k-space Microscopy of Bi2Sr2CaCu2O8+: Fermiology and Many-body Effects
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This chapter consists of two main sections. In the first section, we summarise briefly the phenomena of superconductivity appearing at low and at high temperature. After that, the crystalline structure and the electronic structure of high temperature superconducting cuprates are described. Since one of the cuprate systems, namely Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, becomes the main subject of the investigations presented in this thesis, then one part of this section is going to be dedicated to reviewing of a number of issues related to the aim of our studies.

The second main section describes the experimental technique used in this thesis which is angle resolved photoemission spectroscopy (ARPES). The first part of this section will describe the essence of ARPES which is based on the photoelectric effect and how this simple principle can be used to extract fascinating knowledge and information from complex systems such as superconducting cuprates. The second part of this section will describe the experimental set-up and the last part will devoted to the measurement methods and the details of how to analyse the data obtained using this technique.

2.1. Low temperature superconductors vs. high temperature superconducting cuprates

The term high temperature superconducting cuprates refers to the new class of superconductors first discovered in the La-Ba-Cu-O system by George Bed-
norz and Karl Alex Müller in 1986 [1]. As seen in Fig. 2.1, until 1986, the highest $T_C$ ever observed was 23 K in Nb$_3$Ge. Initially, superconductivity, a novel phenomena in which charge carriers can move freely in the lattice without resistance, was discovered in 1911 by the Dutch physicist Kammerlingh Onnes when he measured the resistivity of mercury at very low temperature (at the temperature scale of liquid helium’s boiling point i.e.: 4.2K) [2, 3].

Superconductivity is characterised by the presence of an energy gap close to the Fermi energy. This parameter describes the energy required to break the Cooper pairs, the bound pairs of charge carriers (electrons). In most low temperature superconductors such as elemental superconductors (Zn, Hg, Pb, etc.) and Nb-based superconductors, the binding of electrons in a Cooper pair is due to an effective attractive electron-electron interaction, mediated by the exchange of virtual phonons [5]. This bound pair has zero net angular momentum and possesses $s$-wave symmetry (see Fig. 2.2(a)). Due to the presence of the energy gap, the density of states of single particle excitations in the superconducting state is modified as can be seen in Fig. 2.2(c). On the contrary, in the high-$T_C$ cuprates the Cooper pairs have non-zero angular momentum and are said to have $d$-wave symmetry. This departure from $s$-wave symmetry was suggested from early ARPES measurements of the superconducting gap around the Fermi
surface [6, 7], and has since been proven by phase sensitive experiments [8–10]. Consequently, the superconducting gap function around the Fermi surface, which is related to the order parameter, follows a cosine function with nodes at $k_x = \pm k_y$ where the value of superconducting gap vanishes (see Fig. 2.2(b)).

Another novel characteristic of superconductivity is the occurrence of the so-called the Meissner-Ochsenfeld effect in which a weak external magnetic field $H$ is expelled by the material when it becomes a superconductor. Furthermore, this effect provides evidence that a superconductor is a perfect diamagnet, in which its magnetic susceptibility, $\chi$, the change of the magnetization with respect to the external magnetic field, has the value of -1. Diamagnets screen out part of the external magnetic field, and so they become magnetised oppositely to the external field.

If $H$ becomes stronger it turns out that the superconductivity is destroyed either in one of two following cases. The first case is that the magnetic field $B$ remains zero inside the superconductor until suddenly the superconductivity is destroyed completely when $H$ reaches the critical value, $H_C$. This case is known as a type I superconductor. In the second case, known as a type II superconductor, there are two different critical fields, denoted $H_{C1}$, the lower critical field, and $H_{C2}$, the upper critical field. For small values of $H$ again the Meissner-Ochsenfeld effect occurs, however, once $H$ exceeds $H_{C1}$, magnetic flux starts to enter the superconductor but the superconductivity is not entirely destroyed and hence $B \neq 0$, and $M$ is closer to zero. Upon increasing the field $H$, the magnetic flux density gradually increases until in the end at $H_{C2}$ the su-

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**Figure 2.2:** The sketch of order parameter symmetry in (a) conventional superconductors, (b) high-$T_C$ cuprates. (c) Density of states of an $s$-wave superconductor in the normal state (black line). Due to the presence of the gap near the Fermi level the density of state in superconducting state, within BCS model, is strongly modified (grey line).
perconductivity is fully destroyed. The behaviour of these type I and type II superconductors are sketched in Fig. 2.3(a).

The critical field, $H_C$, varies as a function of the temperature, and it becomes zero at the critical temperature. Typical phase diagram of type I and type II superconductors as a function of external magnetic field and temperature are sketched in Fig. 2.3(b).

Prior to the discovery of the high temperature superconducting cuprates in 1986, there have been many discoveries of superconductivity in various materials such as “heavy Fermion”-based (CeCu$_2$Si$_2$ was discovered by Frank Steglich’s group in 1979 [11]) and other U-based systems such as UPt$_3$ [12]. Although these compounds exhibit superconductivity at very low temperature (in order of 1 Kelvin), they can be classified as unconventional superconductors since their order parameter, which related to the pairing symmetry of the Copper pairs, is not of simple $s$-wave symmetry but rather has anisotropic $d$-wave symmetry for CeCuSi$_2$ and $p$-wave symmetry for UPt$_3$, although some do argue that $d$-wave terms also appear in the pairing symmetry of UPt$_3$ [13]. In these compounds, superconductivity appears to be often associated with the proximity of magnetic (antiferromagnetic or ferromagnetic) spin fluctuations [13]. Another novel example of this class of materials is UGe$_2$, which exhibits simultaneously
ferromagnetism and superconductivity under pressure, and the newly discovered UCoGe \[14\] in which the system also remains ferromagnetic in the superconducting state under ambient pressure.

The big breakthrough happened in 1986 when a superconductor was discovered in the La-Ba-CuO system with quite a high $T_C$ for that time ($T_C = 25$ K). In this system, the $\text{La}^{3+}$ in the parent compound La$_2$CuO$_4$ which is experimentally determined to be an antiferromagnetic (AF) insulator \[15\], is substituted by $\text{Ba}^{2+}$, $\text{Sr}^{2+}$ or $\text{Ca}^{2+}$ in order to produce metallic behavior and superconductivity. After that, a higher $T_C$ of 93 K was achieved in the YBCO system namely in YBa$_2$Cu$_3$O$_7$ \[16\]. Again, this represented another breakthrough since YBCO’s $T_C$ surpasses the boiling point of liquid nitrogen (\textit{i.e.} 77 K). Further research on new superconducting materials has led to the discovery of the BSCCO (Bi-Sr-Ca-Cu-O) system \[17\], the TBCCO (Tl-Ba-Ca-Cu-O) system \[18\] and the HBCCO (after Hg-Ba-Ca-Cu-O) system \[19\] (for a review see \textit{e.g.} \[4, 6\]). Currently HgBa$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ has the record of the highest value of $T_C$ of 135 K at ambient pressure \[20\].

Unlike the conventional low temperature superconductors (with $s$-wave pairing symmetry) which are already explained fully by BCS (Bardeen, Cooper, Schrieffer) theory developed in 1957 \[5\], the microscopic mechanism behind the high temperature superconducting cuprates is still not fully understood until now and this makes this one of the most challenging subjects in condensed matter physics. There are two main camps considering the pairing mechanism of Cooper pairs in high temperature superconductors: the pairing is phonon mediated or spin fluctuation mediated.

### 2.1.1. The basic crystalline structure of superconducting cuprates

All of the cuprate (copper oxide) superconductors mentioned in section 2.1 possess a common structural unit: the CuO$_2$ plane, and interstitial insulating layers. As one can see from Fig. 2.4(a) to 2.4(i), the insulating layers (\textit{e.g.}: BiO, SrO, BaO, LaO and TIO) form blocks between the CuO$_2$ planes and thus get the name “block layers”. These act as a charge reservoir for the CuO$_2$ planes.

Depending on the geometry of the oxygen ions surrounding the copper sites (whether it is in apical position or in plane), there are three different basic structures within the CuO layer, namely: CuO$_4$ plaquette, CuO$_5$ pyramid and CuO$_6$
Figure 2.4: The sketch of crystal structures of a number of known cuprate families. (a-c) BSCCO system with general formula Bi$_2$Sr$_2$Ca$_{2-n}$Cu$_n$O$_{4+2n}$ with n = 1, 2, 3. (d) LBCO system: (LaBa)$_2$CuO$_4$. (e) YBCO system: YBa$_2$Cu$_3$O$_7$ and (f) TBCCO system: TiBa$_2$Ca$_2$Cu$_3$O$_9$. Schematic pictures of the basic elements in the CuO$_2$ layer of the cuprates. (g) CuO$_4$ plaquette, (h) CuO$_5$ pyramid, and (i) CuO$_6$ octahedron. Adapted from [4].
Figure 2.5: (a). Sketch of a Mott-Hubbard insulator. Due to correlation effects between the electrons, the highest occupied state (d-band) is split into the upper empty band known as the upper Hubbard band and the lower filled band known as the lower Hubbard band. The energy gap is characterised by the on-site Coulomb repulsion $U$. (b) The sketch that represents the super-exchange mechanism described in the text. (c) The long range antiferromagnetic order appearing in undoped cuprates.

octahedron (see Fig. 2.4(g)-2.4(i)), which will determine different properties for each configuration. It is evident that cuprates which have $T_C$ higher than 30 K, consist of at least one CuO$_6$-based or CuO$_5$-based CuO$_2$-layer per structural repeat unit. Among the same family of cuprates, the number of CuO$_2$-layers within a unit cell determines the $T_C$. For example, in the BSCCO system shown in Fig. 2.4(a) - 2.4(c), single layered Bi2201 has $T_C$ of 40 K, double layered has $T_C$ of 95 K while three layered BSCCO has maximum $T_C$ of up to 110 K [21].

2.1.2. The electronic structure of superconducting cuprates

As mentioned in the previous subsection, the CuO$_2$ layers play the dominant role in the determination of the properties for all cuprates since the Cu-O bands are the lowest-energy electronic states and therefore determine the macroscopic electronic properties [6].

In the undoped case, the parent material is an antiferromagnetic insulator [15], with energy gap of 2 eV which contradicts the prediction of band theory since within the one electron picture, the odd number of electrons per Cu site would make this material metallic. This situation was already described earlier by Mott and Hubbard, and later became known as the “Mott-Hubbard insulator” [22, 23]. In this system, the insulating properties occur due to strong correlation effects between the electrons. In the ground state of the undoped system, the Cu site would have a d$^9$ configuration. If one electron hops to a neighbour-
ing site, the site left behind would have a \( \text{d}^8 \) configuration while the site hopped to would have \( \text{d}^{10} \) configuration (see Fig. 2.5(b)). If the Coulomb repulsion between these two electrons (or two holes) is stronger than the kinetic energy \( (t) \) gained from hopping, the electrons would be localised and such hopping processes will be suppressed. This affects the electron removal and electron addition spectral weight for the system, such that the highest band (the conduction band), as seen in Fig 2.5(a), is split into two sub-bands: the occupied, lower band (known as the lower Hubbard band) and the unoccupied, upper band (known as the upper Hubbard band). There is an energy gap between them of size \( U \). With one electron per site, the lower Hubbard band will be filled and the upper Hubbard band will be completely empty, and as a consequence of this the system is an insulator. In such a situation, the spins of these Cu ions will arrange themselves in the form of long range antiferromagnetic order, because the interaction between two spins arising from virtual hopping favors the antiparallel configuration (due to the Pauli exclusion principle see Fig. 2.5(b)). This process is known as the super-exchange interaction with an energy \( J \) which is proportional to \( t^2/U \) [24]. The long range antiferromagnetic ordering gives rise to the well-known Néel lattice with a high \( T_N \) (Néel temperature) of 300 K [13].

However, the situation in cuprates, which belong to the late transition metal oxide group of materials, is complicated due to the fact that the Cu \( 3d_{x^2−y^2} \) and O \( 2p_{x,y} \) states are strongly hybridised. This means that there is an \( 2p \)-dominated valence band between the upper and lower Hubbard bands, making the undoped, parent compound of the high-\( T_C \) superconductors a charge transfer insulator [25], more correctly described in a three band model suggested by Emery [26]. Note that as a result, the energy gap in the cuprates is characterised by the charge transfer energy \( \Delta \) rather than the on-site Coulomb repulsion, \( U \), since the CuO \( \Delta \) is smaller than \( U \), where \( \Delta \) is defined as the energy difference between the Cu \( 3d \) and O \( 2p \) orbitals (see Fig. 2.5(a)). This type of insulator is known as a charge-transfer insulator following the classification scheme of Zaanen, Sawatzky, and Allen [25]. To summarise, the electronic structure of undoped cuprates is that of an antiferromagnetic insulator, whereby the energy gap is between the UHB and the \( O2p \) band with the Fermi energy lying between these two bands.

The electronic structure of undoped cuprates can be changed by substituting atoms within the charge reservoir layer (e.g.: La with Sr) or by changing the
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Figure 2.6: (a) Sketch of a charge-transfer insulator. Due to correlation effects between the electrons, the highest occupied state ($Cu3d$-band) is split into the empty upper Hubbard band (UHB) and the lower, filled lower Hubbard band (LHB). The energy gap is characterised by the charge transfer energy $\Delta$ rather than the on-site Coulomb repulsion $U$. (b) An illustration of how the electronic structure in cuprates is changed upon doping. Upper panel: undoped situation. Middle panel: hole doping ($p$-type). Lower panel: electron doping ($n$-type). Grey shading indicates the occupied states while white area represents the unoccupied states (from [27]).

oxygen content, and in this manner additional charge carriers are doped into the CuO$_2$ layer. There are two types of doping possible: firstly by doping the CuO$_2$ layer with holes and the second with electrons. As can be seen in middle panel of Fig. 2.6(b), upon hole doping the Fermi level ($E_F$) is shifted into the $O2p$-dominated valence band, whereas it would be shifted to the UHB in the electron-doped case (lower panel of Fig. 2.6(b)). Upon both $p$-or $n$-type doping of a suitable degree, a metallic and superconducting state occurs.

Fig. 2.7 shows the widely accepted generic phase diagram of both electron and hole-doped cuprates. An example for the electron-doped system is Nd$_{2-x}$Ce$_x$CuO$_4$ compounds [28]. The $T_C$ of the material is less than that of the analogous hole doped systems.

The LSCO, BSCCO, YBCO, TBCCO and HBCCO systems are the main examples of the hole-doped cuprates. When holes are introduced into the CuO plane by partially replacing a trivalent cation in the crystal structure with a divalent one, or by introduction of excess oxygen atoms, the Néel lattice (long range order of the AFI Cu $d^9$ spins) will be rapidly destroyed because the holes are mobile, and can hop from one Cu site to the next without experiencing the
Figure 2.7: The sketch of generic phase diagram of the electron and hole-doped cuprates. This phase diagram illustrates the rich physical properties exhibited by these materials: including superconductivity (SC), antiferromagnetic insulating (AFI) behaviour, with a normal state or pseudogap, and normal metal. Adapted from [6].

Coulomb interaction. This situation will break the magnetic bond between the Cu spins hence destroying the AFI order.

At the right doping level, a superconducting state emerges at low temperatures from this destroyed AFI state. For example, for the BSCCO system, it becomes superconducting at hole doping level of 5% per Cu atom, reaches a maximum $T_C$ at 16% and loses its superconducting properties at 27% [29]. After that, the material becomes an ordinary metal and can be described as a Fermi liquid.

The region under the superconducting dome in the hole-doped part of the phase diagram where $T_C$ increase with hole concentration is known as the underdoped (UD) region, and the region where $T_C$ decreases upon further hole-doping is known as the overdoped (OD) region. The region at which $T_C$ reaches its maximum value for each particular cuprate system is known as optimal-doping (OPT).

The superconducting region of the phase diagram is characterised by the formation of Cooper pairs from charge carriers and its pairing symmetry is represented by the unconventional $d$-wave pairing symmetry. Apart from the superconductivity itself, one of the main puzzles in the phase diagram in cuprates is the underdoped (or pseudogap) phase. This phase covers the area between 5% and 16% doping level and exhibits interesting phenomena in the sense that the gap, which is observed for temperature below $T_C$, persists up until a tempera-
ture $T^*$ which is well above $T_C$. This gap state is known as the pseudogap and its origin is still under considerable discussion. The pseudogap weakens as the doping level increases.

The first experimental observation of this phase was from NMR (nuclear magnetic resonance) measurements, which measure the imaginary part of the dynamic susceptibility divided by the energy and show that the spin lattice relaxation rate of underdoped cuprates begins to decrease above $T_C$ [30, 31]. The presence of the gap above $T_C$ is also apparent from infrared measurements and it gave a different result for the c-axis polarised and planar measurement. From c-axis measurements of underdoped cuprates, the optical conductivity at low frequencies is suppressed at a certain frequency and its value is roughly constant in temperature. This charge gap would vanish as $T^*$ is approached [32]. On the contrary, the planar response gave a different result in which the data show a peak (the Drude peak) centered at zero frequency which narrows, leading to a dip in the optical conductivity between the peak and the higher frequency response. This peak represent the in plane, coherent charge transport and the dip is thought to be a gap in the scattering rate of the charge carriers [33].

Another convincing result from the pseudogap phase in cuprates was revealed by an ARPES measurement. First ARPES studies showed that the pseudogap is also highly anisotropic and has a momentum dependence which is very similar to that of the superconducting gap below $T_C$ [36–38]. Later work by Norman et al. show that the anisotropy of the pseudogap has a very interesting temperature dependence. As can be seen from Figs. 2.8(e) and 2.8(f), the pseudogap vanishes along segments of the Fermi surface centered at the node (the point where $k_x = \pm k_y$ and the value of the superconducting gap is zero). These segments are known as Fermi arcs [35]. The $d$-wave node below $T_C$ (top panel of Fig. 2.8(f)) becomes a gapless arc above $T_C$ (middle panel of Fig. 2.8(f)) which expands with increasing $T$ to form the full Fermi surface at $T^*$ (bottom panel of Fig. 2.8(f)).

The origin of the pseudogap observed in cuprates, like the superconductivity itself, is still under intense and considerable discussion. Two main interpretations are emerging considering this phase. On the one hand, a scenario involving preformed pairs was proposed. Given that the symmetry of the pseudogap is the same as that of the superconducting gap, it is natural to relate the pseudogap phase with fluctuations that lead to $d$-wave superconductivity. In this
Figure 2.8: (a,b,c): Spectra taken at three different points in the Brillouin zone (shown in (d)) of underdoped Bi2212 with $T_c$ of 83K. They were recorded at various temperatures (solid curves). The dotted, red curves in (a,b,c) are reference spectra from polycrystalline Pt which is in electrical contact with the sample. Note the closing of the spectral gap at different $T$ for different Fermi surface locations $k$’s, which is also apparent from the plot (e) of the midpoint of the leading edge of the ARPES spectra as a function of $T$. (f) Schematic illustration of the temperature dependence of the Fermi surface in underdoped cuprates (see text). From [34, 35].
picture, in the normal state \((T > T^*)\), there are no coherent excitations. As the temperature is lowered \((T^* > T > T_C)\), a gap appears long before superconductivity is established. This pseudogap is produced by non-coherent fluctuations of the pairing field. Finally, below \(T_C\) the coherence sets in, and this will give rise to superconductivity and the observation of a sharp peak close to the Fermi level in ARPES data [13]. Recent ARPES measurement from Kanigel et al. support this scenario [39]. In this study, they showed that the Fermi arc length can be scaled by the reduced temperature, \(t = T/T^*(x)\), where \(T^*(x)\) is the temperature below which the pseudogap first develops at a given hole doping \(x\). In particular, the Fermi arc length collapses linearly with \(T/T^*(x)\) and extrapolates to zero as \(T\) goes to zero. This suggest that the ground state of the pseudogap phase is a nodal liquid, a strange metallic state whose gapless excitations are located only at points in momentum space \((k_x = \pm k_y)\), just as in a \(d\)-wave superconductor [39].

On the other hand, the alternative scenarios are based upon pseudogap that is not related to superconductivity, including scenarios which involve stripes [40], antiferromagnetic fluctuations [41], spin-charge separation, circulating orbital currents [42, 43] and quantum critical points [44]. In these scenarios, the pseudogap is not merely unrelated to superconductivity but rather competes with it. In addition, mostly these pictures involve either a charge density wave or spin density wave like phenomena, usually without long range order [13]. A consequence of the competition between superconductivity and the pseudogap phase is the coexistence of two gaps below \(T_C\) in all samples possessing a \(T^*\) that is greater than \(T_C\).

Recent results from superconducting gap anisotropy measurements in deeply underdoped Bi2212 compounds by Tanaka et al. are quite convincing in favour of the two gap scenario [45]. In this picture, the gap at the nodal and antinodal regions of \(k\)-space arise from different mechanisms. By careful analysis at two different regions in the Bi2212 BZ, it was observed that the superconducting gap value close to the nodal direction follows the doping dependence of the superconducting transition temperature (where a coherent peak in the spectrum can be observed), while the gap value at the antinodal position looks to have an intimate relation to the pseudogap also for \(T < T_C\). The observation of two distinct gaps has also been proposed from Raman [46, 47], penetration depth [48], and Andreev reflection experiments [49].

In the "normal metal" phase (see Fig. 2.7), the behaviour is consistent with
Fermi liquid theory developed by Landau. In this theory, the properties of the single electron are changed or renormalised by interactions with other electrons to give rise to a "quasiparticle". One of the characteristics of the quasiparticle is a narrow linewidth at low energy. This has been observed in ARPES data in the superconducting state for the whole doping region and in the normal state of the overdoped region. Within the Fermi liquid model, the quasiparticle linewidth is proportional to $E^2$ where $E$ is the energy of the excitation with respect to the Fermi level.

In the non-Fermi liquid region, the region between the UD and Fermi liquid regions and above the area with the highest $T_C$, the thermodynamic properties of the high $T_C$ superconductors are, in fact, similar to those of a Fermi liquid, but numerous experiments, such as resistivity, nuclear magnetic resonance (NMR) relaxation time, Hall conductivity and magnetoresistance, reveal unusual things in the sense that they are characterised by unusual power laws as a function of temperature.

### 2.1.3. Previous ARPES measurements on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

In this subsection, we will focus on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) since this compound is the topic of the experimental studies presented in this thesis. The
following literature review focusses mostly on ARPES results obtained for this compound and to be more structured it will consist of three main subjects of interest which are relevant to the topics of this thesis namely: the Fermi surface, the presence of superconducting and pseudogap, and many body effects.

Bi2212, perhaps the most extensively studied material among high-$T_c$ cuprates using ARPES [6], has a layered, orthorhombic structure (as seen in Fig. 2.9(a)) with $a \approx b \approx 5.4 \text{ Å}$ and $c \approx 30.7 \text{ Å}$. From x-ray studies it is known that the central Bi atom in the BiO plane is shifted about 2% from the tetragonal position in the crystallographic $a$-direction. If this displacement were to be ignored, the unit cell can be approximated by the smaller tetragonal unit cell with $a' \approx b' \approx 3.83 \text{ Å}$ which is rotated 90° in the $ab$ plane with respect to the orthorhombic unit cell.

The presence of a flat and mirror-like surface after cleavage of Bi2212 single crystals is one of the advantages of this compound and it thereby meets the requirement for surface sensitive experimental techniques such ARPES (the surface sensitivity or this technique will be discussed in the ARPES subsection later). This excellent cleavage plane is obtained by breaking the weak van der Waals bonds between two adjacent BiO layers (see Fig. 2.9(a)).

As mentioned previously, since the Cu-O related bands are the lowest-energy electronic states, the macroscopic electronic properties are the result of the behaviour of the CuO$_2$ planes. As in Bi2212 the electronic coupling of the CuO$_2$ blocks with one another along the $c$-direction is very poor, the electronic states in the CuO$_2$ are highly two dimensional. As a consequence, only the parallel component of the wavevector ($k_{||}$) is important in determining the dispersion relation. In Bi2212, to all intents and purposes, the perpendicular component of the wavevector ($k_{\perp}$) can be ignored.

The Fermi surface topology

Considering its eminent qualifications as a subject for study using ARPES, there have been extensive investigations of the Fermi surface (FS) of Bi2212. The Fermi surface is a surface of constant energy in reciprocal space which separates the occupied and unoccupied states. Since electronic excitations at low energies across the FS determine the material’s properties, this makes the FS an important subject to be studied.

In the following, the conventional notation for the tetragonal 2D Brillouin zone (BZ) is applied for the Bi2212 system and will be used throughout the whole thesis. The $\Gamma - M$ line is along the Cu-O bond direction, with $\Gamma = (0,0)$,
$M = (\pi,0)$, $X = (\pi,-\pi)$, and $Y = (\pi,-\pi)$. All these points in BZ have units of $1/a'$, where $a' = 3.83 \text{ Å}$ is the distance between the nearest-neighbor planar Cu ions (see Figs. 2.9(b)-2.9(c)). The tetragonal crystallographic $a'$-axis is parallel to the $\Gamma - X$ line while the $b'$-axis is parallel to the $\Gamma - Y$ line. There are also common notations used at particular momentum positions in the 2D BZ of Bi2212 e.g.: the nodal (N) point which refers to the point where the superconducting order parameter is zero (in the $\Gamma$-$Y$ and $\Gamma$-$X$ directions) and the antinodal (AN) point which refers to points on the FS where superconducting order parameter is maximum (in the X-M-Y direction).

Many features have been observed in the study of the Bi2212’s FS. Firstly, the presence of umklapp or diffraction replica (DR’s) bands which essentially complicate the data analysis. These DR’s originate from the diffraction of outgoing photoelectrons due to the incommensurate (IC) modulation present in pristine Bi2212 and related superstructures in the crystallographic $bc$-plane direction. This IC modulation has a wavelength of approximately $4.76b$ ($q \approx 0.21b'$) and spans 5 unit cells (it is also known as $5\times1$ reconstruction) [52]. The excess oxygen atoms in the BiO planes or the lattice mismatch between the CuO$_2$ and the BiO planes could be the driving force of such modulations [53, 54]. By substituting Pb atoms for Bi atoms one can suppress the modulation [55] and it has been reported that a modulation-free phase can be achieved for $\sim 40\%$ Pb atoms per formula unit [56, 57].

The second FS feature of Bi2212 to be mentioned here is the shadow Fermi
surface (SFS) which was observed for the first time by Aebi et al. [58]. In the 2D tetragonal BZ of Bi2212, the SFS band is located around the $\Gamma$ point. The microscopic origin of the shadow Fermi surface forms the subject of the Chapter 3 of this thesis.

The third characteristic of the FS of Bi2212 to be dealt here is the presence of a splitting of the CuO$_2$ bands into a bonding (BB) and antibonding (AB) combination due to the inter-plane interaction within each (CuO$_2$)$_2$ bilayer. This splitting was predicted by band structure calculations [59–61]. The wavefunctions of the bilayer split bands are even for the BB and odd for the AB under the reflection in a mirror plane located in the middle of the two adjacent CuO$_2$ planes.

This c-axis bilayer splitting was observed for the first time in overdoped Bi2212 [62, 63] as at high doping level the normal state ARPES features in Bi2212 are generally sharper and more pronounced. In a simple tight-binding calculation, the origin of these two bands is easily understood. Their dispersion relation in terms of the dispersion for a single layer is given by [64, 65]

$$\begin{align*}
\xi_{k}^{(BB)} &= \xi_k - t_\perp (k) \\
\xi_{k}^{(AB)} &= \xi_k + t_\perp (k)
\end{align*}$$

with a band structure term $\xi_k$ which has the form

$$\xi_k = \Delta \varepsilon - 2t[\cos(k_xa) + \cos(k_ya)] + 4t' \cos(k_xa) \cos(k_ya)$$

$$-2t''[\cos(k_xa) + \cos(k_ya)],$$

where $t$ denotes the hopping integral between 2 neighboring Cu sites along the Cu-O bonding direction, $t'$ denoting hopping to the second nearest Cu neighbour along the diagonal and $t''$ denoted the hopping to the third nearest Cu neighbour. The interlayer hopping term $t_\perp (k)$ which describes the hopping of a charge carrier between two neighbouring CuO$_2$ planes is given by

$$t_\perp (k) = \frac{1}{4}[\cos(k_xa) - \cos(k_ya)]^2$$

According to Eqs. (2.1), (2.2), and (2.3), the bilayer splitting is zero along the nodal direction (i.e.: $k_x = k_y$) and it is maximal near the M-point of the 2D BZ. This prediction is clearly experimentally verified in Refs. [62, 63]. Recent observations related in Refs. [66, 67] show that there is still a small splitting of
23 meV between the bonding and antibonding bands along the nodal direction for Bi2212 regardless of the doping level. This nodal splitting is due to vertical interplane hopping between O 2pσ orbitals (the orbitals that bond with the Cu 3dₓ²−ᵧ²) [66].

The bilayer splitting has been observed both in the normal and superconducting states. For example, in heavily overdoped samples, the maximum splitting is found to be about 88 meV in the normal state and about 20 meV in the superconducting state by measuring the difference between energy distribution curve (EDC) peak dispersion of these two FS sheets [63]. It was also reported that the bilayer splitting appears in optimal and underdoped compounds, and its magnitude was shown to be independent of doping [68, 69]. Though this feature is generally less clear in the data at reduced hole-doping, it is not lost, meaning that although the coherence between the electronic states in neighbouring CuO₂ planes in the bilayer lessens as hole-doping decreases [70], it is still non-zero. The bilayer splitting is argued to be more prominent in heavily overdoped compounds simply because these compounds become more Fermi-liquid like, with a higher degree of 3D dimensional coherence and better defined quasiparticles [63].

Since the bonding and antibonding bands have different symmetry along the c-axis, their photoemission matrix elements are different as the incident photon energy is varied [50, 63]. This means that resolving the bilayer splitting in ARPES experiment would be possible by employing an appropriate photon energy. As can be seen from Fig. 2.11, using a photon energy of 38-39 eV will give the
most contrast between the BB and AB intensity which is a very useful property when one wants to study the electronic structure of each FS sheet separately.

In the late 1990’s, the topology of the Bi2212 FS became a matter of controversy. In particular the question arose as to whether the FS topology was hole like (i.e. closed shape around the (X,Y) points, see Fig. 2.12(a), upper left panel) or electron-like (see Fig. 2.12(b)), enclosing the occupied state [3], and centered upon the Γ point.

Through the improvements in energy and angular resolution of ARPES spectrometers that went coupled with the introduction of a 2D detection system (see section 2.2.2), resolving all the features appearing in the ARPES spectrum become possible. As an example, by using Pb-doped Bi2212 Kordyuk et al. [68] could show that the FS topology remains a hole-like upon changing the doping level, as can be seen in Fig. 2.12(c). As the doping level is altered, the size of FS ”barrel” is changed. The more overdoped, the bigger the FS area enclosing hole states. In addition, the shape of the FS of Bi2212 becomes more square as the doping is increased. By fitting a model of the FS shape to the experimental FS maps (shown as solid yellow and dashed red line in the sketch in Fig. 2.12(c)),
the hole doping level $\delta$ can be derived from the simple relation,

$$\delta + 1 = \frac{2S_B}{S_{BZ}},$$

where $\delta$ denotes the doping level, $S_B$ is the area of the FS barrel and $s_{BZ}$ is the area of 1st (tetragonal) Brillouin zone. Eqn. (2.4) can be understood as follows: since the parent compound of Bi2212 has Cu $3d_{x^2-y^2}$ orbitals playing host to one localised electron, then the CuO$_2$-derived bands in undoped Bi2212 are half-filled, which can be described by Eqn. (2.4) if $\delta=0$. If hole doping, $\delta$, is now increased, this leads to an increase in the area of the hole-like FS beyond a value of one half of the BZ area. At a certain (high) doping level, the hole-like FS’s will touch one another (see Fig. 2.11(b)), leading to a topological transition to an electron-like situation.

Recent measurement and analysis of the different sheets of the Bi2212 FS (i.e.: bonding and antibonding) reveal that the bonding FS sheet always stays hole-like, whereas for the antibonding FS sheet, a cross-over from hole to electron-like has been observed at a doping level of 0.23 which corresponds to a $T_C$ of 55 K [70].

**The superconducting gap**

One of the most important results obtained using ARPES in the high $T_C$ cuprates is the observation of the anisotropy of the superconducting (SC) gap and of the pseudogap. Regardless of the fact that it is not explicitly phase sensitive, ARPES has been considered as one of the only experimental tools in which both the anisotropy of the superconducting and pseudogap can be derived quantitatively [7, 71–74].

The anisotropy of the superconducting gap was first observed in ARPES data of overdoped Bi2212 compounds as a difference in the position of the leading edge of the spectrum for $k = k_F$ at two different positions on the Fermi surface. As can be seen from Fig. 2.13(a), in the nodal direction (B), the spectra taken above and below $T_C$ are very similar which indicates a small or vanishing superconducting gap. In the antinodal direction (near the $(\pi,0)$ point, marked (A) in Fig. 2.13(a)), the superconducting and normal state spectra clearly exhibit not only a shift in the leading edge, but also a change in lineshape, whereby the superconducting spectrum consists of what has become known as peak-dip-hump lineshape. These results strongly support the existence of a $d$-wave order
In most ARPES studies of the superconducting gap, the gap is determined by measuring the leading-edge position (LEP) of the ARPES spectra. By comparing the LEP of the BSCCO ARPES spectra to the LEP of a polycrystalline metal like Pt or Au, one can determine the superconducting gap qualitatively. Another method to quantify the superconducting gap is by fitting the spectrum, or energy distribution curve (EDC) at different momenta with a model spectral function (EDC and spectral function are specific terms used in the discussion of ARPES data will be discussed in more detail in the measurements and data analysis subsection). In this sense, if the model used for the fit is correct, then its outcome is the real superconducting gap value, but of course this requires a good knowledge of superconducting gap itself. As an example, Ding et al. employed a phenomenologically broadened BCS spectral function in order to quantify the size of the superconducting gap at different momenta and the results agree nicely with the $d_{x^2-y^2}$ functional form $\Delta(k) = \Delta_0[\cos(k_xa) - \cos(k_ya)]$ [73] (see Fig. 2.13(b)).

A slight departure from pure $d$-wave character in the superconducting gap anisotropy has been observed for underdoped Bi2212 compounds. Instead of a "V"-shape as shown in Fig. 2.13(b), the superconducting gap anisotropy has an "U" shape where the area with vanishing gap is slightly extended around the node. Such a "U" shape of superconducting gap anisotropy is not only
observed in pristine Bi2212 but also in Pb-doped Bi2212 where the bilayer splitting is more readily resolved due to the lack of complicating diffraction replica features, therefore making the analysis more reliable. In order to account for this behavior, a higher harmonic term, such as $[\cos(2k_xa) - \cos(2k_ya)]$ should be included in the expansion of the gap function $\Delta(k)$, in addition to the simple $"V"$-like term.

Recent results of superconducting gap anisotropy measurements in deeply underdoped Bi2212 compounds by Tanaka et al. [45] have argued in favour of a two gap scenario. In this sense, the superconducting gap at the nodal and antinodal regions arise from different mechanisms. Within this scenario, the gap seen for $T < T_C$ at the antinodal region is suggested to have an intimate relation with the pseudogap. As one can see from Fig. 2.14(a), the gap near the nodal region did not increase with underdoping, (in fact, it decreases as doping level decreases below optimal doping), whereas the gap at the antinode does increase with successive underdoping [45]. A temperature dependent study of the superconducting gap near the nodal region in underdoped compounds reveals that the gap value has a temperature dependence like the temperature dependence of BCS superconductor [75].

Figure 2.14: (a) Doping dependence of the peak position for Fermi surface points close to the nodal region (coloured points) and in the antinodal region (black points). The dashed line indicates the pseudogap line at the antinodal region as reported from previous ARPES measurement on Bi2212 compounds (from [45]). (b) Temperature dependence of the gap size at Fermi surface crossing points near the nodal region as indicated in the inset. The dashed line shows the temperature dependence of the superconducting gap based on weak coupling BCS theory and serves as the guide to the eye (from [75].)
The many body effects: the coupling of charge carriers to bosonic degrees of freedom

One of the advantages of ARPES measurements is their capability to cope with the many-body effects in solids through the electron self-energy appearing in the ARPES spectral function (the latter will be elaborated in more detail in the next section). The self-energy, \( \Sigma \), is a complex function \( \Sigma = \Sigma' + i\Sigma'' \) whereby its real and imaginary parts correspond to the energy renormalisation with respect to the bare band dispersion \( \varepsilon_k \) and to the finite lifetime of the quasiparticles in the interacting system, respectively \([6, 77]\). It is the unique prospect of obtaining \( k \)-dependent, quantitative information regarding the self-energy that has driven many recent ARPES investigations.

The energy renormalisation is seen as a deviation of the electronic band dispersion from the bare-band dispersion close to the Fermi energy. Such deviations are widely believed to be a manifestation of the interaction of the charge carriers with particular bosonic degrees of freedom such as lattice vibrations (phonons), or with magnetic spin fluctuations. Therefore the study of the renormalisation and scattering rate of the quasiparticle as a function of doping, temperature and location in the BZ may help to reveal the details of the many-body interaction felt by the charge carriers, and therefore may help to uncover the mechanism of high-\( T_C \) superconductivity.

In Bi2212, renormalisation of the electronic bands was first observed at the nodal region of \( k \)-space in the form of a dispersion anomaly or “kink”: the deviation of the electronic band dispersion from the bare band dispersion at a...
particular energy scale. In nodal direction, as can be seen in Fig. 2.15(a), a dispersion kink at 70 meV was observed whose strength varied (increased) as doping was altered (decreased) [76, 80]. From temperature dependent ARPES data, it was proposed that this nodal kink still persists above the superconducting critical temperature, which has led to the argument that it originates from the interaction between electrons and phonons, since such phonon excitations should persist above $T_C$ (see Fig. 2.15(b)) [76].

In the antinodal region, a dispersion anomaly is observed at an energy scale of ca. 40 meV and it is seen only below the superconducting critical temperature $T_C$. Initially, the discussions of the antinodal kink have been less clear, since there are complications due to the presence of the incommensurate modulation of the BiO planes in non Pb-doped samples and the c-axis bilayer splitting. Here, the importance of Pb-doping to suppress the superstructure and the correct choice of photon energy in order to deliver sufficient bilayer splitting contrast needs to be stressed. In this vein, one study of antinodal kink by Kim et al. revealed that the renormalisation has a doping dependence both for the bonding and antibonding band as is shown in Fig. 2.16(c) [79]. By comparing the superconducting state ARPES spectra to the normal state spectra, the coupling parameter $\lambda$, which describes the interaction between the charge carriers and bosonic degrees of freedom was shown to decreases as the doping level increases up to the overdoped region.

In Ref. [78], Gromko et al. reported that the renormalisation strength and,
Figure 2.17: Temperature and doping dependence of the imaginary part of the self energy in Bi2212 related compounds determined from the full width at half maximum of the momentum distribution curves (MDC). (a-b) The temperature dependence for optimal doped (Opt) Pb-doped Bi2212. The contribution from a highly overdoped (OD) sample at 130 K (inset and gray line) is subtracted to obtained the imaginary mode-related component of the self-energy. $T_C$ of this OD sample is 69 K. (c) Doping dependence of nodal quasiparticle scattering rate (from [81]).

in particular, the energy scale of the renormalisation decreases as the doping level goes to the overdoped region as shown in Fig. 2.16(b). In addition, it was observed that the renormalisation is sensitive to the position in the Brillouin zone (BZ), being maximal at the M ($\pi$,0) point [78]. These points make a strong case that the kink in the nodal and antinodal region could be separate entities arising from different phenomena. Since the ca. 40 meV kink is only observed in the superconducting state and is maximal at the antinode then it was considered that the magnetic resonance mode could be its driving force, as the antiferromagnetic scattering vector $Q=($π,π) - which plays host to this mode - connects the two antinodal points in the tetragonal Bi2212 2D BZ. In earlier work, Kaminski et al. also reported that the dispersion anomaly continually evolved and grew stronger as ($\pi$,0) was approached. In addition, they argued that this dispersion anomaly was the main origin of the peak-dip-hump line shape [82] seen in this region of $k$-space.

The scattering rate or inverse lifetime of quasiparticles from photoemission of Bi2212 has also been studied extensively [81, 83–85]. The normal state scattering rate of optimally doped Bi2212 for $\omega \ll k_BT$, depends on temperature linearly but is independent of frequency. On the contrary for $\omega \gg k_BT$, it is linearly depending on frequency but temperature independent [83]. In optimally
doped Bi2212, the normal state scattering rate has a momentum dependence consisting of constant and frequency dependent terms around the Fermi surface [84].

In the superconducting state, there is clear evidence for a non-linear frequency dependence of the scattering rate, but in general, for large binding energies the scattering rate behaves linearly with respect to the frequency. However, recent studies of the nodal quasiparticle scattering rate (from the width of the $E_F$ MDC’s) as a function of energy [67, 81, 86] have revealed that at moderate energies there is an anomaly also in the imaginary part of self-energy - as can be seen in Fig. 2.17 - in keeping with the dispersion anomalies due to structure in its real part [67, 80]. The kink in the imaginary part of self-energy vanishes above $T_C$ as seen in Fig. 2.17(b) and has a doping dependence in which it is stronger in underdoped rather than in overdoped. This is consistent with the behavior of the real part of the self-energy in the nodal direction, as well as with the doping and temperature dependence of the intensity of the spin-1 magnetic resonance mode observed in inelastic neutron scattering (INS) [81, 86].

The many body effects observed in the Bi2212 compounds (particularly in overdoped samples and in the antinodal region of $k$-space) will be discussed in more detail in chapters 4 and 5 of this thesis.

2.2. Angle Resolved Photoemission Spectroscopy (ARPES)

This section is devoted to Angle Resolved Photoemission Spectroscopy (ARPES), the experimental technique that we have used in probing the electronic structure of Bi2212 and related compounds presented in this thesis. The description starts from the basic principle of photoemission and is then followed by a description of the experimental set-ups. The last part of this section then describes the measurements and the data analysis methods employed.

2.2.1. Basic principle

The basic principle of photoemission spectroscopy is the photoelectric effect, a phenomenon that was first explained by Einstein’s theory based on the quantisation of light in 1905. If photons with energy $h\nu$ from a light source, in our case either originating from a He gas discharge or from synchrotron radiation,
impinge onto the crystal then an electron can absorb the energy and escape from the sample into the vacuum with the kinetic energy:

$$E_K = h\nu - E_B - \Phi_W,$$

(2.5)

where $E_B$ is the binding energy of the electrons in the valence band and $\Phi_W$ is the work function, the quantity that acts as a potential barrier to the electrons at the surface and prevents the valence electrons from escaping the sample. Its magnitude is 3-5 eV in typical metals.

By collecting the outgoing photoelectrons with an electron analyser, one can map out the number of photoelectrons as a function of their kinetic energy. In the angle resolved (ARPES) mode, one can map out the number of outgoing electrons both as a function of their kinetic energy and emission angle $\theta$. The state-of-the-art ARPES experiment can measure and analyse multiple emission angles $\theta$ simultaneously (see Fig. 2.18). Following the momentum conservation law, the in-plane momentum of the photoelectrons is given by

$$p_\parallel = \hbar k_\parallel = \sqrt{2mE_{\text{kin}} \sin(\theta)},$$

(2.6)
whereby

\[ k_\parallel^2 = k_x^2 + k_y^2 \]
\[ k_x = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \sin(\theta) \cos(\Phi) \]
\[ k_y = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \sin(\theta) \sin(\Phi). \]  

(2.7)

The out-plane component of the photoelectron momentum is not conserved across the sample surface due to the lack of translational symmetry along the surface normal.

As will be related in more detail in section 2.2.2, the angle multiplexing energy analyser has as its basic measurement mode a line-scan in \( k_\parallel \), resulting in a two dimensional plot with in-plane momentum \( k_\parallel \) on one axis and energy as the other axis. In a crystal in which the electronic structure is strongly two dimensional (i.e. the band energy is only a very weak function of \( k_z \) or \( k_\perp \)), the fact that we have explicit access only to \( k_x \) and \( k_y \) is hardly a hindrance, and means that in such cases ARPES can directly measure the dispersion, the \( E \) versus \( k_\parallel \) relation of the many-body interacting electron system in a complete manner.

ARPES (photoemission in general) is a surface sensitive technique in the sense that the outgoing photoelectrons have a short mean-free-path length (\( \lambda \)). This means that they lose their kinetic energy very quickly due to the interactions in the solid during transport to the surface and subsequently, penetration through the surface and escaping to vacuum. The magnitude of \( \lambda \) is typically in the order of a few tenths of a nm. As a consequences, ARPES experiments have to be carried out under ultra high vacuum (UHV) conditions (the pressure of the system being in the range of \( 10^{-10} \) mbar or less) in order to prevent rapid adsorption of molecules from the surrounding atmosphere onto the surface of the sample within the timescale of the experiment.

**Three step model and sudden approximation**

In ARPES, during photoexcitation the system finally becomes a (N-1) electron system, as a hole will be left in the solid. The remaining electrons can interact with this hole, giving the constraint that photoemission is not merely a simple single electron removal process but it is a process in which many-body effects should be taken into account.

A rigorous method to describe the photoemission process is through the one
\textit{step model} in which the photon absorption, electron transport to the surface and electron escape are treated as a single process. In this model, the bulk, surface and vacuum have to be included in the Hamiltonian describing the crystal, implying that not only bulk states have to be considered but also surface states and surface resonances as well (for a review of the \textit{one step model}, see [34]).

Despite its accuracy, the computational complexity of the \textit{one step model} means that a more accessible picture is often used to describe photoemission; one in which three steps are considered. In the \textit{three step model}, the photoemission process is divided into three separate steps. Firstly, an electron is excited into an empty state through the absorption of the photon. Secondly, the electron travels to the surface of the sample, during which the electron might lose energy due to interactions and collisions with other electrons in the sample. As a consequence, secondary electrons with lower kinetic energy are created. The second step also can be described in terms of an effective mean free path which is proportional to the probability that the excited electron will reach the surface without scattering: in other words with no change in energy and momentum. The third step is for the photoelectron to overcome the surface potential barrier and escape into the vacuum. This can be represented by a probability of transition through the surface. Its value is unity if the photoelectron has sufficient energy to overcome the surface barrier or work function $\Phi$ and escape into the vacuum, and it is zero otherwise.

Both the one and three step model rely on the sudden approximation in the
sense that there is no interaction between the escaping electron and the remaining systems. This approximation in principle works only with the electrons which have high kinetic energy. In high $T_C$ cuprates, there is evidence that the sudden approximation is already applicable at the low kinetic energies resulting from use of a photon energy of 20 eV [87].

The formalism of the photoemission process should include the transition probability (let us call this $W_{fi}$) for an optical excitation between the N-electron ground state $\Psi_i$ and one of the possible final states $\Psi_f$. This can be approximated by the Fermi’s golden rule expression [77]:

$$W_{fi} = \frac{2\pi}{\hbar} |\mathcal{M}_{fi}|^2 \delta(E_F - E_i - h\nu) = |\langle \Psi_f | \mathcal{H}_{int} | \Psi_i \rangle|^2 \delta(E_F - E_i - h\nu).$$  \hspace{1cm} (2.8)

Fermi’s golden rule describes the transition probability in terms of the coupling strength between the initial ($\Psi_i$) and final ($\Psi_f$) state and considering the number of ways that the transition can take place. $\mathcal{H}_{int}$ is the Hamiltonian which describes the interaction between the electrons in solid and incoming photon which acts as a external electromagnetic field $\mathbf{A}$, and the $\mathcal{H}_{int}$ is the perturbation term of the overall Hamiltonian $H = H_0 + H_{int}$ given by

$$H_0 = \frac{p^2}{2m} + e\Phi$$
$$H_{int} = -\frac{e}{2mc} [\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}] + \frac{e^2}{2mc^2} \mathbf{A} \cdot \mathbf{A},$$ \hspace{1cm} (2.9)

where $\Phi$ and $\mathbf{p}$ are the scalar potential (not to be confused with the work function) and momentum operator respectively. For low intensities of the external field, first order perturbation theory can be used and yields the $\mathcal{H}_{int}$ as given in Eqn. (2.9). By using the commutator $[\mathbf{p}, \mathbf{A}] = -i\hbar \cdot \nabla$ and choosing an appropriate gauge (the common procedure is to invoke the Coulomb gauge in which $\Phi = 0$ and therefore in the dipole approximation, where the spatial variation of the vector potential $\mathbf{A}$ is small$^1$, yielding $\nabla \cdot \mathbf{A} = 0$), the $\mathcal{H}_{int}$ reduces to

$$\mathcal{H}_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p},$$ \hspace{1cm} (2.10)

$^1$In the dipole approximation, the wavelength of the electromagnetic radiation which induces transitions between different atomic levels is greater than the typical atomic distance. Thus, the $\exp(ik \cdot r)$ term in $\mathcal{A}$, which can be expressed as a series ($1 + ik \cdot r + ...$), can be approximated by its first term, unity. Thus, this means that $\mathbf{A}$ becomes a constant.
where the quadratic term in $A$ is omitted as well since it is negligible for the low electromagnetic field strength relevant for present day photon sources.

In the sudden approximation, the wave function of the initial and final state can be factorised into the optical transition and the remaining condition term which can be described as [6]:

$$\Psi_i = A \Phi^k_i \Psi_i^{N-1}$$  \hspace{1cm} (2.11)

$$\Psi_f = A \Phi^k_f \Psi_f^{N-1},$$  \hspace{1cm} (2.12)

where $A$ is an operator that properly antisymmetrises the $N$-electron wave function so that the Pauli principle is satisfied. $\Phi^k_i$ and $\Phi^k_f$ are the wave functions of the photoelectrons with momentum $k$ before and after the optical transition takes place, $\Psi_i^{N-1}$ and $\Psi_f^{N-1}$ describe the remaining (N-1) electron system. The final state $\Psi_f^{N-1}$ can be expressed as an excited state with an eigenfunction $\Psi_m^{N-1}$ and its corresponding eigenvalue $E_m^{N-1}$. This will mean that the summation of all possible excited states $m$ defines the total transition probability. In general, however, $\Psi_i^{N-1}$ should be written as $\Psi_i^{N-1} = c_k \Psi_i^N$, where $c_k$ is the annihilation operator for an electron with momentum $k$. This expression shows that $\Psi_i^{N-1}$ is not an eigenstate of the (N-1) electron Hamiltonian, but it is just what remains from the $N$-particle system after one electron is pulled out. Within this approximation, the matrix element can be written as:

$$\langle \Psi_f | H_{int} | \Psi_i \rangle = \langle \Psi_f^k | H_{int}^k | \Phi^k_i \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle,$$  \hspace{1cm} (2.13)

where $\langle \Psi_f^k | H_{int}^k | \Phi^k_i \rangle \equiv M_{f,i}^k$ is the one-electron dipole matrix element, and $\langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$ is the (N-1) electron overlap integral. The total photoemission intensity measured with momentum $k$ and kinetic energy $E_{kin}$ is proportional to

$$I \propto \sum_{f,i} |M_{f,i}^k|^2 \sum_m |c_{m,i}|^2 \delta(E_{kin} - E_{m}^{N-1} - E_i^N),$$  \hspace{1cm} (2.14)

where $\sum_m |c_{m,i}|^2 = \sum_m \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle^2$ is the overlap integral which describes the probability to remove the electron from state $\Psi_i^{N-1}$ to the excited state $\Psi_m^{N-1}$ in the (N-1)-particle system.

In a system for which correlation effects are strong, such as the superconducting cuprates, many of the different $|c_{m,i}|^2$ terms will not vanish, since photoelectron removal will affect the effective potential of the system, and it turns out that $\Psi_i^{N-1}$ will overlap with many of the eigenstates $\Psi_m^{N-1}$. Consequently,
the ARPES spectra will be described by a main line and several satellites which represent the number of excited states that were created in the photoemission process (see [6]).

**Many-body effects, spectral function and self energy**

In correlated systems such as cuprates, the interactions involving many participating bodies are the fundamental ingredient which need to be solved to understand the physical properties. The many-body problem can be defined as the study of how the interactions between single particles affect the non-interacting system. The photoemission process, as described in the preceding section, initially is viewed as a single particle probe in which the (photo)electron is excited to the final state but, nevertheless, it also represents the many-body problem in which the remaining (N-1) electrons in fact can interact with the created hole.

One way to solve the many-body problem is through the Green’s function (GF) formalism. Instead of solving the Schrödinger equation (SE) with the full many-body wave functions which is not a tractable problem, this formalism employs the expansion of the single particle eigenfunction and solves it in an iterative way [88, 89]. This GF, the inverse differential operator, gives the probability to find the single particle at time $t$, given its probability at some previous time $t'$. But how should this single particle approach describe the many-body aspects seen in the photoemission process? The answer lies in the scattering processes that appear between the electrons when they are within a certain range of each other. In the limit when the critical range at or below which the scattering processes cuts in is very small, this situation reduces to the single particle case. The electron propagates through the medium and gives rise to infinite series of multiply scattered waves which sum to provide the GF for the single particle (in this case one electron) interacting with the medium (which may consist of other electrons), thus yielding the many-body effects. In this way one can obtain the response of complex interacting systems to simple forms of excitation without having to find the full eigenvalue and eigenfunction [88, 89].

The propagation of a single electron in a many-body system, as described in preceding paragraph, is given by the *time ordered* one-electron GF

$$G^\pm(\vec{r}_1, \vec{r}_2, t_1, t_2) = \begin{cases} 
-i \langle \Psi^N_0 | C_{r_1}(t_1) C^\dagger_{r_2}(t_2) | \Psi^N_0 \rangle & \text{for } t_1 > t_2 \\
+ i \langle \Psi^N_0 | C^\dagger_{r_2}(t_2) C_{r_1}(t_1) | \Psi^N_0 \rangle & \text{for } t_1 < t_2,
\end{cases}$$  

(2.15)
which describes the probability that an electron at \( r_1 \) and time \( t_1 \) will be found at \( r_2 \) at a later time \( t_2 \). The plus and minus sign refer to addition and removal of an electron respectively. \( C^\dagger_r(t) \) and \( C_r(t) \) are, the creation and annihilation operators at time \( t \) in space representation of a single-particle state while \( \langle \Psi_N^N | \ldots | \Psi_0^N \rangle \) is an average over the ground state of the \( N \)-particle system.

For a free (non-interacting) electron system, the operators \( C^\dagger_r(t) \) and \( C_r(t) \) in Eqn. (2.15) are connected to those in momentum space through the relation [90]

\[
C(\vec{r}, t) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{k}} C_{\vec{k}} e^{i(\vec{k} \cdot \vec{r} - \varepsilon_{\vec{k}} t)},
\]

(2.16)

where \( \Omega \) and \( \varepsilon_{\vec{k}} \) denote the volume and the bare spectrum of the non-interacting electrons, respectively. Substituting Eqn. (2.16) into the time ordered GF expression Eqn. (2.15) and considering the situation where \( r_1 = r_2 = r \) and \( t_1 = 0; t_2 = t \), one can obtain the GF of the free (non-interacting) electron, [90]

\[
G_0(r, t) = \frac{i}{\Omega} \sum_{\vec{k}} e^{i(\vec{k} \cdot \vec{r} - \varepsilon_{\vec{k}} t)} \left\{ \begin{array}{cl} 1 - f_{\vec{k}} & t > 0 \\ -f_{\vec{k}} & t < 0 \end{array} \right.,
\]

(2.17)

where the anticommutator for fermions has been used and \( f_{\vec{k}} = \langle n_{\vec{k}} \rangle = \langle C^\dagger_{\vec{k}} C_{\vec{k}} \rangle \) is the Fermi function at \( T = 0 \) which has a value either unity for \( |k| < k_F \) or zero for \( |k| > k_F \). The GF in momentum representation \( G(k, \omega) \) and that in space representation \( G_0(r, t) \) are related through the following Fourier transform (FT) [90]

\[
G_0(r, t) = \int_{-\infty}^{\infty} \frac{d^3 \vec{k}}{(2\pi)^3} e^{-i\omega t} G(k, \omega) \frac{d\omega}{2\pi}.
\]

(2.18)

Finally, employing Eq. (2.18), one can obtain the non-interacting single electron GF as function of momentum and energy,

\[
G_0(k, \omega) = \frac{1}{\omega - \varepsilon_k - i\eta},
\]

(2.19)

where \( \eta \) is a positive infinitesimal for \( \varepsilon_k \) greater than Fermi energy \( E_F \) or \( k \) greater than \( k_F \), and it is a negative infinitesimal otherwise.

Now we wish to switch on the interactions and see how we can describe the many-body effects. In systems with weak or moderately strong interactions, the single-particle GF for the interacting electron system is closely related to GF for the non-interacting system. In this situation since the many-body effects are
embraced in the system via the scattering between the electron and the rest, then a perturbative expansion describing this situation can be introduced to the formally non-interacting GF. Following the similar procedure as we applied to the non-interacting system, one arrives at an expression for the interacting electron GF in the momentum representation [90]:

$$G^\pm(k, t) = \begin{cases} 
-i\langle \Psi_0^N | C_k(0) e^{-i\mathcal{H}t} C_k^\dagger(0) | \Psi_0^N \rangle e^{iE_0^N t}, & t > 0 \\
+i\langle \Psi_0^N | C_k^\dagger(0) e^{i\mathcal{H}t} C_k(0) | \Psi_0^N \rangle e^{-iE_0^N t}, & t < 0 
\end{cases} \quad (2.20)$$

where $E_0^N$ is the ground state energy of the interacting $N$-particle system. When deriving Eqn. (2.20), the definition of the GF from Eqn. (2.15), the Heisenberg representation namely $C_k(t) = e^{i\mathcal{H}t} C_k(0) e^{-i\mathcal{H}t}$, and the same condition as employed in the non-interacting case in which $r_1 = r_2 = r$ and $t_1 = t; t_2 = 0$ have been used. On inserting between $C$ and $C^\dagger$ in Eqn. (2.20) the complete set of eigenfunctions $\sum_m |\Psi_m^{N+1}\rangle \langle \Psi_m^{N+1}| = 1$ of $\mathcal{H}$ (here $m$ is an index of a quantum state; the plus sign in $N \pm 1$ denotes the system with one electron is added while minus sign denoted the system with one electron removed), one can obtain [90]:

$$G(k, t) = \begin{cases} 
-i \sum_m |\langle \Psi_m^{N+1} | C_k^\dagger | \Psi_0^N \rangle|^2 \delta(\omega - \varepsilon_m^{N+1} - \mu + i\eta), & t > 0 \\
+i \sum_m |\langle \Psi_m^{N-1} | C_k | \Psi_0^N \rangle|^2 \delta(\omega - \varepsilon_m^{N-1} - \mu - i\eta), & t < 0, 
\end{cases} \quad (2.21)$$

After Fourier transforming, one arrives at the following expressions:

$$G^+(k, \omega) = \sum_m \frac{|\langle \Psi_m^{N+1} | C_k^\dagger | \Psi_0^N \rangle|^2}{\omega - \varepsilon_m^{N+1} - \mu + i\eta}, \quad (2.22)$$

$$G^-(k, \omega) = \sum_m \frac{|\langle \Psi_m^{N-1} | C_k | \Psi_0^N \rangle|^2}{\omega - \varepsilon_m^{N-1} - \mu - i\eta}, \quad (2.23)$$

$$G(k, \omega) = G^+(k, \omega) + G^-(k, \omega), \quad (2.24)$$

in which we have substituted the eigenvalues $\varepsilon_m^{N \pm 1}$ with $\varepsilon_m^{N \pm 1}$ and the ground state energy $E_0^N$ with the chemical potential $\mu$ for convenience. $\eta$ is a positive infinitesimal.

From Eqs. (2.22) and (2.23) one can define an important quantity, namely the spectral function which is given by:

$$A^\pm(k, \omega) = \sum_m |\langle \Psi_m^{N+1} | C_k^\pm | \Psi_0^N \rangle|^2 \delta(\omega - \varepsilon_m^{N \pm 1} + \mu), \quad (2.25)$$
where \( C_k^+ = C_k^\dagger \) and \( C_k^- = C_k \) are the creation and annihilation operators. The spectral function \( A^\pm(k, \omega) \) is intimately related to the overlap integral \( \sum_m |c_{m,0}|^2 = \sum_m |\langle \Psi_{N-1}^{-1} | \Psi_0^{N-1} \rangle|^2 \) described in Eqn. (2.14) (here the index \( i \) in (2.14) which denoted the initial state has been replaced with 0, representing the ground state which can act as the initial state), since by applying the operators \( C_k^\pm \) to the state \( |\Psi_0^N\rangle \) one can obtain the new state \( |\Psi_0^{N\pm1}\rangle \). Thus, the spectral function \( A^\pm(k, \omega) \), depending on the sign, defines the probability of single-electron addition (plus sign) and the probability of single-electron removal (minus sign) for the interacting system.

The single-particle GF for the interacting system described in Eqn. (2.24) can then be expressed in terms of spectral function \( A(k, \omega) \) as follows:

\[
G(k, \omega) = \int_0^{\infty} dE' \frac{A^+(k, \omega)}{\omega - E' + i\eta} + \int_0^{\infty} dE' \frac{A^-(k, \omega)}{\omega + E' - i\eta},
\]

where \( E' = \epsilon_m^{N\pm1} - \mu \). This expression can be simplified by using the Dirac identity in the limit of \( \eta \to 0^+ \): \( (\omega \pm i\eta)^{-1} = \mathcal{P}(\frac{1}{\omega - E'}) \mp i\pi\delta(\omega - E') \), where \( \mathcal{P} \) denotes the principal value, which in turn yields the relation between the spectral function and the GF via:

\[
A^\pm(k, \omega) = \mp \frac{1}{\pi} \text{Im} G(k, \pm \omega),
\]

Comparing the spectral function of the non-interacting system to that of interacting system, will give us an indication of how important this spectral function is. By inserting the GF for the non-interacting system from Eqn. (2.20) into Eqn. (2.27), the spectral function will be a \( \delta \)-function which is peaked at \( \omega = \epsilon_k \). In this case the spectral function can be written as \( A(k, \omega) = \delta(\omega - \epsilon_k) \).

For the interacting system, there is a correction of the GF due to the electron-electron correlations, and other interactions, which can be conveniently expressed in term of the electron self-energy, given by:

\[
\Sigma(k, \omega) = \Sigma'(k, \omega) + i\Sigma''(k, \omega)
\]

The self-energy includes all the particle interaction effects involved. The outgoing photoelectron perturbs the other particles of the system in such a way that its motion is correlated with the other particles in the system. In other words, the outgoing photoelectron affects the many-body system, which in turn feed
Figure 2.20: (a) Momentum-resolved single electron removal and addition spectra for the non-interacting system in which a single energy band dispersing across \( E_F \). (b) Same spectra for interacting Fermi liquid system. Momentum distribution function \( n(k) \) is shown for both systems at corresponding ground state \( (T = 0K) \). Adapted from [6].

back to the outgoing photoelectron, thus altering its energy [88].

Since the self-energy describes the dynamic response or the time dependence of the rest of the system correlated with the outgoing photoelectron, the self-energy can be thought as an external effective potential which is time dependent. Due to this self-energy, the interacting GF is corrected and is then given by:

\[
G(k, \omega) = \frac{1}{\omega - \varepsilon_k + \Sigma(k, \omega)}.
\] (2.29)

By employing the relation between the GF and spectral function (SF) given by Eqn. (2.27), one can obtain the interacting SF:

\[
A^\pm(k, \omega) = \pm \frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \varepsilon_k - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}. \tag{2.30}
\]

It is evident that \( \Sigma'(k, \omega) \) describes the correction to the the value of the bare particle dispersion \( \varepsilon_k \), while \( \Sigma''(k, \omega) \) describes the lifetime broadening of the non-interacting spectrum at \( \omega = \varepsilon_k \), which occurs due to the many-body interactions in the system.

In the interacting electron systems described in preceding paragraph, de facto the concept of the quasiparticle (QP) has been introduced, in which the real particle is surrounded by a cloud of excitations of the system. In this way, the physical electron is dressed or renormalised with a variety of excitations of the various degrees of freedom of the solids. This leads to new properties for the QP compared to the physical electron such as an effective mass \( m^* \), a renormalised energy \( \varepsilon_k - \Sigma'(k, \omega) \), and a finite lifetime \( \tau_k \).

In this case of an interacting electron system, the momentum distribution \( n_k \)
of the QP will display a discontinuity smaller than unity at \( k = k_F \), which is in sharp contrast to the case of the electron gas in which \( n_k \) has a discontinuity equal to unity, showing a perfect step-like function at \( T = 0 \) K. The size of the discontinuity at \( k = k_F \) is known as \( Z_k \), the coherence factor or the pole strength. Since the spectral weight should be conserved, then the remaining spectral weight must be transferred to an "incoherent part" (see Figs. 2.20(a) and 2.20(b)).

As discussed in the preceding part about the overlap integral \( \sum_m |c_{m,0}|^2 = \sum_m |\langle \Psi_m^{N-1}|\Psi_0^{N-1} \rangle|^2 \) described in Eqn. (2.14), it then follows that the eventual photoemission spectrum consists of a main line (coherent part) and the satellite part (incoherent). The latter corresponds to the non-zero \( |c_{m,0}|^2 \), arising from the interaction of a particular ground state \( \Psi_0^{N-1} \) and a number of excited states \( \Psi_m^{N-1} \) created as a result of the photoemission process.

In conclusion for this part, we have shown that the intensity in angle resolved photoemission is directly proportional to the spectral function \( A(k, \omega) \), multiplied by the matrix element, thus giving:

\[
I(k, \omega) = I_0(k, \nu, A) f(\omega) A(k, \omega) \otimes R_\omega \otimes R_k + BG, \tag{2.31}
\]

where \( I_0(k, \nu, A) \) denotes the single-electron dipole matrix element \( M_{k,i} \) which depends on the momentum and energy of the photoelectron as well as the polarisation of the incoming photon. \( f(\omega) \) denotes the Fermi-Dirac function which is given by:

\[
f(\omega) = \frac{1}{(\exp[\frac{\hbar \omega - E_F}{k_B T}] + 1)}, \tag{2.32}
\]

where \( E_F \) is the Fermi energy. The momentum resolution \( R_k \) and energy resolution \( R_\omega \) of the experiment as a whole (from the light source, crystal, and electron energy analyser) should also be included when the physical interpretation is extracted from photoemission intensity because the measurement possesses a linear response nature. The effect of the finite energy resolution can be simulated by convoluting a constant momentum cut through \( A(k, \omega) \) ‘data’ with a one-dimensional Gaussian with an appropriate full width at half maximum (FWHM). The momentum resolution can be simulated by summing up the constant wavevector cuts through a theoretical \( A(k, \omega) \) dataset across a certain \( k \)-range. This procedure is permitted since the data from a real angle multiplexing electron energy analyser are usually resulted from an angular slice integration across a \( k \)-range already greater than the nominal angular resolution of the elec-
**Figure 2.21:** Schematic representation of an experimental geometry that can give rise to a strong matrix element effect in the photoemission intensity. A $3d_{x^2-y^2}$ orbital in a CuO$_2$ planes possesses two minor planes (perpendicular to the xy plane). (a) M1 is the mirror plane along the Cu-O bond; in this mirror plane, the $3d_{x^2-y^2}$ orbital has even reflection symmetry. (b) The second mirror plane, M2, is that running at an azimuthal angle of 45° with respect to the first. In M2 the $3d_{x^2-y^2}$ orbital has odd symmetry. Adapted from [6].

The matrix element effects

The implication of the matrix element, which was given earlier in the dipole approximation as $|M_{fi}|^2 = |\langle \Phi^k_f | A \cdot p | \Phi^k_i \rangle|^2$ for the photoemission intensity will be discussed in more detail in this section. It is clearly evident that the matrix elements should be taken into account as well as possible when photoemission spectroscopic data is analysed.

The matrix element, as appearing in Eqn. 2.31 depends on a number of factors including the photon energy, the $k$-location of state being probed and the polarisation of the exciting radiation (with respect to the orientation of the crystal and the detector) [77]. There are particular situations in which the matrix elements can be exploited to give information regarding the symmetry of the initial states in a photoemission experiment. The effect of a crystal mirror plane is a good and relevant example of this. For clarity, let us consider the photoemission from a sample which contains occupied orbitals of the same symmetry.
Table 2.1: The polarisation condition which is needed in order to get a non-vanishing photoemission intensity in the experimental geometry given in Fig. 2.21.

<table>
<thead>
<tr>
<th>mirror plane</th>
<th>( \Phi_i ) symmetry</th>
<th>matrix element</th>
<th>required polarisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>even</td>
<td>( \langle +</td>
<td>+</td>
</tr>
<tr>
<td>M2</td>
<td>odd</td>
<td>( \langle +</td>
<td>-</td>
</tr>
</tbody>
</table>

as a \( d_{x^2-y^2} \) orbital (for example the Zhang-Rice singlet in the CuO\(_2\) planes of BSCCO). The \( d_{x^2-y^2} \) orbital pictured in Fig. 2.21(a) has even symmetry with respect to reflection in the mirror plane M1 and has odd symmetry with respect to the mirror plane M2 shown in Fig. 2.21(b).

The electron analyser will be able to detect a non-zero photoemission intensity if the whole integrand in the overlap integral is an even function (including the final states \( \Phi_f \)) under reflection in the relevant mirror plane. This is so because the odd-parity final states would be zero everywhere in the presence of the mirror plane and therefore also at the electron analyser which lies in the mirror plane. This implies that for the experimental geometry shown in Fig. 2.21(a), the \( A \cdot p(\Phi^k_i) \) must have even symmetry. Consequently, if the initial state \( \Phi^k_i \) is even with respect to the mirror plane M1 then the light polarisation A must be even too, meaning that only components of A that are parallel to the mirror plane M1 will contribute to a non-vanishing intensity at the detector. In the case when the initial state \( \Phi^k_i \) is odd with respect to the mirror plane M1 such as in Fig. 2.21(b), the polarisation A will also need to be odd in the sense that only the component of A that is perpendicular to the mirror plane M1 will allow the dipole transition and therefore yield photoemission intensity.

In summary, the experimental geometry in combination with the polarisation of the light will enable us - in particular cases - to study the orbital symmetry of the initial states. Hence, there are preferable polarisation and experimental conditions for photoemission measurements at high symmetry points of the Fermi surface of, for example high-\( T_C \) cuprates: for measurement along the Cu-O bond direction (\( \Gamma-M \), see Fig. 2.9), the polarisation vector of the incoming light should be parallel to the \( \Gamma-M \) \( ((0,0)-(\pi,0)) \) line, while for measurement along the zone diagonal (nodal line, \( \Gamma X \) or \( \Gamma Y \), the polarisation vector of the incoming light should be perpendicular to the \( \Gamma - (X)' \) \( ((0,0)-(\pi,\pi)) \) line. Note that the arguments provided in the preceding paragraph will be no longer valid if the detector is located out of the mirror plane of the sample or the sample itself
2.2.2. Experimental set-up

This section will discuss the experimental set-ups used to carry out the ARPES measurements presented in this work. In general, performing ARPES measurement requires: a light source, an electron energy analyser, detector and a sample cryostat (also possibly allowing rotation of the sample). All of these components should be housed in an ultra-high vacuum (UHV) chamber. In addition, one requires high quality single crystals which should be cleaved \textit{in situ} in UHV (with a pressure of less than $10^{-10}$ mbar), in order to provide clean surfaces for investigation.

Measurements presented in this thesis were performed at different laboratories but they shared the same basic experimental set-up. For example, Fig. 2.22 shows the experimental set-up at van der Waals-Zeeman Institute, University of Amsterdam (the experiment is named FAMoS, after FOM-Amsterdam Momentum Space microscope) which has been used to produce the Fermi surface map of the PbBi2212 compound shown in Fig. 3.1. This set-up is equipped with a two-angular axis cryomanipulator which can rotate the sample position in the polar degree of freedom (the rotation axis is parallel to the sample surface and in the vertical plane of Figs. 2.22(b) and 2.23(b), an angle we denote $\theta$, and in the azimuthal degree of freedom (the rotation axis is perpendicular to the sample surface), an angle denoted $\Phi$ (see Fig. 2.23(b)). The (cryo)manipulator is
mounted on a commercial x,y,z translation stage to enable an adjustment of the sample position in the vacuum chamber.

Almost all experimental results presented in this thesis were performed at synchrotron radiation laboratories, namely, the SLS (Swiss Light Source) in Villigen, Switzerland, at the X90LA-SIS beamline [92] and at BESSY in Berlin, Germany, at the UE112 PGM1 beamline [93]. At both beamlines, end-stations conceptually similar to the FAMoS system were used in all aspects except that of light source.

**Light sources**

In the case of the FAMoS set-up in Amsterdam, the light source is a helium discharge source, namely the VUV 5000 system from the company Gamma-data, driven by a VUV 5010 microwave generator.

The photons that are provided by this equipment, are emitted due to de-excitation of electrons in He atoms from the $1s^12p^1$ state to the $1s^3$ state in a He plasma. This process yields the most intense "line" in the spectrum, that is known as HeI$\alpha$ with an energy of 21.218 eV. Another main transition line is the transition of electrons in He ions from $2p^1$ state to $1s^1$ state, known as HeII $\alpha$ with an energy of 40.812 eV. The He I line has the most intense output accounting for ca. 88% of the intensity, while the He II accounts for 5% of the total VUV intensity.

To sustain the helium plasma mentioned in the preceding paragraph, an elec-
Figure 2.24: (a) Schematic of a beamline set-up at a synchrotron radiation source with an undulator (the straight section in the storage ring which produces the photons), the monochromator which selects the energy of the photons and the hemispherical analyser. Adapted from [6]. (b) A schematic example of a synchrotron radiation facility at BESSY in Berlin, Germany. Electrons moving around in a storage ring emit radiation when passing through an undulator device.

electron cyclotron resonance (ECR) condition is used, whereby, the helium plasma experiences a Lorentz force due to a static magnetic field and thus starts to rotate perpendicular to the magnetic field. The angular frequency of the electrons, in the presence of the perpendicular electric field, is given by the cyclotron frequency $\omega_{ce}$:

$$\omega_{ce} = \frac{eB}{mc},$$

(2.33)

where $e$ denotes the electron charge, $B$ denotes the static magnetic field, $m$ is the electron mass, and $c$ is the electron velocity. The ECR is achieved by fine tuning the electric and magnetic field such that the angular frequency $\omega_{ce}$ of the electrons is equal to the frequency of the oscillating electric field. Typically the frequency of the oscillating electric field is in the microwave region, in this case 10 GHz and therefore the VUV 5010 microwave generator is used in order to generated these waves.

The advantage of this ECR He source compared to traditional high voltage He discharge sources is that the excitation efficiency is so much higher that a considerably lower He gas pressure in the discharge region can be employed ($10^2$ mbar instead of a few mbar). This leads to a substantial decrease in self absorption of the radiation by the He atoms in the plasma. In turn, this not only leads to higher intensities but also to significantly narrower linewidths of the VUV radiation.

Besides the main HeI $\alpha$ and HeII $\alpha$ lines, weaker satellite lines are also produced by the ECR source. As a consequence, a toroidal grating monochromator is used to select a single line out of the He discharge spectrum.
Measurement using a synchrotron radiation source offer many advantages. For example: the availability of photons with a wide range of different energies and polarisations, the photon flux is much higher as well as the smaller size of the light spot. The latter is very helpful in terms of reducing the need for very large and extremely flat single crystal samples.

Synchrotron radiation is created when charged particles travelling at relativistic speeds are accelerated. In a storage ring-based synchrotron radiation facility, this acceleration is realised by a deflection of the trajectory of a usually GeV electron beam by magnetic structures. In the research presented here these structure are periodic arrays of magnets called undulators, situated in straight sections of the storage ring (see Fig. 2.24). Upon passing through the periodic magnetic field of the undulator, the electron beam oscillates, emitting synchrotron radiation. The result is a highly collimated, intense (in our case) VUV beam of an energy that can be tuned to with a few eV by adjustment of the strength of the magnetic field, which is altered by adjusting the distance between two arrays of magnets. In order to obtain circularly polarised light, another undulator can be installed perpendicular to the first undulator. By introducing a phase difference between these two undulators, circular polarised light will be achieved. The light is then monochromatised to the desired photon energy using a grating monochromator (see Fig. 2.24). Details of the two beamlines used can be found here [92, 93],

**Hemispherical electron analyser and detector**

An electron energy analyser consists of two concentric hemispheres (of radii $R_{in}$ and $R_{out}$) which actually carry out the energy dispersion. The electrons travel in trajectories which are generated by the voltage difference between the two hemispheres, in the radial electrostatic field. The potential on these hemispheres is given by

\begin{align}
V_{in}(R_{in}) &= \frac{E_0}{e} \left[ \frac{2R_0}{R_{in}} - 1 \right] \tag{2.34} \\
V_{out}(R_{out}) &= \frac{E_0}{e} \left[ \frac{2R_0}{R_{out}} - 1 \right], \tag{2.35}
\end{align}

where $E_0$ and $R_0$ are the pass energy and mean radius respectively. Only the electrons with energy close to $E_0$ will then arrive at the detector. The pass energy used in the experiments related here was varied between 2, 5, 10, and 20
Figure 2.25: Schematic of the electron analyser and detector system.

eV. The range of energies that can simultaneously be recorded is ca. $E_0/10$. The energy resolution can be determined, in part, from the pass energy. The lower the pass energy, the higher the resolution and the lower the intensity at the detector since the energy range that can simultaneously be probed depends on the pass energy. Another factors that determine pass energy are the size of the entrance slit and $R_0$.

In this work, the emitted photoelectrons have been analysed using commercial hemispherical electron analysers from the company Gammadata-SCIENTA: a SCIENTA SES 100 (with mean radius $R_0$ of 100 mm) at the BESSY end station$^2$ and a SCIENTA SES 2002 (with $R_0$ of 200 mm) at University of Amsterdam and at the SLS end-station.

Before the electrons pass through the entrance slit and thus the hemispherical analyser, a multi-element lens retards the electrons to an energy close to the pass energy and can additionally focus the electrons in either an angularly or spatially resolved manner. In the angularly resolved mode (called angular mode), the electrons are sorted by the lens system according to their emission angle from the sample surface. In the spatially resolved mode (called transmission mode), the lens system analyses the original position of the electrons and therefore a real space image of the sample is obtained.

After the electrons, with a certain energy width centered on the pass energy, have passed by the analyser, they land on the detector as shown in Fig. 2.25. The detector consists of a two dimensional multichannel plate that multiplies the incoming electrons, and an phosphor screen that produces a light flash when

$^2$kindly made available to us due to the generosity of the ARPES group of the IFW Dresden.
it is hit by the electrons. A CCD camera detects the light flashes. Thus, the
detector enables one to image the electron’s kinetic energy and emission angles
simultaneously. The SES 2002 and SES 100 analysers have an acceptance angle
range of $\sim 14^\circ$ and $\sim 7^\circ$ respectively, leading to angular resolutions of $0.2^\circ$ and
$0.3^\circ$, respectively.

**Low energy electron diffraction (LEED)**

In this subsection, a brief description of low energy electron diffraction (LEED)
is given. This technique is used to study single crystalline surfaces by means of
back scattering of monochromatic electrons. The electrons with a energy of typ-
ically 20 to 200 eV are ejected from an electron gun and are back-scattered by the
atoms on the surface of the sample. These backscattered electrons then are de-
tected as bright spots on a fluorescent screen. If these electrons satisfy the Bragg
condition $n\lambda = 2d \sin \theta$ then constructive and destructive interference results in
the appearance of a diffraction pattern.

LEED is a surface sensitive technique like ARPES, since the electrons have
similar kinetic energy to the photoelectrons and thus a similarly short inelastic
mean free path. The diffraction pattern yielded by LEED reflects the symmetry
of the 2D reciprocal lattice belonging to the surface layer.

Before doing any ARPES measurements it is worthwhile to do LEED first
because with LEED one can immediately get an impression of the quality of
the sample (for example: to judge whether the sample has a superstructure or
whether the sample is tilted). Another advantage of using LEED before doing
ARPES is to quickly align the sample, so as to know how to align the energy
analyser’s angular dispersive direction in a particular orientation in reciprocal
space.

**Sample preparation**

The vast majority of the single crystal Bi2212 samples (both pristine and lead
doped) used in this work were grown using the optical floating zone method
by Dr. Yingkai Huang, the crystal grower in our institute at the University of
Amsterdam. For the ARPES measurements presented in Chapter 3, part of the
samples were kindly provided by Dr. Helmuth Berger from the Institute of
Physics of Complex Matter, EPFL, Lausane, Switzerland.

In order to obtain modulation-free single crystals, they were doped with lead
Pb$_x$Bi$_{2-x}$Sr$_2$CaCu$_2$O$_{8+\delta}$ with $x \sim 0.4$). To vary the doping level (by varying
δ), the newly grown crystals (known as “as grown” or AG) are subjected to a post-annealing treatment in order to add or remove oxygen from the crystal and therefore change the doping level. Annealing in flowing oxygen is more likely to add oxygen to the crystal and hence overdope the crystal, while annealing in flowing Ar or N\textsubscript{2} will take oxygen from the sample and thus tend to underdope it. For the measurements presented in Chapters 4 and 5, overdoped samples with $T_C$’s of 78 K, 80 K, and 84 K were used.

All Bi2212 crystals were cleaved in vacuum using loops made from adhesive tape. Only cleavage surfaces that were shiny, flat and non-leafy, and which gave high quality LEED patterns, were used to do the ARPES measurements.

2.2.3. The data analysis method

This section discusses how to present the measured signal and how to do the analysis of the ARPES spectra, so as to enable the extraction of important quantities such as quasiparticle lifetime and dispersion in an evident and robust manner.

In an ARPES measurement, photons of fixed energy $h\nu$ and polarisation are used. The experiment itself comprises the measurement of the number of photoelectrons per time interval as a function of both their kinetic energy and emission angle with respect to the sample normal. As discussed in an earlier subsection, the electron energy analysers used in the course of this thesis yield a simultaneous measurement of the photoelectron intensity as a function of ki-
netic energy and along a line scan in $k_x$ and $k_y$, the position and orientation of
which with respect to the 2D Brillouin zone can be set by the values of the polar
($\theta$) and azimuthal ($\phi$) angles via the cryo-manipulator.

Fig. 2.26(a) shows the three dimensional ARPES data set: intensity as a function of parallel momentum (the aforementioned line scan in $k_x$, $k_y$) and the kinetic energy of the detected photoelectrons. This data is recorded along the nodal line ($\Gamma Y$) in the first BZ of OD Bi2212, a cut which is shown schematically in the inset to panel (d) of Fig. 2.26. As mentioned in the discussion about the ARPES basic principles, the measured signal is made up of different contributions which one should take into account correctly when the data analysis is performed. For example, one should aware of the presence of the inelastic background due to secondary electrons as shown in Fig. 2.26(c). Consequently, one of the steps in analysing ARPES data can be the subtraction of the background.

Before we discuss the background subtraction procedure, it is worthwhile to describe a basic unit of ARPES data obtained from an angle multiplexing analyser. The middle panel of Fig. 2.27 shows the projection of the 3D ARPES data which is called the EDM, or energy distribution map. Slicing such a data set parallel to the momentum axis yields an MDC (momentum distribution curve), a constant energy quantity. Slicing parallel to the $E$ axis gives the EDC (energy distribution curve), which is to a good approximation a constant $k_\parallel$ quantity.

The EDM shown in Fig. 2.27 is therefore composed of a large number of EDC’s each of which has been recorded on a different angular channel on the detector. As differences in detector efficiency are averaged out across the energy direction by sweeping the spectrum across the detector, there only remains the necessity for a normalisation across the angular direction of the detector i.e. from one EDC to the next. A common procedure is to normalise the EDC’s for different emission angles to the intensity for the unoccupied states above the Fermi level, as this intensity comes from excitation of deep lying levels excited with higher order light and thus is, to a first approximation, angle independent. Alternatively, one can use a reference EDM from a polycrystalline gold film for the normalisation.

To determine the background to be subtracted from the measured MDC recorded along the $\Gamma Y$ line (nodal direction) shown in Fig. 2.26(d), a line is drawn from the lowest intensity ($U$) to another lowest intensity point ($O$). $U$ is located at $k > k_F$ therefore for any $k_x$ and $k_y$ value, there is no occupation for $E \leq E_F$. $O$ is located in the occupied states ($E < E_F$) yet at that $k_x$, $k_y$ value there is no band
Figure 2.27: Approaches toward analysing ARPES data. The EDM, energy distribution map, is a two dimensional representation of ARPES data as a function of energy and a parallel component of the photoelectron momentum. Analysing a constant energy cut of the EDM graph will yield the MDC (right panel) while analysing a constant momentum cut will yield the EDC or energy distribution curves (left panel). The inset in the MDC panel shows the experimental nodal cut through $k$-space that gave rise to the pictured EDM.

Another way to represent the ARPES data is as a constant energy plot versus $k_x$ and $k_y$. This is called an MDM (momentum distribution map). As an example one can refer to the Fig. 3.1 which represents a Fermi surface map recorded from overdoped PbBi2212.

The EDC line shape (Fig. 2.27, left) shows a non-trivial form which makes data analysis based on EDC’s more complicated. The asymmetric shape is introduced by the Fermi function $f(\omega)$ as it cuts the spectral function in the positive $\omega$ region. Another factor behind the complicated EDC line shape comes from the non-trivial $\omega$ dependence of the self-energy as given by Eqn. (2.30), yielding a non-Lorentzian shape of the spectral function $A(k, \omega)$. The latter constraint forces one to model the self-energy in order to simulate the EDC and therefore makes the EDC analysis itself dependent on the details of the self-energy model used.

On the contrary, the MDC line shape is simpler since it resembles a Lorentzian lineshape. Indeed, close to the Fermi level the dispersion can be considered linear such that for $k$ near $k_F$, the bare dispersion can be approximated as $\varepsilon_k \simeq v_F^0 (k - k_F)$, where $v_F^0 = \frac{\partial \varepsilon}{\partial k}$ is the bare Fermi velocity. Hence, from Eqn. (2.30), it is easy to see that the MDC has a Lorentzian line shape which is centered at $k = k_F + [\omega - \Sigma'(\omega)]/v_F^0$ and has half-width (HWHM) $W_M = |\Sigma''(\omega)|/v_F^0$. The peak position will give one point in the renormalised disper-
sion, while its half-width describes the life time of the quasiparticles and is proportional to the imaginary part of the self-energy. Note that such an analysis is valid in a regime without a (superconducting) energy gap.