurity* ($V_{imp} = 8$). Effect of correlations for the singlet (left) and triplet (right) components of the orbital d_{xz} . Correlation strength: (a)-(b) $U = 0$, (c)-(d) $U = 0.4$, (e)-(f) $U = 1.2$ and (g)-(h) $U = 1.35$.

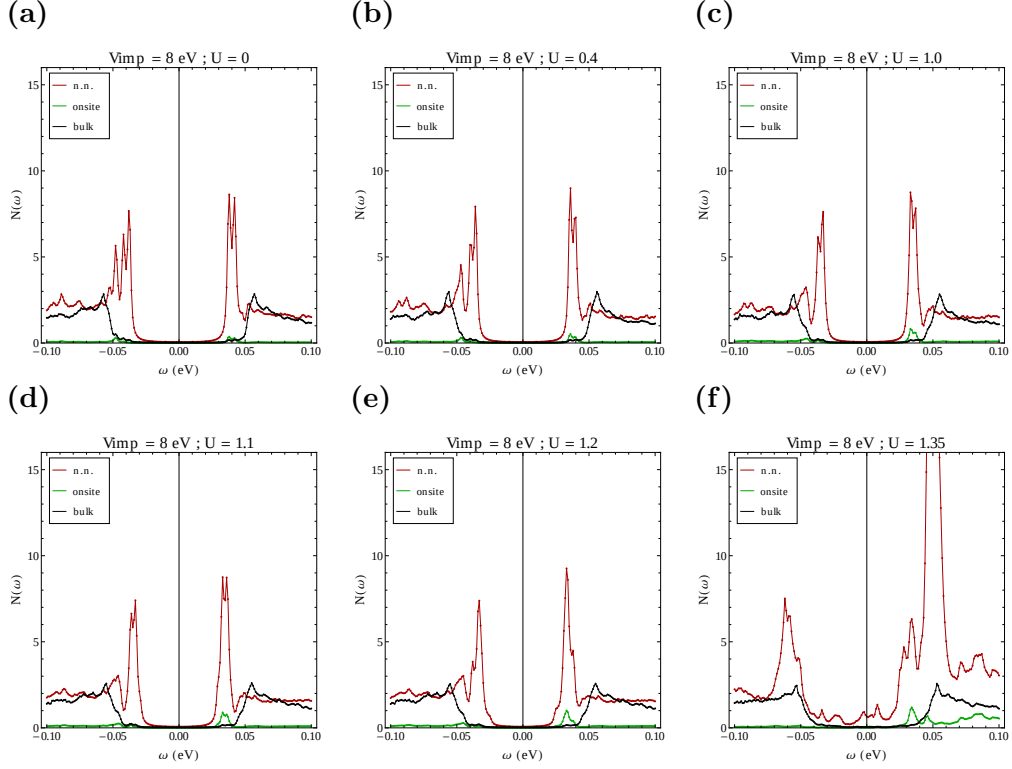


Figure 4.8: LDOS around a *strong impurity* ($V_{imp} = 8$), for various correlation strengths. The black curve is the DOS far away from the impurity, and red and green curves the nearest neighbor and impurity sites respectively. (a) $U = 0$, local in-gap bound states, closer to the gap edge than in the weak impurity case. (b)-(d) $U = 0.4$, $U = 1.0$ and $U = 1.1$, the states remain the same as in (a). (e) $U = 1.2 \sim U_c$, the local bound-state structure is still very similar, but the interaction parameter U is strong enough to cross the Stoner instability. (f) $U = 1.35 > U_c$, strong magnetization sets in and the same magnetic features as in the weak impurity case appear.

4.4 Conclusion

In this chapter, local properties of the single-nonmagnetic-impurity problem for the superconducting $s_{\pm}$ state have been presented. The impurity is placed in a non-magnetic system, but close to the SDW.

Local orbital ordering is induced around repulsive and attractive potentials, because of an effective hopping asymmetry due to the different spatial orientation of orbitals d_{xz} and d_{yz} .

Repulsive impurities are pair-breaking and develop local in-gap bound states around the potential; attractive impurities on the contrary, are non-pair-breaking, and have a clean gap in the whole system. Magnetization for high enough U values is locally induced just around the impurities with in-gap bound states (repulsive potentials). This can be understood by the fulfillment of the Stoner criterion in the single-band system, which in the static, long-wave limit becomes $UN(E_F) \rightarrow 1$. The repulsive impurities have a higher local DOS at the Fermi level due to the in-gap bound states, and can then satisfy the Stoner condition around the impurity for $U > U_c$. The resulting induced magnetic order $Q = (\pi, \pi)$ however, is different from the stripe-like antiferromagnetic order $Q = (\pi, 0)$ that was found for the homogeneous system. As will be explained in chapter 5, at this doping the structure of the susceptibility of the homogeneous system has changed. The $(\pi, 0)$ peak has been suppressed and a plateau around (π, π) dominates the response function. The impurity locally crosses the leading magnetic instability, which is the checkerboard ordering at this filling.

Finally, we discuss the effect of correlations for a weak and a strong impurity.

In the former case, at low correlations, the bound states are pushed towards the gap edges, and the singlet components are peaked around the impurity site. However, the superconducting gap in the LDOS does not locally increase. At high correlations, the in-gap bound states are pushed into the gap again, the Stoner instability is crossed and there is induced magnetization in the system. The singlet components start to be suppressed again, showing a competing effect with the magnetic order. When magnetization is completely settled down, extra local magnetic features appear in the DOS.

In the strong impurity limit, at low correlations, the in-gap bound states are closer to the gap edge and not affected by increasing the strength of the interactions. The singlet components are always suppressed around the impurity site. At high correlations, when $U > U_c$, the Stoner instability is crossed, and the same magnetic local in-gap features as in the weak impurity case appear.

Chapter 5

Effective pairing

The main motivation of this chapter is to improve our model by removing the dependence on the choice of the pairing couplings $V_{ij}^{\mu\nu}$. Until now, superconductivity was included by a phenomenological BCS term (see equation (2.9)), with an effective attraction between next-nearest neighbor electrons included by hand. We will assume now that the driving force for superconductivity comes from a spin fluctuation mechanism, and calculate the resulting effective pairings within this approach. Once we have these new couplings, we can repeat the whole analysis of chapter 3 for a homogeneous system, and the single-impurity problem of chapter 4, with a reduced parameter space. We can also contrast our results with previous spin fluctuation studies of the gap symmetry and structure.

5.1 The spin fluctuation glue

The electron-phonon mechanism is not strong enough to produce the observed high critical superconducting temperatures [11] in FeSC. The point of departure is the following: the BCS theory in essence still suffices to explain the physics of the high temperature superconductors. One just needs a different agent that can take the role of phonons, mediating attractive interactions. An option is then to look for “glue” that emerges from the interacting electron system itself. Magnetism is usually nearby in FeSC, and the most popular candidate is the spin fluctuation (also called paramagnon) theory of pairing. This mechanism is similar to a conventional superconductor, in which the exchange of paramagnons, instead of phonons, results in an effective attraction between electrons.

The effective electron-electron interaction is calculated by making use of perturbation theory, i.e. summing a series of diagrams to infinite order. An example of such diagrammatic series is shown in figure 5.1. The first term of the series represents the simple Coulomb interaction (red dashed line) between fermion lines

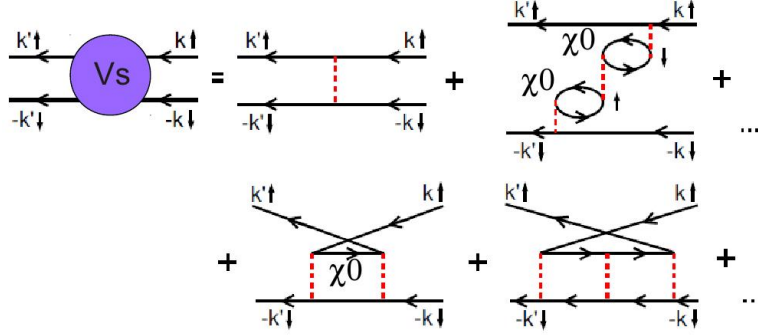


Figure 5.1: Effective pairing interaction between opposite spins. Solid lines are single-particle propagators, and red dashed lines the interaction U between opposite spins in the single-band system.

(black lines) with opposite spin. The next term in the series, a third order term (three red dashed interaction lines), stands for the simplest diagram of exchange of longitudinal spin fluctuations. It involves two particle-hole bubbles χ_0 (bare spin susceptibility involving two single-particle propagators) connected by interacting U lines. Note that it is not possible to have an uneven number of bubbles due to spin, i.e. since U is an onsite interaction it must connect fermion lines of opposite spin only. Higher order terms of longitudinal spin fluctuations (shown as “...” in the first row) are built by adding even number of bubbles. The next two terms (second line of the series), a second and a third order terms, represent the exchange of transverse spin fluctuations. Summing this graphs to all orders gives rise to the effective electron electron interaction V_s mediated by spin fluctuations.

Extensive studies of this theoretical approach have been done in the one-band system for cuprates, by for example, D. J. Scalapino[28]. In these compounds, the spin fluctuation theory naturally led to a $d_{x^2-y^2}$ superconducting order parameter.

5.2 The spin and charge susceptibilities

In this section, charge and spin susceptibilities are calculated in the paramagnetic regime, and are used in the next section to construct the pairing interaction vertex. In order to calculate those response functions, we will work in momentum space. The kinetic energy term of the Hamiltonian takes the following form in momentum representation:

$$H_0 = \sum_{k\sigma} \sum_{\mu\nu} \xi_{\mu\nu}(k) \hat{c}_{\mu\sigma}^\dagger(k) \hat{c}_{\nu\sigma}(k) - \mu_0 \sum_{k\mu\sigma} \hat{c}_{\mu\sigma}^\dagger(k) \hat{c}_{\mu\sigma}(k). \quad (5.1)$$

Here, the terms $\xi_{\mu\nu}(k)$ are linear combinations of $t_{ij}^{\mu\nu} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}}$ resulting from Fourier transforming equation (2.2). They are listed in [24].

We start by calculating the two-particle correlation function of the non-interacting Hamiltonian. For a multiorbital system, it is given by the general expression

$$\chi_{0st}^{pq}(q, \tau) = \frac{1}{N} \sum_{k\sigma k'\sigma'} \langle T_\tau \hat{c}_{p\sigma}^\dagger(k, \tau) \hat{c}_{q\sigma}(k+q, \tau) \hat{c}_{t\sigma'}^\dagger(k', 0) \hat{c}_{s\sigma'}(k'-q, 0) \rangle_0, \quad (5.2)$$

where p, q, s and t are orbital indexes and N is the normalization factor. In order to get the Matsubara frequency-dependent function, we Fourier transform the previous expression,

$$\begin{aligned} \chi_{0st}^{pq}(q, iq_n) &= -\frac{1}{N} \int_0^\beta d\tau e^{iq_n\tau} \sum_{k\sigma} G_0^{qt}(k+q, \tau) G_0^{sp}(k, -\tau) \\ &= -\frac{1}{N\beta} \sum_{ik_n} \sum_{k\sigma} G_0^{qt}(k+q, ik_n + iq_n) G_0^{sp}(k, ik_n) \end{aligned} \quad (5.3)$$

where we have used Wick's theorem, the single-particle Green's function

$$G_0^{sp}(k\tau, k'\tau') = -\langle T_\tau \hat{c}_{s\sigma}(k, \tau) \hat{c}_{p\sigma'}^\dagger(k', \tau') \rangle_0, \quad (5.4)$$

and transformed a convolution integral. The spectral representation of the Green's function is given by,

$$G_0^{\mu\nu}(k, iq_n) = \sum_n \frac{u_\mu^n(k) u_\nu^{n*}(k)}{iq_n - E_n(k)}. \quad (5.5)$$

Here, $u_\mu^n(k)$ are the components of the eigenvectors resulting from the diagonalization of the initial Hamiltonian (5.1) by a unitary transformation similar to the one we did in chapter 2, namely $\hat{c}_{\mu\sigma}(k) = \sum_n u_\mu^n(k) \hat{\gamma}_{n\sigma}(k)$. Now we just have to insert (5.5) in expression (5.3), do the Matsubara frequency summation, and the replacement $iq_n \rightarrow \omega + i\eta$ by analytical continuation. The final expression for the non-interacting susceptibility is then

$$\chi_{0st}^{pq}(q, \omega) = -\frac{1}{N} \sum_{k,mn} \frac{u_s^m(k) u_p^{m*}(k) u_q^n(k+q) u_t^{n*}(k+q)}{\omega + E_n(k+q) - E_m(k) + i\eta} [f(E_n(k+q)) - f(E_m(k))]. \quad (5.6)$$

This is the well known Lindhard function of the non-interacting electron gas, with the extra contribution of the matrix elements $u_\mu^n(k)$ that arised from the diagonalization of (5.1). In order to get a physical intuition of this multi-orbital response function, we calculate the bare static susceptibility

$$\chi_0(q) = \frac{1}{2} \sum_{sp} \chi_{0ss}^{pp}(q, 0), \quad (5.7)$$

which includes only the single-particle propagators projected on the same orbital, i.e. the $q = p$ and $t = s$ terms in equation (5.2) (the rest of the elements involve projection on different orbitals and are smaller). The real part of $\chi_0(q)$ is shown in figures 5.2 (a) and (b) for two different chemical potentials corresponding to the undoped ($x = 0$) and the electron doped ($x = 0.15$) systems. In figure 5.2 (a) one can see that the weight is suppressed for small q vectors and the main contribution comes from the high momentum vectors (q_y, π) and (π, q_x) . There are two peaks at $\mathbf{q}_y = (\pi, 0)$ and $\mathbf{q}_x = (0, \pi)$ resulting from the nesting between the hole and electron pockets, and a plateau around (π, π) from the nesting between the two electron pockets. When the doping is increased in figure 5.2 (b), these two peaks are slightly suppressed while the plateau around (π, π) appears slightly larger. This new structure can be attributed to the change in the Fermi surface shown in figures 5.2 (c) and (d).

Interactions add other fundamental excitations into the system, and the response function is modified. We include the interactions within the RPA approximation, in which the infinite sum of the most divergent diagrams for each order is performed (the ones with maximum number of pair-bubbles, which dominate the physics in the high-density limit). For a multi-band system, the RPA charge and spin susceptibilities are obtained in the form of Dyson-type equations as [24]

$$\chi_c^{RPA}(q, \omega) = \chi_0(q, \omega)[1 + U^c \chi_0(q, \omega)]^{-1}, \quad (5.8)$$

and

$$\chi_s^{RPA}(q, \omega) = \chi_0(q, \omega)[1 - U^s \chi_0(q, \omega)]^{-1}, \quad (5.9)$$

where for our five orbital problem χ_0 , U^c and U^s are 25×25 matrices in the (pq, st) basis. The matrices U^c and U^s are given as

$$(U^c)_{aa}^{aa} = U, \quad (U^c)_{aa}^{bb} = 2U - 5J, \quad (U^c)_{ab}^{ab} = \frac{13}{4}J - U, \quad (U^c)_{ab}^{ba} = J, \quad (5.10)$$

and

$$(U^s)_{aa}^{aa} = U, \quad (U^s)_{aa}^{bb} = J, \quad (U^s)_{ab}^{ab} = -\frac{9}{4}J + U, \quad (U^s)_{ab}^{ba} = J. \quad (5.11)$$

The details about susceptibilities and interaction matrices can be found in the Appendix of [37]. Again, in order to have a physical intuition of the multiorbital interacting response functions, we calculate the static charge and spin susceptibilities

$$\chi_c^{RPA}(q) = \frac{1}{2} \sum_{sp} (\chi_c^{RPA})_{ss}^{pp}(q, 0), \quad (5.12)$$

$$\chi_s^{RPA}(q) = \frac{1}{2} \sum_{sp} (\chi_s^{RPA})_{ss}^{pp}(q, 0), \quad (5.13)$$

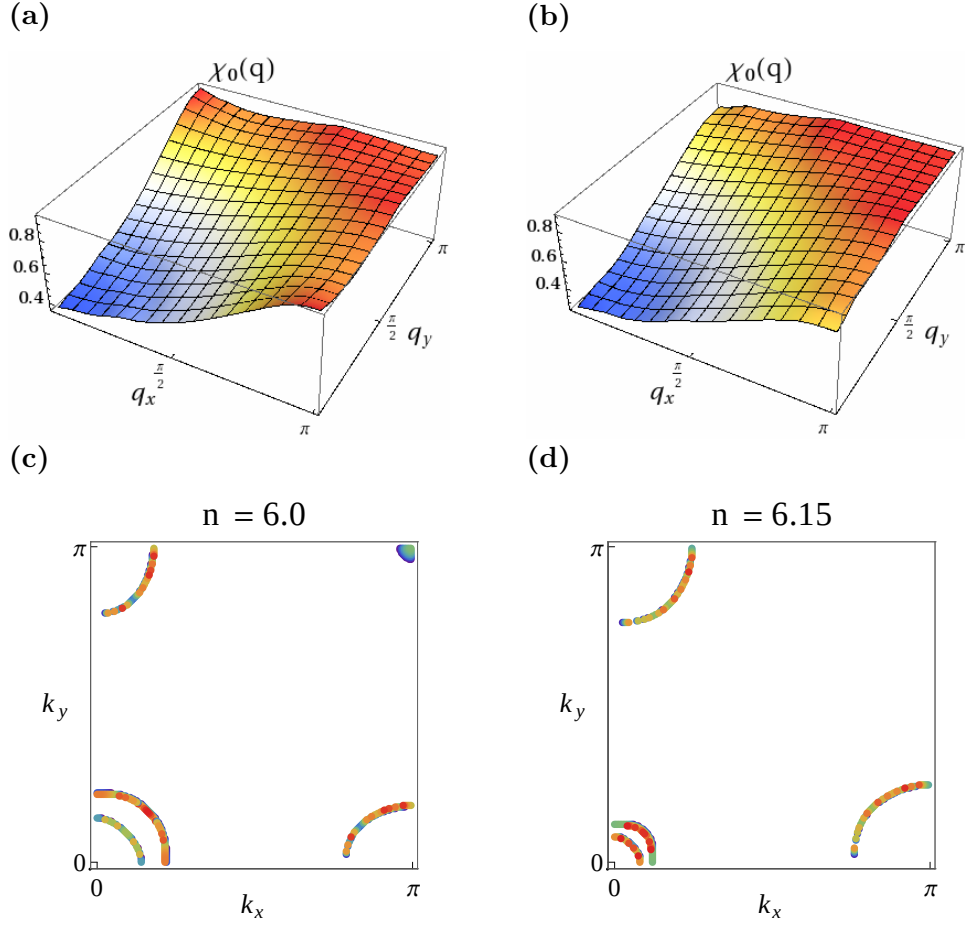


Figure 5.2: The real part of the bare static spin susceptibility, $\text{Re}\chi_0(q)$, in the first quadrant of the BZ for the (a) undoped ($n = 6.0$) and (b) electron doped ($n = 6.15$) systems. (c) and (d) are the non-interacting Fermi surfaces of H_0 in the first quadrant of the BZ for the doping in (a) and (b), respectively. In the undoped compound (c), the hole and electron pockets are nested by $\mathbf{q}_y = (\pi, 0)$ and $\mathbf{q}_x = (0, \pi)$ (the notation comes from the orbital weight of the electron pockets d_{yz} or d_{xz} , see chapter 3), which enhance the peaks in (a) at those vectors. In addition, the nesting between the two electron pockets $\mathbf{q}_{ee} = (-\pi + \delta_x, \pi + \delta_y)$ results in the plateau around (π, π) in (a). (d) In the electron doped FS, $\mathbf{q}_y$ and $\mathbf{q}_x$ are very deteriorated, due to the opposite growth of the electron and hole pockets with doping, and the structure at those vectors in (b) is suppressed with respect to (a). $\mathbf{q}_{ee}$ on the contrary takes a bigger region because of the larger electron pockets, and the plateau in (b) has increased.

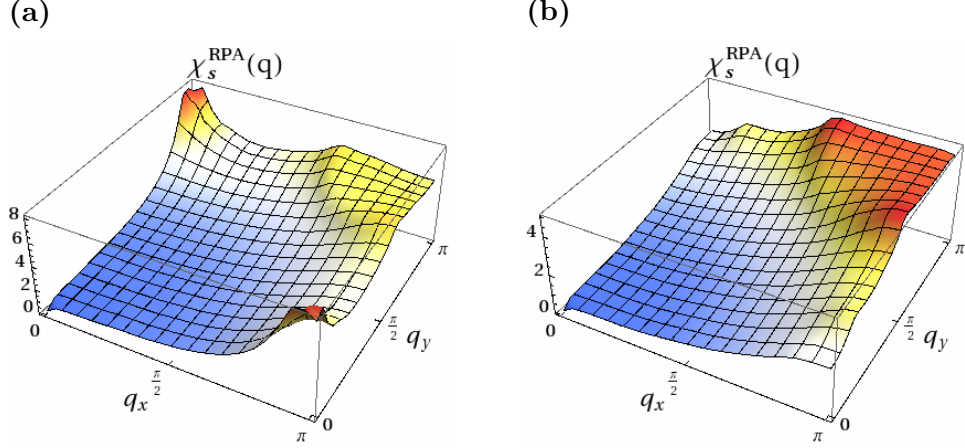


Figure 5.3: Real part of the RPA spin susceptibility $\chi_s^{RPA}(q)$ for $U = 1.1$ and $J = U/4$ in the (a) undoped (b) electron doped $n = 6.15$ systems. The spin response function is enhanced at the stripe-type SDW vector $(\pi, 0)$ for the undoped compound (a). The structure changes upon doping, the peak is suppressed and the plateau around (π, π) is the pronounced region, instead at (b).

which include only the diagonal density-density and spin-spin processes ($q = p$ and $t = s$ like we did in equation (5.7)). In the single-band system, the inclusion of interactions within an RPA approach is known to enhance existing structures in the bare susceptibility. In the case of a multi-orbital system, it is not obvious how the structures of the charge and spin susceptibilities will be changed by the variation of the onsite intra-orbital repulsion U and Hund's coupling J . There is a matrix in the denominator instead of the single parameter U of the single-band system. We have not performed a systematic analysis of the $\{U, J\}$ parameter space dependence in the structure of the RPA susceptibilities, and had to stick to our usual choice $U \sim 1.0$ and $J = U/4$. Figure 5.3 shows the real part of the RPA spin susceptibility $\chi_s^{RPA}(q)$ for the two dopings discussed earlier in figure 5.2. In the undoped compound, the main peak is found at $\mathbf{q}_y = (\pi, 0)$ (and the C_4 symmetric $\mathbf{q}_x = (0, \pi)$), which agrees with the stripe-like antiferromagnetic state that we found in chapter 3. The plateau around (π, π) that was found in the bare susceptibility in figure 5.2 (a) is still there with the inclusion of the interactions, but is less pronounced than the $(\pi, 0)$ peak. At higher electron doping the scenario changes, as can be seen in figure 5.3 (b). The pronounced structure is now around (π, π) and the $(\pi, 0)$ peak appears suppressed. These results agree with the magnetic phase diagram that we found in chapter 3. The $(\pi, 0)$ peak responsible for the striped SDW gets suppressed upon doping, and at a certain filling ($n = 6.1$) the interacting parameter U is not strong enough to cross the Stoner instability. For the parameters chosen, the charge susceptibility is more than one order of

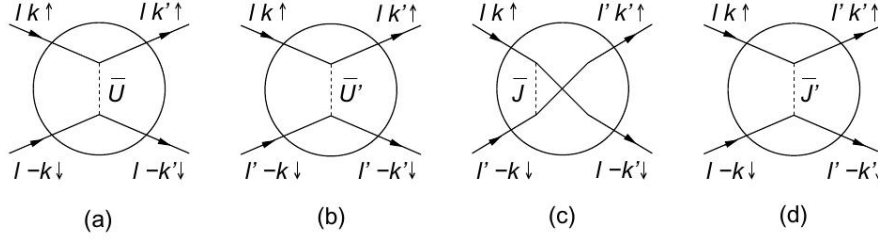


Figure 5.4: First order scattering vertices corresponding to (a) intra-, (b)-(c) mixed- and (d) inter-orbital pair scattering processes. l and l' are orbital indexes and the interaction parameters $\bar{U} \equiv U$, $\bar{U}' \equiv U' - J$, $\bar{J} \equiv J$ and $\bar{J}' \equiv J'$. The Coulomb matrix elements were derived in equation (2.6).

magnitude smaller than the spin susceptibility, and has no pronounced structures.

We close this section by making a connexion to the single-impurity problem in chapter 4. The Stoner criterion is in fact more complex in multiorbital systems than the usual single-band criterion. There is a matrix in the denominator which implies a specific combination of the elements of the bare susceptibility with the interaction parameters (cf equation (5.9)). How an impurity affects a multi-orbital system's response function, depends then not only on the modified structure of the bare susceptibility $\chi_0(q)$, but also on the combination of U and J which determines the final enhanced structures of the function.

5.3 Effective pairings

Assuming that the pairing interaction responsible for superconductivity arises from the exchange of spin fluctuations, we can calculate the pairing vertex using the fluctuation exchange approximation. For a given doping, U and J values we calculate the multi-orbital pairing vertex in the singlet channel (from [24])

$$\Gamma_{pqst}(k - k', 0) = \left[\frac{3}{2} U^s \chi_s^{RPA}(k - k', 0) U^s + \frac{1}{2} U^s - \frac{1}{2} U^c \chi_c^{RPA}(k - k', 0) U^c + \frac{1}{2} U^c \right]_{pq}^{st} \quad (5.14)$$

First order scattering vertices for the multiorbital Hubbard model are shown in figure 5.4. The interaction Hamiltonian H_{sc} of this pairing vertex is given by

$$H_{sc} = \sum_{pqst} \sum_{kk'} \Gamma_{pqst}(k - k', 0) c_{p\uparrow}^\dagger(k') c_{t\downarrow}^\dagger(-k') c_{s\downarrow}(-k) c_{q\uparrow}(k). \quad (5.15)$$

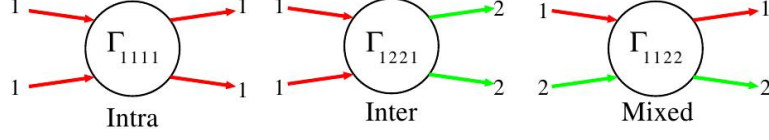


Figure 5.5: Representative examples of classes of orbital vertices: intra-, inter- and mixed-orbital vertices.

Examples of the particle-particle scattering of electrons in orbitals q, s into p, t are shown in figure 5.5. Rewriting the annihilation and creation operators in the real space formulation, and after doing some algebra we arrive to

$$\begin{aligned}
H_{sc} &= \sum_{pqst} \sum_{kk'} \sum_{r_p r_q r_s r_t} \Gamma_{pqst}(k - k', 0) e^{-ik'(r_p - r_t)} e^{ik(r_q - r_s)} \\
&\quad c_{p\uparrow}^\dagger(r_p) c_{t\downarrow}^\dagger(r_t) c_{s\downarrow}(r_s) c_{q\uparrow}(r_q) \\
&= \sum_{pqst} \sum_{r_i r_j} \sum_q \Gamma_{pqst}(q, 0) e^{ik(r_i - r_j)} c_{p\uparrow}^\dagger(r_i) c_{t\downarrow}^\dagger(r_j) c_{s\downarrow}(r_j) c_{q\uparrow}(r_i) \\
&= \sum_{pqst} \sum_{ij} \Gamma_{pqst}(r, 0) c_{ip\uparrow}^\dagger c_{jt\downarrow}^\dagger c_{js\downarrow} c_{iq\uparrow},
\end{aligned} \tag{5.16}$$

where $r_i \equiv r_p = r_q$ and $r_j \equiv r_s = r_t$. Here we have use the fact that (5.15) only depends on the difference of momentum $q \equiv k - k'$ leaving us with two spatial coordinates $\delta_{r_q - r_t, r_p - r_s}$. It has also been assumed that $\delta_{r_p + r_t, r_q + r_s}$. H_{sc} has now the form of the real space BCS Hamiltonian $H_{BCS} = -V_{ij}^{\mu\nu} \sum_{i \neq j, \mu\nu} \hat{n}_{i\mu\uparrow} \hat{n}_{j\nu\downarrow}$ that was introduced by hand in chapter 2. The pairing couplings $V_{ij}^{\mu\nu}$ are then replaced by the effective couplings calculated within the spin fluctuation mechanism,

$$\Gamma_{pqst}(r, 0) = \sum_q \Gamma_{pqst}(q, 0) e^{ik(r_i - r_j)}, \tag{5.17}$$

for the onsite ($r = 0$), nearest neighbor ($r = (0, \pm 1)$ and $r = (\pm 1, 0)$) and next-nearest neighbor ($r = (\pm 1, \pm 1)$) electron pairs.

Results

We have calculated the effective intra-, inter and mixed-orbital pairings within this approach for different dopings. Figures 5.6, 5.7, 5.8 and 5.9 show the main results of this section. In all these figures, subfigure (a) shows the real space intra-orbital couplings $\Gamma_{pppp}(r)$ at the nearest neighbor (NN) and next-nearest neighbor (NNN) sites versus the interaction paramter U (and keeping the rate $J = U/4$ fixed). The maximum value of U is below the magnetic instability, since once it has been

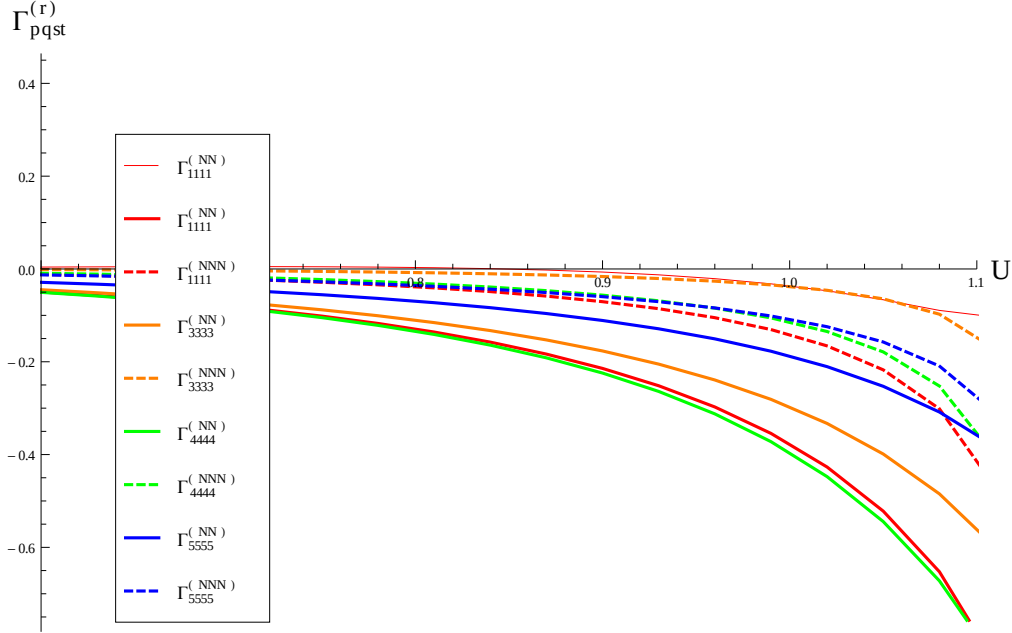
crossed, the spin susceptibility diverges and so do the pairings (cf equation 5.14). The other two subfigures, (b) and (c), show for a fixed value of $U = 1.0$, the intra-orbital couplings in momentum space $\Gamma(q)$ in (b), and their Fourier transform to real space until 5th nearest neighbors in (c). The color scale in (c) should be taken qualitatively (for quantitative values see (a)). The orbital numbering [$1 = d_{xz}$, $2 = d_{yz}$, $3 = d_{x^2-y^2}$, $4 = d_{xy}$, $5 = d_{3z^2-r^2}$] remains the same as in chapter 2.

The main conclusions are the following:

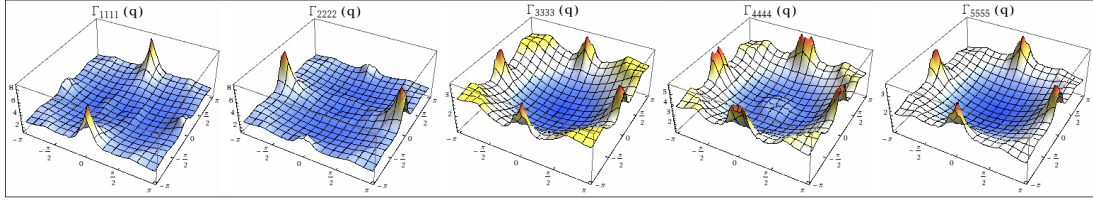
- $\Gamma^{(NN)}$ is the dominant attractive pairing for all dopings, $\Gamma^{(NN)} > \Gamma^{(NNN)}$ (normal versus dashed curves). When increasing the doping, this difference increases and at high dopings $\Gamma^{(NNN)}$ even starts becoming repulsive (see figures 5.8 (a) and 5.9 (a)).
- $\Gamma_{4444}^{(NN)}$ (the d_{xy} orbital) is the most attractive pairing, followed closely by the degenerate orbitals $\Gamma_{1111}^{(NN)}$ (d_{xz}) and $\Gamma_{2222}^{(NN)}$ (d_{yz}).
- The pairings of the orbitals d_{xz} and d_{yz} are twofold symmetric, and the rest of the orbitals couplings are fourfold symmetric. To understand where these symmetries come from, we plot the pairings in momentum representation (subfigures (b)).
- The intra- and mixed-orbital couplings (see figure 5.5) are comparable in magnitude and the largest components. These are the ones we will be using in the self-consistent BdG equations. The inter-orbital pairings are several orders of magnitudes smaller, and we do not consider them.

(a)

$$n = 5.95 ; J = U/4$$



(b)



(c)

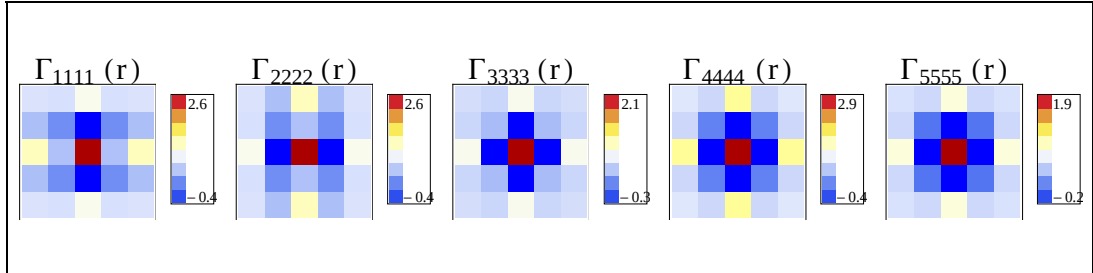


Figure 5.6: Hole doped ($n = 5.95$) intra-orbital pairings. (a) The NN (full lines) and NNN (dashed lines) sites couplings orbitally resolved. Because the orbitals 1 and 2 are degenerate just one of them is plotted. Note the thin and thick red lines for the two type of NN coming from the twofold symmetry of these two orbitals (see (c)). (b) and (c) show the same couplings in momentum space and their Fourier transform to real space, for the fixed $U = 1.0$ in (a).

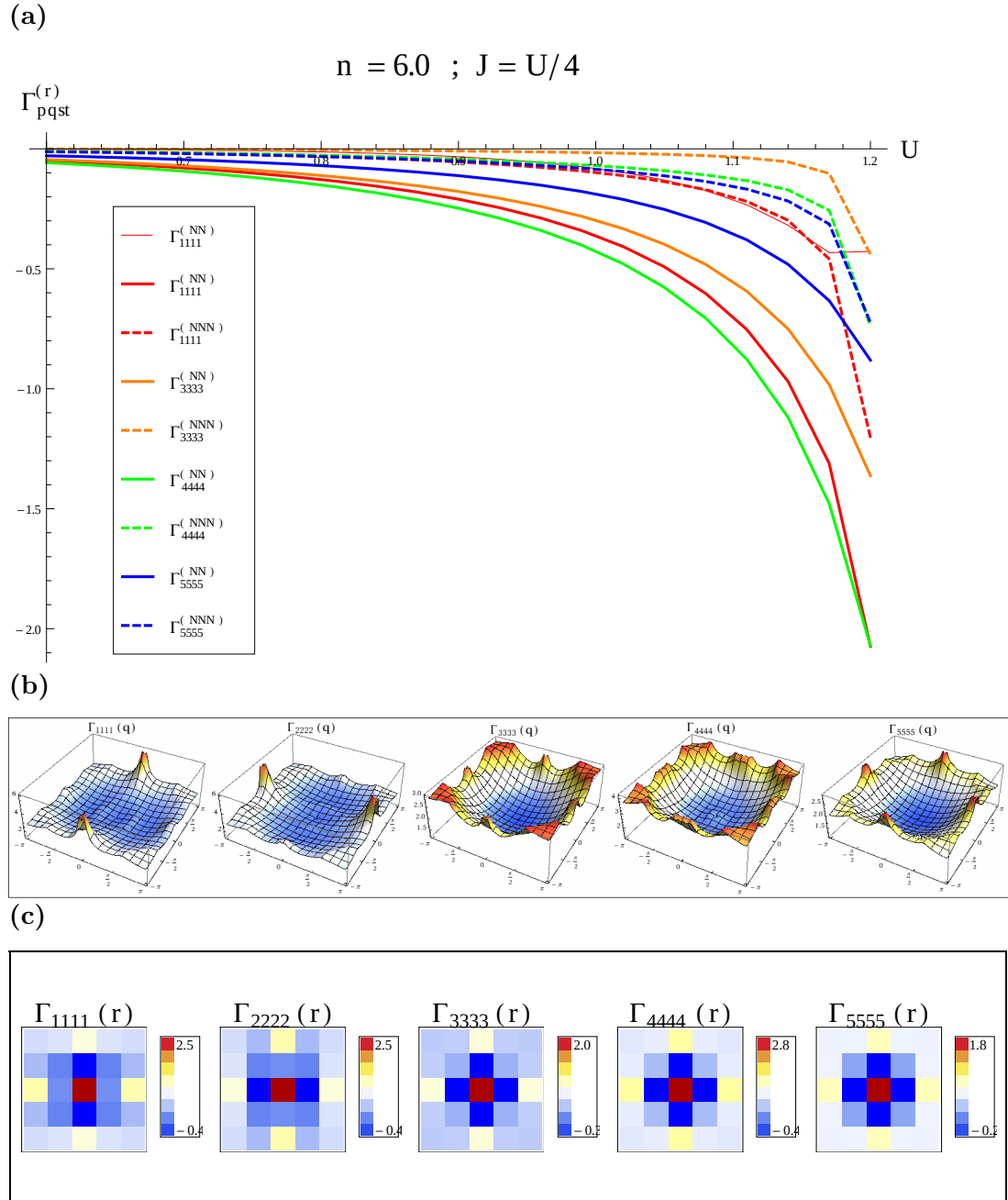
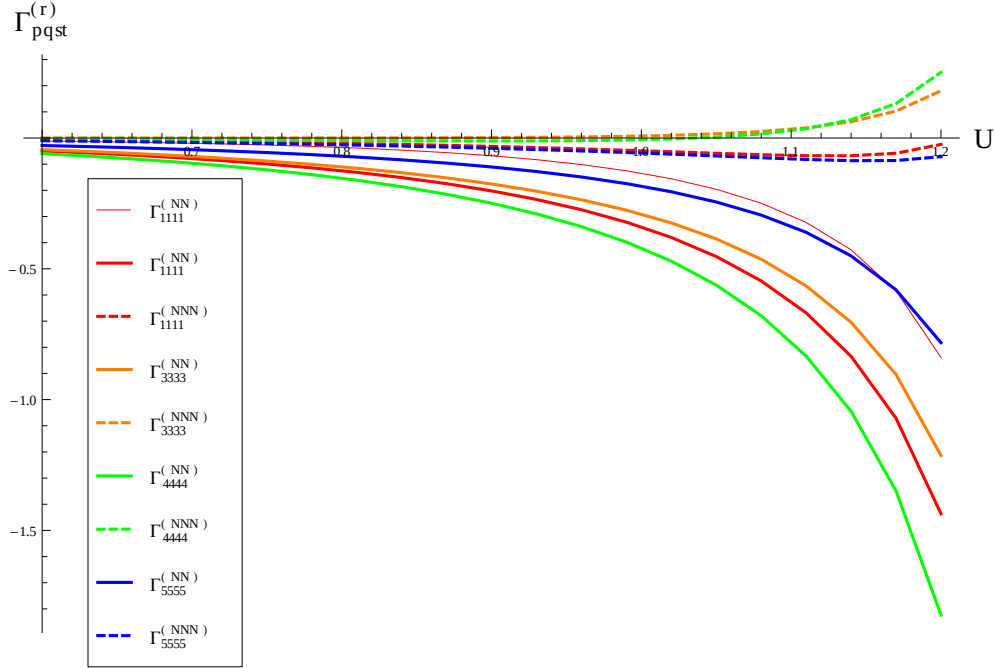


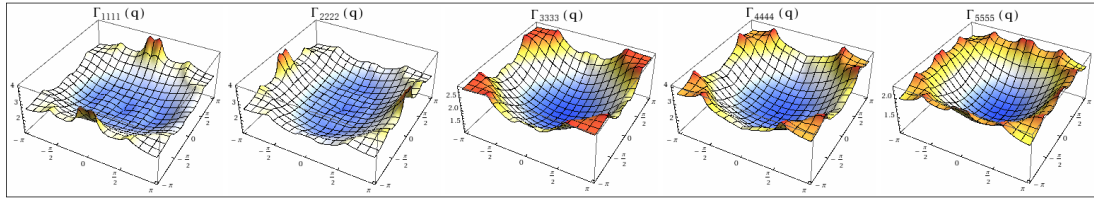
Figure 5.7: Same as in 5.6 for the undoped ($n = 6.0$) system. The difference between $\Gamma^{(NN)}$ and $\Gamma^{(NNN)}$ pairings is bigger.

(a)

$$n = 6.075 \quad ; \quad J = U/4$$



(b)



(c)

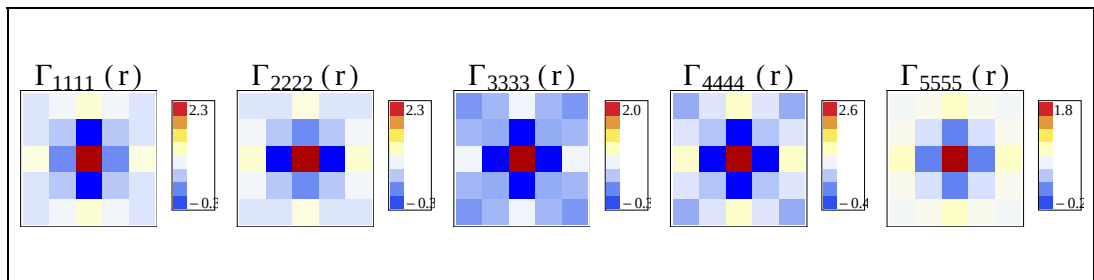
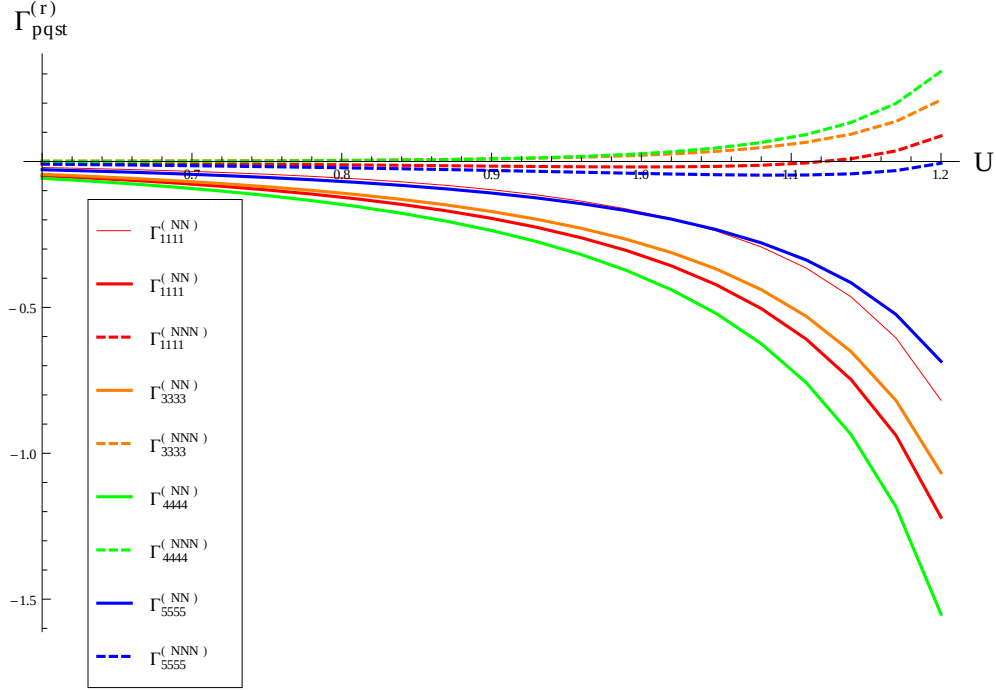


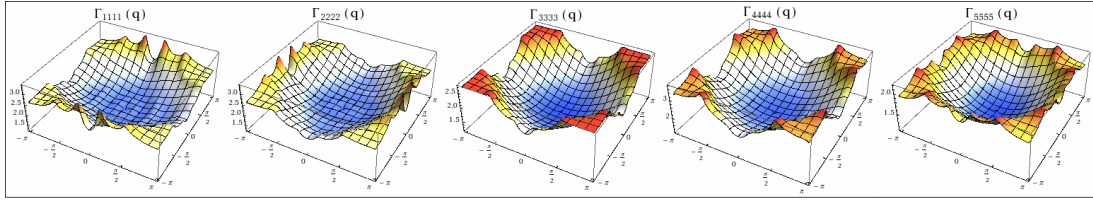
Figure 5.8: Same as in 5.6 for the electron doped ($n = 6.075$) system. $\Gamma^{(NNN)}$ starts being repulsive for some of the orbitals and the strength of the attractive $\Gamma^{(NN)}$ is slightly smaller.

(a)

$$n = 6.15 \quad ; \quad J = U/4$$



(b)



(c)

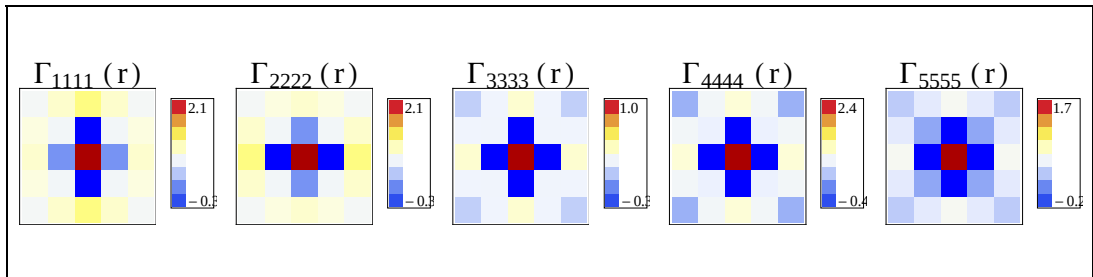


Figure 5.9: Same as in 5.6 for the electron doped ($n = 6.15$) system. The $\Gamma^{(NNN)}$ of the most important orbitals (1, 2 and 4) are repulsive at this doping. $\Gamma^{(NN)}$ are still attractive.

5.4 Homogeneous system

Now that we have calculated the effective pairings for different doping values x , $\Gamma^{6+x}(r)$, we can repeat the analysis of chapter 3, i.e. generate a phase diagram for the same $U = 1.35$ and $J = U/4$ interacting values, and calculate the new superconducting gap.

The whole study is done for the lowest and the highest dopings: the hole doped effective pairings $\Gamma^{5.95}(r)$ (figure 5.6), and the electron doped effective pairings $\Gamma^{6.15}(r)$ (figure 5.9). The difference between the nearest neighbor couplings $\Gamma^{(NN)}$ and the next-nearest neighbor couplings $\Gamma^{(NNN)}$ is smallest in the hole doped case and largest in the electron doped case (among the different dopings we presented in the previous section). So we will analyze the evolution of the mean field parameters with doping, for these two extreme effective couplings.

5.4.1 Hole and electron doped effective pairings

Figure 5.10 shows the new phase diagrams of the self-consistent fields for both cases: $\Gamma^{5.95}(r)$ in (a) and $\Gamma^{6.15}(r)$ in (b). The magnetic and a representative superconducting fields are given by,

$$m = (-1)^{(ix)} \sum_{\mu} (n_{i\mu\uparrow} - n_{i\mu\downarrow}), \quad (5.18)$$

$$\Delta = \sum_{\mu} (\Delta_{\mu\mu}^{nn} + \Delta_{\mu\mu}^{nnn}),$$

where

$$\Delta_{\mu\nu}^{nn} = \sum_j \Delta_{\mu\nu}^{S(nn)} = \frac{1}{2} \sum_j (|\Delta_{ij}^{\mu\mu}| - |\Delta_{ji}^{\mu\mu}|), \quad (5.19)$$

$$\Delta_{\mu\nu}^{nnn} = \sum_j \Delta_{\mu\nu}^{S(nnn)} = \frac{1}{2} \sum_j (\Delta_{ij}^{\mu\mu} - \Delta_{ji}^{\mu\mu}).$$

are the singlet components of the nearest neighbor (nn) and next-nearest neighbor (nnn) sites in orbital space. Note that we include the absolute value in $\Delta_{\mu\nu}^{nn}$ to account for the sign change in d-wave states. Both phase diagrams are very similar to the one we got for the constant $V_{ij}^{\mu\nu}$ in chapter 3 (cf figure 3.8(a)), except that the magnetic OP vanishes at lower dopings for the electron doped effective pairings (figure 5.10(b)).

However, the resulting superconducting gaps are now more complex, as will be shown below. Figure 5.11 shows the gap that develops for different dopings in the hole doped effective pairings case. At low dopings, in subfigures (a)-(c),

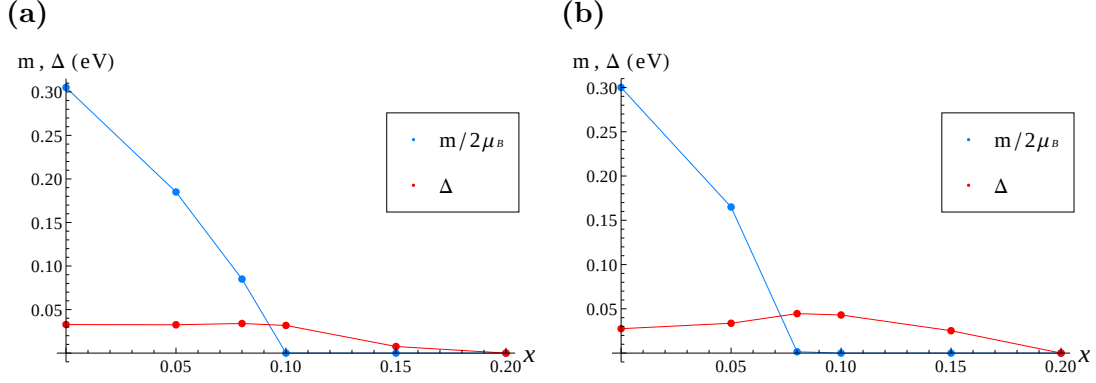


Figure 5.10: Phase diagrams of the self-consistent fields for the two effective pairings cases, (a) the hole doped $\Gamma^{5.95}(r)$ and the (b) electron doped $\Gamma^{6.15}(r)$.

the gap is nodeless, s-wave symmetric and has multi-gap features. The symmetry is deduced from how the superconducting order parameter $\Delta_{\mu\nu}^{S(nn)}$ (which pairs the nearest neighbor sites i and j) transforms under a $\pi/2$ rotation in real space. At low dopings, the gap is nodeless, and all the $\Delta_{\mu\nu}^{S(nn)}$ maintain their sign upon rotation. Their amplitude, however, is changed under this rotation, as expected from the broken translational invariance induced from the order of spins in the magnetic state. When magnetization vanishes at higher dopings ($n = 6.1$), the system chooses a different superconducting state, and the gap becomes nodal. The new state has d-wave symmetry, which is deduced from a sign change under a $\pi/2$ rotation of the $\Delta_{\mu\nu}^{S(nn)}$. The multi-gap feature is still visible. With the increase of doping the gap becomes smaller and eventually closes at $n = 6.2$.

Figure 5.12 shows the density of states against doping for the other case, i.e. the electron doped $\Gamma^{6.15}(r)$ effective pairings case. The only difference from the $\Gamma^{5.95}(r)$ pairings case, is that the superconducting state develops the same nodal two-gap d-wave symmetry for both low and high dopings, as can be seen in subfigures (a)-(e). As in the previous case, the gap closes again around $n = 6.2$.

Two-gap superconductivity has been reported by several groups. Two examples of STM measurements of a nodal and a nodeless gap are shown in figure 5.13. The measurements were made in the same compound (BaFe_2As_2) for hole (a) and electron (b) dopings.

After this study, we conclude that the resulting superconducting state in our system depends both on the effective pairings $\Gamma^{6+x}(r)$ and on the electronic filling of the system:

- Role of the effective pairings. It was mentioned in the previous section that the difference between Γ^{NN} and Γ^{NNN} is smallest for the hole doped effective pairings $\Gamma^{5.95}$. The resulting superconducting state at low electron dopings

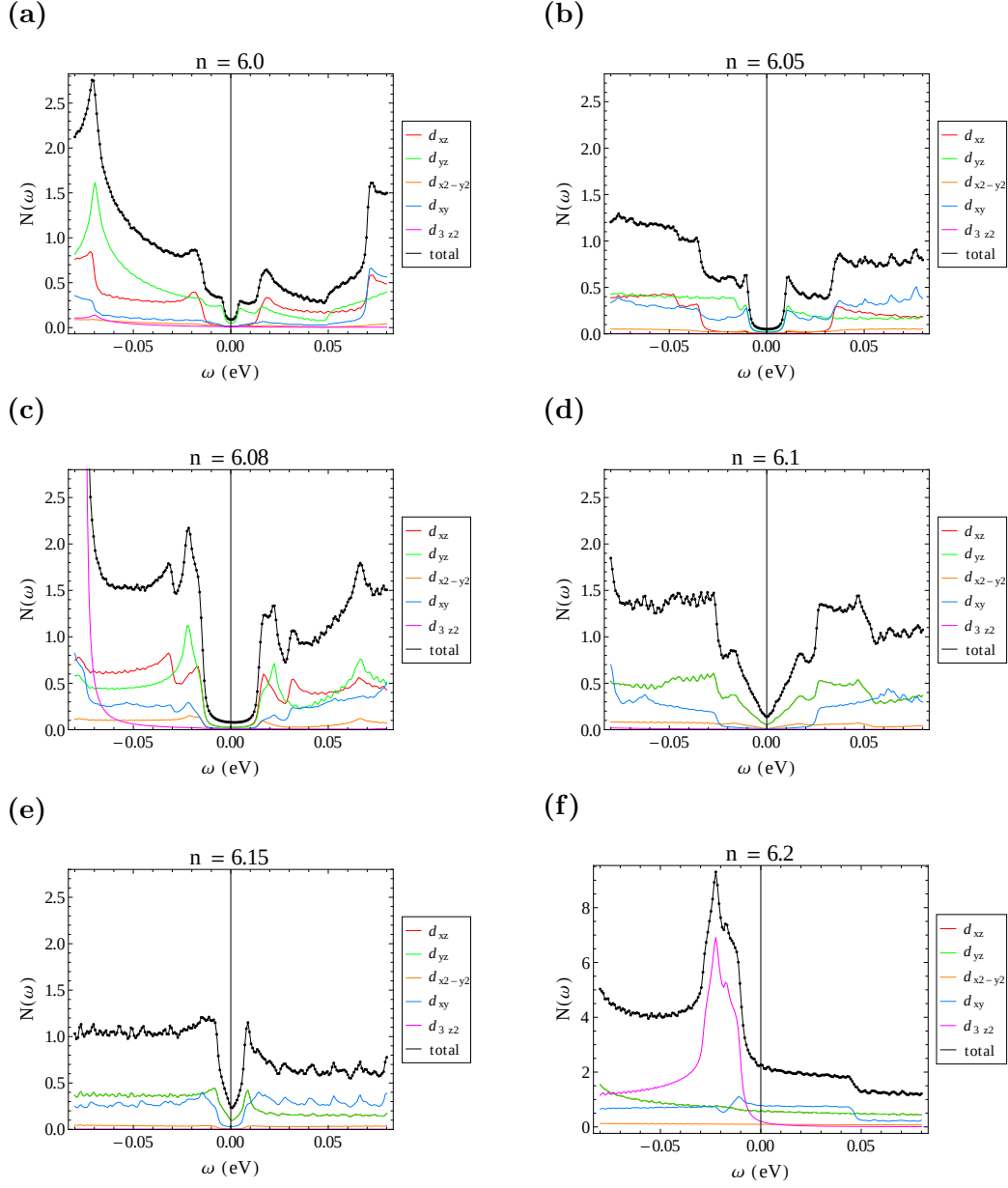


Figure 5.11: *DOS vs doping for $\Gamma^{5.95}(r)$. Orbitaly resolved (colored curves) and total (black curve) DOS. (a)-(c) At low dopings the state develops a U-shaped full two-gap. Note the orbital ordering of d_{xz} and d_{yz} generated because of magnetization. d_{yz} has a bigger magnetic moment and a smaller gap, reflecting the competing effect of superconductivity with magnetization. (d) When the magnetic OP vanishes the gap becomes V-shaped nodal and the new superconducting state is d-wave symmetric. (e)-(f) Doping the system move the gap edges closer to the Fermi level until the gap completely closes at $n = 6.2$.*

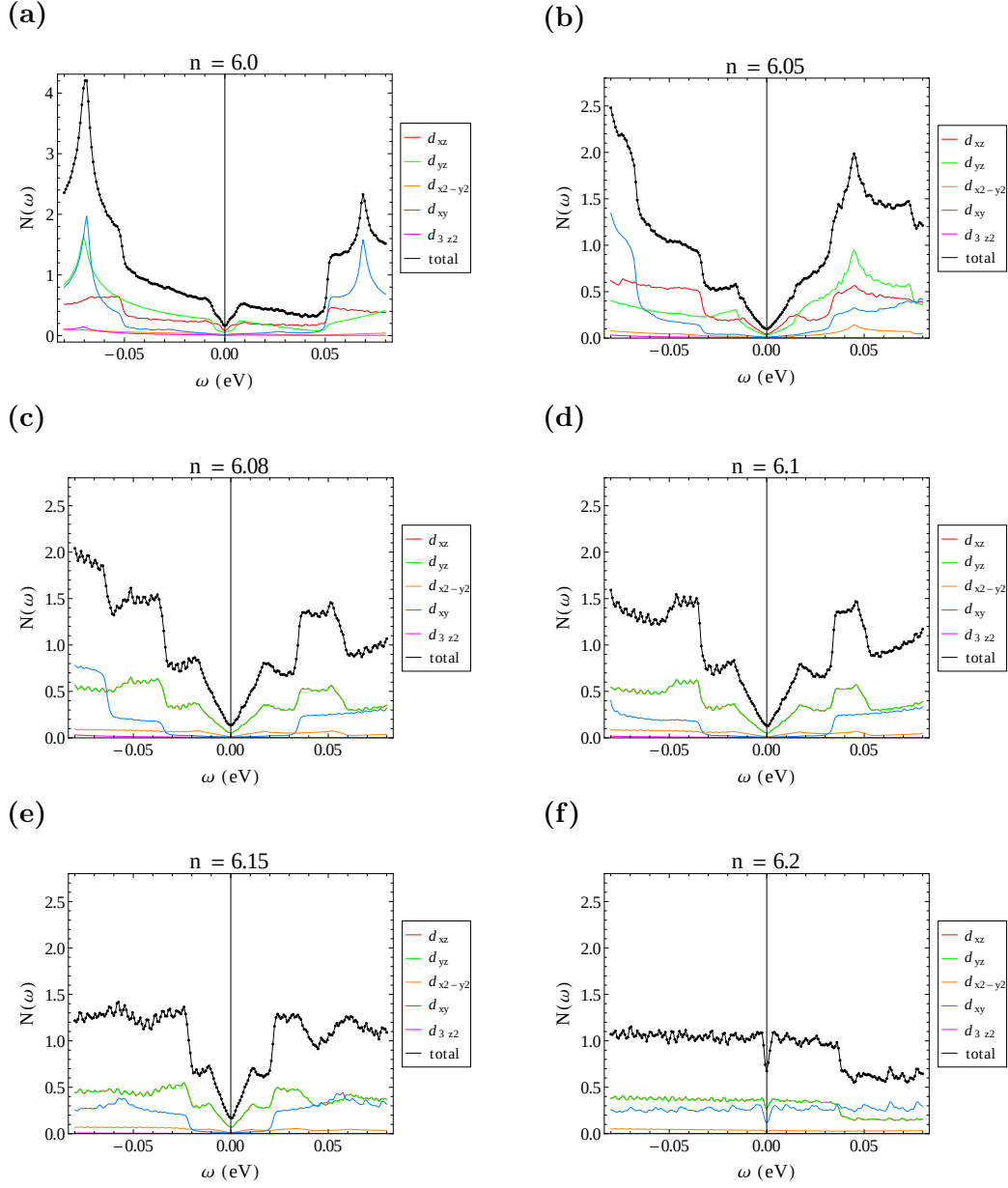


Figure 5.12: *DOS vs doping for $\Gamma^{6.15}(r)$* . Same as in figure 5.11. In this case the superconducting state is V-shaped nodal and d-wave symmetric for all the dopings (a)-(f). The gap closes also at $n \sim 6.2$.

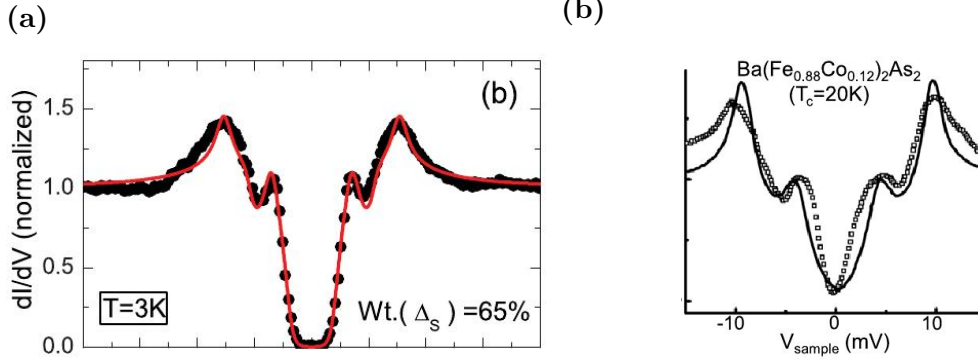


Figure 5.13: STM measurements of different superconducting gaps of a 122 compound. (a) Spectra of a nodeless two-gap ($\Delta_1 \sim 4$ meV and $\Delta_2 \sim 8$ meV) of the hole doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ compound. They needed to include anisotropic factors to fit (red curve) the data (black dots). From [50]. (b) Spectroscopic evidence for two-gap nodal superconductivity in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with an electron doped sample ($x = 0.12$). The black dots are the data and the black line is a fit. From [51].

(low $x < 0.08$) is a full gapped s-wave state. In the high electron doped pairings $\Gamma^{6.15}(r)$, Γ^{NN} are the dominant pairing couplings and Γ^{NNN} are very small and even repulsive for some orbitals. The resulting superconducting state is a nodal d-wave state.

- Role of doping. Even with the hole doped pairings $\Gamma^{5.95}(r)$, which favor an s-wave state, the system changes to the d-wave state at high electron doping. The filling of the band and the corresponding Fermi surface then also affects in choosing the lowest energy state.
- The nodal s-wave state (cf figure 1.7) was not found at any doping for the analyzed two pairing cases. From previous studies [24] and [37], we know it should develop when using the undoped effective pairings $\Gamma^{6.0}(r)$ (cf figure 5.7).

5.4.2 Superconducting gaps in k space

Throughout this work, we have focused on the density of states to get a picture of the superconducting gap (for example in figures 5.11 and 5.12). We take now a different approach in order to find the structure of the gap in momentum space, i.e. we want to know how the gap develops on the different Fermi surface pockets. It is also useful for contrasting our results with other previous five-band theoretical studies, since most of them are in momentum space.

We start from the reduced BCS mean field Hamiltonian in momentum representation,

$$H = \sum_{k\sigma\mu\nu} (\xi_{\mu\nu}(k) \hat{c}_{\mu\sigma}^\dagger(k) \hat{c}_{\nu\sigma}(k) - \mu_0 \delta_{\mu\nu}) + \sum_{k\mu\nu} (\Delta_{\mu\nu}(k) \hat{c}_{\mu\uparrow}^\dagger(k) \hat{c}_{\nu\downarrow}^\dagger(-k) + H.c.), \quad (5.20)$$

where the first term is the kinetic energy term (5.1) and the second term describes the Cooper pairs with the superconducting order parameter

$$\Delta_{\mu\nu}(k) = \sum_{k'} V_{kk'} \langle \hat{c}_{\nu\downarrow}(-k) \hat{c}_{\mu\uparrow}(k) \rangle. \quad (5.21)$$

The Hamiltonian can be rewritten in matrix form as,

$$H = \sum_{k\mu\nu} \begin{pmatrix} \hat{c}_{\mu\uparrow}^\dagger(k) & \hat{c}_{\mu\downarrow}(-k) \end{pmatrix} \begin{pmatrix} \xi_{\mu\nu}(k) - \mu_0 \delta_{\mu\nu} & \Delta_{\mu\nu}(k) \\ \Delta_{\mu\nu}^*(k) & -\xi_{\mu\nu}^*(-k) + \mu_0 \delta_{\mu\nu} \end{pmatrix} \begin{pmatrix} \hat{c}_{\nu\uparrow}(k) \\ \hat{c}_{\nu\downarrow}(-k) \end{pmatrix} \quad (5.22)$$

Note that the orbital degree of freedom makes this expression a 10×10 matrix (in the single-band system is a 2×2 instead). The Bogoliubov unitary transformation equivalent to the one we introduced in chapter 2

$$\begin{pmatrix} \hat{c}_{\mu\uparrow}(k) \\ \hat{c}_{\mu\downarrow}(-k) \end{pmatrix} = \begin{pmatrix} u_\mu^n(k) & -v_\mu^n(k) \\ v_\mu^{n*}(k) & u_\mu^{n*}(k) \end{pmatrix} \begin{pmatrix} \hat{\gamma}_{n\uparrow}(k) \\ \hat{\gamma}_{n\downarrow}(-k) \end{pmatrix} \quad (5.23)$$

is used to bring the Hamiltonian into a diagonal form. Here, n is the diagonal *band* index. In the simplest case, where the superconducting part of the matrix is diagonal and proportional to the identity matrix, $\Delta_{\mu\nu}(k) \equiv \Delta(k)$, one recovers the usual BCS spectrum for each diagonal band n (see Appendix C),

$$E_n(k) = \pm \sqrt{(\xi_n(k) - \mu_0)^2 + |\Delta(k)|^2}. \quad (5.24)$$

For a more general $\Delta_{\mu\nu}(k)$ (for example not proportional to the identity matrix, non-diagonal etc.), we do not recover the simple Bogoliubov spectrum (5.24) in each band, but rather some complicated function of the superconducting $\Delta_{\mu\nu}(k)$. What we do then, is solve this problem numerically, find the energy spectrum $E_n(k)$, and obtain the superconducting gap structure in momentum space from the spectrum. We have not included the Hartree-Fock mean field correlations in this alternative k space approach, so we are restricted to nonmagnetic superconducting states. The two cases we are going to discuss are shown in figure 5.14: a nodeless s -wave and a nodal d -wave multiple-gap states. Their effective pairings are the hole ($n = 5.95$) and electron doped ($n = 6.15$) cases that have been analyzed in the previous section, respectively. Both kind of nodeless and nodal multi-gaps have

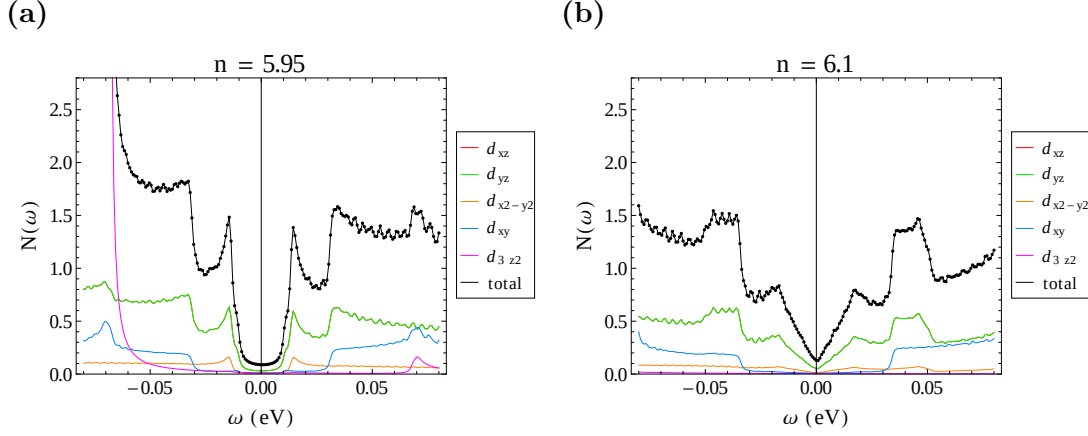


Figure 5.14: Orbitaly resolved and total DOS of the two nonmagnetic superconducting states that we are going to analyze in k space. (a) Hole doped effective pairings $\Gamma^{5.95}(r)$ and $n = 5.95$ filling. The system is kept in a nonmagnetic state by lowering the interacting parameter to $U = 1.0$. It is a fully gapped s-wave superconducting state. (b) Electron doped effective pairings ($\Gamma^{6.15}(r)$). At the $n = 6.1$ doping, the system is in a nonmagnetic state for $U = 1.35$. The superconducting gap is nodal and d-wave symmetric. Note that the two representative cases we have chosen correspond to similar DOS measured by STM for hole and electron doped compounds that were shown in figure 5.13.

been reported in STM experiments that were shown in figure 5.13. So we introduce in (5.22) the gap functions resulting from the nearest neighbor (nn) pairing,

$$\Delta_{k\mu\nu}^{nn} = 2\Delta_{\mu\nu}^{S(nn)}(\cos k_x \pm \cos k_y), \quad (5.25)$$

and the next-nearest neighbors (nnn) pairing,

$$\Delta_{k\mu\nu}^{nnn} = 4\Delta_{\mu\nu}^{S(nnn)} \cos k_x \cos k_y, \quad (5.26)$$

where $\Delta_{\mu\nu}^{S(nn)}$ and $\Delta_{\mu\nu}^{S(nnn)}$ are the superconducting field parameters that have been obtained by self-consistently solving the real space BdG equations (cf equation (5.19)) for each of the cases in figure 5.14. The positive sign in (5.25) stands for an s-wave state, and the minus sign for a d-wave state.

Figure 5.15 shows the resulting energy spectrum and gap structure for the fully gapped s-wave case. Both the hole-like bands around Γ and the electron-like bands around X and Y develop full gaps (figures 5.15(a)-(c)), in agreement with the DOS of this state (cf figure 5.14(a)). The outer hole gap structure is anisotropic with a C_4 symmetry of gap maxima along $k_x = k_y$ and minima at $(0, k_0)$ and $(k_0, 0)$ (or Fe-Fe direction) (see figure 5.15(d)). This kind of anisotropy in the hole pockets

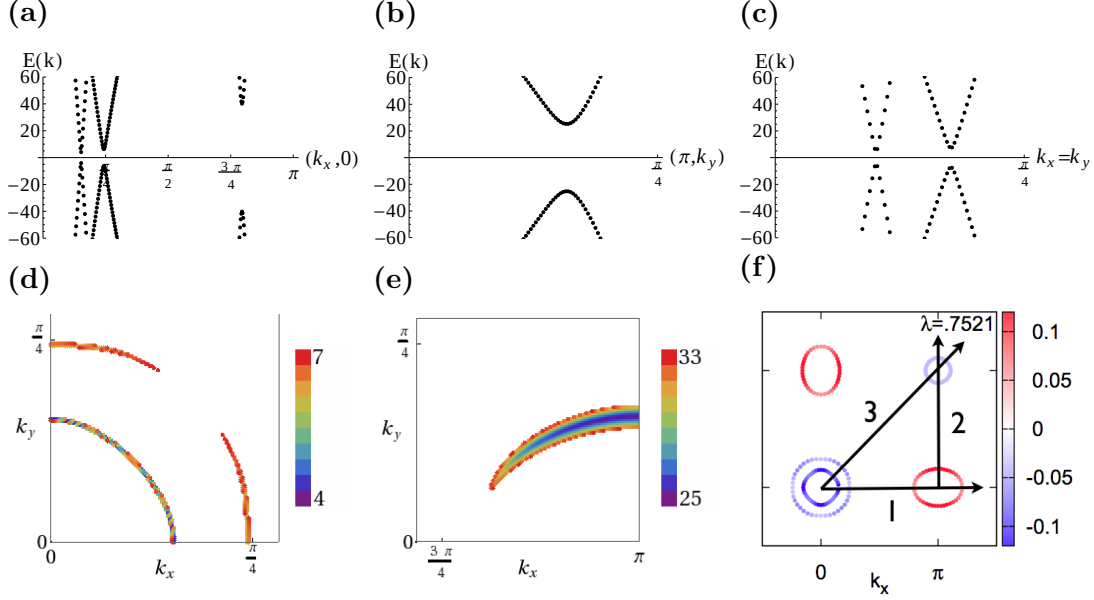


Figure 5.15: Results in momentum space for the fully gapped s-wave nonmagnetic state shown in 5.14 (a). (a)-(c) The energy gap spectrum $E(k)$ in meV along the three symmetry directions Γ -X, X-M and Γ -M shown by arrows 1, 2 and 3 in (f). (a) The hole-like bands around Γ , and an electron-like band at X. The gap opening of the electron pocket is larger than the hole bands gaps. (b) The same electron band with a smaller opening along this direction, reflecting the anisotropy of the gap. Note that the cut is only until $k_y = \pi/4$. (c) The two hole bands again, in the diagonal cut 3. Note that the cut is only until $k_y = \pi/4$. (d) Constant energy cuts of $E(k)$ around Γ from 4 to 7 meV. The anisotropy of the outer hole pocket gap is obvious in this figure, it has a maximum along cut 3 (9 meV) and minimum along cut 1 (6 meV). The inner hole pocket has a very small gap and it is difficult to get any clear conclusion about its structure, which with this resolution (400×400 k points) was nearly isotropic. (e) The same as in (d) but for the electron pocket at X, from 25 to 33 meV. The electron gap is clearly anisotropic, with the minimum along cut 2 (25 meV) and the maximum along cut 1. (f) Momentum dependence of the gaps on the Fermi surfaces of a different study [37] in the hole doped ($n = 5.95$) system. The gap function is a nodeless s-wave.

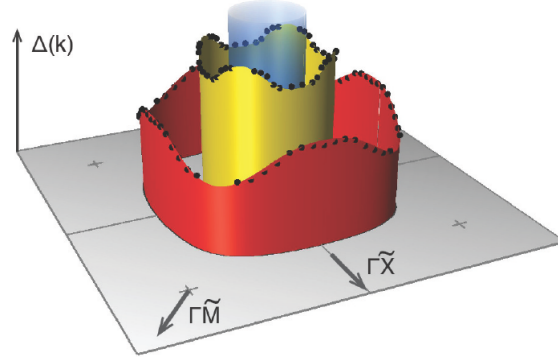


Figure 5.16: A three-dimensional anisotropic energy gap structure on the hole bands measured by quasiparticle interference (QPI) [15]. Each gap function exhibits distinct $\pi/2$ rotational symmetry and a specific relationship of gap minima/maxima relative to the BZ axes. The Γ - $\tilde{M}$ arrow points into the Fe-Fe direction (the $(0, k_y)$ and $(k_x, 0)$ vectors in our system).

has been recently reported by M. P. Allan *et al.* and is shown in figure 5.16.

The second representative case, the electron doped nodal d-wave case, is shown in figure 5.17. The electron-like bands at X and Y develop a large anisotropic full gap (figures 5.17(a)-(b)). The hole-like bands, however, develop much smaller gaps with nodes along the $k_x = k_y$ direction (figure 5.17(c)). This coincides with the nodal lines of the $d_{x^2-y^2}$ state (cf figure 1.8(c)), as expected.

In both cases the gaps are anisotropic in momentum space (respecting the C_4 symmetry of the tetragonal lattice). What is the origin of the anisotropy in our system? To answer this question, we discuss below possible factors that can induce a complex structure of the superconducting gap:

- Proximity of nodal lines. The gap amplitude decreases as it gets closer to a nodal line. This is unlikely in our case, since it can not explain the anisotropy in the hole gaps of the s-wave state (see figure 5.15(d)).
- Momentum dependence of the density of states. If the gap is proportional to the spectral function $A(k, 0)$ at the Fermi energy (as in the single-band BCS gap $\Delta_0 \propto e^{-1/N(E_F)}$), the k structure of this function should be reflected in the gap.
- The asymmetry of the effective pairings is the most plausible explanation. The calculated $\Gamma_{pqst}(q)$ have a momentum dependence in orbital space.

A way to test the last two effects, would be the following. We can remove the anisotropy of the effective pairings by inserting the Δ_k^{nnn} into (5.26) self-consistently obtained from a simple constant $V_{ij}^{\mu\mu} = V$ pairing interaction. The

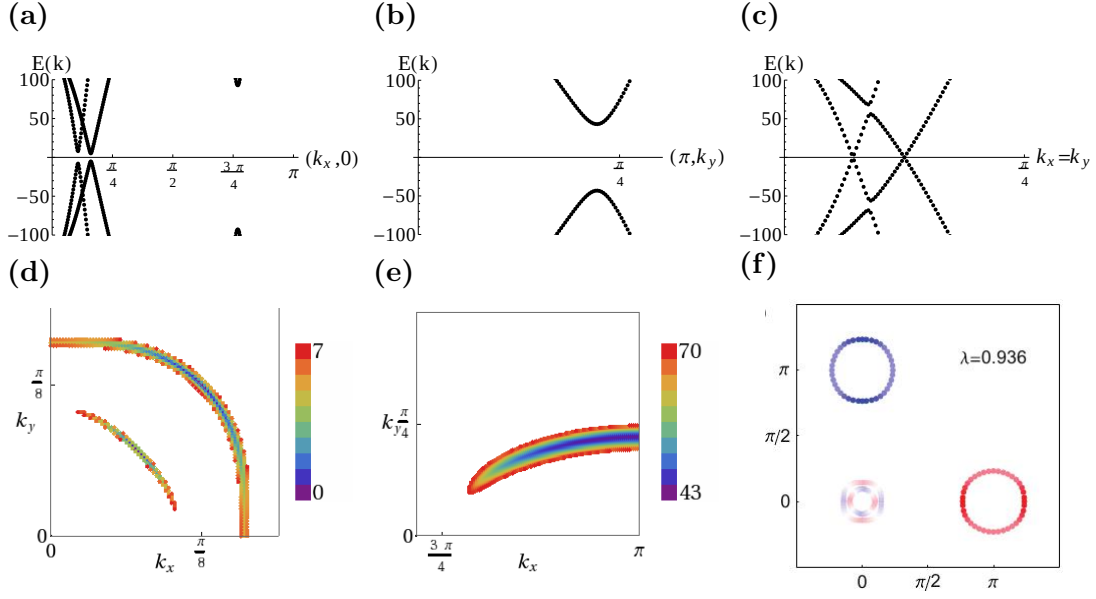


Figure 5.17: Same as in 5.15 for the nodal d-wave nonmagnetic state shown in 5.14 (b). (a) Two hole pockets around Γ and the electron pocket at X . The gap of the electron pocket is around 50meV larger than the hole gaps. (b) The same electron pocket with a smaller opening along this direction, again anisotropic as in the hole-doped case. (c) The nodes of the two hole pockets appear along this ($k_x = k_y$) direction. (d) The hole pockets energy dispersion from 4meV to 7meV. The gap closes at (π,π) in both pockets and peak along cut 1. (e) The electron spectrum from 43 to 70 meV. The gap minimum is again along cut 2 (43 meV) and the maximum along cut 1 (80 meV). (f) Momentum dependence of the gaps on the Fermi surfaces of a different study [24] in a $n = 6.125$ electron doped compound. The gap function is a nodal d-wave.

resulting superconducting OP Δ_μ are different for each orbital, because of the different $N_\mu(E_F)$ of each orbital. If the anisotropy survives, the momentum dependence of the effective pairings would not be necessary for the anisotropic structure. We can further remove the momentum $N(E_F)$ effect to explicitly check the proximity of the nodes effect, by including the simplest superconducting state into (5.22), the same Δ_k in all the orbitals. But in this case we know that the dispersion is the well known Bogoliubov spectrum (5.24). And again, the $\cos k$ functions in (5.25) and (5.26) cannot induce the observed anisotropy in the hole pockets.

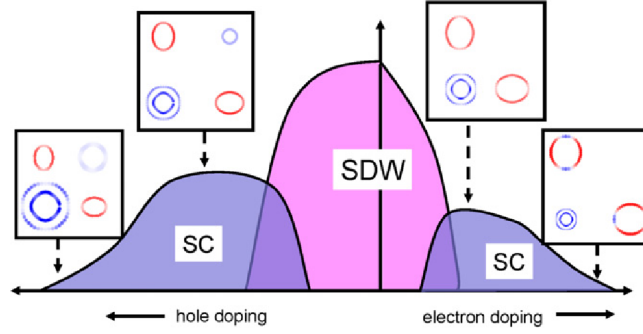
We close this section by comparing the presented results with earlier spin fluctuation calculations. In A.F. Kemper *et al.* [37], it was found that for the $n = 5.95$ compound and similar interaction parameters U and J , the leading instability is in the fully gapped $s_\pm$ state. S. Graser *et al.* [24] performed the same analysis for the $n = 6.125$ electron doped compound, and found that the instability was in the nodal d-wave channel instead. These two gap structures are shown in figures 5.15(f) and 5.17(f) and agree with our results. For most of the $\{U, J\}$ combinations that preserve the spin and orbital rotational invariance (where the relations that we have assumed $U' = U - 2J$ and $J' = J$ hold), the leading pairing instabilities resulting from the spin fluctuation approximation are summarized below:

- Low hole doping: anisotropic but nodeless s-wave solution (see figure 5.15(f)).
- Low electron doping: anisotropic nodal s-wave solution (see figure 5.18).
- High hole and electron doping: a d-wave solution overtakes the anisotropic s-wave (see figure 5.17(f)).

These results are consistent with the change of the superconducting state in our system from s- to d-wave at high electron dopings with $\Gamma^{5.95}(r)$ (see figures 5.11(c)-(d)). The two leading channels, with s-wave and d-wave symmetries, appear in the spin fluctuation studies however, nearly degenerate. One can in fact find a tuning of the U and J values, and preserve an s-wave solution for all the fillings. A nice analysis of the parameter-sensitive properties of the resulting gap symmetry and structure can be found in [52]. Figure 5.18(a) shows a schematic phase diagram of the FeSC versus doping, with the superconducting gap function expected from the spin fluctuation theory for specific interacting parameters. The symmetry of the superconducting gap is s-wave, and its structure changes for different fillings. The gap structure is closely related to the details of the Fermi surface and the band structure, and evolves across the phase diagram from hole to electron doped systems. This fact opens the possibility that different members of the FeSC may have different gap symmetries and/or structures.

In fact, as was mentioned in chapter 1, experimental studies show a wide diversity of behaviors, some consistent with fully gapped states, and others with

(a)



(b)

Family	Full gap	Highly anisotropic	Strong nodal
1111	PrFeAsO _{1-y} [52K] [290] SmFeAs(O, F) [55K] [211]	LaFeAs(O, F) [26K] [212] NdFeAs(O, F) [212]	LaFePO [6K] [201, 202, 291]
122	(Ba, K)Fe ₂ As ₂ [40K] [144, 234, 240, 292] Ba(Fe, Co) ₂ As ₂ [OP, 23K] [236, 206]	Ba(Fe, Co) ₂ As ₂ [OD] [236, 239]* Ba(Fe, Ni) ₂ As ₂ [293]* Ba(Fe, Co) ₂ As ₂ [UD] [239]*	KFe ₂ As ₂ [4K] [209, 304] BaFe ₂ (As, P) ₂ [OP, 31K] [203, 147] (Ba, K)Fe ₂ As ₂ [UD] [240]
111	LiFeAs [18K] [294, 256]		LiFeP [6K] [295]
11		Fe(Se, Te) [27K] [229, 244]	

Figure 5.18: (a) Schematic phase diagram of the FeSC, with the gap structure expected from the spin fluctuation theory. [red= +, blue= -] (b) Table of the four FeSC subfamilies 1111, 122, 111 and 11, grouped into three gap structure categories (nodeless, anisotropic and nodal), from bulk measurements. Both figures were taken from [4].

evidence of nodal gaps. This non-universality is shown in figure 5.18(b), where the gap structure is deduced from experimental results for each FeSC subfamily (1111, 122, 111 and 11). Most of the subfamilies have compounds in the three different structures, i.e. the fully gapped, anisotropic and nodal gaps, for different fillings. This evolution of the gap can be explained by the spin fluctuation approximation, as was pointed out in figure 5.18(a).

5.4.3 Sensitivity to details of band structure

In chapter 3 we observed a noncompeting effect of superconductivity and magnetism in some of the orbitals, specially in orbital d_{xy} . Looking carefully at this orbital contribution to the DOS, an increasing step-like feature around the Fermi level was found (cf figure 3.1 at $\omega = 0$). We study in this section how this details in the band structure affect our results. We remove the two steps around the Fermi level (d_{xy} blue curve and $d_{3z^2-r^2}$ pink curve in figure 3.1) by slightly shifting the onsite energies and checking that the Fermi surface is not changed. Once we have

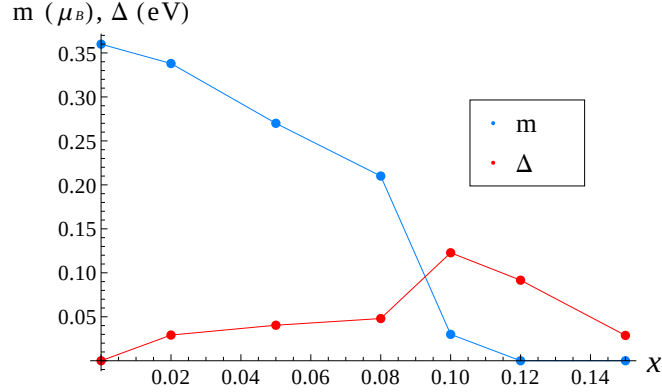


Figure 5.19: Phase diagram for the *modified band* of the magnetic and superconducting order parameters versus doping. The pairing couplings $V_{ij}^{\mu\nu}$ are calculated within the spin and charge fluctuation mechanism in the nonmagnetic $n = 6.15$ state and included until next-nearest neighbors.

the new band without steps in the DOS around the Fermi level, we calculate the couplings for the $n = 6.15$ nonmagnetic electron doped case (very similar to figure 5.9) and repeat the BdG analysis for different dopings. Figure 5.19 shows the resulting phase diagram for $U = 1.34$ and $J = U/4$. The magnetic order parameter varies with doping in the same way as in the old band. The maximum magnetic momentum for the stripe-like order is $m \sim 0.36 \mu_B$ in the undoped system and vanishes at around $n = 6.11$. The representative superconducting order parameter vanishes at zero doping. There is now a clear competing effect between superconductivity and magnetism, especially obvious in the sudden decrease of magnetism from $n = 6.08$ to $n = 6.1$ and the corresponding increase in the superconducting OP.

The evolution of the superconducting gap for different dopings is shown in figure 5.20. The results are very similar to the DOS calculated for the original band (cd figure 5.12), but the gap closes now at zero doping.

We conclude that details in the band structure matter, at least to some extent. Since the resulting self-consistent fields depend on the filling of the band, and by extension on the structure of the density of states, they are influenced by the details of the band.

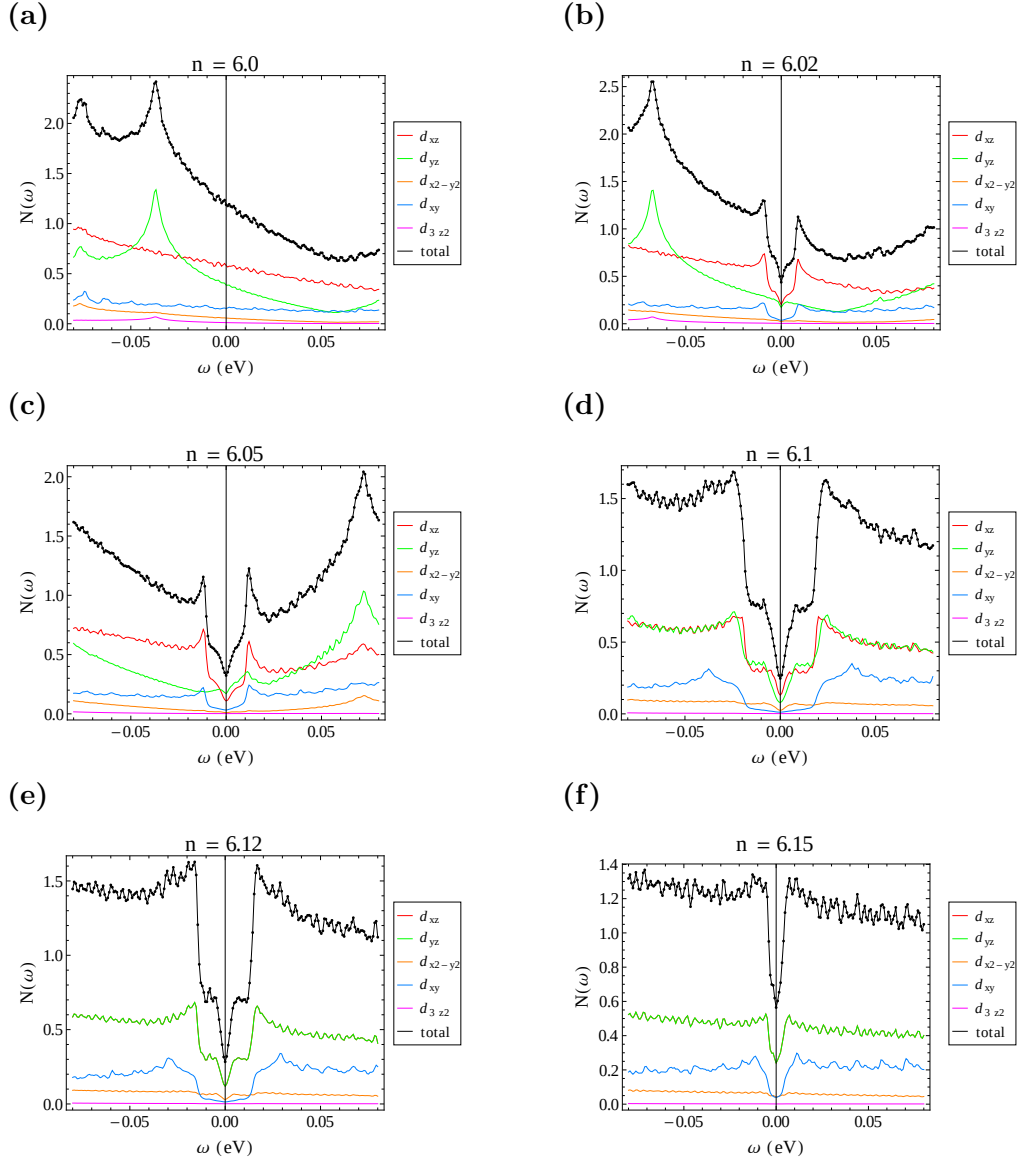


Figure 5.20: *Modified band*. Same as in figure 5.11 and 5.12. (a) The undoped compound has only magnetic features: orbital d_{yz} (green curve) has develop a SDW gap, and only the left magnetic coherence peak is visible in this energy range (see again figure 3.6 (b)). (b) The system evolves into a nodal d-wave superconducting state. The magnetic orbital d_{yz} has the smallest gap, reflecting the competing effect with magnetism and superconductivity. (c)-(d) The two-gap region grows and is biggest when magnetization has almost vanished. (e)-(f) The superconducting coherence peaks start getting closing, until the gap closes at $n \gtrsim 6.15$.

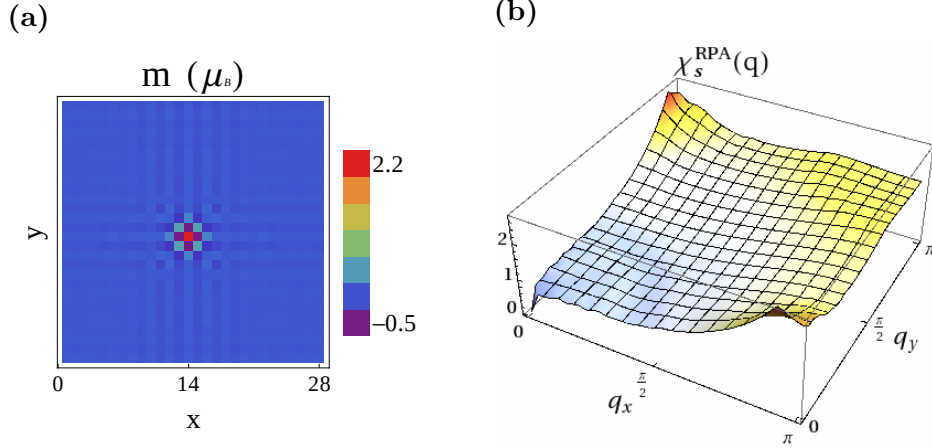


Figure 5.21: (a) Induced local (π, π) magnetic ordering around a nonmagnetic repulsive impurity $V_{imp} = 1$ for the hole doped $n = 5.95$ system with $\Gamma^{5.95}(r)$ effective couplings. (b) Real part of the RPA spin susceptibility $\chi_s^{RPA}(q)$ of the $n = 5.95$ hole doped system for $U = 1.2$ and $J = U/4$.

5.5 Single-impurity problem

After studying the homogeneous system, we want to analyze how the single-impurity effects change with the new effective couplings $\Gamma^{6+x}(r)$. We will again stick to two effective couplings: the hole doped pairings $\Gamma^{5.95}(r)$ in the fully gapped s-wave state, and the electron doped pairings $\Gamma^{6.15}(r)$ in the nodal d-wave state. In order to contrast with the results of chapter 4, we choose the system to be in a nonmagnetic state, but close to a SDW.

So we take the two homogeneous nonmagnetic cases we discussed in section 5.4.2 (cf figure 5.14), place a single nonmagnetic impurity in the middle of the lattice, and ask: what has changed with the new effective couplings?

5.5.1 Mean fields

For both cases, we get again the same induced local orbital ordering (cf figure 4.1) and the same local magnetization with the (π, π) order (see figure 5.21(a)). In the hole doped case, the dominant peaks are clearly the stripe-like ordering vector $(\pi, 0)$ as can be seen in figure 5.21(b). The impurity is then locally inducing large changes in the structure of the bare spin susceptibility. $V_{imp} = 1$ is a rather strong impurity indeed, comparable to the interacting parameters $U = 1.35$ and $J = 0.33$ (the smallest energy scale of our system). The density at the impurity site is $n_{i^*} = 4.5$ far from the homogeneous $n_{i^*} = 5.95$. Now, one should remember from figure 5.3, that electron doping the system $x = 0.15$ resulted in a

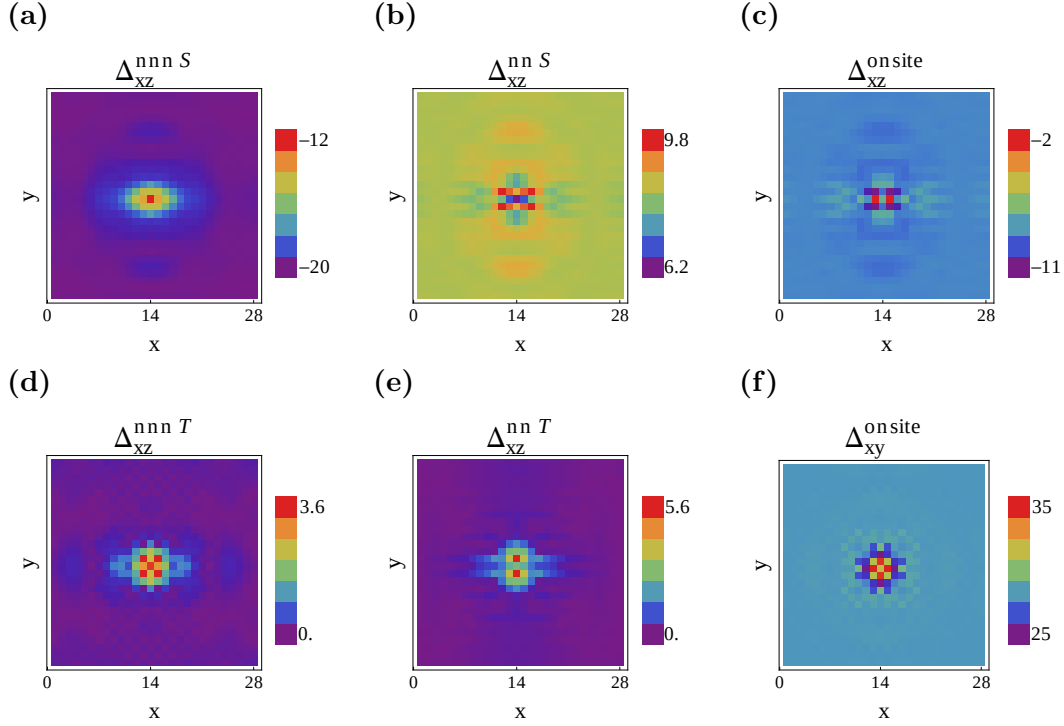


Figure 5.22: Superconducting order parameters for the normal-band at $n = 5.95$ filling, the hole doped effective pairings $\Gamma^{5.95}(r)$ and $V_{imp} = 1$. The system is in a nonmagnetic ($U = 1.2$) state with a nodeless s-wave symmetric gap. (a) and (d) are the singlet and triplet components of the d_{xz} orbital between the next-nearest neighbor sites. (b) and (e) the same but between the nearest neighbors. (c) and (f) are the onsite superconducting order parameters for the d_{xz} and d_{xy} , respectively.

change of scenario, where the (π, π) plateau responsible for the checkerboard magnetic ordering is more prominent than the $(\pi, 0)$ stripe-like SDW peak, dominant in the undoped compound. Our impurity heavily hole dopes the system locally ($x_{i^*} \sim -1.5$), making possible to have completely different local structure of the bare susceptibility, with a (π, π) enhanced structure instead. How could we change the situation? Linear response theory should be recovered for weak enough impurities (compared to the interacting parameters U and J). We expect for these weak impurities to change just slightly the bare susceptibility. The induced local magnetic order would then correspond to the most prominent peak in the homogeneous spin susceptibility, i.e. a $(\pi, 0)$ in the hole doped or small electron doped system.

We move on now to the superconducting mean fields, where some changes can be found, as perhaps, expected. First of all, there are now three types of

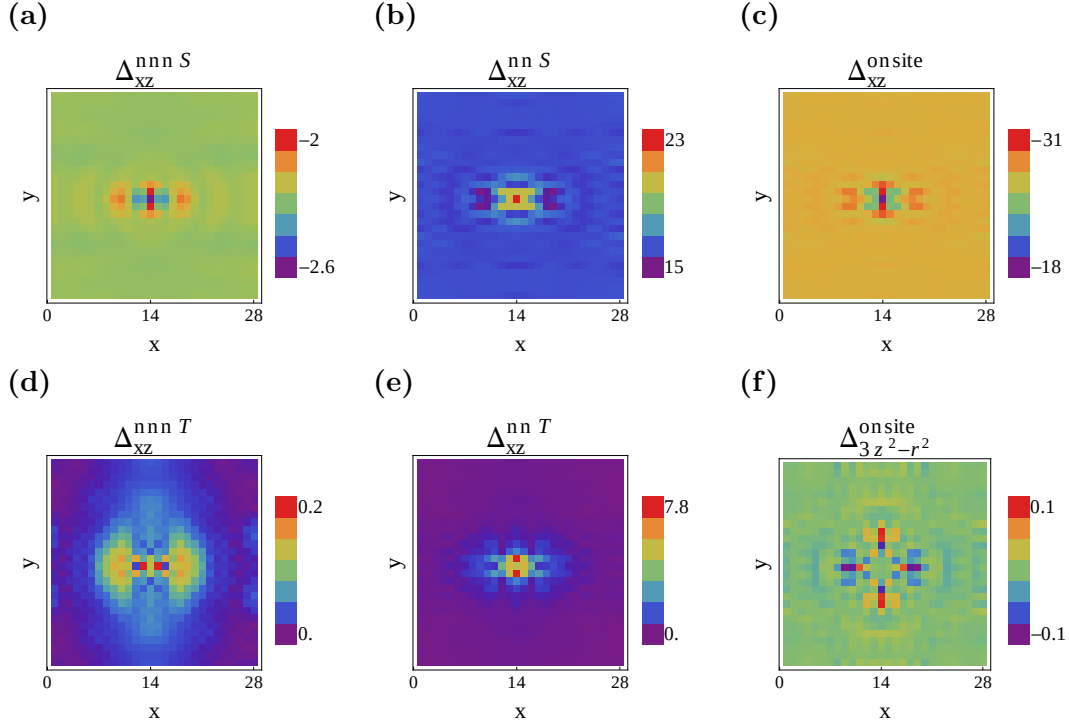


Figure 5.23: Superconducting order parameters for the new-band and electron doped effective pairings ($\Gamma^{6.15}(r)$). The system is in a nonmagnetic ($n = 6.1$) state with a nodal d-wave symmetric gap. Figures (a)-(e) are the same as in 5.22 and (f) is the onsite field for the $d_{3z^2-r^2}$ orbital.

superconducting order parameters: the onsite $\Delta_{\mu\nu}^{onsite}$, the nearest neighbors $\Delta_{\mu\nu}^{nn}$ and the next-nearest neighbors $\Delta_{\mu\nu}^{nnn}$. Figure 5.22 shows some examples of the three types of intra-orbital fields, in (a)-(e) the ones of orbital d_{xz} , and in (f) of orbital d_{xy} . The order parameters respect the symmetry of the orbital, as they did in chapter 4. But now there is also a sign change between the nearest and next-nearest neighbors order parameters as can be seen from figures 5.22(a) and (b). This sign change develops between different orbitals too and does not depend on our initial guess.

The surprising results are the onsite superconducting fields in figures 5.22(c) and (f). The onsite effective couplings calculated within the spin fluctuation approximation $\Gamma(r = 0)$ are repulsive and of the order of electron volts. One would then expect small expectation values of the onsite electron pairing; their values are, however, comparable to the rest of the non-onsite expectation values. We checked that this effect vanished if the nearest and next-nearest couplings were assumed to be repulsive too. It is then induced by the effective attractive interaction in the

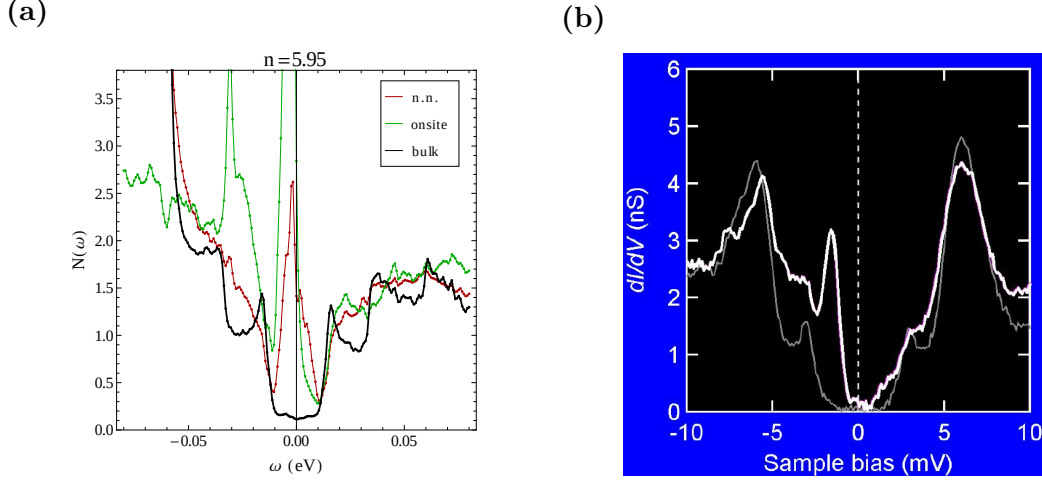


Figure 5.24: (a) LDOS of the hole doped s-wave case for $U = 1.2$ and $V_{imp} = 1$. There is induced magnetization around the impurity. Local in-gap bound states are generated at the nearest neighbor and impurity site. (b) STM measurements on LiFeAs in the bulk (line) and close to an impurity (thick white line). From [53].

surrounding sites, and is once again a consequence of the multi-band coupled gap equations. This large onsite fields effect was also reported in a previous five-orbital model [45].

The superconducting fields of the d-wave case are shown in figure 5.23. The sign changes between different fields are again present (compare subfigures (a) and (b)). For this pairing, the onsite fields are also large and reflect the d-wave symmetry of the superconducting gap, i.e. there is a sign change under a $\pi/2$ rotation, as can be seen in figure 5.23(f).

5.5.2 Local density of states

We finish the impurity-problem analysis by presenting local density of states results for the s-wave superconducting state. Figure 5.24(a) shows the calculated LDOS in the fully gapped s-wave case with induced local magnetization around the impurity (see figure 5.21(a)). Local in-gap bound states are generated at the nearest neighbor and impurity sites (red and green curves). In subfigure (b), STM measurements on the LiFeAs compound [53] are shown for comparison with our model's results. This material has a nodeless two-gap structure in the homogeneous state (white thin curve) with coherence peaks located at around ± 3 meV and ± 7 meV. The thick white line is a scan close to an impurity in the system. The in-gap bound state appears at negative energies and close to the smaller gap edge. Our model is then able to reproduce similar features of STM measurements.

Of course the present study is set up for a 1111-type band structure, whereas the 111-type materials (the STM measurements are done on LiFeAs) are known for having an extra large hole pocket centered at (π, π) . Recently, we have extended the present study to a band structure realistic for 111, and found that indeed the RPA couplings tend to naturally generate a fully gapped $s_{\pm}$ state. It will be very interesting to extend the impurity study to this new band and compare the final LDOS directly with the growing number of STM experiments on the high-quality surfaces of 111 materials.

5.6 Conclusion

In this last chapter, we have tried to improve our model, assuming that superconductivity is driven by the spin fluctuation mechanism, and calculating the effective pairings.

First, we have analyzed the RPA spin and charge susceptibilities in momentum space. For the undoped compound, a peak at $(\pi, 0)$ dominates the real part of the spin susceptibility, consistent with the stripe-like magnetic order. Electron doping the system deteriorates the nesting and the enhanced structure of the spin response function is changed; the $(\pi, 0)$ peak is suppressed and the main structure appears around (π, π) instead.

With the RPA susceptibilities, we can calculate the effective electron-electron superconducting pairings within the spin fluctuation approach. For all the dopings we tried, the dominant attractive coupling is between nearest neighbor sites. When the system is electron doped, the next-nearest neighbor couplings are suppressed, even becoming repulsive, while the nearest neighbors remain attractive. The onsite couplings are large and repulsive.

We use the effective pairings from the lowest and highest dopings, $\Gamma^{5.95}(r)$ and $\Gamma^{6.15}(r)$, and repeat the analysis of the homogeneous system. At low hole- and electron- dopings, a nodeless two-gap s-wave state is found for $\Gamma^{5.95}(r)$. At high electron dopings, a nodal two-gap d-wave state is found in both cases. Multi-gap structures have been reported by STM measurements. The gap structure is studied in momentum space for the two different superconducting states (nodeless s-wave and nodal d-wave) in the nonmagnetic phase. The gaps are anisotropic in both cases. The hole-like gaps present a specific C_4 symmetric anisotropy that was reported in a QPI experiment. Our results are also consistent with previous spin fluctuation studies, which find a evolution of the gap from nodeless, anisotropic and finally nodal structure, against doping. This agrees with the non-universality reported by the experiments.

Details of the band structure were found to influence in the final mean fields through the DOS. With small changes in the original band, a correct phase diagram

of the order parameters versus doping was reproduced.

Finally, we revisit the single-impurity problem for both superconducting gap states. The induced local orbital ordering and checkerboard magnetization are found again. The onsite superconducting fields are not small, despite the large repulsion of the effective couplings. We conclude this is a consequence of the coupled multi-gap equations. Realistic LDOS with local in-gap bound states are obtained by our model, which can be directly compared to recent STM measurements on impurities.

Chapter 6

Conclusions

In this thesis we have built a real space microscopic five-orbital Hubbard model relevant to the Fe-based superconductors. The interactions include the intra- and inter- Coulomb repulsion and the Hund's coupling, and are considered at the mean field level. Superconductivity is included in two ways: originally by a phenomenological BCS term, and in the last chapter, by the effective interaction driven by the exchange of spin fluctuations.

In the homogeneous system, we obtain a SDW stripe-like antiferromagnetic order for the parent compound. This order of spins leads to a reconstructed Fermi surface with orbital order, and a particle-hole asymmetric SDW gap around the Fermi level. A reasonable phase diagram was reproduced by setting the pairing couplings by hand. It can be divided into three zones: the magnetic, the coexistence, and the superconducting zones.

Local properties of the single-impurity problem for the superconducting phenomenological $s_{\pm}$ state are subsequently studied. We find orbital ordering around attractive and repulsive impurities, due to an effective hopping asymmetry of the ordered orbitals. Repulsive impurities are pair-breaking and develop local in-gap bound states. As a consequence, a checkerboard-type of antiferromagnetism is induced around the potential. Attractive impurities on the contrary, are non-pair-breaking, have an almost uniform clean gap, and do not induce local magnetization. The role of correlations in the impurity bound states is also analyzed. In the presence of weak correlations these states are generally pushed to the edges of the gap, whereas for larger correlations the onsite impurity potential induces a magnetic region which reintroduces the low-energy bound states into the gap.

Finally, we try to improve the model by calculating the effective pairings by the spin fluctuation approach. For all the dopings we tried, the dominant attractive coupling is between nearest neighbors sites, followed by next-nearest neighbors couplings. The onsite couplings are large and repulsive. We use those effective pairings to repeat the analysis of the homogeneous system and the single-impurity

problem. For the clean system, anisotropic fully gapped s-wave and nodal d-wave superconducting states were found for different sets of effective couplings. In the impurity study, huge onsite superconducting fields were found, probably as a consequence of the multi-band physics. We obtain realistic local density of states with impurity in-gap bound states that can be directly compared to recent STM measurements.

Recently, we have extended our study to a 111 band structure and found that the effective couplings naturally generate a nodeless two-gap superconducting state. It would be very interesting to extend the impurity study to this new band, and compare it to the growing number of STM experiments on the high-quality surfaces of 111 materials. Another interesting project would be to study impurity effects in the magnetic state, where experimentally nematic electronic structures have been reported [54].

Appendix A

Mean Field Treatment

We make use of the mean field theory to make our Hamiltonian quadratic in the electron operators. The interaction term,

$$H_{int} = U \sum_{i\mu} \hat{n}_{i\mu\uparrow} \hat{n}_{i\mu\downarrow} + U' \sum_{i,\mu<\nu,\sigma} \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\bar{\sigma}} + (U' - J) \sum_{i,\mu<\nu,\sigma} \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma} \\ + J \sum_{i,\mu<\nu,\sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\nu\bar{\sigma}}^\dagger \hat{c}_{i\mu\bar{\sigma}} \hat{c}_{i\nu\sigma} + J' \sum_{i,\mu<\nu,\sigma} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}}^\dagger \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\nu\sigma}.$$

is mean field decoupled in the “density” and “Cooper” channels, i.e., we keep terms like $\langle \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma} \rangle$ and $\langle \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\mu\sigma} \rangle$ and throw away the quadratic terms in fluctuations. The H_{int} term becomes,

$$H_{int}^{MF} = \sum_{i,\mu \neq \nu,\sigma} [U \langle \hat{n}_{i\mu\bar{\sigma}} \rangle + U' \langle \hat{n}_{i\nu\bar{\sigma}} \rangle + (U' - J) \langle \hat{n}_{i\nu\sigma} \rangle] \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma} \quad (A.1) \\ + \sum_{i,\mu \neq \nu,\sigma} [(\frac{1}{2} U \langle \hat{c}_{i\mu\bar{\sigma}} \hat{c}_{i\mu\sigma} \rangle + J' \langle \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\nu\sigma} \rangle) \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\bar{\sigma}}^\dagger + h.c.] \\ + \sum_{i,\mu \neq \nu,\sigma} [(U' \langle \hat{c}_{i\nu\bar{\sigma}} \hat{c}_{i\mu\sigma} \rangle + J \langle \hat{c}_{i\mu\bar{\sigma}} \hat{c}_{i\nu\sigma} \rangle) \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\nu\bar{\sigma}}^\dagger + h.c.].$$

We do the same for the BCS term,

$$H_{BCS} = -V_{ij} \sum_{i \neq j, \mu\nu} \hat{n}_{i\mu\uparrow} \hat{n}_{j\nu\downarrow}.$$

Decoupling it in the “Cooper” channel, by allowing for both intra- and inter-orbital pairing, we arrive to

$$H_{BCS}^{MF} = -\frac{1}{2} \sum_{i \neq j, \mu\nu, \sigma} [\langle \hat{c}_{j\nu\bar{\sigma}} \hat{c}_{i\mu\sigma} \rangle \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\bar{\sigma}}^\dagger + H.c.]. \quad (A.2)$$

Appendix B

Bogoliubov de-Gennes equations

The first step in the diagonalization process is to compute the commutators $[H^{MF}, \hat{c}_{i\mu\sigma}]$. We will do this in two differing ways. In the first way, we split the mean field Hamiltonian up and find the commutator of each piece. The kinetic energy term,

$$\begin{aligned} [H_0, \hat{c}_{i\mu\sigma}] &= \sum_{klab\sigma'} t_{kl}^{ab} [\hat{c}_{ka\sigma'}^\dagger, \hat{c}_{lb\sigma'}, \hat{c}_{i\mu\sigma}] \\ &= - \sum_{klab\sigma'} t_{kl}^{ab} \{\hat{c}_{ka\sigma'}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{lb\sigma'} \\ &= - \sum_{j\nu} t_{ij}^{\mu\nu} \hat{c}_{j\nu\sigma}. \end{aligned} \quad (\text{B.1})$$

The Hartree-Fock part of the interacting term,

$$\begin{aligned} [H_{int-HF}^{MF}, \hat{c}_{i\mu\sigma}] &= \sum_{ka \neq b\sigma'} (U n_{ka\bar{\sigma}} + U' n_{kb\bar{\sigma}} + (U' - J) n_{kb\sigma}) [\hat{c}_{ka\sigma'}^\dagger, \hat{c}_{ka\sigma'}, \hat{c}_{i\mu\sigma}] \\ &= - \sum_{ka \neq b\sigma'} (U n_{ka\bar{\sigma}} + U' n_{kb\bar{\sigma}} + (U' - J) n_{kb\sigma}) \{\hat{c}_{ka\sigma'}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{ka\sigma'} \\ &= - \sum_{\mu \neq \nu} (U n_{i\mu\bar{\sigma}} + U' n_{i\nu\bar{\sigma}} + (U' - J) n_{i\nu\sigma}) \hat{c}_{j\nu\sigma}. \end{aligned} \quad (\text{B.2})$$

The onsite intra-orbital superconducting part of the interacting term,

$$\begin{aligned} [H_{int-intraSC}^{MF}, \hat{c}_{i\mu\sigma}] &= 2 \sum_{ka \neq b} \left(\frac{1}{2} \Delta_k^{a(U)} + \Delta_k^{b(J')} \right) [\hat{c}_{ka\uparrow}^\dagger, \hat{c}_{ka\downarrow}^\dagger, \hat{c}_{i\mu\sigma}] \\ &= 2 \sum_{ka \neq b} \left(\frac{1}{2} \Delta_k^{a(U)} + \Delta_k^{b(J')} \right) (\{\hat{c}_{ka\downarrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{ka\uparrow}^\dagger - \{\hat{c}_{ka\uparrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{ka\downarrow}^\dagger) \\ &= 2 \sum_{\mu \neq \nu} \left(\frac{1}{2} \Delta_i^{\mu(U)} + \Delta_i^{\nu(J')} \right) (\hat{c}_{i\mu\uparrow}^\dagger \delta_{\sigma\downarrow} - \hat{c}_{i\mu\downarrow}^\dagger \delta_{\sigma\uparrow}). \end{aligned} \quad (\text{B.3})$$

The inter-orbital superconducting part,

$$\begin{aligned}
[H_{int-interSC}^{MF}, \hat{c}_{i\mu\sigma}] &= 2 \sum_{ka \neq b} (\Delta_k^{ab(U')} + \Delta_k^{ba(J)}) [\hat{c}_{ka\uparrow}^\dagger \hat{c}_{kb\downarrow}^\dagger, \hat{c}_{i\mu\sigma}] \\
&= 2 \sum_{ka \neq b} (\Delta_k^{ab(U')} + \Delta_k^{ba(J)}) (\{\hat{c}_{kb\downarrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{ka\uparrow}^\dagger - \{\hat{c}_{ka\uparrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{kb\downarrow}^\dagger) \\
&= 2 \sum_{\mu \neq \nu} [(\Delta_i^{\nu\mu(U')} + \Delta_i^{\mu\nu(J)}) \hat{c}_{i\nu\uparrow}^\dagger \delta_{\sigma\downarrow} - (\Delta_i^{\mu\nu(U')} + \Delta_i^{\nu\mu(J)}) \hat{c}_{i\mu\downarrow}^\dagger \delta_{\sigma\uparrow}].
\end{aligned} \tag{B.4}$$

And the last term in the Hamiltonian, the BCS term,

$$\begin{aligned}
[H_{BCS}^{MF}, \hat{c}_{i\mu\sigma}] &= - \sum_{klab} \Delta_{kl}^{ab(V_{kl})} [\hat{c}_{ka\uparrow}^\dagger \hat{c}_{lb\downarrow}^\dagger, \hat{c}_{i\mu\sigma}] \\
&= - \sum_{klab} \Delta_{kl}^{ab(V_{kl})} (\{\hat{c}_{lb\downarrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{ka\uparrow}^\dagger - \{\hat{c}_{ka\uparrow}^\dagger, \hat{c}_{i\mu\sigma}\} \hat{c}_{lb\downarrow}^\dagger) \\
&= - \sum_{j\nu} [\Delta_{ji}^{\nu\mu(V_{ij})} \hat{c}_{j\nu\uparrow}^\dagger \delta_{\sigma\downarrow} - \Delta_{ij}^{\mu\nu(V_{ij})} \hat{c}_{i\nu\downarrow}^\dagger \delta_{\sigma\uparrow}].
\end{aligned} \tag{B.5}$$

We turn now to the second method, where we use the spin-generalized Bogoliubov transformation and note that

$$\begin{aligned}
[H^{MF}, \hat{\gamma}_{n\sigma}] &= -E_{n\sigma} \hat{\gamma}_{n\sigma}, \\
[H^{MF}, \hat{\gamma}_{n\sigma}^\dagger] &= E_{n\sigma} \hat{\gamma}_{n\sigma}^\dagger.
\end{aligned} \tag{B.6}$$

We get then by the second method:

$$\begin{aligned}
[H^{MF}, \hat{c}_{i\mu\uparrow}] &= \sum_n (-E_{n\uparrow} u_{i\mu\uparrow}^n \hat{\gamma}_{n\uparrow} + E_{n\downarrow} v_{i\mu\uparrow}^{n*} \hat{\gamma}_{n\downarrow}^\dagger), \\
[H^{MF}, \hat{c}_{i\mu\downarrow}] &= \sum_n (E_{n\uparrow} v_{i\mu\downarrow}^{n*} \hat{\gamma}_{n\uparrow}^\dagger - E_{n\downarrow} u_{i\mu\downarrow}^n \hat{\gamma}_{n\downarrow}).
\end{aligned} \tag{B.7}$$

We now have two equivalent ways of expressing the commutators. By equating the coefficients of the $\hat{\gamma}$ operators, we arrive to the Bogoliubov-de Gennes equations:

$$\begin{aligned}
-E_{n\uparrow} u_{i\mu\uparrow} &= - \sum_{j\nu} t_{ij}^{\mu\nu} u_{j\nu\uparrow}^n - \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\downarrow} + U' n_{i\nu\downarrow} + (U' - J) n_{i\nu\uparrow}) u_{i\mu\uparrow}^n \\
&\quad - 2 \sum_{\mu \neq \nu} \left(\frac{1}{2} \Delta_i^{\mu(U)} + \Delta_i^{\nu(J')} \right) v_{i\mu\downarrow}^n - 2 \sum_{\mu \neq \nu} (\Delta_i^{\mu\nu(U')} + \Delta_i^{\nu\mu(J)}) v_{i\nu\downarrow}^n \\
&\quad + \sum_{j\nu} \Delta_{ij}^{\mu\nu} v_{j\nu\downarrow}^n,
\end{aligned} \tag{B.8}$$

$$\begin{aligned}
E_{n\uparrow} v_{i\mu\downarrow}^{n*} = & - \sum_{j\nu} t_{ij}^{\mu\nu} v_{j\nu\downarrow}^{n*} - \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\uparrow} + U' n_{i\nu\uparrow} + (U' - J) n_{i\nu\downarrow}) v_{i\mu\downarrow}^{n*} \quad (\text{B.9}) \\
& + 2 \sum_{\mu \neq \nu} \left(\frac{1}{2} \Delta_i^{\mu(U)} + \Delta_i^{\nu(J')} \right) u_{i\mu\uparrow}^{n*} + 2 \sum_{\mu \neq \nu} (\Delta_i^{\nu\mu(U')} + \Delta_i^{\mu\nu(J)}) u_{i\nu\uparrow}^{n*} \\
& - \sum_{j\nu} \Delta_{ji}^{\nu\mu} u_{j\nu\uparrow}^{n*},
\end{aligned}$$

$$\begin{aligned}
E_{n\downarrow} v_{i\mu\uparrow}^{n*} = & - \sum_{j\nu} t_{ij}^{\mu\nu} v_{j\nu\uparrow}^{n*} - \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\downarrow} + U' n_{i\nu\downarrow} + (U' - J) n_{i\nu\uparrow}) v_{i\mu\uparrow}^{n*} \quad (\text{B.10}) \\
& - 2 \sum_{\mu \neq \nu} \left(\frac{1}{2} \Delta_i^{\mu(U)} + \Delta_i^{\nu(J')} \right) u_{i\mu\downarrow}^{n*} - 2 \sum_{\mu \neq \nu} (\Delta_i^{\mu\nu(U')} + \Delta_i^{\nu\mu(J)}) u_{i\nu\downarrow}^{n*} \\
& + \sum_{j\nu} \Delta_{ij}^{\mu\nu} u_{j\nu\downarrow}^{n*},
\end{aligned}$$

$$\begin{aligned}
-E_{n\downarrow} u_{i\mu\downarrow} = & - \sum_{j\nu} t_{ij}^{\mu\nu} u_{j\nu\downarrow}^n - \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\uparrow} + U' n_{i\nu\uparrow} + (U' - J) n_{i\nu\downarrow}) u_{i\mu\downarrow}^n \quad (\text{B.11}) \\
& + 2 \sum_{\mu \neq \nu} \left(\frac{1}{2} \Delta_i^{\mu(U)} + \Delta_i^{\nu(J')} \right) v_{i\mu\uparrow}^n + 2 \sum_{\mu \neq \nu} (\Delta_i^{\nu\mu(U')} + \Delta_i^{\mu\nu(J)}) v_{i\nu\uparrow}^n \\
& - \sum_{j\nu} \Delta_{ji}^{\nu\mu} v_{j\nu\uparrow}^n,
\end{aligned}$$

Upon a little manipulation we can write these equations in matrix form:

$$\begin{pmatrix} \hat{\xi}_{\uparrow} & \hat{\Delta}_{ij}^{\mu\nu} \\ \hat{\Delta}_{ji}^{\nu\mu*} & -\hat{\xi}_{\downarrow} \end{pmatrix} \begin{pmatrix} u_{\uparrow}^n \\ v_{\downarrow}^n \end{pmatrix} = E_{n\uparrow} \begin{pmatrix} u_{\uparrow}^n \\ v_{\downarrow}^n \end{pmatrix}, \quad (\text{B.12})$$

and

$$\begin{pmatrix} \hat{\xi}_{\downarrow} & -\hat{\Delta}_{ji}^{\nu\mu} \\ -\hat{\Delta}_{ij}^{\mu\nu*} & -\hat{\xi}_{\uparrow} \end{pmatrix} \begin{pmatrix} u_{\downarrow}^n \\ v_{\uparrow}^n \end{pmatrix} = E_{n\downarrow} \begin{pmatrix} u_{\downarrow}^n \\ v_{\uparrow}^n \end{pmatrix}. \quad (\text{B.13})$$

Here the matrix operators are defined as:

$$\begin{aligned}
\hat{\xi}_{\sigma} u_{i\mu} = & \sum_{j\nu} t_{ij}^{\mu\nu} u_{j\nu} + \sum_{\mu \neq \nu} (-\mu_0 + U n_{i\mu\bar{\sigma}} + U' n_{i\nu\bar{\sigma}} + (U' - J) n_{i\nu\sigma} + V_{imp}) u_{i\mu}, \quad (\text{B.14}) \\
\hat{\Delta}_{ij}^{\mu\nu} u_{i\mu} = & \sum_{\mu \neq \nu} (\Delta_i^{\mu(U)} + 2\Delta_i^{\nu(J')}) u_{i\mu} + \sum_{\mu \neq \nu} (2\Delta_i^{\mu\nu(U')} + 2\Delta_i^{\nu\mu(J)}) u_{i\nu} - \sum_{j\nu} \Delta_{ij}^{\mu\nu} u_{j\nu}.
\end{aligned}$$

Since we are concerned only with eigenvectors corresponding to positive eigenvalues and the symmetry

$$\begin{pmatrix} u_{\uparrow}^n \\ v_{\downarrow}^n \\ E_{n\uparrow} \end{pmatrix} \rightarrow \begin{pmatrix} v_{\uparrow}^{n*} \\ u_{\downarrow}^{n*} \\ -E_{n\downarrow} \end{pmatrix} \quad (\text{B.15})$$

holds, we only need to diagonalize a single Hermitian matrix.

$$\begin{pmatrix} \hat{\xi}_{\uparrow} & \hat{\Delta}_{ij} \\ \hat{\Delta}_{ji}^* & -\hat{\xi}_{\downarrow}^* \end{pmatrix} \begin{pmatrix} u^n \\ v^n \end{pmatrix} = E_n \begin{pmatrix} u^n \\ v^n \end{pmatrix}. \quad (\text{B.16})$$

B.1 Self-consistent fields

We can now express the self-consistent parameters of our mean field Hamiltonian in terms of the eigenvectors and eigenvalues:

$$\begin{aligned} n_{i\mu\uparrow} &= \langle \hat{c}_{i\mu\uparrow}^\dagger \hat{c}_{i\mu\uparrow} \rangle = \sum_n |u_{i\mu\uparrow}^n|^2 \langle \hat{\gamma}_{n\uparrow}^\dagger \hat{\gamma}_{n\uparrow} \rangle + \sum_n |v_{i\mu\uparrow}^n|^2 \langle \hat{\gamma}_{n\downarrow} \hat{\gamma}_{n\downarrow}^\dagger \rangle \\ &= \sum_n |u_{i\mu\uparrow}^n|^2 f(E_{n\uparrow}) + \sum_n |v_{i\mu\uparrow}^n|^2 f(-E_{n\downarrow}) \\ &= \sum_{n, E_{n\uparrow} > 0} |u_{i\mu\uparrow}^n|^2 f(E_{n\uparrow}) + \sum_{n, E_{n\uparrow} < 0} |u_{i\mu\uparrow}^n|^2 f(E_{n\uparrow}) \\ &= \sum_l |u_{i\mu\uparrow}^n|^2 f(E_{n\uparrow}) \end{aligned} \quad (\text{B.17})$$

where $\sum_n$ sums only for those n values which have positive (or negative when specified) eigenvalues, $E_{n\sigma}, E_{n\bar{\sigma}} > 0$, and $\sum_l$ sums for *all* states with positive and negative eigenvalues. The symmetry (B.15) has been used. A very similar calculation gives for the spin down density,

$$\begin{aligned} n_{i\mu\downarrow} &= \langle \hat{c}_{i\mu\downarrow}^\dagger \hat{c}_{i\mu\downarrow} \rangle = \sum_n |u_{i\mu\downarrow}^n|^2 \langle \hat{\gamma}_{n\downarrow}^\dagger \hat{\gamma}_{n\downarrow} \rangle + \sum_n |v_{i\mu\downarrow}^n|^2 \langle \hat{\gamma}_{n\uparrow} \hat{\gamma}_{n\uparrow}^\dagger \rangle \\ &= \sum_n |u_{i\mu\downarrow}^n|^2 f(E_{n\downarrow}) + \sum_n |v_{i\mu\downarrow}^n|^2 f(-E_{n\uparrow}) \\ &= \sum_{n, E_{n\uparrow} < 0} |v_{i\mu\downarrow}^n|^2 f(-E_{n\uparrow}) + \sum_{n, E_{n\uparrow} > 0} |v_{i\mu\downarrow}^n|^2 f(-E_{n\uparrow}) \\ &= \sum_l |v_{i\mu\downarrow}^n|^2 (1 - 2f(E_{n\uparrow})) \end{aligned} \quad (\text{B.18})$$

Starting for the most complex superconducting field, we can recover the rest of the onsite fields without repeating the whole calculation:

$$\begin{aligned}
\Delta_{ij}^{\mu\nu} &= V_{ij}^{\mu\nu} \langle \hat{c}_{j\nu\downarrow} \hat{c}_{i\mu\uparrow} \rangle \\
&= V_{ij}^{\mu\nu} \left[\sum_n u_{j\nu\downarrow}^n v_{i\mu\uparrow}^{n*} \langle \hat{\gamma}_{n\downarrow} \hat{\gamma}_{n\downarrow}^\dagger \rangle + \sum_n v_{j\nu\downarrow}^{n*} u_{i\mu\uparrow}^n \langle \hat{\gamma}_{n\uparrow}^\dagger \hat{\gamma}_{n\uparrow} \rangle \right] \\
&= V_{ij}^{\mu\nu} \left[\sum_{n, E_{n\uparrow} < 0} v_{j\nu\downarrow}^{n*} u_{i\mu\uparrow}^n f(E_{n\uparrow}) + \sum_{n, E_{n\uparrow} > 0} v_{j\nu\downarrow}^{n*} u_{i\mu\uparrow}^n f(E_{n\uparrow}) \right] \\
&= V_{ij}^{\mu\nu} \sum_l v_{j\nu\downarrow}^{n*} u_{i\mu\uparrow}^n f(E_{n\uparrow}).
\end{aligned} \tag{B.19}$$

From here, the onsite superconducting fields:

$$\Delta_i^{\mu\nu(X)} = X \langle \hat{c}_{i\nu\downarrow} \hat{c}_{i\mu\uparrow} \rangle = X \sum_l v_{i\nu\downarrow}^{n*} u_{i\mu\uparrow}^n f(E_{n\uparrow}). \tag{B.20}$$

Appendix C

Unitary transformation in k space

Our Hamiltonian can be written in matrix form:

$$H = \sum_{k\mu\nu} A_{k\mu}^\dagger H_{k\mu\nu} A_{k\nu} \quad (\text{C.1})$$

where μ and ν are *orbital* indexes and

$$A_{k\mu} = \begin{pmatrix} \hat{c}_{\mu\uparrow}(k) \\ \hat{c}_{\mu\downarrow}^\dagger(-k) \end{pmatrix}, \quad H_{k\mu\nu} = \begin{pmatrix} H_{0\mu\nu}(k) & \Delta_{\mu\nu}(k) \\ \Delta_{\nu\mu}^*(k) & -H_{0\mu\nu}^*(-k) \end{pmatrix}. \quad (\text{C.2})$$

To bring the Hamiltonian into a diagonal form, we introduce the special unitary transformation that only affects H_0 :

$$B_{k\mu} = \begin{pmatrix} \hat{\gamma}_{n\uparrow}(k) \\ \hat{\gamma}_{n\downarrow}^\dagger(-k) \end{pmatrix} = U_{k\mu}^{-1} A_{k\mu}, \quad U_{k\mu} = \begin{pmatrix} u_\mu^n(k) & 0 \\ 0 & u_\mu^{n*}(k) \end{pmatrix}. \quad (\text{C.3})$$

so that

$$U_{k\mu}^\dagger H_{k\mu\nu} U_{k\nu} = \begin{pmatrix} u_\mu^{n*}(k) & 0 \\ 0 & u_\mu^n(k) \end{pmatrix} \begin{pmatrix} H_0(k) & \Delta(k) \\ \Delta^*(k) & -H_0^*(-k) \end{pmatrix} \begin{pmatrix} u_\nu^n(k) & 0 \\ 0 & u_\nu^{n*}(k) \end{pmatrix} \quad (\text{C.4})$$

$$= \begin{pmatrix} \xi_n(k) - \mu_0 & \Delta(k) \\ \Delta^*(k) & -\xi_n(-k) + \mu_0 \end{pmatrix} \quad (\text{C.5})$$

Here, the diagonal blocks of the matrix are diagonal represented by the new *band* index n . The only way the block matrix $\Delta(k)$ to be diagonal after the unitary transformation, is if it is proportional to the identity matrix, since

$$u_\mu^{n*}(k) \Delta(k) u_\nu^n(k) = \Delta(k) u_\mu^{n*}(k) u_\nu^n(k) = \Delta(k), \quad (\text{C.6})$$

from the definition of the unitary transformation. The eigenvalues of this matrix are the usual Bogoliubov quasiparticle spectrum,

$$E_n(k) = \pm \sqrt{(\xi_n(k) - \mu_0)^2 + |\Delta(k)|^2}. \quad (\text{C.7})$$

Note that a more general expression of the matrix $\Delta(k)$ (diagonal but with different diagonal elements), would result in a non-diagonal $\Delta(k)$ after the unitary transformation. The last step of getting the well known BCS spectrum would require more operations, and result in a complex function of the $\Delta_{\mu\nu}(k)$ elements.

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