Photoemission and magnetic response in the bipolaronic superconductor

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Photoemission and magnetic response in the bipolaronic superconductor

by

C.J. Dent

A Doctoral Thesis
submitted in partial fulfilment of the requirements
for the award of the degree
Doctor of Philosophy
of
Loughborough University

Supervisor: Professor A.S. Alexandrov

April 2001

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Abstract

A theory of angle-resolved photoemission (ARPES) in doped charge-transfer Mott insulators is developed taking into account the realistic band structure, (bi)polaron formation due to the strong electron-phonon interaction, and a random field potential. We derive the coherent part of the ARPES spectra with the oxygen hole spectral function calculated in the non-crossing (ladder) approximation and with the exact spectral function of a one-dimensional hole in a random potential. On the basis of this theory, explanations are proposed for several features of the ARPES spectra taken from the cuprate superconductors. These include the polarization dependence and spectral shape in YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$. The theory is compatible with the doping dependence of kinetic and thermodynamic properties of the cuprates as well as with the d-wave symmetry of the superconducting order parameter.

The scattering cross section of a Coulomb potential screened by a charged Bose gas (CBG) is calculated both above and below the Bose-Einstein condensation temperature, using the variable phase method. In contrast with the BCS superconductor, the screened scattering potential and quasiparticle lifetime are found to be very different in the superconducting and normal states. We apply the result to explain the appearance of a sharp peak in the ARPES spectra in some cuprates below the superconducting transition.

The charged Bose gas model for the upper critical field in the cuprates is extended to explain the crossing point in the curves of induced magnetization divided by the square root of field against temperature in the less anisotropic cuprates. This model has already been shown to provide a parameter-free expression for $T_c$ in a wide range of cuprates. We compare our results with experiment in YBa$_2$Cu$_3$O$_{7-\delta}$. 

Acknowledgements

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Chapter 1

Introduction

The Bose-Einstein condensation (BEC) of electron pairs was first used as an explanation for superconductivity in a specific system by Ogg in 1946 [1]. In this letter he claimed to have observed superconductivity in a very dilute solution of sodium in liquid ammonia. Unfortunately, Ogg's claimed results have not been verified elsewhere. He did however postulate that this 'superconductivity' was due to the condensation of bound electron pairs present in the solution [2], referring to F. London's discussion of BEC in the context of superfluidity [3].

The charged Bose gas (CBG) was first proposed as the basis for a theory of superconductivity in a proven superconductor by Schafroth in 1954-55 [4]. He demonstrated that the ideal CBG exhibits many of the equilibrium properties of a superconductor, but found some differences, e.g. the response to an external magnetic field and the discontinuity of the specific heat at the transition in the CBG. In any case, in 1957 Bardeen, Cooper and Schrieffer published their famous paper [5] and Bose condensation disappeared as a model for a real superconductor for several decades.

In 1981, Alexandrov and Ranninger published a pair of papers [6] predicting that superconductivity could occur in a system of bipolarons (electrons or holes bound into real space pairs by a strong electron-phonon interaction.) At the time, no candidate materials for this behaviour had been discovered, but their work is now the basis of one of the many theories of high-temperature superconductivity in the cuprates [7]. In
the next Chapter, we briefly discuss the BCS theory and some of the disagreements between its predictions and experiment in the cuprates. We then describe the bipolaron theory of superconductivity, which can be regarded as the extension of the BCS theory to the case of strong electron-phonon coupling, and in Chapters 3-6 we derive several new applications of the theory and compare them with experiment. Finally, in Chapter 7, we present our conclusions and offer suggestions for further research based on the work presented here.
Chapter 2

Bipolaronic superconductivity

2.1 Introduction - breakdown of the BCS theory in the cuprates

The BCS theory was developed in the 1950s to describe the superconductors which were then known. It is based on a Fermi liquid normal state, and an interaction with a Boson field (e.g. phonons.) Bardeen, Cooper and Schrieffer showed that via the interaction with phonons, electrons near the Fermi level may attract each other. Within the BCS picture, superconductivity is due to the formation of pairs of electrons with equal and opposite momenta (Cooper pairs.) An important feature of the theory is that the pair formation temperature and the superconducting critical temperature are one and the same. This is in contrast to the mechanism for superfluidity in He^4, where bosons (i.e. helium atoms) exist above the superfluid temperature, and the superfluidity is related to Bose-Einstein condensation.

The BCS/Fermi liquid theory predicts many experimental properties of classical low-temperature superconductors, some of which are listed in Table 2.1. Among these is a gap in the single-particle density of states at the Fermi energy, which may be observed in tunneling experiments. This gap is due to the binding energy of the paired electrons near the Fermi level. The BCS theory predicts that the gap at zero temperature will be
3.5k_BT_c, where T_c is the critical temperature, that the gap decreases to zero as \((T_c - T)^{1/2}\) as \(T \to T_c\) from below, and that there is no gap in the normal state as there are no pairs.

One of the other famous BCS predictions is the isotope effect on T_c. This arises from the fact that changing the mass of the ions in the crystal changes the phonon frequency, which in turn affects the critical temperature. The 'isotope exponent' \(\alpha\) is defined as

\[
\alpha = - \frac{d \ln T_c}{d \ln M},
\]

where \(M\) is the ion mass (i.e. \(T_c \propto M^{-\alpha}\)). The BCS theory predicts \(\alpha = 1/2\).

As its derivation is independent of the precise nature of the Fermions in the system or the Bosons mediating their interaction, the BCS theory is rather universal. As well as describing superconductivity in many superconducting metals and alloys, it can also be applied to superfluidity in He\(^3\) (\(T_c\) a few mK) and possibly atomic nuclei (\(T_c \sim 10^{10}\)K) [8]. Thus after the discovery, particularly in view of the fact that no other mechanism was generally accepted as the origin of superconductivity in a real material, it was natural to think that the explanation for cuprate superconductivity would be BCS-like as well. Only experiment could say whether this was correct, and it has become clear that cuprate superconductivity is not BCS-like (at least not in any trivial sense), Table 2.1.

In this chapter, we present an overview of the bipolaron theory of superconductivity developed by Alexandrov and Mott [7, 9]. We derive from first principles the polaron and bipolaron Hamiltonians, and then go on to discuss the bipolaron theory as applied to the cuprates, including several examples of application to experiment.

### 2.2 The polaronic Hamiltonian

#### 2.2.1 The Fröhlich Hamiltonian

Our starting point is the Hamiltonian describing the interaction of electrons with a crystal lattice:

\[
H = H_0 + H_{e-ph},
\] (2.2)
### Table 2.1: BCS/Fermi Liquid (FL) predictions and experimental results for high-$T_c$ copper oxides.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>BCS/FL prediction</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T &lt; T_c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMR $1/T_1$</td>
<td>coherent peak</td>
<td>absent</td>
</tr>
<tr>
<td>Isotope effect</td>
<td>$\alpha = 0.5$ or less</td>
<td>$-0.013 &lt; \alpha &lt; +1.0$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>decrease</td>
<td>enhancement</td>
</tr>
<tr>
<td>Gap</td>
<td>$3.5T_c$</td>
<td>$7 - 8T_c$ (for $T_c = 90K$)</td>
</tr>
<tr>
<td>$T &gt; T_c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hall Ratio</td>
<td>constant</td>
<td>$\sim 1/T$</td>
</tr>
<tr>
<td>Korringa ratio $1/T_1T$</td>
<td>constant</td>
<td>temperature dependent</td>
</tr>
<tr>
<td>Thermopower</td>
<td>$\sim T$, small</td>
<td>nonlinear, large</td>
</tr>
<tr>
<td>Infrared conductivity</td>
<td>Drude-law</td>
<td>mid-infrared maxima</td>
</tr>
</tbody>
</table>

Here

$$H_0 = \sum_{k,n,s} \xi_{k,n,s} c_{k,n,s}^\dagger c_{k,n,s} + \sum_{q,\nu} \omega_{q,\nu} \left( d_{q,\nu}^\dagger d_{q,\nu} + \frac{1}{2} \right)$$

(2.3)

describes independent Bloch electrons and phonons with $k, n, s$ the electron Bloch momentum, band number and spin, $q, \nu$ the phonon momentum and branch, $\xi_{k,n,s} = E_{k,n,s} - \mu$ the band dispersion, $\omega_{q,\nu}$ the phonon frequency, $c_{k,n,s}$ the electron annihilation operator, $d_{q,\nu}$ the phonon annihilation operator and $\mu$ the chemical potential. Here and throughout this thesis we use units where $\hbar = 1$.

The electron-phonon interaction is

$$H_{e-ph} = \frac{1}{\sqrt{2N}} \sum_{k,q,n,n',\nu,s} \gamma_{n,n'}(q,k,\nu) \omega_{q,\nu} c_{k,n,s}^\dagger c_{k-q,n',s} d_{q,\nu} + h.c.$$  

(2.4)

with a dimensionless matrix element

$$\gamma_{n,n'}(q,k,\nu) = -\frac{N}{M^{1/2} \omega_{q,\nu}^{3/2}} \int d\Omega (e_{q,\nu} \cdot \nabla v(r)) \psi_{k,n,s}(r) \psi_{k-q,n',s}(r),$$

(2.5)

where $N$ is the number of ions in the crystal, $M$ the ionic mass, $e_{q,\nu}$ a unit vector representing the phonon polarisation, $v(r)$ is the interaction potential of an electron with a single ion, and $\psi_{k,n,s}(r)$ a Bloch wavefunction.
CHAPTER 2. BIPOLARONIC SUPERCONDUCTIVITY

If the matrix element depends only on the momentum transfer, i.e.

$$\gamma_{n, n'}(q, k, \nu) = \gamma(q, \nu), \quad (2.6)$$

then we have the Fröhlich Hamiltonian.

2.2.2 From Fröhlich to polarons

Due to the self-trapping of the electrons, it is natural in the strong coupling regime to use the Wannier (site) representation:

$$c_i = \frac{1}{\sqrt{N}} \sum_k e^{ik\cdot m} c_{k,s}, \quad (2.7)$$

where the quantum number $i = (m, s)$ includes both site position $m$ and electron spin $s$. The Hamiltonian is then

$$H = \sum_{i,j} (T(m - n) \delta_{i,s'} - \mu \delta_{i,j}) c_i^\dagger c_j + \sum_{q,i} \omega_q \tilde{n}_i (u_i(q) d_q + h.c.) \quad (2.8)$$

$$+ \frac{1}{2} \sum_{i,j} V_c(m - n) c_i^\dagger c_j^\dagger c_j c_i + \sum_q \omega_q \left( d_q^\dagger d_q + \frac{1}{2} \right),$$

with bare hopping integral

$$T(m) = \frac{1}{N} \sum_k E_k e^{ik\cdot m}, \quad (2.9)$$

electron-phonon interaction matrix element

$$u_i(q) = \frac{1}{\sqrt{2N}} \gamma(q) e^{ik\cdot m}, \quad (2.10)$$

and Coulomb interaction

$$V_c(m) = \frac{1}{N} \sum_q \frac{4\pi e^2}{\varepsilon q^2} e^{ik\cdot m}. \quad (2.11)$$

In the above, $i = (m, s), j = (n, s')$, and the occupation number $\tilde{n} = c_i^\dagger c_i$, and a single electron band is considered.

In the strong coupling regime, $\lambda > 1$, it is convenient to make the Lang-Firsov canonical transformation [10], which diagonalises the Hamiltonian in the infinite coupling $\lambda \rightarrow \infty$ limit:

$$\tilde{H} = e^S H e^{-S}, \quad (2.12)$$
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with

\[ S = \sum_{q,i} n_i(u_i(q)d_q - h.c.) \]  

(2.13)

The transformed electron and phonon operators are

\[ \tilde{c}_i = c_i \exp \left( \sum_q u_i(q)d_q - h.c. \right) \]  

(2.14)

and

\[ \tilde{d}_q = d_q - \sum_i n_i u_i(q). \]  

(2.15)

From Eq. 2.15, the physical interpretation of the Lang-Firsov transformation is that it shifts the equilibrium positions of the ions. The transformed Hamiltonian is

\[ \tilde{H} = \sum_{i,j} (\delta_{ij} - \mu \delta_{ij})c_i^\dagger c_j - E_p \sum_i n_i \]

\[ + \frac{1}{2} \sum_{i,j} v_{ij} c_i^\dagger c_j^\dagger c_j c_i + \sum_q \omega_q \tilde{d}_q^\dagger \tilde{d}_q \]  

(2.16)

where the new hopping integral (now dependent on the phonon variables) is

\[ \delta_{ij} = T(m - n)\delta_{s,s'} \exp \left( \sum_{q,i} [u_i(q) - u_j(q)]d_q - h.c. \right), \]  

(2.17)

the new polaron-polaron interaction is

\[ v_{ij} = V_c(m - n) - 2 \sum_q \omega_q(u_i(q)u_j^*(q)), \]  

(2.18)

comprising the Coulomb repulsion and an additional attractive term via a non-retarded lattice deformation, and the polaron level shift is

\[ E_p = \frac{1}{2N} \sum_{q,v} \gamma^2(q,v)\omega_{q,v}. \]  

(2.19)

As it stands, the Hamiltonian may be diagonalised exactly if the hopping matrix element is zero. The solution then consists of completely localised polarons with an effective non-retarded interaction, Eq. 2.18, and independent phonons. In order to treat the problem for finite hopping (but still in the strong-coupling \( \lambda > 1 \) regime), one can make a perturbation expansion in \( 1/\lambda \) [11]. Due to degeneracy, terms of the first order in \( T(m) \) should be included in the zero-order Hamiltonian \( H_0 \):

\[ H_0 = \sum_{i,j} (\sigma(m - n) - \mu \delta_{ij})c_i^\dagger c_j + \sum_q \omega_q \tilde{d}_q^\dagger \tilde{d}_q. \]  

(2.20)
Here

\[ \sigma(m - n) = \langle \hat{\sigma}_{ij} \rangle = T(m - n) \delta_{ss'} \exp \left[ -g^2(m - n) \right] \]  

(2.21)

is the hopping matrix element averaged with the equilibrium phonon distribution,

\[ g^2(m) = \frac{1}{2N} \sum_q \gamma^2(q) \coth \left( \frac{\omega(q)}{2T} \right) \left[ 1 - \cos(q \cdot m) \right] \]  

(2.22)

and \( T \) is the temperature. For clarity we have omitted the phonon branch \( \nu \). Note that the atomic level is renormalised so that \( T(0) = -E_p \). The interaction term in the Hamiltonian \( \tilde{H} = H_0 + H_{\text{int}} \) is then the sum of the residual polaron-phonon interaction \( H_{p-ph} \) and the polaron-polaron interaction \( H_{p-p} \):

\[ H_{\text{int}} = H_{p-ph} + H_{p-p}, \]  

(2.23)

with

\[ H_{p-ph} = \sum_{i,j} \left[ \hat{\sigma}_{ij} - \sigma(m - n) \right] c_i^\dagger c_j \]  

(2.24)

and

\[ H_{p-p} = \frac{1}{2} \sum_{i,j} \omega q_i c_i^\dagger c_j^\dagger c_j c_i. \]  

(2.25)

Due to the translational symmetry of the problem, the unperturbed Hamiltonian \( H_0 \) is diagonal in the Bloch representation:

\[ H_0 = \sum_{k,s} (\epsilon_k - \mu) c_{k,s}^\dagger c_{k,s} + \sum_q \omega q \left( d_{q}^\dagger d_{q} + \frac{1}{2} \right), \]  

(2.26)

with the polaron band dispersion

\[ \epsilon_k = \sum_m \sigma(m) e^{i k \cdot m}. \]  

(2.27)

Thus the polaronic bandwidth \( \omega \) has been exponentially reduced compared with the bare electronic bandwidth \( D \),

\[ \omega = D e^{-g^2}, \]  

(2.28)

where \( g^2 \) is obtained from Eq. 2.22 with nearest neighbour hopping \( |m| = a \). Physically, this increase in the effective mass is due to the phonon cloud which surrounds a small polaron.

We note in passing that as the polarons obey Fermi statistics, a BCS-like polaronic superconducting state may be obtained from the above Hamiltonian [7].
2.3 Bipolarons and superconductivity

2.3.1 Bipolaron formation

In the limit of strong electron-phonon coupling, $g^2$ is large, and the polaron-polaron interaction becomes attractive. In general therefore the attractive energy of two polarons is greater than the polaron bandwidth, and there is an instability towards bipolaron formation.

The situation may be treated perturbatively using the new small parameter $w/\Delta$ where $\Delta \sim 2g^2\omega$ is the bipolaron binding energy (which is of the same order as the strength of the attraction) [6]. We thus rewrite the Hamiltonian as

$$\hat{H} = H_0 + H_{\text{pert}}$$

(2.29)

where the unperturbed Hamiltonian represents immobile bipolarons and free phonons,

$$H_0 = \frac{1}{2} \sum_{i,j} v_{ij} c_i^\dagger c_j^\dagger c_j c_i + \sum_q \omega_q \left( d_q^\dagger d_q + \frac{1}{2} \right),$$

(2.30)

and the perturbation represents polaron tunneling,

$$H_{\text{pert}} = \sum_{i,j} \delta_{ij} c_i^\dagger c_j.$$  

(2.31)

In the following, we shall treat the case of on-site bipolarons, where the two polarons forming the bipolaron occupy the same site. In this case, due to the Pauli principle, the only way for a bipolaron to hop is for one of the polarons to hop onto an adjacent site to form a virtual inter-site pair, and then for the other to follow it. The other possibility is an inter-site bipolaron, where the two polarons are on neighbouring sites, which is believed to be relevant in the cuprates. In this second case, the bipolaron moves around the lattice by alternate hopping of the polarons, as one might move a heavy filing cabinet by 'walking' it.

If $\Delta \gg w$, the ground state consists solely of bound bipolarons. We therefore make another canonical transformation which removes the bipolaron-breaking $c_i^\dagger c_j^\dagger c_i c_j$ term in the Hamiltonian. This leaves as the leading order perturbation term the second-order one representing simultaneous hopping of two polarons, i.e. the hopping of an on-site
bipolaron. The transformation is given by:

\[(H_b)_{f,f'} = \left( e^{S_2} \tilde{H} e^{-S_2} \right)_{f,f'} \]  
(2.32)

with

\[ (S_2)_{f,p} = \sum_{i,j} \frac{\langle f | \hat{c}_i \hat{c}_j^+ | p \rangle}{E_f - E_p} \]  
(2.33)

where \(E_{f,p}\) and \(\langle f | p \rangle\) are the energy levels and eigenstates of \(H_0\).

Taking into account that \(H_b\) operates on the subspace of the eigenstates of the original Hamiltonian in which all polarons are bound into bipolarons, we may rewrite the bipolaron Hamiltonian in terms of (singlet) bipolaron creation, \(b_m^+ = c_{m,\uparrow}^t c_{m,\downarrow}^t\) and annihilation operators (here as always \(m\) is the coordinate of a lattice point):

\[
H_b = -\sum_m \left( \Delta + \frac{1}{2} \sum_{m'} \nu_{m,m'}^{(2)} \right) n_m \\
+ \sum_{m \neq m'} \left( -t_{m,m'} b_m^+ b_{m'} + \frac{1}{2} \nu_{m,m'} n_m n_{m'} \right),
\]  
(2.34)

where \(n_m = b_m^+ b_m\) is the bipolaron occupation number operator,

\[
\nu_{m,m'}^{(2)} = 4\nu_{m,m'} + \nu_{m,m'}^{(2)},
\]  
(2.35)

is the bipolaron-bipolaron interaction, including the direct Coulomb repulsion and the attraction via phonons between pairs of polarons (both included in \(4\nu_{m,m'}\)), and a second-order repulsive correction

\[
\nu_{m,m'}^{(2)} = 2i \int_0^\infty dt \Phi_{m,m'}^{m,m}(t) \exp(-i\Delta t),
\]  
(2.36)

with

\[
\Phi_{m,n}^{m,m}(t) = \sigma^2(a) e^{-\sigma^2} \exp \left( \frac{1}{N} \sum_q |\gamma(q)|^2 \left[ 1 - \cos(q \cdot a) \frac{\cosh \left[ \frac{\omega_q (\frac{1}{2} \Gamma + t)}{\sinh \frac{\omega_q}{2T}} \right] \right] \right),
\]  
(2.37)

a real time multiphonon correlation function between nearest neighbour sites where \(a = m - n\). The physical origin of this repulsive correction is simple - a virtual hop of one part of a pair to an adjacent occupied site is forbidden by the exclusion principle.

The bipolaron hopping integral is as one expects of second order in the electron hopping integral \(T(m-n)\):

\[
t_{m,m'}^{(2)} = 2i \int_0^\infty dt \Phi_{m,m'}^{m,m}(t) \exp(-i\Delta t),
\]  
(2.38)
where the expression for $\Phi_{m,m'}^{n,m'n'}$ is the same as that for $\Phi_{m,n}^{n,m}$ apart from the second exponent having the opposite sign.

The bipolaron operators obey mixed Fermi-Bose commutation relations in the subspace of sites unoccupied or doubly occupied by polarons to which they are applied:

$$b_m b_m^\dagger + b_m^\dagger b_m = 1,$$  \hspace{1cm} (2.39)

(i.e. the exclusion principle is enforced on site by Fermi commutation relations) and

$$b_m b_m^\dagger - b_m^\dagger b_m = 0$$  \hspace{1cm} (2.40)

(i.e. Bose commutation relations between different sites.)

### 2.3.2 Nature of the bipolaronic ground state

Due to the mixed statistics of the bipolaron operators, it is convenient to transform to the 'pseudospin' representation \[6\). We rewrite the bipolaronic Hamiltonian as

$$H_b = -\mu \sum_m n_m + \sum_{m \neq m'} \left( \frac{1}{2} \delta_{m,m'} n_m n_{m'} - t_{m,m'} b_m^\dagger b_{m'} \right),$$  \hspace{1cm} (2.41)

where the energy of a single localised bipolaron is included in the definition of the bipolaron chemical potential $\mu$. We then make the substitution

$$b_m^\dagger = S_m^x - iS_m^y$$  \hspace{1cm} (2.42)

from which it follows that

$$n_m = \frac{1}{2} - S_m^z.$$  \hspace{1cm} (2.43)

$S_z = 1/2$ corresponds to an empty cell and $S_z = -1/2$ to a cell occupied by a bipolaron. The Hamiltonian transforms to the familiar anisotropic Heisenberg Hamiltonian

$$H_b = \mu \sum_m S_m^z + \sum_{m \neq m'} \left( \frac{1}{2} \delta_{m,m'} S_m^x S_{m'}^x - t_{m,m'} (S_m^z S_{m'}^y + S_{m'}^y S_m^y) \right).$$  \hspace{1cm} (2.44)

The chemical potential $\mu$ plays the role in the Heisenberg Hamiltonian of an external magnetic field. In the present application however, the 'magnetic field' is fixed by the total 'magnetisation' as the bipolaron density $n$ is conserved,

$$\frac{1}{n} \sum_m \langle S_m^z \rangle = \frac{1}{2} - n.$$  \hspace{1cm} (2.45)
If only nearest neighbour hopping is taken into account, there are two possibilities for the nature of the ground state of this system; one is 'ferromagnetic' (FM) where bipolarons are uniformly distributed over the lattice, and the other is 'antiferromagnetic' (AFM), where there are two sublattices with different densities. The AFM state only exists for boson density above a certain value:

$$n > n_c = \frac{1}{2} \left[ 1 - \sqrt{\frac{\bar{\vartheta} - t}{\bar{\vartheta} + t}} \right], \quad (2.46)$$

where $\bar{\vartheta} = (z/2)t_{mn}$, $t = z t_{mm}$, $m$ and $m'$ are nearest neighbour sites and $z$ is the coordination number of the lattice. For densities where it does exist, the AFM state is the actual ground state. A more detailed analysis of the Hamiltonian, including next neighbour hopping, has revealed other phases, including an incommensurate charge-ordered phase [12].

Alexandrov and Mott [7] have proposed that in real solids, the long-range Coulomb repulsion, as opposed to the hard-core interaction is the only relevant term for low energy kinetics and thermodynamics in real bipolaronic solids. It is therefore useful to map the bipolaronic Hamiltonian onto a charged Bose gas.

2.3.3 Mapping onto a charged Bose gas

We make the following transformation to a representation containing only Bose operators $a_m, a_m^\dagger$:

$$b_m = \sum_{k=0}^{\infty} \beta_k a_m^k a_{m+1}^k \quad (2.47)$$

$$b_m^\dagger = \sum_{k=0}^{\infty} \beta_k a_{m+1}^k a_m^k \quad (2.48)$$

with

$$a_m a_{m'}^\dagger - a_{m'} a_m^\dagger = \delta_{m,m'}. \quad (2.49)$$

The coefficients $\beta_k$ are determined by substituting Eqs. 2.47,2.48 into the bipolaron commutation relations Eqs. 2.39,2.40. The first few are:

$$\beta_0 = 1, \beta_1 = -1, \beta_2 = \frac{1}{2} + \frac{\sqrt{3}}{6}. \quad (2.50)$$
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We finally introduce the field bipolaron and boson operators

\[ \phi(r) = \frac{1}{\sqrt{N}} \sum_m \delta(r - m) b_m \] (2.51)

\[ \psi(r) = \frac{1}{\sqrt{N}} \sum_m \delta(r - m) a_m. \] (2.52)

The field operators transform as

\[ \phi(r) = \left( 1 - \frac{\psi^\dagger(r) \psi(r)}{N} + \frac{(1/2 + \sqrt{3}/6) \psi^\dagger(r) \psi^\dagger(r) \psi(r) \psi(r)}{N^2} + \ldots \right) \psi(r), \] (2.53)

and the bipolaronic Hamiltonian may then be written in the form

\[ H_b = - \int d \mathbf{r} d \mathbf{r}' \psi^\dagger(r) [t(r - r') + \mu] \psi(r') + H_{int}. \] (2.54)

Here

\[ H_{int} = H_t + H_s, \] (2.55)

where \( H_t \) is the dynamic part of the interaction

\[ H_t = \frac{1}{2} \int d \mathbf{r} d \mathbf{r}' \psi(r - r') \psi^\dagger(r') \psi(r) \psi(r') \] (2.56)

and \( H_s \) describes the kinematic hard core effects

\[ H_s = \frac{2}{N} \int d \mathbf{r} d \mathbf{r}' [\psi^\dagger(r) \psi^\dagger(r') \psi(r') \psi(r') + \psi^\dagger(r) \psi^\dagger(r) \psi(r) \psi(r')] + H^{(3)}, \] (2.57)

where

\[ t(r - r') = \sum_k (t - E_k) e^{ik \cdot (r - r')}, \] (2.58)

\[ \bar{v}(r - r') = \frac{1}{N} \sum_k \bar{v}_k e^{ik \cdot (r - r')}, \] (2.59)

\[ \bar{v}_k = \sum_{m \neq m'} \bar{v}_{m,m'} e^{ik \cdot (m - m')}. \] (2.60)

The term \( H^{(3)} \) is of higher order in the field operators. The essential physics of bipolarons is determined by the two-particle interaction, which includes the short range term \( H_s \) resulting from the hard-core effect. As \( \bar{v} \) already includes hard core effects, \( H_s \) may be absorbed into its definition.

We have now demonstrated that \( H_s \) is identical in leading order, if the carrier density is small enough, to the Hamiltonian of charged bosons tunneling in a band. Thus by making the Bogoliubov transformation one can show immediately that a system of bipolarons satisfies the Landau criterion for superfluidity and exhibits the Meissner effect \([7]\).
Figure 2.1: Unit cell of YBa$_2$Cu$_3$O$_7$. The common feature among all the cuprates is the CuO$_2$ plane with an apical oxygen in the next layer above the copper forming a series of ‘pyramids’. These are represented schematically in Fig. 2.2.

2.4 Polarons and bipolarons in the cuprates

In the earlier sections of this chapter, we have discussed purely theoretically how bipolaronic superconductivity can occur in a system with a strong electron-phonon interaction. We now go on to discuss the concrete application of this theory to the phenomenon of high-temperature superconductivity in the cuprates. There are many different cuprate superconductors, but they are all have a layered crystal structure, and they all have CuO$_2$ planes as part of that structure, Fig. 2.1.

In the above discussion of polarons and bipolarons we considered only the on-site bipolaron. The situation in the cuprates is rather different; numerical minimisation of the ground state energy without the kinetic energy term reveals that in the cuprate perovskite structure intersite pairing of an in-plane oxygen hole with an apex one is favourable [13]. In La$_2$CuO$_4$, the binding energy $\Delta = 0.119$eV. This bipolaron may tunnel from one cell to a neighbouring one by a direct single-polaron tunneling of the apical hole, Fig. 2.2. Here we derive the essential features of the bipolaron energy spectrum; for a complete derivation of the Hamiltonian, see Section 6.2 of [9].
Figure 2.2: Apex bipolaron tunneling in perovskites. The apical polaron tunnels from one apical oxygen to the next, and the basal can move between cells more easily as each of the cells shares a basal oxygen.

The bipolaron hopping integral $t$ may be obtained by projecting the Lang-Firsov transformed Hamiltonian $\tilde{H}$ onto the space of empty or doubly-occupied unit cells (i.e. the space containing only bipolarons.) The wavefunction of an apex bipolaron localised in the cell $m$ is:

$$|m\rangle = \sum_{i=1}^{4} A_i c_{i}^{\dagger} c_{\text{apex}}^{\dagger}|0\rangle,$$

where the sum is over in-plane $p_{x,y}$ orbitals in the cell, Fig. 2.2. If the in-plane hole is shared equally between the four plane orbitals $p_{x1}, p_{y2}, p_{x3}$ and $p_{y4}$, then the probability amplitudes $A_i$ are normalised to $|A_i| = 1/2$. While this is the case for an isolated CuO$_5$ pyramid, in the cuprate crystal structure the in-plane oxygen band wavefunctions must have the same symmetry as the point group of the crystal. In this case the combination of the oxygen orbitals may be different, e.g. the hole could be shared between $p_{x1}$ and $p_{x3}$ in which case $|A_1| = |A_3| = 1/\sqrt{2}$ and $A_1 = A_3 = 0$.

In the case where the basal hole is shared equally between the four oxygens, the transfer integral for bipolaron tunneling to a neighbouring cell is then

$$t = \langle m|\tilde{H}|m+a\rangle = \frac{1}{4} T_{pp'}^{\text{apex}} e^{-g^2},$$

where $T_{pp'}^{\text{apex}}$ is the single particle hopping integral between two apex ions,

$$g^2 = \frac{1}{2N} \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 [1 - \cos(q_xa)]$$

is the polaron band-narrowing factor, and $a$ is the in-plane lattice constant which equals
the distance between neighbouring apical sites. The in-plane hopping occurs more easily; as in the wavefunction of an in-plane hole the probability amplitude for each site is 1/2, this introduces the factor of 1/4 in Eq. 2.62. In the other case discussed in the previous paragraph, the factor of 1/4 would be replaced by 1/2, and the bipolaron would be even lighter.

Hence in the tight-binding approximation the bipolaron spectrum consists of two bands resulting from the $p_{x,y}$ apex polaron bands respectively:

$$E_k^X = -t \cos(k_x) + t' \cos(k_y)$$  \hspace{1cm} (2.64)

$$E_k^Y = t' \cos(k_x) - t \cos(k_y),$$  \hspace{1cm} (2.65)

where the in-plane lattice constant $a$ is set to 1, $t$ is the $(pp\sigma)$ hopping integral between $p$ orbitals of the same symmetry elongated in the same direction and $t'$ is the $(pp\pi)$ integral for hopping in the perpendicular direction. The ratio $t/t' = T_{pp}^{\text{apex}} / T_{pp}^{\text{apex}} = 4$ may be found from tables of hopping integrals in solids [18]. The two bands do not mix as $T_{pp,pp}^{\text{apex}} = 0$ for nearest neighbours. One feature specific to the inter-site perovskite bipolaron, as opposed to the on-site bipolaron discussed earlier, is that the bipolaron bandwidth is of the same order as the polaron one due to the different method of hopping. For a large part of the Brillouin zone near $(0, \pi)$ for the `$x$' and $(\pi, 0)$ for the `$y$' bipolaron, one can make the effective mass approximation

$$E_{k,x,y} = \frac{k_x^2}{2m_{x,y}} + \frac{k_y^2}{2m_{x,y}},$$  \hspace{1cm} (2.66)

with $k_{x,y}$ taken relative to the bottoms of the bands, $m_x = 1/t$ and $m_y = 4m_x$. This mass anisotropy has a significant impact under some circumstances, e.g. the Hall effect.

### 2.5 Relation to experiment

In this section, we discuss some of the experimental predictions which have been made from the bipolaron theory of cuprate superconductivity, with a particular emphasis on more recent applications. A summary of earlier work may be found in the two books on the subject by Alexandrov and Mott [7, 9]. Also, here we do not discuss in detail the experiments which have a direct bearing on this thesis; these will be presented in greater depth in the relevant chapters.
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Figure 2.3: Inter-site bipolaron energy bands (in this schematic representation each band extends between the two horizontal lines either side of its label.) The chemical potential above $T_c$ is below the bottom of the bipolaron band, and the condensate at the bottom of the band below $T_c$ is represented by the shaded region. As polarons exist as thermal excitations a minimum of $\Delta/2$ above the bottom of the bipolaron band even in the normal state there should be a reduction in the single-particle density of states at the ‘Fermi level’. For intersite bipolarons there is a triplet bipolaron band at a higher energy than the singlet one.

2.5.1 Pseudogap

Differently from the BCS case, in a bipolaronic superconductor, the pairs form above the superconducting $T_c$, and then the mechanism for superconductivity is Bose-Einstein condensation of preformed pairs. It is to be expected that at temperatures $T > \Delta/2$, where $\Delta$ is the bipolaron binding energy, the majority of carriers will be thermally excited single polarons, and below this temperature the majority of carriers will be bound bipolarons. There should therefore be observed at some temperature above $T_c$ a cross-over between different sets of properties. One of these will be a depression in the single-particle density of states below the crossover, Fig. 2.3.

This feature has been observed in many experiments, ranging from direct probes of the energy density of states such as single-particle tunneling [14] to others such as NMR [15] and specific heat [16]. Recently, it has become clear however that a different value
is found for the pseudogap in experiments such as single-particle tunneling as opposed to those which probe spin excitation such as NMR. This has been explained in terms of the different energies of pair breaking excitations and spin-flip excitations [17], Fig. 2.3.

2.5.2 d-wave order parameter

In any superconductor, the superconducting state is described by an order parameter (pair wavefunction.) Within the BCS approach, this necessarily has the same symmetry as the superconducting gap, but can be either s-wave (spherically symmetric) as in the original formulation or d-wave. The bipolaron case is rather different, as the bipolaron condensate wavefunction must be distinguished from the internal wavefunction of a single bipolaron [19].

In the case of the cuprates, as described above, the bipolaron energy spectrum has its minima at the points of the Brillouin zone $(\pm \pi, 0)$ and $(0, \pm \pi)$, and therefore it is these states into which the bipolarons condense. As these states are degenerate, the condensate wavefunction (order parameter) in the Wannier site representation is

$$\Psi_\pm (\mathbf{m}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}=(\pm \pi, 0),(0,\pm \pi)} b_\mathbf{k} \exp(-i \mathbf{k} \cdot \mathbf{m}) = \sqrt{\frac{x}{2}} \left[ \cos(\pi m_x) \pm \cos(\pi m_y) \right], \quad (2.67)$$

where $\mathbf{m} = (m_x, m_y)$ is the site coordinate and $b_\mathbf{k}$ is the bipolaron (boson) operator, which for the macroscopically occupied condensate states is a complex number. The two solutions $\Psi_\pm$ are physically identical as on may be mapped onto the other by the translation $(m_x, m_y) \rightarrow (m_x, m_y + 1)$. They both have d-wave symmetry, changing sign when the CuO$_2$ plane is rotated through $\pi/2$ about $(0,0)$ for $\Psi_-$ and $(0,1)$ for $\Psi_+$. It is important to recognise that this d-wave symmetry is entirely due to the bipolaron energy dispersion having its minimum at the Brillouin zone boundaries; if the minimum was at the $\Gamma$ point, the analogue of Eq. 2.67 would give s-wave symmetry. There is substantial evidence for a d-wave order parameter in the cuprates from phase-sensitive experiments, which has been reviewed by Annett et al [20].

One of the pieces of evidence for a d-wave order parameter reviewed in [20] is the linear temperature ($T$) dependence of the London penetration depth at low $T$. In an s-wave BCS superconductor, the deviation of the penetration depth $\lambda$ at low temperatures from
its value at $T = 0$ is exponentially small. If the cuprates were BCS superconductors, the linear dependence would imply a more complicated pairing symmetry. Within the bipolaron theory, this linear temperature ($T$) dependence may be explained by a model including the localisation of bipolarons in a random potential, independently of the symmetry of the order parameter [21]. This theory can explain both a linear increase and a linear decrease in $\lambda$ depending on the shape of the potential wells within the random potential. Increasing the temperature thermally excites bipolarons from states localised by disorder into the condensate. If the random potential exhibits the correct nature, this thermal excitation of bosons into the condensate may outweigh the thermal excitation of bipolarons out of the condensate, thus decreasing the penetration depth.

2.5.3 Single particle tunneling

To derive the single-particle conductance for Superconductor-Insulator-Normal metal (SIN) tunneling, one can apply a one-particle tunneling Hamiltonian describing the injection of an electron into a single hole polaronic state with matrix element $P_{k,\nu}$ or a bipolaronic state with matrix element $P_{k,\nu,\mu}$:

$$H_{\text{tun}} = \sum_{k,\nu} P_{k,\nu} a_k p_{\nu} + B_{k,\nu,\mu} a_k p_{\nu} a_{k+} b_{\mu} + h.c.,$$

(2.68)

Here $k, \nu, \mu$ are quantum numbers describing electrons in the tip of the probe (annihilation operator $a_k$), and hole polarons ($p_{\nu}$) and bipolarons ($b_{\nu}$) in the CuO$_2$ plane respectively. Physically, this means that an electron can tunnel into the superconductor either by 'filling' an unpaired hole or by filling one of the holes in a bipolaron, leaving an unpaired hole polaron, Fig. 2.4.

After making a series of approximations (Fermi golden rule, density of states in the tip approximately constant near the Fermi level, temperature smaller than other relevant energy scales, polaron and bipolaron matrix elements constant), the tunneling conductance is found to be

$$\sigma(V) = 4\pi e^2 N_{\text{tip}} \left[ D^2 \rho(-eV - \Delta/2) + xB^2 \rho(eV - \Delta/2) \right],$$

(2.69)

where $\rho(E)$ is the polaronic DOS, $x$ the bipolaron density per cell (proportional to the doping) and $N_{\text{tip}}$ is the density of states near the Fermi level in the tip. In the cuprates,
due to the in-plane anisotropy of the bipolaron bands, one can make a one-dimensional approximation to the density of states, and then introducing a random potential to represent disorder one obtains

\[ \sigma(V) \propto A \rho \left( \frac{2eV - \Delta}{\epsilon_0} \right) + \rho \left( \frac{-2eV - \Delta}{\epsilon_0} \right), \tag{2.70} \]

with \( \epsilon_0 \) an energy scale characterising the random potential and with the DOS of 1D hole in a random potential, which is derived in Appendix B:

\[ \rho(\xi) = \frac{4}{\pi^2} \times \frac{\text{Ai}(\xi)\text{Ai}'(\xi) + \text{Bi}(\xi)\text{Bi}'(\xi)}{[\text{Ai}^2(\xi) + \text{Bi}^2(\xi)]^2}. \tag{2.71} \]

It is clear that the gap \( \Delta \) in the above equation is independent of the pair wavefunction or order parameter, and depends instead on the difference between the bottoms of the polaron and bipolaron bands.

With a BCS-like mechanism and a \( d \)-wave order parameter one would expect to see \( \sigma = 0 \) only when \( V = 0 \), and a 'V-shaped' spectrum nearby. Many sets of data however show a full \( s \)-wave gap in the tunneling spectra, some very clearly (Fig. 2.5). This tunneling data, as well as a variety of other measurements [24], suggests that a theory where the
2.5.4 Parameter-free expression for $T_c$

One of the goals of any theory of superconductivity is to provide an expression for $T_c$ as a function of some well-defined parameters characterising the material. As in the bipolaron theory the mechanism of superconductivity is Bose-Einstein condensation, the critical temperature is determined by the bipolaron energy spectrum. As discussed earlier, making the effective mass approximation, the following result is obtained for the $x$ and $y$ bipolaron bands:

$$E_k^{x,y} = \frac{k_x^2}{2m_{x,y}} + \frac{k_y^2}{2m_{y,x}} + t_c [1 - \cos(k_z d)], \quad (2.72)$$

where $k_{x,y}$ are taken relative to the band minima at the $(\pi,0)$ and $(0,\pi)$ points of the Brillouin zone, $d$ is the interplane distance and $t_c$ is the interplane bipolaron hopping integral.
The condensation temperature of these bipolarons has recently been calculated [25]. Substituting the spectrum into the sum rule

$$\sum_{k,i=(x,y)}^{1} \frac{1}{\exp \left( \frac{E_k}{k_B T_c} \right) - 1} = n_B$$

(2.73)

one obtains:

$$k_B T_c = f \left( \frac{t_c}{k_B T_c} \right) \frac{3.31 h^2 (n_B/2)^{2/3}}{(m_x m_y m_c)^{1/3}},$$

(2.74)

where the coefficient $f$, dependent on the ratio of the c-axis hopping integral to the condensation temperature, is a correction for having made the effective mass approximation in the c-direction. It may be shown that provided $t_c / k_B T_c \geq 0.01$, $f$ is approximately 1. In this equation, one may eliminate the effective masses and the boson density in favour of the penetration depths and the Hall coefficient $R_H$ just above the transition by making the substitution:

$$\lambda_{ab} = \left[ \frac{m_x m_y}{8\pi n_B e^2 (m_x + m_y)} \right]^{1/2}$$

(2.75)

$$\lambda_c = \left[ \frac{m_c}{16\pi n_B e^2} \right]^{1/2}$$

(2.76)

$$R_H = \frac{1}{2cn_B} \times \frac{4m_x m_y}{(m_x + m_y)^2}.$$  

(2.77)

We then arrive at a parameter-free expression which can indicate how far cuprates are from the BEC regime:

$$T_c = 1.64 \left( \frac{e R_H}{\lambda_{ab}^4 \lambda_c^2} \right)^{1/3}.$$  

(2.78)

The theory has been compared with experiment for more than thirty different samples. For almost all samples, the experimental critical temperature agrees with the theoretical one to within the error in the penetration depths ($\sim 10\%$), Fig. 2.6. It is important to note that in order to obtain this agreement it is necessary to assume a two-band model. Indeed, the only samples in which agreement is very poor are several Zn-substituted YBCO samples. The authors of this theory have suggested that the Zn-doping removes the degeneracy between the bands, in which case the expression for $T_c$ should be multiplied by $2^{2/3}$. The theoretical estimates are then $T_c = 73, 57, 41K$, in good agreement with the measured $T_c = 68, 55, 46K$. 


**Figure 2.6:** Theoretical critical temperature compared with experiment for 
La$_{2-x}$Sr$_x$CuO$_4$ samples (squares), Zn-substituted YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_7$ (circles), 
YBa$_2$Cu$_3$O$_{7-\delta}$ (triangles) and HgBa$_2$CuO$_{4+\delta}$ (diamonds). For experimental references 
see [25].

2.5.5 Spin susceptibility

In a system of singlet bipolarons, the spin susceptibility is obviously due entirely to 
thermally excited polarons [26]. The polaron spin susceptibility is given by

\[
\chi_s(T) = -2\mu_B^2 \int_0^\infty dE N_p(E) \frac{\partial f_p}{\partial E},
\]

where \( f_p = [y^{-1/2} \exp(E/T + \Delta/2T) + 1]^{-1} \) is the polaron distribution function, \( y = \exp(\mu/T) \), \( \mu \) is the chemical potential, \( \mu_B \) the Bohr magneton and \( \Delta \) the bipolaron binding energy. As the polarons are not degenerate, one can make a classical Boltzmann approximation for the polaron distribution function. Also due to the large difference between the \( p\sigma \) and \( p\pi \) hopping integrals in the cuprates, a one-dimensional approximation for the density of states is applicable:

\[
N_p(E) \simeq \frac{1}{4\pi d a} \sqrt{\frac{m^*}{2E}},
\]

where \( d \) is the inter-plane distance and \( a \) the in-plane lattice constant. With these approximations, and calculating the chemical potential by taking into account the Anderson localisation of bipolarons due to a random potential [27], the spin susceptibility is

\[
\chi_s(T, x) = \frac{B_{so}}{\sqrt{T}} \exp \left(-\frac{\Delta}{2T}\right),
\]
Figure 2.7: Temperature dependence of the normal state susceptibility for La$_{2-x}$Sr$_x$CuO$_4$ (from [28]). The horizontal line marks the contribution from the core diamagnetic and Van Vleck paramagnetic susceptibility. The solid lines represent a fit by Müller et al using the bipolaron model.

where $x$ is the doping, $B_\infty \propto x^{1/2}(m^*/m_{ab}^{**})^{1/2}$, $m^* \approx m_c^*$ is the single polaron mass and $m_{ab}^{**}$ is the in-plane bipolaron mass.

Müller et al have used the above expression to fit the temperature dependence of the spin susceptibility of La$_{2-x}$Sr$_x$CuO$_4$ for a range of doping levels [28], Fig. 2.7. In the same paper, they also analysed the doping dependence of the bipolaron binding energies used in the fits, and found them to be consistent with theoretical predictions, Fig. 2.8.

### 2.5.6 Effective mass and anisotropy

As described above, the effective hopping integral for the inter-site bipolarons along the CuO$_2$ planes in the cuprates is

$$ t_{ab}^{**} = \frac{1}{4} t_{ab}^{anex} \exp(-g^2). $$

In the $c$-direction, however, the hopping integral must be calculated in the same way as for the on-site bipolaron as the intersite hopping mechanism is not available [9]:

$$ t_{c}^{**} = 2t^2 \sqrt{\frac{2\pi}{\hbar \omega \Delta}} \exp \left[ -2g^2 - \frac{\Delta}{\omega} \left( 1 + \ln \frac{2g^2 \omega}{\Delta} \right) \right] $$

(2.83)
Figure 2.8: Doping dependence of the bipolaron binding energy $\Delta$ (triangles) and theoretical prediction (solid lines) [28]. The experimentally obtained $\Delta$ agrees well with the theory ($\sim 1/x$) for $0.06 \leq x \leq 0.15$, where most of the data is taken.

with $t_c$ the bare single-particle hopping integral in the $c$-direction, $\omega$ the characteristic phonon frequency and $\Delta$ the bipolaron binding energy. Taking into account that the bipolaron binding $\Delta \propto 1/\delta$ where $\delta$ is the doping, the doping dependence of the anisotropy is [29]

$$\gamma = \sqrt{\frac{m^b_{22}}{m^b_{11}}} = \left[ \frac{a_1}{\delta^{1/2}} \exp \left( \frac{a_2}{\delta} \right) \right]$$  \hspace{1cm} (2.84)

where $a_{1,2}$ are independent fitting parameters and $m^b_{ab,c}$ are the components of the bipolaron effective mass. A fit of this expression to experimental data is shown in Fig. 2.9.

Zhao et al have also used the above expressions for the effective mass and anisotropy to investigate the effect on the anisotropy when $^{16}$O is substituted by $^{18}$O in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [30, 31]. In these papers, they use values of the various parameters taken from other experiments to predict both the value of the anisotropy and the isotope effect on it using the bipolaron theory, and find good agreement between this and their own data. They also deduced from the isotope shift in $m^*_{ab}$ that $g^2 = 2.8$ [32], which agreed with the value they deduced from earlier optical conductivity measurements [33].
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Figure 2.9: Circles: Anisotropy as a function of doping in HgBa$_2$CuO$_{4+\delta}$ taken from magnetisation measurements [29]. Solid line: Fit from Eq. 2.84.

2.5.7 Electronic specific heat

In a BCS superconductor, there is a well-defined step in the specific heat at the transition temperature, and this moves downwards in temperature with the resistive transition when a magnetic field is applied. Most high-$T_c$ cuprates however show a sharp 'λ' type peak in the specific heat at the critical temperature in zero field, and the effect of magnetic field on this peak is to reduce its height but leave its temperature largely unchanged [34]. A possible explanation of this effect in terms of the charged Bose gas was proposed by Alexandrov et al [35].

In a Bose system, the specific heat is calculated from the temperature derivative of the energy:

$$C(T, H) = \frac{d}{dT} \int d\epsilon \rho(\epsilon) e n_B(\epsilon), \quad (2.85)$$

where $\rho(\epsilon)$ is the density of states and $n_B(\epsilon)$ the Bose distribution function. The result is

$$C(T, H) = \frac{<\epsilon^2>}{T^2} - \frac{<\epsilon>^2}{T^2} <\nu^2> \quad (2.86)$$

where

$$<\epsilon^\nu> = -T \int d\epsilon \rho(\epsilon) \frac{\partial n_B(\epsilon)}{\partial \epsilon} \epsilon^\nu. \quad (2.87)$$
Figure 2.10: Change in the specific heat of CBG in an applied magnetic field [35] compared with experiment [36] in Hg-1223. The lines correspond to $H = 0, 0.52, 2T$.

In the ideal 3D charged Bose gas, the density of states in zero magnetic field is given by

$$\rho(\epsilon) = \frac{m^{3/2} \sqrt{\epsilon}}{\sqrt{2\pi^2}},$$

where $m = (m_{ab}^2 m_c)^{1/3}$, and in a magnetic field by

$$\rho(\epsilon, H) = \frac{m^{3/2} \omega_H}{2\sqrt{2\pi^2}} \sum_{n=0}^{\infty} \left[ \epsilon - \omega_H(n + \frac{1}{2}) \right]^{-1/2},$$

where $\omega_H = 2eH/m_{ab}$ is the cyclotron frequency. Despite the fact that due to the one-dimensional density of states in the lowest Landau level the 3D ideal CBG cannot be condensed in a magnetic field, the authors of [35] deliberately chose to retain it as a model for this experiment to test their premise that the specific heat in a magnetic field is unrelated to the superconducting transition. The results of their calculations are shown in comparison with experiment in Fig. 2.10.

2.6 Summary

In this chapter, we have provided an overview of the bipolaron theory of superconductivity, and discussed a number of recent applications to experiment. The theory can
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explain many of the properties of the high-\(T_c\) cuprates, including the pseudogap, a \(d\)-wave order parameter, the tunneling spectra, the spin susceptibility, the effective mass anisotropy and the electronic specific heat near the transition. The theory also provides a parameter-free expression for the superconducting critical temperature. It is interesting to note that the mechanism for superconductivity in the theory is phononic, and in a sense the theory is the strong-coupling extension of the BCS theory, where the electron-phonon interaction is strong enough to bind single carriers into real space pairs.

There are some important experiments which we have omitted from this introductory chapter. These include angle-resolved photoemission and observations of the upper critical field and unusual diamagnetic effects, which motivate the original work in this thesis, and which will be discussed in greater detail in the relevant chapters.
Chapter 3

ARPES in bipolaronic superconductors

3.1 Introduction

In Chapter 2, we discussed how single-particle tunneling experiments may be used to measure the energy density of states in the cuprates. Recently, due to increasingly sophisticated experimental techniques, there has been a great deal of interest in Angle-Resolved PhotoEmission Spectroscopy (ARPES) where one distinguishes between photoelectrons of different momenta. By the conservation of momentum, this can provide information about the band dispersion in the sample. The ARPES experiment is shown schematically in Fig. 3.1.

In this chapter, we discuss on a largely theoretical basis ARPES in the cuprates from the point of view of the bipolaron theory. We review the experimental data from ARPES and make comparisons with our theory in Chapter 5.
3.1.1 Theory of the ARPES technique

In principle, it is possible to write down a very detailed description of the ARPES experiment, for instance in terms of three-current correlation functions [37]. These however are very difficult to compute, and various simplifications are usually made, which reduce the theory to the simple version presented here. The interaction of the electrons in a crystal with an electromagnetic field of frequency $\nu$ is described in the dipole approximation by the Hamiltonian

$$H_{\text{int}} = (8\pi I)^{1/2} \sin(\nu t) \sum_{k,k'} (\mathbf{e} \cdot \mathbf{d}_{k,k'}) c_k^\dagger h_{k'}^\dagger + \text{h.c.},$$  \hfill (3.1)

where $I$, $\mathbf{e}$ and $\nu$ are the intensity, polarisation and frequency of the incident radiation, $k$ is the momentum of the emitted photoelectron registered by the detector, $k'$ is the Bloch momentum of the hole remaining in the sample, and $c_k^\dagger$ and $h_{k'}^\dagger$ are their creation operators, respectively. For simplicity we suppress the band index in $h_{k'}^\dagger$. The dipole matrix element is

$$\mathbf{d}_{k,k'} = -e \langle \mathbf{k} | \mathbf{r} | \mathbf{k}' \rangle.$$

Here $|\mathbf{k}\rangle$ represents the final state of the photoelectron and $|\mathbf{k}'\rangle = u_{-\mathbf{k'}}(\mathbf{r}) \exp(-i\mathbf{k}' \cdot \mathbf{r})$ is the initial Bloch state of the electron in the crystal. We denote the Schrödinger wavefunctions for the initial and final states as $\psi^i(\mathbf{r}_k)$ and $\psi^f(\mathbf{r}_{k'})$ respectively.

Due to the translational symmetry of the crystal, we may derive a conservation of
momentum relation between \( k \) and \( k' \). Making the substitution \( r = r' + a \), where \( a \) is a lattice vector, we obtain for the dipole matrix element

\[
d_{k,k'} = -e \int dr \psi^{*}_k(r) r \exp(-i k' \cdot r) u_{-k'}(r)
\]

(3.3)

\[
d_{k,k'} = -e \exp(-i(\mathbf{k} - \mathbf{k'}) \cdot a) \times \int dr' \psi^{*}_k(r') (r' + a) \exp(-i k' \cdot r') u_{-k'}(r').
\]

(3.4)

We are able to use the Bloch relation \( \psi_k(r + a) = e^{-i \mathbf{k} \cdot \mathbf{a}} \psi_k(r) \) for the initial and final states as they are both Bloch states of the system. We thus obtain

\[
d_{k,k'} = \exp(-i(\mathbf{k} + \mathbf{k'}) \cdot a) \left[ d_{k,k'} + a \int dr' \psi^{*}_k(r') \psi^{*}_k(r') \right]
\]

(3.5)

\[
d_{k,k'} = \exp(-i(\mathbf{k} + \mathbf{k'}) \cdot a) d_{k,k'},
\]

(3.6)

as \( \psi_k(r') \) and \( |k'\rangle \) are orthogonal. It follows that, if the matrix element is to be non-zero, \( k' = -k + G \), where \( G \) is a reciprocal lattice vector. From now on, we use the notation \( d(k) = d_{k,-k+G} \).

The Fermi Golden Rule gives the photocurrent to be

\[
I(k, E) = 4\pi^2 \frac{n}{|e \cdot d(k)|^2} \sum_{i,f} e^{\beta + \mu N_i - E_i} \left| \left< f \left| h_{k-G}^\dagger \right| i \right> \right|^2 \delta(E + E_f - E_i),
\]

(3.7)

where \( E \) is the binding energy, \( E_{i,f} \) is the energy of the initial and final states of the crystal, and \( \Omega, \mu, N_i \) are the thermodynamic and chemical potentials and the number of holes, respectively. By definition the sum in Eq. 3.7 is \( n(E)A(k - G, -E) \) where the spectral function \( A(k - G, E) = (-1/\pi) \Im G^R(k - G, E) \) is proportional to the imaginary part of the retarded Green function (GF), and \( n(E) = \frac{\exp(E/T) + 1}{1} \), the Fermi distribution. ARPES thus measures the spectral function of hole polarons multiplied by the Fermi distribution and a matrix element dependent on \( k \) and the polarisation of the incident radiation. For convenience, in the following we put \( G = 0 \). In ARPES experiments, the photoelectron energies are measured relative to that of an electron emitted from the Fermi level. This level is found by comparison with the Fermi step in the spectra from a good metal such as platinum in electrical contact with the sample.

In a real system, Eq. 3.7 applies only in the two dimensions parallel to the surface of the crystal, as the potential between the surface and the vacuum level breaks the conservation of momentum in the third dimension. This is why ARPES has been particularly
important in the cuprates; due to their highly anisotropic nature, it is appropriate when interpreting ARPES data to make a two-dimensional approximation. Thus if the crystal is cleaved parallel to the \( ab \)-plane, ARPES measures the dependence of the spectral function on the components of Bloch momentum in that same plane.

It is important to note that the ARPES experiment measures the spectral density of the hole created in the sample, Eq. 3.7. In our theory, bipolaron formation pins the chemical potential \( \mu \) below the bottom of the \( p \)-oxygen polaron band as Bose statistics imply that \( \mu \) cannot enter the bipolaron band. The polaron band will thus have its minimum half the bipolaron binding energy (i.e. the single particle gap) above the chemical potential.

3.1.2 Polaronic ARPES

The hole polaron GF may be derived using the Lang-Firsov canonical transformation, described in the previous chapter [38]. One obtains for the hole Matsubara GF a convolution of the free hole GF and a multiphonon correlation function:

\[
G(k, \omega_n) = \frac{T}{N} \sum_{\omega_n', m, k'} \frac{\sigma(m, \omega_n' - \omega_n) e^{i(k-k') \cdot m}}{i\omega_n' - \xi_{k'}} \tag{3.8}
\]

where

\[
\sigma(m, \tau) = \exp \left( \frac{1}{2N} \sum_q |\gamma(q)|^2 f_q(m, \tau) \right) \tag{3.9}
\]

Here

\[
f_q(m, \tau) = [\cos(q \cdot m) \cosh(\omega_q |\tau|) - 1] \coth \frac{\omega_q}{2T}
\]

\[
+ \cos(q \cdot m) \sinh(\omega_q |\tau|) \tag{3.10}
\]

where \( m \) is a lattice vector, \( \omega_n = \pi T (2n + 1) \) and \( n = 0, \pm 1, \pm 2, \ldots \).

For dispersionless phonons (\( \omega_q \)) and a short-range (Holstein) electron-phonon interaction with a \( q \)-independent matrix element \( \langle |\gamma(q)|^2 = 2g^2 \rangle \) the Fourier component of \( \sigma(m, \tau) \) may be evaluated to give

\[
G(k, \omega_n) = \frac{e^{-g^2}}{i\omega_n - \xi_k} + \frac{e^{-g^2}}{N} \sum_{l=1}^{\infty} \frac{g^{2l}}{l!}
\]
There are thus two terms in a polaronic carrier's GF. The first, coherent, \( k \)-dependent term arises from the polaron band tunneling. Its spectral weight is strongly suppressed by a factor \( Z = \exp(-g^2) \), and its effective mass is strongly enhanced, \( \xi_k = Z E_k - \mu \), where \( E(k) \) is the bare band dispersion (as before, we include the polaronic level shift in the chemical potential.) The second, \( k \)-independent, term describes excitations accompanied by the emission and absorption of phonons. This term spreads over a wide energy range, about twice the polaron level shift \( E_p = g^2 \omega \).

As we have demonstrated above, ARPES measures the spectral function (i.e. the imaginary part of the retarded GF \( G^R \)) multiplied by the Fermi-Dirac distribution function and by the square of the dipole matrix element. \( G^R \) is obtained from the Matsubara GF \( G(k, \omega_n) \) by substituting \( i \omega_n \to E + i0^+ \). Hence, neglecting the finite instrumental resolution, the ARPES intensity is

\[
I(k, E) \sim |d(k)|^2 n(E) Z \delta(E + \xi_k) + I_{\text{incoh}}(E), \tag{3.12}
\]

where \( I_{\text{incoh}}(E) \) is a structureless function of the binding energy, spreading from about \(-\omega\) down to \(-2E_p\).

As \( g^2 = E_p/\omega \), the small Holstein polaron is very heavy unless the phonon frequency is extremely high. However, the situation in the cuprates is very different. The Holstein case above occurs when the electron-phonon interaction becomes short range due to screening. Due to the low mobility of polaronic carriers, in the cuprates the electron-phonon interaction remains long range \[39\] and \( \gamma(q) \sim 1/q \), leading to a much lighter, mobile small Fröhlich polaron (SFP). It can be shown using Eqs. 3.8 and 3.9 that for any finite-radius interaction with a \( q \)-dependent matrix element the coherent part of the ARPES spectrum has the same form as Eq. 3.12 but with different spectral weight \( (Z) \) and effective mass \( (Z') \) renormalisation exponents \[40\]. The incoherent background also becomes \( k \)-dependent if \( \gamma \) depends on \( q \) \[41\]. Thus in general

\[
I(k, E) \sim |d(k)|^2 n(E) Z \delta(E + \xi_k) + I_{\text{incoh}}(k, E), \tag{3.13}
\]

with \( Z = \exp(-E_p/\omega) \) as in the Holstein case. The reduction of the SFP bandwidth is
much smaller, \( \zeta_k = Z'E(k) - \mu \), where \( Z' = \exp(-\gamma E_p/\omega) \). In the general case,

\[
\gamma = \sum_q |\gamma(q)|^2 \frac{[1 - \cos(q \cdot a)]}{\sum_q |\gamma(q)|^2}.
\]

(3.14)

The coefficient \( \gamma \) has been calculated as 0.44 and 0.255 in the cuprate lattice for the apex and in-plane oxygen holes [39]. Thus on the one hand small polarons and intersite bipolarons are mobile and can account for the high transition temperatures in the cuprates, and on the other the coherent spectral weight is still strongly suppressed.

The present experimental resolution in ARPES [42] allows probing of the intrinsic damping of the coherent polaron tunneling. This damping appears due to the random field and low-frequency lattice and spin fluctuations described by the polaron self-energy \( \Sigma_p(k, E) \), so that the coherent part of the spectral function is given by

\[
A_p(k, E) = -\frac{1}{\pi} \frac{3\Sigma_p(k, E)}{[E + \Re \Sigma_p(k, E) - \xi_k]^2 + [\Im \Sigma_p(k, E)]^2}.
\]

(3.15)

In the next section, we calculate the spectral shape of the coherent part of the \( A_p(k, E) \).

### 3.2 Spectral shape of the ARPES signal

#### 3.2.1 Self-energy of a 1D hole in the non-crossing approximation

Small polarons exist in the Bloch states at temperatures below the optical phonon frequency \( T < \omega/2 \) no matter how strong their interaction with the phonons is. This is because when the bandwidth is less than the phonon frequency, by the conservation of energy one phonon decays are not allowed. Two-phonon processes require pre-existing phonons, which are exponentially small in number at low temperatures. A finite polaron self-energy therefore appears only due to (quasi)elastic scattering, which is modelled by a random potential \( V(r) \), with

\[
\langle V(x) \rangle = 0,
\]

(3.16)

\[
\langle V(x)V(x') \rangle = \frac{1}{2} D \delta(x - x').
\]

(3.17)

In this section, we apply the simple non-crossing (ladder) approximation, which is described in Appendix A. Within this approximation the self-energy is \( k \)-independent,
and
\[ \Sigma_p(E) \sim \sum_k G_p^R(k, E), \] (3.18)
with
\[ G_p^R(k, E) = \frac{1}{E - \xi_k - \Sigma_p(E)}. \] (3.19)

As discussed in Chapter 2, the oxygen polaron spectrum is parametrised in the tight-binding model as
\[ \xi^{x,y}_k = 2[t \cos(k_x a) - t' \cos(k_y a) + t_c \cos(k_z d)] - \mu, \] (3.20)

If the oxygen hopping integrals in Eq. 3.20, reduced by the narrowing effect, are positive, the minima of the polaron bands are found at the Brillouin zone boundary at the X point \((\pi, 0)\) and the Y-point \((0, \pi)\). The oxygen hole is (quasi) one-dimensional due to the large difference between the oxygen hopping integrals for the orbitals elongated parallel to and perpendicular to the oxygen-oxygen hopping \(t', t_c \ll t\). Making this approximation, the equation for the self-energy in the non-crossing approximation, takes the form
\[ \Sigma_p(\epsilon) = \frac{-1}{2^{3/2} \sqrt{\Sigma_p(\epsilon) - \epsilon}}, \] (3.21)
for each of the two bands. Here we introduce a dimensionless energy (and self-energy), \(\epsilon \equiv (E + \mu)/\epsilon_0\) using \(\epsilon_0 = (D^2m^*)^{1/3}\) as the energy unit. The constant \(D\) is the second moment of the Gaussian white noise potential, comprising thermal and random fluctuations as \(D = 2(V_0^2T/M + n_{im}v^2)\), where \(V_0\) is the amplitude of the deformation potential, \(M\) is the elastic modulus, \(n_{im}\) is the impurity density, and \(v\) is the coefficient of the \(\delta\)-function impurity potential. The solution is
\[ \Sigma_p(\epsilon) = \frac{\epsilon}{3} - \left[ \frac{1}{16} + \frac{\epsilon^3}{27} + \left( \frac{1}{256} + \frac{\epsilon^3}{216} \right)^{1/2} \right]^{1/3}, \] (3.22)

More details of this approximation can be found in Appendix A.

There exists an exact result for the convolution of this spectral function with a Gaussian momentum resolution to obtain the experimental photocurrent,
\[ I(k, E) \sim Z \int_{-\infty}^{\infty} dk' A_p(k', -E) \exp \left[ -\frac{(k - k')^2}{\delta^2} \right]. \] (3.23)
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3. ARPES IN BIPOLARONIC SUPERCONDUCTORS

Figure 3.2: Spectral functions of a 1D hole in a random potential for $k = 0$, using the non-crossing approximation (dotted line) and the exact theory of [43] (solid line). The energy unit is $\epsilon_0$, as used in Eq. 3.21.

The integral is expressed in terms of $\Sigma_p(\epsilon)$, Eq. 3.21 and the tabulated Error function $w(z)$ as

$$
I(k, E) \sim -2Z \frac{\gamma}{\delta} \Re \{ \Sigma_p(\epsilon) [w(z_1) + w(z_2)] \},
$$

(3.24)

where $z_{1,2} = [\pm k - i/2\Sigma_p(\epsilon)]/\delta$, $w(z) = e^{-z^2} \text{erfc}(-iz)$ and $\epsilon = (-E + \mu)/\epsilon_0$.

The imaginary part of the self-energy, Eq. 3.21, disappears below $\epsilon = -3/2^{5/3} \approx -0.9449$. The non-crossing approximation fails to describe the Lifshitz tail of localised states below the bottom of the band, Fig. 3.2. One has to go beyond the simple ladder approximation, to describe the single-electron tunnelling inside the gap [19] and the ARPES spectra at very small binding energy.

3.2.2 Exact spectral function of a 1D hole

The exact spectral function for a one dimensional particle in a random Gaussian white noise potential was derived by Halperin [43] and the density of states by Frisch and Lloyd [44]. Halperin derived two pairs of differential equations from whose solutions the spectral function of a ‘Schrodinger’ particle (i.e. in the effective mass approximation)
and of a 'discrete' particle (tight-binding approximation) may be calculated. We provide a brief summary of his results here - more details of the methods involved may be found in Appendix B. Quantum Monte Carlo calculations show that the polaronic bandwidth is about 100 meV or larger [45], which allows us to apply the 'Schrodinger' particle spectral function, given by [43] (for the derivation, see appendix B)

$$A_p(k, \epsilon) = 4 \int_{-\infty}^{\infty} p_0(-z) p_1(z) \, dz,$$

where $p_{0,1}(z)$ obey the two differential equations

$$\left[ \frac{d^2}{dz^2} + \frac{d}{dz} (z^2 + 2\epsilon) \right] p_0 = 0,$$

and

$$\left[ \frac{d^2}{dz^2} + \frac{d}{dz} (z^2 + 2\epsilon) - z - ik \right] p_1 + p_0 = 0,$$

with boundary conditions

$$\lim_{z \to \infty} z^{2-n} p_n(z) = \lim_{z \to -\infty} z^{2-n} p_n(z)$$

where $k$ is measured in units of $k_0 = (D^{1/2} m^*)^{2/3}$. The first equation may be integrated to give

$$p_0(z) = \exp \left( -\frac{z^2}{3} - 2\epsilon \right) \int_{-\infty}^{z} \exp \left( \frac{u^2}{3} + 2\epsilon u \right) \, du$$

The equation for $p_1(z)$ has no known analytic solution, and hence must be solved numerically. There is however an asymptotic expression for $A_p(k, \epsilon)$ in the tail where $|\epsilon| \gg 1$:

$$A_p(k, \epsilon) \sim 2\pi \sqrt{-2\epsilon} \exp \left( -\frac{4}{3}(-2\epsilon)^{3/2} \right) \cosh^{2} \left( \frac{\pi k}{(-8\epsilon)^{1/2}} \right).$$

$A(k, 0)$, calculated using this theory, is plotted as an example in Fig. 3.2. In practice, for computational efficiency we use the exact spectral density for $-1.4 < \epsilon < 1$, and outside this range we use the asymptotic result, Eq. 3.30, for $\epsilon < -1.4$, and the non-crossing approximation for $\epsilon \geq 1$, where they are almost indistinguishable from the exact result on the scale of the diagrams we will be concerned with.

### 3.3 Summary

In this chapter, we have first given a simple derivation of the theory behind ARPES experiments, and we have then discussed the ARPES lineshape in a bipolaronic superconductor on a purely theoretical basis. In order to investigate the spectral shape near
the band minima, we have taken advantage of the quasi-one dimensional nature of the band dispersion near that point. At low temperatures, the intrinsic linewidth of the spectra is due to elastic scattering off impurities etc.. In Chapter 5, we shall compare this theory with experiment in the Yttrium based cuprates. Specifically, we shall discuss the spectral shape and band dispersion, and calculate the angular and polarisation dependence of the dipole matrix element.
Chapter 4

Screened impurity in the CBG

4.1 Introduction

In the previous chapter, we noted that the intrinsic linewidth of ARPES spectra within the bipolaron approach to cuprate superconductivity is largely due to impurity scattering. In this chapter we develop a theory which will allow us in Chapter 5 to propose an explanation for the temperature and doping dependence of the ARPES peak. As discussed in the previous chapter, ARPES measures the spectral density of a single hole created in the sample. The carriers which screen impurities however are bipolarons. In this chapter, we therefore calculate the cross-section for the scattering of a hole off a Coulomb impurity screened by the charged Bose gas.

4.2 The variable phase method for potential scattering

The general theory of potential scattering in terms of phase shifts was developed in the earliest days of quantum mechanics (see for instance [46].) While in principle this allows scattering cross sections to be calculated for an arbitrary potential, in practice the equations for the radial part of the wavefunction may only be solved analytically for a few potentials, and in the standard formulation are not in an ideal form for numerical
computation. The 'variable phase' approach [47] solves this problem by making the phase shifts functions of the radial coordinate, and then the Schrödinger equation for each radial component of the wavefunction reduces to a first order differential equation for the corresponding phase shift.

We consider here a charged particle of mass \( m \) and wavevector \( k \) scattered by a potential \( V(r) \), and use dimensionless units with \( \hbar = 2m = 1 \). The scattering situation is described by a stationary wavefunction \( \psi(r) \), which is a solution of the time-independent Schrödinger equation

\[
\left[ \nabla^2 + k^2 - V(r) \right] \psi(r) = 0,
\]

(4.1)

with asymptotic boundary condition

\[
\psi(r) \xrightarrow{r \to \infty} e^{ikz} + f(\theta) \frac{e^{ikr}}{r}.
\]

(4.2)

Here, the \( z \)-axis is taken parallel to the wavevector of the incoming particles, and \( \theta \) is the normal spherical polar coordinate. The first term in Eq. 4.2 represents the incident particles, the second term the scattered particles moving radially outwards. The differential cross-section is then

\[
\frac{d\sigma(\theta)}{d\Omega} = |f(\theta)|^2.
\]

(4.3)

As the potential is spherically symmetric, we may exploit the symmetry of the problem and substitute

\[
\psi(r) = \frac{1}{r} \sum_{l=0}^{\infty} u_l(r) P_l(\cos \theta),
\]

(4.4)

where the \( P_l \)'s are the Legendre polynomials. The condition that \( \psi(r) \) must everywhere be finite implies the boundary condition

\[
u_l(0) = 0
\]

(4.5)

for the 'radial wavefunction' \( u_l(r) \). Substituting Eq. 4.4 into the Schrödinger equation, we obtain the 'radial Schrödinger equation'

\[
u_l''(r) + \left[ k^2 - \frac{l(l+1)}{r^2} - V(r) \right] u_l(r) = 0.
\]

(4.6)

From now on, we assume that

\[
V(r) \xrightarrow{r \to \infty} \frac{V_0}{r^n},
\]

(4.7)
CHAPTER 4. SCREENED IMPURITY IN THE CBG

with \( n < 2 \). The angular momentum \( l \) scattering phase shift may then be obtained by comparison with the asymptotic solution

\[
u_l(r) \sim r \to \infty \sin \left( kr - \frac{l \pi}{2} + \delta_l \right).
\]

The scattering amplitude is then given by

\[
f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l} \sin(\delta_l) P_l(\cos \theta),
\]

and the total scattering cross section by

\[
\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} \sin^2 \delta_l.
\]

The variable phase method \([47] \) introduces a new function \( \delta_l(r) \) (the 'phase function'), from which the phase shifts may be calculated as

\[
\delta_l = \lim_{r \to \infty} \delta_l(r).
\]

The derivation of the variable phase method is rather long, and we therefore include it as Appendix A. The function \( \delta_l(r) \) satisfies the 'phase equation'

\[
\delta_l'(r) = -\frac{V(r)}{k} \left[ \cos \delta_l(r) j_l(kr) - \sin \delta_l(r) n_l(kr) \right]^2,
\]

with

\[
\delta_l(r) \sim r \to 0 \frac{V_0}{r^2 k^2} \frac{(kr)^{2l+3}}{(2l+3-n)[(2l+1)!!]^2}.
\]

\( j_l(x) \) and \( n_l(x) \) are the Riccati-Bessel functions. Some of their properties, and a full derivation of this technique, may be found in Appendix C. The notation

\[
(2l+1)!! = 1.3...(2l-1)(2l+1)
\]

is also used.

In the \( l = 0 \) case, the phase equation may be simplified to give

\[
\delta_0'(r) = -\frac{V(r)}{k} \sin^2[kr + \delta_0(r)].
\]

This is particularly useful when the scattered particles have small momentum, more specifically when the particle wavelength is small compared with the radius of action of the scattering potential, and the particle energy is small compared with the field within
Figure 4.1: The phase function $\delta_1(r)$ for the attractive potential $V(r) = -(10/r)e^{-r}$, for (from top to bottom as $r \to \infty$) $k = 0.1, 0.5, 1.0, 2.0, 10$. Note that by Levinson's Theorem, the potential has one $P$-wave bound state.

that radius. In this case we may neglect $l > 0$ contributions to the total scattering cross-section, so that

$$\sigma = \frac{4\pi}{k^2} \sin^2 \delta_0. \quad (4.16)$$

The phase shifts for a given potential may now be calculated easily by numerical solution of the first order ordinary differential equation Eq. 4.12. Some examples of the phase function for the Yukawa potential with different particle energies are plotted in Fig. 4.2.

There are two further important analytical results; the first (Levinson's Theorem [47]) states that for 'regular' potentials (which include all those with which we shall be concerned), the zero-energy phase shift is equal to $\pi$ multiplied by the number of bound states of the potential. The second is the well-known Wigner resonance scattering formula [46], which states that for slow particle scattering of a particle with energy $E$ off a potential with a shallow bound state of binding energy $\epsilon < E$ the total scattering cross section is

$$\sigma = \frac{2\pi}{m E + |\epsilon|}. \quad (4.17)$$

We have used this to check that our calculation method works correctly by comparing
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Figure 4.2: Plot of scattering cross section $\sigma_n$ against scattered particle momentum $k$ for small $k$ (solid line) and fit using the Wigner formula (broken line) for potential $V_n(r) = (-1/r) \exp(-0.55r)$. There is good agreement between the numerical and Wigner results.

our results with Eq. 4.17 for various potentials with shallow bound states (Fig. 4.2).

4.3 Screened Coulomb potential in the charged Bose gas

The effective potential about a point charge in the CBG was calculated by Hore and Frankel using the dielectric formalism. [48]. If the unscreened potential is $V_{\text{unscr}}(r)$, the real-space screened potential will then be given by

$$V_{\text{scr}}(r) = \frac{1}{(2\pi)^3} \int d^3q e^{iq\cdot r} \frac{V_{\text{unscr}}(q)}{\epsilon(q,0)}.$$  

(4.18)

The static dielectric function of the non-interacting CBG is

$$\epsilon(q,0) = 1 + \sum_p \frac{4\pi(e^*)^2}{q^2\Omega} \left( \frac{F_0(p) - F_0(p - q)}{-(1/m_b)p \cdot q + q^2/2m_b} \right),$$  

(4.19)

in which $e^* = 2e$ the boson charge, and $F_0(p)$ the equilibrium distribution of the bosons. We may therefore take $F_0(p) = (e^{(p^2/2m_b - \mu)/k_BT} - 1)^{-1}$, the Bose distribution function.
Eliminating the chemical potential, for small $q$ the dielectric function for $T < T_c$ is

$$\epsilon(q, 0) = 1 + \frac{4m_b^2 \omega_p^2}{q^4} \left[ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right] + \frac{1}{q^2} \frac{\omega_p^2 m_b^3 k_B T}{2} + O \left( \frac{1}{q^2} \right), \quad (4.20)$$

and for $T \to \infty$ is

$$\epsilon(q, 0) = 1 + \frac{1}{q^2} \frac{\omega_p^2}{k_B T} \left[ 1 + \zeta \left( \frac{3}{2} \right) \left( \frac{T_c}{T} \right)^{3/2} + \ldots \right] + O(q^2), \quad (4.21)$$

with $\omega_p^2 = 4\pi (e^*)^2 \rho / m_b$, and $\rho$ the boson density. Alexandrov and Beere [49] showed that that the result for $T < T_c$, Eq. 4.20 is also valid for the case of interacting charged bosons on an oppositely charged background at low temperatures. In the high temperature, the classical result, Eq. 4.21, will also be valid.

The unscreened Coulomb potential is $V_c(r) = Q/r$, whose Fourier transform is $V_c(q) = 4\pi Q / q^2$. Unfortunately, for this potential, it is only possible to compute the inverse Fourier transform in Eq. 4.18 exactly for $T = 0$ and $T \to \infty$. For other temperatures, Hore and Frankels’ approach is to take $\epsilon(q, 0) = 1+$ (the term that gives the largest contribution as $q \to 0$). This ‘small $q$’ approach should give the correct form of the potential as $r \to \infty$, which is the relevant region for the scattering of slow particles. Performing the inverse Fourier transforms, we obtain for $T < T_c$

$$\lim_{r \to \infty} V_{\text{screened}}(r) = \frac{V_0}{r} \exp[-K_s r] \cos[K_s r] \equiv V_s(r) \quad (4.22)$$

with

$$K_s = \left( m_b^2 \omega_p^2 \left[ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right] \right)^{1/4}, \quad (4.23)$$

and for $T \to \infty$,

$$\lim_{r \to \infty} V_{\text{screened}}(r) = \frac{V_0}{r} \exp[-K_n r] \equiv V_n(r) \quad (4.24)$$

with

$$K_n = \left( m_b \omega_p^2 \right)^{1/2} \left[ 1 + \zeta \left( \frac{3}{2} \right) \left( \frac{T_c}{T} \right)^{3/2} + \ldots \right]^{1/2}. \quad (4.25)$$

The zero-energy scattering cross-sections for the potentials $V_n(r) = -(V_0/r)e^{-K_n r}$ and $V_s(r) = -(V_0/r)e^{-K_s r} \cos(K_s r)$ are shown in Fig. 4.3. These graphs are plotted for $V_0 = 1$; in each case, the equivalent graph for arbitrary $V_0$ may be found by rescaling $\sigma$ and $K_{n,s}$. According to the Wigner formula (Eq. 4.17), as $K$ is decreased, when a new bound state appears there should be a peak in the cross-section, as there will then be a
Figure 4.3: Plots of zero-energy scattering cross sections (a) $\sigma_n$ and (b) $\sigma_s$ against screening wavevector $K$ for the potentials (a) $V_n(r) = -(1/r)e^{-Knr}$ and (b) $V_s(r) = -(1/r)e^{-Ksr}\cos(Ksr)$. 
minimum in the binding energy of the most shallow bound state. This is the origin of the peaks in Fig. 4.3, which may be checked using Levinson's Theorem. It can also be seen that as \( K = K_n = K_s \) is decreased, the first few bound states appear at higher \( K \) in the ordinary Yukawa potential; this agrees with the intuitive conclusion that the bound states should in general be deeper in the non-oscillatory potential. Another intuitive expectation which is also bourne out is that for a given \( V_0 \) and \( K_n = K_s = K \), the non-oscillatory potential should be the stronger scatterer; in Fig. 4.3 it may be seen that this is the case when \( K \) is large enough for neither potential to have bound states (the difference in cross sections is then in fact about three orders of magnitude.)

### 4.4 Summary

In this chapter, we have calculated the scattering cross section of a charged particle off a Coulomb scattering centre in the charged Bose gas both above and below the condensation temperature. In the high-temperature limit \( T \gg T_c \), the screened potential is the normal Yukawa one; at \( T = 0 \), the potential is still spherically symmetric, but has an additional cosine factor. We find that when the two potentials have no bound states,
the normal state cross-section is about three orders of magnitude larger than that for
the superconducting state if the screening length is the same. In the next chapter, we
shall discuss the application of these results to the variation of the ARPES linewidth in
the cuprates with temperature and doping.
Chapter 5

ARPES in the cuprates

5.1 Introduction

As mentioned in Chapter 3, ARPES in principle it allows direct measurement of the electronic structure. In this chapter, we provide an overview of the experimental results from ARPES and the current problems in their interpretation, and discuss how some of them may be explained by the theoretical work contained in the previous two chapters of this thesis.

We first provide a brief summary of the expectations from Fermi liquid theory, which will help in our discussion of some of the outstanding problems in the interpretation of ARPES data, and discuss a few of the potential problems in applying the technique to real materials.

5.1.1 Expectations from Fermi liquid theory

ARPES measures the imaginary part of the single hole spectral function $A(k, E)$, where

$$A_p(k, E) = -\frac{1}{\pi} \times \frac{\Im \Sigma_p(k, E)}{(E + \Re \Sigma_p(k, E) - \xi_k)^2 + (\Im \Sigma_p(k, E))^2}.$$ (5.1)

The real part of the self-energy in $A(k, E)$ gives the energy shift relative to the bare bandstructure, the imaginary part may be interpreted as the scattering rate for a particle...
CHAPTER 5. ARPES IN THE CUPRATES

of energy $\xi$, or equivalently $1/\tau$ where $\tau$ is the particle lifetime.

In the Fermi liquid case, we can make a simple estimate of the scattering rate in the vicinity of the Fermi level. We consider an electron with energy $\xi = E - E_F > 0$ where $E_F$ is the Fermi energy, and assume that it undergoes a scattering event involving one other particle. The scattering rate will then be proportional to both the number of available final states and the number of electrons it may scatter off.

If $\xi \ll E_F$ we may also assume that the density of states is constant for our purpose. By the exclusion principle, the particle must scatter into another state above the Fermi level, the number of which is proportional to $\xi$. The number of available scatterers is also proportional to $\xi$, as while the scatterer must come from an occupied state in the Fermi sea, by the exclusion principle it must be scattered into a state above the Fermi level. Thus by the conservation of energy the scatterer must initially be in a state not more than $|\xi|$ below $E_F$, the number of which is again proportional to $\xi$. Hence we may estimate that the scattering rate for an electron of energy $\xi$ is proportional to $\xi^2$. The same analysis applies in the case of single holes, which we are concerned with in photoemission.

On the basis of a Fermi liquid description of the cuprates, one would therefore expect that as $k$ is varied so that a band disperses towards and crosses the Fermi level from the occupied side, the photoemission peak would narrow and sharpen until it crosses the Fermi level at which point the peak will disappear.

5.1.2 The ARPES technique in the cuprates

In Chapter 3, we gave a simple theory of the ARPES experiment. In practice, this interpretation, i.e. that ARPES measures the spectral function multiplied by the Fermi distribution and a momentum-dependent matrix element, is the one generally used. However, with the increasing interest in photoemission arising from its ability in principle to probe directly the electronic structure of the cuprates, a number of researchers have considered in more detail the physical processes involved in the experiment. Before moving on to discuss experimental results relating to the electronic structure of the
cuprates, we describe some of the recent work on understanding the ARPES technique and possible problems with it.

It is well known that ARPES is a surface sensitive probe, and that it is most effective in materials where a very (approaching atomically) flat surface can be obtained. BSCCO has therefore been studied more than the other materials as two of the layers in the unit cell are weakly van der Waals bonded, and therefore a very clean cleaved surface is obtainable. Norman et al have investigated the photoelectron escape depth in Bi2212 using data from electron energy-loss spectroscopy [50]. Their results for the escape depth versus incident photon energy are shown in Fig. 5.1. For the range of photon energies used in ARPES experiments (typically 20 – 30eV), the escape depth is very small, and the electron is emitted from the top CuO2 layer. They went on to use these results to calculate the contribution to the ARPES signal due to photoelectrons which lose energy as they transport out of the crystal, and found that it was not significant compared to the total signal. The conclusion was that the broad incoherent background observed in the material must have some intrinsic origin in the electronic structure, contrary to some earlier estimates which attributed it to inelastic secondaries.

There are however other similar effects which may impact on the intrinsic accuracy of ARPES experiments. Joynt has investigated the interaction between an emitted photo-
electron and the electric field this creates in the sample [51]. He argues that the currents set up in the sample by this electric field will suffer Ohmic losses. This will result in a reduction of the energy of the photoelectron, which will therefore appear to come from further below the Fermi level than is actually the case. In principle this could in turn lead to an erroneous observation of a normal state gap. Joynt argues that this effect is probably not very significant in the cuprates, both from the theoretical point of view that their a−b plane conductivity is reasonably high, and from the experimental point of view that the normal state gap (pseudogap) is also observed in many other experiments. He does however argue that the colossal magnetoresistance manganites are a more likely candidate material for his effect. However, whether or not the suggestions in his paper are relevant to real materials, it serves as a reminder that great care is necessary when interpreting the results of such a surface-sensitive technique.

In addition to these calculations of the significance of possible intrinsic errors in ARPES experiments, there have also been attempts to make a detailed calculation of the matrix elements. Bansil and Lindroos [52] have done this starting from a similar Fermi golden rule expression which we derived in Chapter 3. They work in momentum space with an interaction Hamiltonian \( H_{\text{int}} = e\hbar/2mc(p \cdot A + A \cdot p) \) (vector potential \( A \), electron momentum \( p \)). This expression is manipulated into the form

\[
I(k_{\parallel}, E, \omega) = -\frac{1}{\pi} \Im \left( k_{\parallel} \left| G_2^+(E + i\omega)H_{\text{int}}G_1^+H_{\text{int}}G_2^-(E + i\omega) \right| k_{\parallel} \right), \tag{5.2}
\]

where \( k_{\parallel} \) is the free electron final state momentum, \( \omega \) is the photon frequency and \( G_{1,2}^{+,−} \) denote the retarded and advanced one-electron Green's functions at appropriate energies. It is immediately clear that Eq. 5.2 does not take the simple 'spectral function times matrix element times Fermi distribution' form. Due to the complicated crystal structure of BSCCO, the calculations are very computationally intensive, and they had to make the approximation of a perfectly tetragonal lattice, but they were for instance able to take into account a realistic surface termination. They compare their calculated spectra with in terms of the intensity of the ARPES peak and the integrated weight, rather than actual spectra, and achieve reasonably good agreement. One of their comparisons is shown in Fig. 5.2.

Notwithstanding this brief survey of potential pitfalls and more sophisticated models, for the rest of this chapter we discuss ARPES results using the simple interpretation of
CHAPTER 5. ARPES IN THE CUPRATES

5.2 Experimental results from ARPES

5.2.1 Observation of a large Fermi surface?

ARPES data has generally been interpreted in the literature as showing a Fermi surface. Until recently, most experimental groups active in photoemission agreed that they observed a hole-like Fermi surface (FS) in BCSSO centred around the corners of the Brillouin zone [53]. Along with most other datasets taken around that time this work used photon energies in the range 18 – 23eV. More recently, however, one group claimed that their data taken using 33eV photons showed an electron-like FS centred about the $\Gamma$ point [54, 55], Fig. 5.3. This has excited some considerable controversy in the literature, with some workers confirming the electron-like FS observed at 33eV [56, 57]. Meanwhile others have disputed this, claiming that the correct Fermi surface topology is hole-like.
Figure 5.3: Fermi surface of Bi-2212 as determined in [53] (a) and [54] (b). The dark lines are the main FS pieces, the narrower lines FS replicas due to superstructure modulation.

One item of contention between experimental groups is the method of determining FS crossing points. Those in use include looking for a simultaneous drop in the integrated spectral weight $n(k)$ and maximum in the spectral weight at the Fermi level [54], and taking the maximum value of the gradient of $n(k)$, which should occur at the FS [56]. A third method takes advantage of particle-hole symmetry in the vicinity of the Fermi level at a Fermi surface crossing, i.e. that $A_{FS}(k, E) = A_{FS}(k, -E)$. It 'removes' the Fermi distribution function at a crossing by symmetrising the ARPES spectra: $A_{symm}(k, E) = A(k, E) + A(k, -E)$. $A_{symm}(k, E)$ should then first show a peak at a crossing as one moves from occupied to unoccupied states [58].

A more fundamental issue however is what is actually meant by the term 'Fermi surface' when applied to the cuprates. As discussed above, in a Fermi liquid, as an ARPES peak disperses towards the Fermi level, it should decrease in width until just below the Fermi level it is resolution-limited, and then disappear as it crosses the Fermi level. This is certainly not the case however in the cuprates. The typical observation is shown in Fig. 5.4. Here, the peak does decrease in width as it disperses towards the Fermi level, but its width is still of the order of 0.1eV at the observed crossing, an order of magnitude greater than the experimental resolution. This provides direct evidence that the FS observed in the cuprates cannot be interpreted as evidence of any kind of normal Fermi liquid.
Figure 5.4: Normal-state ARPES data from Bi2212 taken along the $\Gamma - Z$ direction (see Fig. 5.3.) The peak width is still of the order of $0.1eV$ at the observed Fermi level crossing horizontal axis units are $eV$. 
In addition, in the cuprates, many low frequency kinetic and thermodynamic quantities are found to increase with $x$, in contradiction with expectations from the theory of normal Fermi liquid metals. For instance, in the case of the Pauli susceptibility in a metal with a large FS one expects a change in doping to produce a small change in $\chi_{Pauli}$, as the total number of carriers is much greater than the number of dopants. This however is in contradiction with experiment [62].

On the basis of the above observations, our belief is therefore that in connection with ARPES data from the cuprates, the term 'Fermi surface' should be used in the very general sense of a dispersive feature crossing the Fermi level, rather than in the conventional usage within Fermi liquid theory.

5.2.2 Flat bands near the Fermi level

ARPES shows very little peak dispersion around the $Y$-point in the $\Gamma - Y$-direction in YBa$_2$Cu$_4$O$_8$ [63] and around the $\vec{M}$-point in Bi2201 [64] and Bi2212 [65], Fig. 5.5. This feature is commonly referred to as an 'extended saddle point' or an 'extended Van Hove singularity'. Such a feature in the band structure should produce a $1/\sqrt{E}$ singularity.
in the density of states. One theory proposes that superconductivity in the cuprates is BCS-like, with the high transition temperatures caused by the resulting increase in the density of states at the Fermi level [66]. In the data presented in [63], however, the modern symmetrisation method of Fermi surface determination shows that there is no Fermi surface crossing in the $Y - S$ direction, Fig. 5.6. The lack of a peak in the symmetrised ARPES spectra at the Fermi level in this direction may be a manifestation of the pseudogap (discussed in Chapter 2), and does not rule out the possibility of dispersive features crossing the Fermi level in other scanning directions. It does however appear to rule out the Fermi liquid-like normal state required for the extended saddle point scenario.

It is also important to note that a similar extended saddle point has been observed in $\text{Sr}_2\text{RuO}_4$ ($T_c \sim 1K$, isostructural with $\text{LaCu}_2\text{O}_4$) [67], which shows that this feature does not necessarily result in a high transition temperature.
5.2.3 Temperature and doping dependence of the ARPES peak

A number of experimental groups have observed the emergence of a sharp peak below $T_c$ in ARPES spectra taken from Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ near the $(\pi, 0)$ point of the Brillouin zone [68, 69, 70, 71, 72], Fig. 5.7. There is some disagreement among groups as to the quantitative description of this peak. Loeser et al claim that the peak is resolution limited and moves to slightly lower binding energy as the $T$ approaches $T_c$ from below [72], while Fedorov et al [68, 69] believe that it has an intrinsic width of 14meV and the same binding energy at all temperatures. Kaminski et al have also observed a sharp peak at other points in the Brillouin zone [71]. In addition, Loeser et al have observed that the peak increases in height between an underdoped ($T_c = 79K$) and an overdoped ($T_c = 86K$) sample, Fig. 5.8.

The origin of the peak however remains uncertain. Norman and Ding have proposed...
A. Figure 5.8: Doping dependence of the superconducting spectra at $(\pi, 0)$ for the under-doped (dotted) and overdoped (bold) samples [72]. The binding energy is shown on the horizontal axis.

A semi-phenomenological explanation where a step edge in the imaginary part of the self energy is caused by carriers interacting with a dispersionless mode [73]. Their work is based on a model developed in the theory of strong-coupling classical superconductors, where the mode is an Einstein phonon. In the case in question, the peak is only observed below $T_c$, so they base their model on an unspecified collective mode of electronic origin. Shen and Schrieffer explain the effect in terms of a redistribution of the energy of a collective excitation with which the carriers interact [74]. In this chapter we shall propose an alternative explanation based on the results of Chapter 4.

5.2.4 Importance of phonons - recent evidence from ARPES

Lanzara et al have recently reported ARPES results which they interpret as showing that the electron-phonon interaction is important in the cuprates [75]. They observed a kink in the peak dispersion in a wide range of materials, Fig. 5.9. The similar energy scale of the feature ($50 - 80\text{meV}$) in systems with a much greater variation in gap energy (e.g. $10 - 20\text{meV}$ in LSCO and $40 - 50\text{meV}$ in Bi2212) seems to rule out the superconducting gap as the origin. There is also in some cuprates a magnetic mode which appears below
Figure 5.9: Dispersion along the (0,0) - (π,π) direction in various materials. The momenta are normalised such that \( k' = 1 \) at binding energy 170\,meV and \( k = 0 \) at the observed 'Fermi surface crossing'.
5.3 Theory of ARPES in Y123 and Y124

5.3.1 Polarisation dependence in Y123

Using the theory of Chapter 3, we can describe various features of the ARPES spectra in Y123 [77] and Y124 [63]. First we propose an explanation of the experimentally observed polarisation dependence of the ARPES peak intensity near the X and Y points of the Brillouin zone [77]. We make the plane wave approximation \( \psi_k(r) = \exp(ik \cdot r)/(Nv_0)^{1/2} \) \((N = \text{number of unit cells in crystal, } v_0 = \text{volume of unit cell})\) for the final state. We also express the Bloch periodic function \( u_k(r) \) in terms of Wannier orbitals \( w(r) \) as

\[
\psi_k(r) = N^{-1/2} \sum_m e^{ik \cdot (r - m)} w(r - m),
\]

where the sum is over the lattice sites \( m \). From Eq. 3.2, the dipole matrix element is then given by

\[
d_k = -\frac{e}{\sqrt{Nv_0}} \int dr u_{-k}(r)r.
\]

Substituting the Wannier expression for \( u_{-k}(r) \) and making the substitution \( r' = -r + m \),

\[
d_k = \frac{1}{Nv_0} \sum_m \int dr' \exp(i k \cdot r')(r' + m)w(r').
\]

If we define \( f_k \equiv \int dr w(r) \exp(i k \cdot r) \), the Fourier component of the Wannier orbital, then

\[
d_k = e^{-i \nabla_k f_k} \frac{1}{Nv_0} \sum_m \left( -i \nabla_k f_k + f_k \sum_m \right)
\]

\[
= e^{-i \nabla_k f_k} \frac{1}{Nv_0} (-i \nabla_k f_k),
\]
as $\Sigma m_m = 0$.

To estimate $f_k$ we approximate the $x, y$ oxygen orbitals, contributing to the $x$ and $y$ polaron bands respectively, with the ‘hydrogen atom’ orbitals

$$w_x(r) = \sqrt{\frac{1}{8a_0^2\pi}} \frac{x}{2a_0} e^{-r/2a_0}, \quad (5.8)$$

$$w_y(r) = \sqrt{\frac{1}{8a_0^2\pi}} \frac{y}{2a_0} e^{-r/2a_0}. \quad (5.9)$$

As a result we obtain for the $x$ orbital,

$$\frac{\partial f_k}{\partial k_x} = \frac{8a_0^3\pi}{v_0} 2a_0 \left( \left[ (k_0a)^2 + \frac{1}{4} \right]^{-4} - 6(k_0a)^2 \left[ (k_0a)^2 + \frac{1}{4} \right]^{-4} \right), \quad (5.10)$$

and

$$\frac{\partial f_k}{\partial k_{y,z}} = -6 \frac{8a_0^3\pi}{v_0} a_0^3 k_x k_{y,z} \left[ (k_0a)^2 + \frac{1}{4} \right]^{-4}. \quad (5.11)$$

Here $k$ is the photoelectron momentum and $a_0$ is the ‘Bohr radius’ of the Wannier function. For the case of $y$-orbital one should interchange $x$ and $y$. Near the $X$ and $Y$ points of the Brillouin zone, $|k_{y,x}| << k$ respectively. Then it follows from Eq. 5.10 and Eq. 5.11 that the ARPES peak should be seen at $X$ and almost disappear at $Y$ if the photons are polarised along the $x$-direction, i.e. $e \parallel a$. If the polarisation is along the $y$-direction ($e \parallel b$) the peak appears at $Y$ and almost disappears at $X$. Precisely this behaviour is observed in ARPES spectra obtained using polarised photons [77], Fig. 5.10. We also notice a very strong dependence of the dipole matrix element on the photon energy, $d \sim \nu^{-3}$ at large $\nu$. This is consistent with the fact that drastically different results have been obtained at different photon energies in BSCCO [54].

### 5.3.2 Spectral shape and dispersion in Y124

The exact 1D polaron spectral function, Eq. 3.25, integrated with the experimental momentum resolution, provides a quantitative fit to the ARPES spectra in Y124 along the $Y-\Gamma$ direction, Fig. 5.11. The angular dispersion is described with the polaron mass $m^* = 9.9m_e$ in agreement with Monte-Carlo calculations of the Small Frölich Polaron mass [45]. The spectral shape is reproduced well with $e_0 = 19meV$, Fig. 5.12, in close agreement with the value of this parameter found in tunneling experiments [19]. This provides an estimate of the polaron scattering rate which is smaller than the polaron
bandwidth (about 100 meV or larger), in agreement with the notion [78] that many high-
T_c cuprates are in the clean limit. There is also quantitative agreement between theory
and experiment in the perpendicular direction Y - S in a restricted region of small k_x,
where almost no dispersion is observed around Y, Fig. 5.13. Slight dispersion in the
Y - S direction towards the chemical potential might be due to a negative t' in Eq. 3.20.

It is important to note that there is a significant loss of the energy-integrated intensity
along both directions, Fig. 5.14, which the theoretical spectral function alone cannot
account for. The energy-integrated ARPES spectra obey the sum rule

$$ I_k = \int_{-\infty}^{\infty} dE I(k, E) \sim |d(k)|^2 n_k, \quad (5.12) $$

where $n_k = \langle h_k h_k^\dagger \rangle$. If the dipole matrix element is almost k-independent and the
chemical potential is pinned well inside the charge-transfer gap, so that $n_k = 1$ this
integral would be k independent as well. This is not the case for Y124, no matter what
the scanning direction is, Fig 5.14. Therefore, we have to conclude that the dipole matrix
element is k dependent. As we have mentioned above, the incoherent background of the
SFP is angle dependent as well, which might contribute to the intensity loss.
Figure 5.11: Theoretical ARPES spectra for $Y - \Gamma$ direction and experiment [63] in Y124. The parameters are $\epsilon_0 = 19\text{meV}$, momentum resolution $\delta = 0.28\pi/a$ and polaron mass $m^* = 9.9m_e$. The bipolaron binding energy $2|\mu| = 40\text{meV}$. The theory provides a quantitative fit to experiment in this scanning direction.

Figure 5.12: Theoretical fit (dashed lines) to two experimental ARPES curves from Y124 corresponding to $k = 0.04\pi/a$ (upper curves), and $k = 0.30\pi/a$. Momenta are measured relative to the $Y$-point of the Brillouin zone.
CHAPTER 5. ARPES IN THE CUPRATES

Figure 5.13: Experimental [63] and theoretical ARPES spectra in Y124 for the Y – S direction.

Figure 5.14: The energy-integrated ARPES intensity in Y124 in the Y – Γ (a) and Y – S (b) directions. Momenta are measured relative to the Y-point of the Brillouin zone.
This strong angular dependence of the integrated spectral weight $I_k$ indicates that methods of Fermi surface determination based on the drop in $I_k$ at a crossing may give systematic errors. The rapid loss of integrated intensity in the 'dielectric' direction, $\Gamma - Y$, where there is clearly no FS crossing, shows that it is dangerous to take this as proof of a crossing without corroborating evidence from other tests.

5.4 ARPES linewidth in BSCCO

In this section, we discuss the possible application of our results on Coulomb potentials screened by the charged Bose gas to the problem of the ARPES linewidth in the cuprates. We believe (see Chapter 3) the ARPES peak is related to photoexcited holes with small group velocity near the top of the oxygen band. The lifetime of these quasiparticles will clearly depend on the nature of the screening of impurities in these materials. The quantities necessary in order to calculate the scattering cross section of the main impurities (the dopants) in the cuprates are the static dielectric constant, the effective mass of the bipolaronic carriers, the charge on the scattering centres and the bipolaron density. The situation is however complicated by the anisotropy of the effective mass tensor. The value of the effective mass of the bipolarons in the cuprates is readily found from the penetration depth [25]. In BSCCO the in-plane bipolaron mass $m_b$ is about $5-6m_e$. The dopants in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ are $O^{2-}$ ions, and thus the Coulomb potential between a scattering centre and a hole is $V(r) = -2e^2/(\epsilon_0 r)$. The issue of the dielectric constant is more contentious; measurements suggest that it may be as high as 1000 [79]. The variable phase method has only been derived for the isotropic problem, so we cannot apply our theory to make a quantitative conclusion about the quasiparticle lifetime at different temperatures in the cuprates. However, we can provide an important general conclusion about the relative value of the cross-sections in the normal and superconducting states. At zero temperature, the screening wavevector is $K_0 = (m_b\omega_p)^{1/2}$, and at a temperature $\alpha T_c$ well above the transition, it is $K_{\alpha T_c} = (m_b\omega_p^2/k_B\alpha T_c)^{1/2}$. Substituting $\omega_p$ and $k_B T_c = 3.3n^{2/3}/m_b$, we obtain:

$$\frac{K_{\alpha T_c}}{K_0} = \left(\frac{2.1em_b^{1/2}}{\epsilon_0^{1/2} \rho^{1/6} \alpha}\right)^{1/2}.$$  \hfill (5.13)
CHAPTER 5. ARPES IN THE CUPRATES

From this, we see that the ratio is only marginally dependent on the boson density, so substituting for \( \rho = 10^{21} \text{cm}^{-3} \), \( e \), and \( m_e \), we obtain

\[
\frac{K_{\alpha T_0}}{K_0} = 3.0 \left( \frac{m_b/m_e}{{\epsilon_0}^{1/2}} \right)^{1/2}.
\]

With realistic boson masses and dielectric constants, \( K_{\alpha T_0} \) and \( K_0 \), while different, are of the same order of magnitude. In the isotropic model, if the screening wavevectors are such that neither the normal state or condensate impurity potentials have bound states, with these parameters it would then follow that the quasiparticle lifetime is much greater in the superconducting state, Fig. 4.3. We propose that this effect also occurs in the realistic non-isotropic model, and could then explain the appearance of a sharp ARPES peak in the superconducting state of BSCCO. With doping, the screening radius decreases both in the normal, Eq. 16, and superconducting states, Eq. 14. In each case the scattering cross section then decreases more rapidly than the density of scatterers; this explains the experimentally observed increase in the sharpness of the peak with doping.

5.5 Summary

In summary, we have applied the theory of ARPES in cuprates derived in Chapter 3 to explain various experimental results. We first used it to explain the narrow flat bands observed in Y123 and Y124, including their polarisation, spectral and angular dependence, as well as a featureless (but dispersive) background. The angular dependence of the peak and of the gap is due to the polaron band dispersion, which agrees well with the QMC results for the small Fröhlich polaron. The peak width is due to a finite imaginary part of the polaron self-energy arising from elastic scattering.

We then investigated in more detail the temperature and doping dependence of the peak width, based on the scattering cross section of a Coulomb impurity in the charged Bose gas (Chapter 4.) In contrast to the BCS superconductor, the scattering potential in the CBG is different in the normal and superconducting states. We find that for the realistic parameters, the scattering cross section above \( T_c \) in the bismuth cuprates might be around three orders of magnitude larger than at \( T = 0 \). We propose that the
appearence of a sharp peak in the ARPES spectra of BSCCO below the superconducting transition and its doping dependence is due to the condensate screening of the scattering potential.
Chapter 6

Magnetic response of the CBG

6.1 Introduction

As mentioned in the introduction to this thesis, Schaffroth considered in some depth the charged Bose gas as a model for superconductivity [4]. One of the quantities he discussed was the induced magnetisation in a magnetic field. In his paper, he calculated this below the zero-field condensation temperature. In this chapter, we extend these calculations to include the diamagnetic response of the CBG at all temperatures, in an extension of Alexandrov's earlier work on the upper critical field in the charged Bose gas and the cuprates [80].
CHAPTER 6. MAGNETIC RESPONSE OF THE CBG

6.2 Magnetisation and critical field
of the CBG

6.2.1 3D anisotropic ideal CBG

The energy spectrum of an ideal 3D CBG in a magnetic field is the famous 'Landau level' result (see for example [46].) If the zero-field Hamiltonian is

$$ H = \frac{p_z^2}{2m_a} + \frac{p_y^2}{2m_b} + \frac{p_z^2}{2m_c}, \quad (6.1) $$

then the energy levels in a magnetic field parallel to the z-axis are given by

$$ E_{n,p_z} = \left(n + \frac{1}{2}\right) \hbar \omega_H + \frac{p_z^2}{2m_c}, \quad (6.2) $$

where \( \omega_H = |q|H/c(m_am_b)^{1/2} \), \( q \) is the boson charge and \( H \) is the applied magnetic field. The density of states per unit volume is then

$$ \rho(E) = \frac{\sqrt{\pi} m_y m_z (\hbar \omega_H)}{2\sqrt{\pi}^3 \hbar^3} \sum_{i=0}^{\infty} \Re \left( \frac{1}{\sqrt{E - \hbar \omega_H (l + 1/2)}} \right). \quad (6.3) $$

As discussed in Chapter 2, in the cuprates there are two degenerate bipolaron bands. In this case the DOS is

$$ \rho(E) = \frac{\sqrt{\pi} m_y m_z (\hbar \omega_H)}{\sqrt{2\pi}^2 \hbar^3} \sum_{i=0}^{\infty} \Re \left( \frac{1}{\sqrt{E - \hbar \omega_H (l + 1/2)}} \right), \quad (6.4) $$

and the boson charge is \(|q| = 2|e|\).

As usual, the density of bipolarons is given by

$$ n_B = \int dE \frac{\rho(E)}{\exp \left( \frac{E - \mu}{T} \right) - 1}, \quad (6.5) $$

where \( T \) is the temperature, \( \mu \) the chemical potential, and the Boltzmann constant \( k_B = 1 \). Making a Taylor series expansion of the denominator of Eq. 6.5, and performing the integral and then the sum over the Landau levels, we obtain

$$ n_B = \frac{\sqrt{\pi} m_y m_z (\hbar \omega_H) \sqrt{T}}{2\sqrt{\pi}^3 \hbar^3} \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k \mu}{T} \right)}{\sqrt{k} \sinh \left( \frac{\hbar \omega_H k}{2T} \right)}. \quad (6.6) $$

The thermodynamic potential \( \Omega \), is given by

$$ \Omega = T \int dE n(E) \ln \left[ 1 - \exp \left( \frac{\mu - E}{T} \right) \right]. \quad (6.7) $$
Evaluating the integral as in Eq. 6.6, we obtain
\[ \Omega = -\frac{\sqrt{m_x m_y m_z (\hbar \omega_H)}}{2\sqrt{2\pi^3 \hbar^3}} \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k\mu}{T} \right)}{k^{\frac{3}{2}} \sinh \left( \frac{\hbar \omega_H k}{2T} \right)}. \] (6.8)

The magnetisation density is then given by
\[ M = -\frac{\partial \Omega}{\partial H} = \frac{2e\sqrt{m_x T^{\frac{3}{2}}}}{2\sqrt{2\pi^3 \hbar^2}} \times \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k\mu}{T} \right)}{k^{\frac{3}{2}} \sinh \left( \frac{\hbar \omega_H k}{2T} \right)} \left[ \frac{1}{k} - \frac{\hbar \omega_H}{2T} \coth \left( \frac{\hbar \omega_H}{2T} \right) \right]. \] (6.9)

It is convenient to introduce the following energy and magnetisation units:
\[ E_0 = 2\pi \hbar^2 \left( \frac{n_B^2}{m_x m_y m_z} \right)^{1/3}, \] (6.10)
\[ M_0 = \frac{2en_B\hbar}{c\sqrt{m_x m_y}}. \] (6.11)

Denoting the dimensionless quantities expressed in these units as \( \bar{T}, \bar{\omega} \) etc., we have then:
\[ M = M_0 \bar{T}^{\frac{3}{2}} \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k\mu}{T} \right)}{k^{\frac{3}{2}} \sinh \left( \frac{\bar{\omega} k}{2} \right)} \left[ \frac{1}{k} - \frac{\bar{\omega}}{2T} \coth \left( \frac{\bar{\omega}}{2T} \right) \right], \] (6.13)
\[ \bar{T}_c \approx 0.332 \] (6.14)

While one can successfully calculate various normal state properties using this model, the ideal CBG cannot be used as even a simple phenomenological model for the superconducting state. In a Bose system, the chemical potential \( \mu \) cannot enter a band as the Bose distribution has a pole at \( E = \mu \). As the temperature is decreased, \( \mu \) increases towards the bottom of the band, and below the temperature where \( \mu \) first reaches the bottom of the band the lowest energy level becomes macroscopically occupied, the phenomenon of Bose-Einstein condensation. One can find \( T_c \), the BEC critical temperature, by fixing \( \mu \) at the bottom of the band in the equation for the Boson density, Eq. 6.5. In the case of the ideal charged Bose gas in an external magnetic field, this would give
\[ n_B = \frac{\sqrt{m_x m_y m_z (\hbar \omega_H)}}{\sqrt{2\pi^3 \hbar^3}} \times \int_{E=0}^{\infty} dE \sum_{l=0}^{\infty} \frac{1}{\exp \left( \frac{E - \hbar \omega_H}{T} \right) - 1} \Im \left( \frac{1}{\sqrt{E - \hbar \omega_H (l + 1/2)}} \right). \] (6.15)
Bose condensation is therefore impossible at temperatures above absolute zero in the ideal charged Bose gas, as the one-dimensional singularity in the density of states of the lowest Landau level causes the integral for the Boson density to diverge. Once elastic scattering due to impurities is taken into account, however, the singularity in the density of states is smoothed out, thus allowing condensation to occur.

### 6.2.2 3D CBG with scattering

As in Chapter 3, we introduce impurity scattering via the non-crossing approximation. The equation for the bipolaron self-energy is then (see Appendix A)

\[ \Sigma_\nu(E) = \sum_{\nu'} \frac{\Gamma_{\nu,\nu'}}{E - E_{\nu'} - \Sigma_{\nu'}(E)}, \]

(6.16)

with \( \nu = (n, p_x, p_z) \) the quantum numbers in the Landau problem, \( \Gamma_{\nu,\nu'} \) the matrix element of the particle-impurity interaction strength. Unfortunately, this equation is analytically intractable as it stands, so we make the approximation that the bipolarons are not scattered between Landau levels, i.e. \( \Gamma_{\nu,\nu'} = \Gamma(n, n') \). This allows us to obtain an analytical result without sacrificing essential physics. The self energy in Landau level \( n \) is then given by:

\[ \Sigma_n(E) = -\frac{\Gamma \sqrt{m_x m_y m_z} (\hbar \omega_H)}{\sqrt{2 \pi^2 \hbar^3}} \frac{1}{\sqrt{\Sigma_n(E) + \hbar \omega_H (n/2) - E}}. \]

(6.17)

We introduce an energy unit characterising the interaction

\[ E_i^3 = \frac{\Gamma (m_x m_y m_z)^{1/2} \hbar \omega_H}{\pi \sqrt{2 \hbar^3}}, \]

(6.18)

so that

\[ \Sigma_n(E) = E_i \sigma \left( \frac{E - \hbar \omega_H (l + 1/2)}{E_i} \right) \]

(6.19)

with

\[ \sigma(\epsilon) = \frac{1}{\sqrt{\sigma(\epsilon) - \epsilon}}. \]

(6.20)

The solution to this equation is

\[ \sigma(\epsilon) = \frac{\epsilon}{3} + e^{-i\frac{\epsilon}{3}} \left( \frac{\epsilon^3}{27} + \frac{1}{2} + \sqrt{\frac{\epsilon^3}{27} + \frac{1}{4}} \right)^{\frac{1}{3}} + e^{i\frac{\epsilon}{3}} \left( \frac{\epsilon^3}{27} + \frac{1}{2} - \sqrt{\frac{\epsilon^3}{27} + \frac{1}{4}} \right)^{\frac{1}{3}}. \]

(6.21)
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If the density of states in level \( n \) without scattering is \( \rho_{n,\text{clean}}(E) \), the density of states with scattering will be

\[
\rho_{n,\text{imp}}(E) = \frac{1}{\pi} \int dE' \rho_{n,\text{clean}}(E') \frac{1}{E - E' - \Sigma_N(E)} \tag{6.22}
\]

\[
= -\frac{1}{\pi^1} \Sigma_n(E) \tag{6.23}
\]

\[
= -\frac{\sqrt{m_x m_y m_z} (\hbar \omega_H)}{2\pi^2 \hbar^3 \sqrt{E_i}} \sigma \left( \frac{E - \hbar \omega (l + 1/2)}{E_i} \right). \tag{6.24}
\]

As for the ideal CBG we may calculate the boson density and magnetisation:

\[
n_B = -\frac{\sqrt{m_x m_y m_z} (\hbar \omega_H) \sqrt{E_i}}{2\pi^2 \hbar^3} \int dE \sigma(e) \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k(\mu - E_i)}{T} \right)}{\sqrt{k} \sinh \left( \frac{\hbar \omega_H k}{2T} \right)}, \tag{6.25}
\]

\[
M = -\frac{2e \sqrt{m_x m_y m_z} (\hbar \omega_H) \sqrt{E_i}}{2\pi^2 \hbar^3 e} \int dE \sigma(e) \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k(\mu - E_i)}{T} \right)}{\sqrt{k} \sinh \left( \frac{\hbar \omega_H k}{2T} \right)}
\times \left[ \frac{4}{3k} - \frac{\hbar \omega_H}{2T} \coth \left( \frac{\hbar \omega_H}{2T} \right) - \frac{2E_i}{3T} \right]. \tag{6.26}
\]

Again, these equations may be expressed using the energy unit \( E_0 \) as:

\[
1 = -\tilde{\omega}_H \sqrt{\frac{E_i}{\pi}} \int dE \sigma(e) \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k(\mu - E_i)}{T} \right)}{\sqrt{k} \sinh \left( \frac{\tilde{\omega} H k}{2T} \right)}, \tag{6.27}
\]

\[
M = -M_0 \tilde{\omega} \sqrt{\frac{E_i}{\pi}} \int dE \sigma(e) \sum_{k=1}^{\infty} \frac{\exp \left( \frac{k(\mu - E_i)}{T} \right)}{\sqrt{k} \sinh \left( \frac{\tilde{\omega} H k}{2T} \right)}
\times \left[ \frac{4}{3k} - \frac{\tilde{\omega}_H}{2T} \coth \left( \frac{\tilde{\omega}_H}{2T} \right) - \frac{2E_i}{3T} \right]. \tag{6.28}
\]

We write \( \tilde{E}_0 = \Gamma \tilde{\omega}^{2/3} \). The density of states in a Landau level with scattering is compared with that without scattering in Fig. 6.1. It is clear that the square root singularity in the density of states has been smoothed out. As in Chapter 3, the non-crossing approximation neglects the Lifshitz tale of localised states at the bottom of the level. The energy at which the density of (extended) states found in this approximation becomes zero at the bottom of the Landau level zero can be taken as the mobility edge.
6.3 Discussion and comparison with experiment

6.3.1 Upper critical field of the BCS superconductor

In 1950, Ginzburg and Landau published a phenomenological description of the superconducting state of the superconductors which were then known [81]. Before we present our results on the critical field of the charged Bose gas, we briefly describe for comparison the Ginsburg-Landau result for the upper critical field of a classical superconductor.

Ginzburg and Landau proposed that the superconducting state is described by a complex order parameter $\psi$, which is zero in the normal state. By minimising their estimate for the free energy of the superconductor, they derived the equation

\[ \frac{1}{2m} (-i\hbar \nabla + 2eA)^2 \psi + (\alpha + \beta \psi^* \psi) \psi = 0 \]  

(6.29)

(this is written in the modern form with the carrier charge equal to $2e$. The correct supercarrier charge was not known when this theory was developed.) Here, $m$ is the pair mass and $A$ the vector potential. Within the theory, near $T_c$, $\alpha$ is proportional to $T - T_c$, with a negative constant of proportionality, and $\beta$ is a positive constant.
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In order to derive the upper critical field near the transition, one first assumes that in this regime the order parameter is small, so that Eq. 6.29 reduces to the linearised Ginzburg-Landau equation

\[ \frac{1}{2m}(\hbar \nabla + 2eA)^2\psi = -\alpha \psi. \tag{6.30} \]

Also, as \( \psi \) is small there is negligible screening by supercurrents, and we may use the uniform applied field for \( A \). It is therefore easy to discover the field at which this solution appears as this is merely the Schrödinger equation for a free particle in a magnetic field. Its solution is the Landau result used earlier in this chapter, giving \( -\alpha = \hbar^2 k_z^2 / 2m + (n + 1/2)\omega_B \). In this case however \( \alpha \) is fixed, and it is necessary to find the largest field for which such a solution can occur, i.e. the upper critical field \( H_{c2} \). This will occur for \( k_z = n = 0 \), giving \( H_{c2}(T) \sim (T_c - T) \) near the transition.

6.3.2 Critical field of the CBG

The unusual upper critical field in the cuprates has been measured by many authors, for instance in \( \text{Tl}_2\text{Ba}_2\text{CuO}_6 \) [82] and \( \text{Bi}_2\text{Sr}_2\text{CuO}_y \) [83] films, and in \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) single crystals [84, 85]. In all cases, positive curvature of the curve \( H_{c2}(T) \) was observed, e.g. Fig. 6.2. This positive curvature appears to be a universal property in the cuprates. In the example shown, \( H_{c2}(T) \) saturates as \( T \to 0 \); in some other samples the critical field diverges.

In a more recent paper, Gantmakher et al [86] have made a very detailed study of the upper critical field in underdoped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+\delta} \) single crystals at different levels of doping. They deliberately used samples with low \( T_c \) (< 30K) so that they could measure \( H_{c2} \) for small values of \( T/T_{c0} \) (\( T_{c0} \) = zero field critical temperature). This makes their results particularly interesting as for samples with higher \( T_c \), the upper critical field can rapidly become experimentally inaccessible as \( T \) decreased below \( T_c \). They found that the shape of the upper critical field curve was independent of precisely how one defines the transition temperature in a magnetic field (e.g. transition onset temperature, maximum gradient of resistivity curve etc.). They also showed that the upper critical field curves from different samples could be all be scaled onto a single universal curve, i.e.

\[ H_{c2}(T) = H_{sc} h_c(T/T_{c0}), \]

where \( H_{sc} \) characterises the sample and \( h_c(t) \) is the universal
Figure 6.2: Upper critical field of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ thin film [82]. Note the positive curvature of the curve everywhere.

curve, Fig. 6.3.

The critical field for charged bosons, $H^*$, is determined as the field in which the first nonzero solution of the linearised stationary equation for the macroscopic condensate wavefunction $\psi_0(r)$ appears [7]:

$$
\left( -\frac{1}{2m} \left( \nabla^2 - 2ieA(r) \right)^2 + U_{\text{imp}}(r) \right) \psi(r) = \mu \psi(r),
$$

(6.31)

where $U_{\text{imp}}(r)$ is the impurity potential. This equation is identical to the Ginzburg-Landau equation, Eq. 6.29, with the Ginzburg-Landau parameter $\alpha$ replaced by the chemical potential $\mu$. It is therefore necessary to use a second equation to calculate $\mu$ at a given temperature, the 'density sum rule' Eq. 6.25. The first non-trivial extended solution of Eq. 6.31 occurs as the temperature is decreased when $\mu = E_c$, the mobility edge. $H^*(T)$ is therefore determined from the density sum rule for the number of particles under the condition that the chemical potential coincides with the mobility edge $E_c$:

$$
n_B = \int_{E_c}^{\infty} \frac{\rho(E)dE}{\exp \left( \frac{E-E_c}{T} \right) - 1},
$$

(6.32)

We find that at temperatures significantly above $T = 0$, our theoretical $H^*(T/T_c0)$ curves can be mapped onto a single universal curve, in a similar manner to the ex-
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Figure 6.3: Left panel: Upper critical field for various YBCO samples, [86]. Right panel: The same curves, scaled onto the single universal curve $b_{sc}(T/T_{c0})$.

Experimental data shown earlier, by dividing by parameters $H_F$ characterising the scattering strengths, Fig. 6.4. We also find that as the scattering strength $\bar{\Gamma}$ is increased, $H_{c2}(T/T_{c0})/H_F$ increases at lower temperatures. The calculated curves for the critical field of charged Bosons provide a very good fit to the experiments of Gantmakher et al, Fig. 6.5.

One can make a simple estimate of the upper critical field of the CBG in low fields [7]. The width of the lowest Landau level will be proportional to the scattering rate, $\Gamma(H)$. The number of Bosons on the lowest level will therefore be proportional to the density of states near the bottom of that, $n_0 \sim H/\sqrt{\Gamma(H)}$. By the Fermi Golden Rule, the scattering rate is proportional to the density of states, i.e. $\Gamma(H) \sim H/\sqrt{\Gamma(H)}$, giving $\Gamma(H) \sim H^{2/3}$ and $n_0 \sim H^{2/3}$. One can calculate the critical field of charged Bosons, $H^*(T)$, by solving the equation

$$n_B = \int dE \frac{\rho(E)}{\exp(E/T) - 1}$$

for $H$ (here for simplicity we have set the zero of energy at the bottom of the lowest Landau level.) In zero field, this gives $n_B \sim T^2$. When a field is applied, one can make
Figure 6.4: Theoretical critical field curves scaled onto a single universal curve for $T \sim T_c$. In our theoretical units, the curves represent $\tilde{n} = 0.01$ (solid), 0.001 (dashed), 0.0001 (dotted).

Figure 6.5: Line: theoretical critical field of charged bosons. Squares: $H_{c2}(T)$ in Y123 ($T_{c0} = 19K$) [86].
the approximation that the zero-field density of states may be used for Landau levels above the first. This is because when performing the integral the other singularities in the DOS are integrated out, and thus one obtains \((n_B - n_0) \sim T^{3/2}\), with the same constant. Hence, \(n_0 \sim T_c^{3/2} - T^{3/2} \sim (T_c - T)\), and we obtain the estimate \(H^*(T) \sim (T_c - T)^{3/2}\) in the vicinity of \(T_c\). It is important to note that this estimate was made without any assumption as to the scattering mechanism, and it predicts the nonlinearity of the \(H_d(T)\) curves in the cuprates. As shown earlier, the BCS/Ginzburg-Landau theory necessarily predicts \(H^*(T) \sim (T_c - T)\) in the same regime.

It remains to discuss briefly the validity of the non-crossing approximation to calculate the density of states. As in Chapter 3, it neglects the Lifshitz tail of states localised by disorder. In his earlier work on the subject [80], Alexandrov models this by introducing an exponentially decaying tail in the lowest Landau level, and using Fermi statistics for the states in the tail (physically, the assumption is that each potential well created by disorder can only contain a single boson due to Coulomb repulsion.) At relatively high temperatures, this will have little effect as most of the localised states will be empty due to thermal excitation, but the effect is significant at lower temperatures. Making the additional approximation mentioned in the previous paragraph that the zero-field density of states can be used for Landau levels above the lowest, he found that at low temperatures increasing the number of localised states decreased the critical field. If the number of localised states becomes equal to the number of bosons, the critical field may even be finite at \(T = 0\), as observed experimentally in [82, 83].

### 6.3.3 Magnetisation of the CBG

The data for the induced magnetisation in the cuprates in a magnetic field show remarkable properties. In the most anisotropic materials, the curves of magnetisation against temperature at a given field all cross at a single point, Fig. 6.6. In the less anisotropic materials, there is a similar crossing point in the magnetisation divided by the square root of the field, Fig. 6.7. In both these cases, the crossing point is observed at a temperature near the zero-field \(T_c\). In our explanation of this phenomenon, we deliberately use the version of our theory which excludes scattering. This is the same methodology
Figure 6.6: Magnetisation $M$ as a function of temperature $T$ in constant fields for a ceramic sample of $\text{Bi}_{2.12}\text{Sr}_{1.90}\text{Ca}_{1.02}\text{Cu}_{1.96}\text{O}_{8+x}$ [87].

Figure 6.7: Magnetisation $M$ divided by square root of field as a function of temperature $T$ for a single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $T_c = 93\text{K}$. Data from [87].
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as used in the work on the electronic specific heat described in Section 2.5.7, and emphasises that in our model the crossing point is a normal state property of the charged Bose gas.

We find values for the boson density $n_B$ and effective masses $m_{x,y,z}$ in Y123 by following the methods of [25]. These may be calculated from the Hall coefficient $R_H$ and the penetration depth $\lambda_{ab,c}$:

$$R_H = \frac{1}{2en_B} \times \frac{4m_xm_y}{(m_x + m_y)^2}$$

$$T_c = 1.64 \left( \frac{eR_H}{\lambda_{ab}\lambda_c^2} \right)^{1/3}$$

It is important to remember that $m_{x,y}$ refer to the effective mass of the carriers in the two bipolaron bands, in the notation used throughout this chapter. Taking the realistic value for the anisotropy $m_x/m_y = 4$, we obtain $m_x = 1.3 \times 10^{-26} g$, $m_y = 3.3 \times 10^{-27} g$ and $n_B = 1.2 \times 10^{21} \text{cm}^{-3}$ for the $T_c = 91.5 K$ sample in [25]. In order to use these values to estimate the magnetisation in the $T_c = 93 K$ sample in [87], we choose our $m_z$ to given a theoretical $T_c$ of 93$K$ from the BEC temperature, i.e. $m_z = 1.9 \times 10^{-25} g$. We thus obtain for our energy and magnetisation units $E_0 = 3.9 \times 10^{-14} \text{erg}$ and $M_0 = 6.1 \text{emu}$. The dimensionless cyclotron frequency in a field of $10^4 \text{Oe}$ is $\tilde{\omega} = 1.3 \times 10^{-3}$. We stress that as our effective masses etc. are taken from a sample other than used in [87], and $m_z$ was chosen to give the correct $T_c$, they should be regarded as rough estimates for the correct parameter values.

Our theoretical curves are shown in Fig. 6.8. We find that while our model gives a crossing point in the magnetisation divided by the square root of field, and gives the correct order of magnitude for the magnetisation, it does not give the correct absolute value or gradient of the curves. Unfortunately, we have been unable to obtain an analogous result for the much more highly anisotropic BSCCO. It may be that a different model is indeed necessary due to this difference in anisotropy (indeed one alternative explanation based on superconducting fluctuations explicitly uses a two-dimensional model for BSCCO and a three-dimensional one for YBCO.)
Figure 6.8: Theoretical curves of magnetisation divided by the square root of field against temperature in Y123.

6.4 Summary

In this chapter, we have derived expressions for the number density of bosons and the diamagnetic response in the charged Bose gas, both with and without impurity scattering. The theory can explain the unusual shape of the upper critical field curves in the cuprates. The theory can also explain the crossing point in the curves of induced magnetisation against the square root of field in Y123, however this three-dimensional theory does not predict the crossing point in the magnetisation curves in the much more anisotropic BSCCO. It is important to note that we explain the induced magnetisation as the normal state Landau diamagnetism of the charged Bose gas.
Chapter 7

Conclusions

The work in this thesis has fallen into two main strands. After an introduction to the bipolaron theory of superconductivity in Chapter 2, in Chapters 3 and 4 we presented a theory of angle-resolved photoemission in charge-transfer Mott insulators. In Chapter 5 we then proposed explanations of various experimental phenomena based on our theory. In Chapter 6, we derived the equations necessary to calculate the magnetisation of the charged Bose gas, and then provided both a theoretical discussion of our results and a comparison with experiment in the cuprates.

In the chapters on photoemission, we first provided a simple derivation of the Physics behind the ARPES experiment. We then presented the polaron Green's function, which consists of two parts; a narrow peak due to coherent polaron tunneling and a broad background due to phonon processes. This incoherent part may be angle-dependent, and it remains to be seen what allowance must be made for it when analysing the spectra. Due to the anisotropy of the polaron bands in the cuprates, we were able to make a one-dimensional approximation for their dispersion near their respective minima. This in turn allowed us to use the exact result for the spectral function of a one-dimensional particle in a random potential to explain the spectral shape and dispersion in Y124. We also showed by using a tight-binding model that the observed polarisation dependence of the spectra in Y123 is compatible with the bipolaron theory. We also discussed the claimed observation of a Fermi surface in the cuprates by angle-resolved photoemission.
CHAPTER 7. CONCLUSIONS

Notwithstanding the current dispute between experimental groups over the topology of this FS, the dispersive feature crossing the Fermi level in many cases shows non-Fermi liquid characteristics. It is therefore important not to assume that these observations imply a Fermi-liquid like normal state, which is contradicted by many other experiments.

The charged Bose gas has previously been shown to explain the unusual positive curvature of the upper critical field curves in the cuprates. We have extended this model to investigate the effect of including the quantisation of all Landau levels, and also to calculate the normal state diamagnetism. The theory can explain the observation that curves of magnetisation divided by square root of field against temperatures at different fields in the less anisotropic materials (such as YBCO) cross at a single point. It would be valuable to investigate whether this theory can explain the dependence of this crossing point on the angle between the magnetic field and the $ab$-plane [89], and also to explain the crossing point in the magnetisation itself in the more anisotropic materials such as BSCCO.

To conclude, we have formulated the theory of ARPES in doped charge-transfer Mott insulators and the necessary equations to calculate the magnetisation of the charged Bose gas. As a result this work, we have proposed new explanations for various phenomena observed in the cuprates based on the bipolaron theory of superconductivity. There is increasing evidence from isotope effects and photoemission among other experiments that the mechanism for superconductivity in these materials is phononic/polaronic, and the bipolaron theory provides such a model which can explain a very wide range of other observations.
Appendix A

The non-crossing approximation

The non-crossing approximation for the self-energy sums all the diagrams in the perturbation expansion for Green's function in which the interaction lines do not intersect, Fig. A.1. The Dyson equation for the Green's function is

\[ G(k, E) = \frac{G_0(k, E)}{1 - G_0(k, E)\Sigma(k, E)} = \frac{1}{E - E_k - \Sigma}, \]

with \( G_0 \) the unperturbed Green's function, \( \Sigma \) the self-energy and \( E_k \) the unperturbed band dispersion. In the non-crossing approximation, we assume that self energy takes the form shown in Fig. A.1.

A.1 1-D particle in a random potential

The model for elastic scattering we have used in the work on photoemission is a particle moving in one dimension in a Gaussian white noise potential \( V(x) \), whose defining properties are:

\[ \langle V(x) \rangle = 0, \]

\[ \langle V(x)V(x') \rangle = \frac{1}{2}D\delta(x - x'). \]
Figure A.1: Self-consistent equation for the Green's function in the non-crossing approximation. A heavy solid line denotes the complete Green's function for the particle; a light solid line denotes the unperturbed Green's function. The approximation sums the subset of Feynman diagrams in which the interaction lines do not intersect.

As this is a local potential, the interaction line in the Feynman diagrams carries momentum but not energy. The non-crossing expression for the self-energy is then

\[ \Sigma(k, E) = D^2 \sum_q G(k - q, E). \]  

(A.4)

It is immediately clear that the self-energy will be independent of \( k \), and may thus be written as

\[ \Sigma(E) = D^2 \int dE G(k - q, E). \]  

(A.5)

Using units for energy \( \epsilon_0 = (D^2 m \hbar^{-2})^{1/3} \) and inverse length \( \kappa_0 = (D m^2 \hbar^{-4})^{1/3} \), this expression reduces to

\[ \Sigma(E) = \frac{1}{2\pi} \int_0^\infty dE' \frac{1}{\sqrt{E'}} \frac{1}{E - E' - \Sigma(E)}. \]  

(A.6)

The integral may be performed by contour integration around the keyhole contour, Fig. A.2, to give

\[ \Sigma(E) = \frac{-1}{2^{3/2} \sqrt{\Sigma(E)} - E}. \]  

(A.7)

Eq. A.7 may be rearranged to give a simple cubic, which one can solve using the standard method.
A.2 CBG in a magnetic field

In this case, the density of states without scattering comprises the well-known Landau levels:

\[
\rho(E) = \frac{\sqrt{m_x m_y m_z}}{\sqrt{2\pi^2 \hbar^3}} \sum_{l=0}^{\infty} \Re \left( \frac{1}{\sqrt{E - \hbar \omega_H (l + 1/2)}} \right) .
\]  

(A.8)

The non-crossing approximation for the self-energy is then

\[
\Sigma_\nu(E) = \sum_{\nu'} \frac{\Gamma_{\nu,\nu'}}{E - E_{\nu'} - \Sigma_{\nu'}(E)},
\]  

(A.9)

with \( \nu = (n, p_x, p_z) \) the quantum numbers in the Landau problem, and \( \Gamma_{\nu,\nu'} \) the matrix element of the particle-impurity interaction. As it stands, this equation cannot be solved analytically, but if we assume that \( \Gamma_{\nu,\nu'} = \Gamma_{\delta n, n'} \) (i.e. no inter-level scattering) then the self-energy for each Landau level may be found as for the 1-D particle in a random potential.
Appendix B

1D particle in a random potential

B.1 Introduction and definitions

In this appendix, we present a summary of Halperin's derivation of the spectral function of a particle moving in one dimension in a Gaussian white noise potential [43]. The particle moves on a line segment $0 \leq x \leq L$ obeying the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad (B.1)$$

where $V$ is the random potential described by a statistical distribution with expectation values

$$\langle V(x) \rangle = 0,$$  

$$\langle V(x)V(x') \rangle = \frac{1}{2}D \delta(x - x'). \quad (B.2)$$

The wavefunctions $\psi_i(x)$ are assumed to satisfy boundary conditions of the form

$$\psi'(0) = z_0 \psi(0),$$

$$\psi'(L) = z_L \psi(L), \quad (B.4)$$

where $z_0, z_L$ are arbitrary real constants. The stationary state wavefunctions are denoted $\psi_j$, with energies $E_j$. The spectral density for the particle is defined by

$$A(k, E) \equiv \frac{1}{L} \left\langle \sum_j \left| \int_0^L e^{ikx} \psi_j(x) \frac{dx}{\sqrt{L}} \right|^2 \delta(E - E_j) \right\rangle. \quad (B.6)$$
Here and throughout this appendix, angle brackets denote a statistical average over an ensemble of potentials, rather than a quantum mechanical ensemble average. The total density of states is defined by

$$\rho(E) = \frac{1}{L} \left\langle \sum_j \delta(E - E_j) \right\rangle.$$  \hspace{1cm} (B.7)

The spectral density is normalised following the convention that

$$\int_{-\infty}^{\infty} A(k, E) dE = 1,$$  \hspace{1cm} (B.8)

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} A(k, E) dk = \rho(E),$$  \hspace{1cm} (B.9)

$$A(k, E) = -\frac{1}{\pi} \Im G(k, E),$$  \hspace{1cm} (B.10)

where $G(k, E)$ is the Green's function for the particle at energy $E$ and wavevector $k$. From now on in this Appendix, we use units of energy $\epsilon_0 = (D^2m\hbar^{-2})^{1/3}$ and inverse length $\kappa_0 = (Dm^2\hbar^{-4})^{1/3}$.

B.2 Derivation of the spectral function

For each potential in the statistical ensemble, $\phi(x; E)$ is defined to be the unique solution of the second-order differential equation with boundary conditions

$$-\frac{1}{2} \frac{\partial^2 \phi}{\partial x^2} + V(x) \phi = e\phi$$  \hspace{1cm} (B.11)

$$\phi(0; E) = 1$$  \hspace{1cm} (B.12)

$$\left. \frac{\partial \phi}{\partial x} \right|_{(0; E)} = z_0 \phi(0; E).$$  \hspace{1cm} (B.13)

It is important to note that while $\phi$ satisfies the Schrödinger equation for the system, it is not an energy eigenstate unless it also satisfies the $x = L$ boundary condition Eq. B.5.

The following functions are also defined:

$$z(x; E) \equiv \frac{\partial \phi(x, E)}{\partial x} / \phi(x; E),$$  \hspace{1cm} (B.14)

$$U_1(x; E) \equiv \left[ \int_0^x e^{ikx'} \phi(x'; E) dx' \right] / e^{ikx} \phi(x; E),$$  \hspace{1cm} (B.15)

$$U_2(x; E) \equiv \left[ \int_0^x \phi(x'; E) dx' \right] / e^{ikx} \phi(x; E)^2,$$  \hspace{1cm} (B.16)

$$U_3(x; E) \equiv \frac{\partial z(x, E)}{\partial E}.$$  \hspace{1cm} (B.17)
It follows from Eqs. B.14 and B.11 that

\[
\frac{\partial^2 \phi}{\partial x^2} - \left( \frac{\partial \phi}{\partial x} \right)^2 = -2z^2 - 2E + 2V(x). \tag{B.18}
\]

In a similar manner, it may be shown that

\[
\begin{align*}
\frac{\partial U_1}{\partial x} &= 1 - zU_1 - ikU_1, \tag{B.19} \\
\frac{\partial U_2}{\partial x} &= 1 - 2zU_2, \tag{B.20} \\
\frac{\partial U_3}{\partial x} &= -2 - 2zU_3. \tag{B.21}
\end{align*}
\]

At \( x = 0 \), \( z = z_0 \) and \( U_1 = U_2 = U_3 = 0 \). At a point \( x = x_n \) where \( \phi(x_n ; E) = 0 \), \( z, U_1, U_2 \) and \( U_3 \) are all infinite. However, the four quantities \( (x-x_n)x, (x-x_n)U_1, (x-x_n)^2U_2 \) and \( (x-x_n)^2U_3 \) are all continuous at \( x_n \), and along with this property Eqs. B.18-B.21 specify \( z, U_1, U_2 \) and \( U_3 \) for all \( x \). It may also be seen from Eqs. B.20 and B.21 that for all \( x \):

\[
U_3(x; E) = -2U_2(x; E). \tag{B.22}
\]

As from Eq. B.16 \( U_2 \) is positive for all \( x \), it follows immediately that \( U_3 \) is negative for all \( x \).

For each potential configuration, the energy \( E_i \) of the \( i \)th eigenstate of the original Hamiltonian is the \( i \)th value of \( E \) for which \( Z(L; E) = z_L \), i.e. for which \( z \) satisfies both the \( x = 0 \) and \( x = L \) boundary conditions associated with the Hamiltonian. From the properties of the Dirac delta function, it follows that

\[
\sum_j \delta(E - E_j) = \delta [z_L - z(L; E)] \left| \frac{\partial z(l; E)}{\partial E} \right|. \tag{B.23}
\]

As a result,

\[
\begin{align*}
A(k, E) &= \frac{1}{L} \left\langle \left| \frac{\int_0^L \phi(x; E)e^{ikx}dx}{\int_0^L \phi(x; E)^2dx} \right|^2 \sum_j \delta(E - E_j) \right\rangle \\
&= \frac{1}{L} \left\langle \left| U_1(L; E) \right|^2 \frac{U_3(L; E)}{U_2(L; E)} \delta [z_L - z(L; E)] \right\rangle \\
&= \frac{2}{L} \left\langle \left| U_1(L; E) \right|^2 \delta [z_L - z(L; E)] \right\rangle. \tag{B.24}
\end{align*}
\]

For clarity, following Halperin, we consider for the time being the case \( k = 0 \); this avoids complications due to the presence of complex numbers. The joint probability
APPENDIX B. 1D PARTICLE IN A RANDOM POTENTIAL

density function (p.d.f.) of $z$ and $U_1$ at the point $x$ is

$$P(z, U_1; x) = \langle \delta[z - z(x; E)]\delta[U_1 - U_1(x; E)] \rangle.$$  \hfill (B.25)

The spectral density may then be re-written as

$$A(0, E) = \frac{2}{L} \int_{-\infty}^{\infty} U_1^2 P(zL, U_1; L) dU_1.$$  \hfill (B.26)

If an expression can be found for the joint p.d.f. of $z$ and $L$ at $x = L$, the spectral density would be determined by Eq. B.26. As the distribution at $x = 0$ is known:

$$P(z; U_1; 0) = \delta(z - z_0)\delta(U_1),$$  \hfill (B.27)

it is sufficient to obtain an 'equation of motion' for $P(z; U_1; x)$ as $x$ moves along the line. If the potential term was absent from Eq. B.18 one could immediately write down the 'conservation of probability' equation

$$\frac{\partial P}{\partial x} = -\frac{\partial}{\partial z} \left( \frac{\partial z}{\partial P} \right) - \frac{\partial}{\partial U_1} \left( \frac{\partial U_1}{\partial P} \right)$$  \hfill (B.28)

$$= \left[ \frac{\partial}{\partial z} (z^2 + 2E) + \frac{\partial}{\partial U_1} (zU_1 - 1) \right] P.$$  \hfill (B.29)

(the analogy is with the conservation of mass equation for a two-dimensional inviscid fluid with 'position' coordinate $(z, U_1)$ and 'time' coordinate $x$.) From Eq. B.18, it follows that within the 'fluid' analogy, the random potential $V(x)$ causes a 'random walk' of the coordinate $z$ with

$$\left[ (z(x + dx; E) - z(x; E))^2 \right] = 2dx.$$  \hfill (B.30)

This adds a 'diffusion' term to Eq. B.29, giving

$$\frac{\partial P}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) + \frac{\partial}{\partial U_1} (zU_1 - 1) \right] P.$$  \hfill (B.31)

Boundary conditions at infinity for the distribution of $z$ and $U_1$ may be derived from their properties at the nodes of $\phi$. Together with these, Eqs. B.27 and B.31 determine $P(z, U_1; x)$ for all $x$. Numerical solution of such a partial differential equation involves significant computational difficulties. Fortunately, Halperin was able to convert this into a form more suitable for calculation. The three functions $P_s(z; x)$ ($s = 0, 1, 2$) are defined as

$$P_s(z; x) = \langle U_1(x; E)^s \delta[z - z(x; E)] \rangle$$  \hfill (B.32)

$$= \int_{-\infty}^{\infty} P(z, U_1; x) U_1^s dU_1.$$  \hfill (B.33)
These equations appear rather complicated. However, $P_0(z; E)$ is just the p.d.f. of $z(x; E)$, and $P_1$ and $P_2$ are the first and second moments with respect to $U_1$ of the joint distribution of $Z$ and $U_1$. Differentiation under the integral sign and integration by parts of the resulting terms including derivatives with respect to $U_1$ give the following equations of motion for the functions $P_2$:

\[
\frac{\partial P_0}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) \right] P_0, \tag{B.34}
\]

\[
\frac{\partial P_1}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) - z \right] P_1 + P_0, \tag{B.35}
\]

\[
\frac{\partial P_2}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + (z^2 + 2E) \frac{\partial}{\partial z} \right] P_2 + 2P_1. \tag{B.36}
\]

The following boundary conditions for $P_{0,1,2}$ may also be derived from the properties of $z$ and $U_1$ at the nodes of $\phi$:

\[
\lim_{z \to +\infty} z^{2-s} P_s = \lim_{z \to -\infty} z^{2-s} P_s. \tag{B.37}
\]

As an example we show this for $P_0$. At a node of $\phi$ at $x = x_n$, $z$ is infinite so Eq. B.18 may be approximated by

\[
\frac{\partial z}{\partial x} = -z^2, \tag{B.38}
\]

giving

\[
z \sim \frac{1}{x - x_n}. \tag{B.39}
\]

Assuming that the nodes are evenly distributed over the line, the probability that for a particular potential $x$ is be within a distance $\delta x$ of a node will be proportional to $1/\delta x$.

Thus from Eq. B.39 the probability that $z > Z$ and the probability that $z < -Z$ ($Z \gg 1$) are both proportional to $Z$, with the same constant of proportionality. This is sufficient to show that the p.d.f. for $z$, $P_0(Z) = dP(z < Z)/dZ$ satisfies Eq. B.37.

From the definitions of $z$ and $U_1$, at $x = 0$

\[
P_0(z; 0) = \delta(z - z_0), \tag{B.40}
\]

\[
P_1(z; 0) = P_2(z; 0) = 0. \tag{B.41}
\]

The equations we now have are much easier to solve numerically than the equation of motion for the $P(z, U_1; x)$. Given the solutions, the spectral may be calculated immediately as

\[
A(k, E) = \frac{2}{L} P_2(z; L). \tag{B.42}
\]
APPENDIX B. 1D PARTICLE IN A RANDOM POTENTIAL

When $k \neq 0$, some of the above equations which were derived for the case $k = 0$ must be modified slightly. $P_2$ is defined in general as

$$P_2(z; x) = \langle |U_1(x; E)|^2 \delta[z - z(x; E)] \rangle. \quad (B.43)$$

The differential equations for $P_1$ and $P_2$ are replaced by

$$\frac{\partial P_1}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) - z - ik \right] P_1 + P_0, \quad (B.44)$$

$$\frac{\partial P_2}{\partial x} = \left[ \frac{\partial^2}{\partial z^2} + (z^2 + 2E) \frac{\partial}{\partial z} \right] P_2 + 2\Re P_1. \quad (B.45)$$

The rest of the equations are still valid.

For macroscopic systems, it is sufficient to calculate the spectral density in the macroscopic limit $L \to \infty$. Halperin gives physical arguments that for large $x$

$$P_0(z; x) \sim p_0(z), \quad (B.46)$$

$$P_1(z; x) \sim p_1(z), \quad (B.47)$$

$$P_2(z; x) \sim Cz + f(z), \quad (B.48)$$

where $p_0, p_1, f$ and the constant $C$ are all independent of $x$. The spectral density is then given for large $x$ by

$$A(k, E) = 2C. \quad (B.49)$$

It is independent both of the length $L$ of the line on which the particle is constrained to move and the boundary conditions imposed at each end.

The functions $p_{0,1}$ obey Eqs. B.34 and B.43 with the left hand sides set to zero:

$$\left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) \right] p_0 = 0 \quad (B.50)$$

$$\left[ \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2 + 2E) - z - ik \right] p_1 + p_0 = 0. \quad (B.51)$$

The same boundary conditions apply, but as $p_0$ is a p.d.f. it satisfies the normalisation

$$\int_{-\infty}^{\infty} p_0(z)dz = 1. \quad (B.52)$$

Substituting $p_0$ and $p_1$ into Eq. B.45, multiplying both sides by $p_0(-z)$ and integrating with respect to $z$, an expression for $C$ is obtained, giving

$$A(k, E) = 4 \int_{-\infty}^{\infty} p_0(-z) \Re p_1(z)dz. \quad (B.53)$$
The simple form of the integral arises from the fact that the differential operator on the right hand side of Eq. B.50 is the adjoint, except from a change of sign in \( z \), of that on the right hand side of Eq. B.45.

### B.3 Analytical results and method for calculation

Eq. B.50 may be integrated immediately to give

\[
p_0(z) = C_0 \exp \left( -\frac{z^3}{3} - 2ze \right) \int_{-\infty}^{z} \exp \left( \frac{u^3}{3} + 2ue \right) du,
\]

where \( C_0 \) is a constant, which may be determined from the normalisation condition for \( p_0 \) to give

\[
C_0 = \left[ \frac{1}{\pi^{1/2}} \int_{0}^{\infty} u^{-1/2} \exp \left( -\frac{u^3}{12} - 2ue \right) du \right]^{-1}.
\]

Halperin shows that \( C_0 \) is equal to the cumulative density of states \( N(E) \), and provides an analytical expression for it in terms of the Airy functions \( \text{Ai} \) and \( \text{Bi} \):

\[
C_0 = N(E) = \frac{1}{\pi^2} \times \frac{1}{[\text{Ai}(-2E)]^2 + [\text{Bi}(-2E)]^2}.
\]

The problem thus reduces to solving Eq. B.51 for \( p_1 \). We used a numerical shooting method, choosing \( p_1(-Z) = \alpha/Z \) and \( p_1'(-Z) = -\alpha/Z^2 \) for a suitably large negative \( Z \) and searching for a value of \( \alpha \) such that \( p_1(+Z) = -1/\alpha \). Halperin also gives an asymptotic result for \( E \ll 0 \):

\[
A_p(k, E) \sim 2\pi \sqrt{-2\varepsilon} \exp \left[ -\frac{4}{3} (-2E)^{3/2} \right] \cosh^2 \left[ \frac{\pi k}{(-8E)^{3/2}} \right].
\]

He also provides the non-crossing approximation result, which works very well for \( E > 1 \) in the units he uses here, and was derived in the previous Appendix.
Appendix C

The variable phase method

C.1 Introduction

The variable phase method reformulates the phase shift theory of potential scattering in a form which makes numerical calculation easier. The derivation given here follows Calogero [47]. The scattering problem is described by a stationary wavefunction \( \psi(r) \), satisfying the time-independent Schrödinger equation

\[
\left[ \nabla^2 + k^2 - V(r) \right] \psi(r) = 0, \tag{C.1}
\]

with asymptotic boundary condition

\[
\psi(r) \xrightarrow{r \to \infty} e^{ikz} + f(\theta) \frac{e^{ikr}}{r}. \tag{C.2}
\]

Here, the system of coordinates is chosen such that the incident beam of particles (wavevector \( k \)) is parallel to the \( z \)-axis, \( \theta \) is the angle between the direction of observation and the incident direction, and units are chosen with \( \hbar = 2m = 1 \). In the boundary condition, the first term represents the incident beam, the second the scattered particles. For the following theory to apply the potential \( V(r) \) must vanish exponentially as \( r \to \infty \).

This equation may be reduced to a set of second order ordinary differential equations.
by making the substitution
\[ \psi(r) = \frac{1}{r} \sum_{l=0}^{\infty} u_l(r) P_l(\cos \theta), \]  
where the \( P_l \)'s are the Legendre polynomials. The condition that \( \psi(r) \) finite everywhere gives the boundary condition
\[ u_l(0) = 0. \]  
Substituting Eq. C.3 into the Schrödinger equation, one obtains the 'radial Schrödinger equation'
\[ \frac{d^2}{dr^2} u_l(r) + \left[ k^2 - \frac{l(l+1)}{r^2} - V(r) \right] u_l(r) = 0. \]  
In the following, it is assumed that
\[ V(r) \sim \frac{V_0}{r^n}, \]  
for \( n < 2 \). Potentials satisfying this condition are called 'regular'. Under this assumption, there are two linearly independent solutions of Eq. C.5, which behave near the origin like \( r^{l+1} \) and \( r^{-l} \). The boundary condition C.4 may therefore be replaced by the more specific condition
\[ u_l(r) \xrightarrow{r \to 0} \text{const} \times r^l. \]  
The radial wavefunction defines the 'scattering phase shift' \( \delta_l \) through the comparison of its behaviour with that of the asymptotic solution
\[ u_l \xrightarrow{r \to \infty} \text{const} \times \sin(kr - l\pi/2 + \delta_l). \]  
The term \( l\pi/2 \) is inserted to ensure that \( \delta_l \) tends to zero for all \( l \) as the potential vanishes. The concept of phase shifts is useful, as it allows calculation of the scattering amplitude. By use of the asymptotic expansion
\[ e^{ikr} \xrightarrow{r \to 0} \frac{1}{kr} \sum_{l=0}^{\infty} (2l+1)^i \sin \left( kr - \frac{l\pi}{2} \right) P_l(\cos \theta), \]  
the following expression is obtained:
\[ f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1)^i e^{i\delta_l} \sin (\delta_l) P_l(\cos \theta). \]  
The variable phase method will reduce this problem of solution of a second order differential equation and comparison with an asymptotic result to the solution of a first order equation, and merely finding the value to which its solution tends as \( r \to \infty \).
APPENDIX C. THE VARIABLE PHASE METHOD

One further result will be used in the derivation. The radial wavefunction satisfies the following integral equation:

\[ u_i(r) = \hat{j}_l(kr) - \frac{1}{k} \int_0^r ds \left[ \hat{j}_l(kr) \hat{n}_l(ks) - \hat{j}_l(ks) \hat{n}_l(kr) \right] V(s) u_i(s). \tag{C.11} \]

The Ricatti-Bessel functions \( \hat{j}_l, \hat{n}_l \) are defined as

\[ \hat{j}_l(x) = \sqrt{\frac{\pi x}{2}} J_{l+1/2}(x), \tag{C.12} \]
\[ \hat{n}_l(x) = (-1)^{l+1} \sqrt{\frac{\pi x}{2}} J_{-(l+1/2)}(x), \tag{C.13} \]

where \( J_p(x) \) is a standard Bessel function. Full details of the Riccati-Bessel functions' properties may be found in Appendix 1 of [47] or in [88]. Using this, Eq. C.7 may be replaced by the more specific form

\[ u_i \overset{r \to 0}{\to} \hat{j}_l(kr) \overset{r \to 0}{\to} \frac{(kr)^{l+1}}{(2l + 1)!!}. \tag{C.14} \]

C.2 Derivation of the phase equation

The derivation begins with the introduction of two more functions defined in terms of the radial wavefunction:

\[ s_l(r) = -\frac{1}{k} \int_0^r dr' V(r') \hat{j}_l(kr') u_i(r') \tag{C.15} \]
\[ c_l(r) = 1 - \frac{1}{k} \int_0^r dr' V(r') \hat{n}_l(kr') u_i(r'). \tag{C.16} \]

From the behaviour of the other functions in terms of which these are defined, they behave near the origin as

\[ s_l(r) \overset{r \to 0}{\to} -\frac{V_0 r^{-(l-m)}}{k^2} \frac{(kr)^{2l+3}}{(2l + 3 - m)(2l + 1)!!^2} \overset{r \to 0}{\to} 0, \tag{C.17} \]
\[ c_l(r) \overset{r \to 0}{\to} 1 + \frac{V_0 r^{2-m}}{(2 - m)(2l + 1)} \overset{r \to 0}{\to} 1. \tag{C.18} \]

Comparison of the definitions of \( s_l(r) \) and \( c_l(r) \) with the integral definition of the radial wavefunction \( u(l)(r) \), Eq. C.11, gives

\[ u_i(r) = c_l(r) \hat{j}_l(kr) - s_l(r) \hat{n}_l(kr), \tag{C.19} \]
\[ u_i(r) \overset{r \to \infty}{\to} c_l(\infty) \sin \left( kr - \frac{l\pi}{2} \right) + s_l(\infty) \cos \left( kr - \frac{l\pi}{2} \right). \tag{C.20} \]
This relies on the asymptotic expansions of \( j_l(x) \) and \( n_l(x) \) for \( x \gg l \),

\[
  j_l(x) \xrightarrow{x \to \infty} \sin \left( x - \frac{l\pi}{2} \right), \quad (C.21)
\]

\[
  n_l(x) \xrightarrow{x \to \infty} \cos \left( x - \frac{l\pi}{2} \right), \quad (C.22)
\]

and the fact that \( s_l(r) \) and \( c_l(r) \) have finite asymptotic limits. This follows from their definitions Eqs. C.15 and C.16, and the assumed asymptotic vanishing of the potential at infinity. By a comparison of Eq. C.20 with the definition of the phase shift Eq. C.8, \( \delta_l \) may be expressed in terms of \( s_l, c_l \) as

\[
  \tan \delta_l = \frac{s_l(\infty)}{c_l(\infty)}. \quad (C.23)
\]

This suggests that it is useful to introduce a new function

\[
  t_l(r) = \frac{s_l(r)}{c_l(r)}. \quad (C.24)
\]

From the small \( r \) expansions of \( s_l \) and \( c_l \), the leading term in the expansion of \( t_l(r) \) is the same as for \( s_l(r) \):

\[
  t_l(r) \xrightarrow{r \to 0} - \frac{V_0 r^{-m}}{k^2} \frac{(kr)^{2l+3}}{(2l + 3 - m)(2l + 1)!} \xrightarrow{r \to 0} 0. \quad (C.25)
\]

Also, the asymptotic behaviour of \( t_l(r) \) gives immediately the tangent of the scattering phase shift:

\[
  \lim_{r \to \infty} t_l(r) \equiv t_l(\infty) = \tan \delta_l. \quad (C.26)
\]

We now have a function whose behaviour at the origin is known, and whose asymptotic value gives the scattering phase shift. It remains to be shown that it is possible to go from the origin to the asymptotic region in order to calculate the phase shifts. Differentiation of the definitions of \( s_l \) and \( c_l \) from Eqs. C.15 and C.16, and substitution for \( u_l(r) \) from C.19 provides the following pair of coupled first order equations:

\[
  s'_l(r) = -\frac{1}{k} V(r) \hat{j}_l(kr) [c_l(r)\hat{j}_l(kr) - s_l(r)\hat{n}_l(kr)], \quad (C.27)
\]

\[
  c'_l(r) = -\frac{1}{k} V(r) \hat{n}_l(kr) [c_l(r)\hat{j}_l(kr) - s_l(r)\hat{n}_l(kr)]. \quad (C.28)
\]

One can now calculate

\[
  t'_l(r) = \frac{s'_l(r)c_l(r) - s_l(r)c'_l(r)}{c_l(r)^2} = -\frac{1}{k} V(r) [\hat{j}_l(kr) - t_l(r)\hat{n}_l(kr)]^2, \quad (C.29)
\]
which seems to allow calculation of \( t_l(\infty) \) from \( t_l(0) \), as required.

The only problem with this equation for \( t_l(r) \) is that \( c_l(r) \) might vanish, giving a pole. This difficulty can be avoided by introducing one more function

\[
t_l(r) = \tan \delta_l(r).
\]  

(C.30)

\( \delta_l(r) \) has the same small \( r \) expansion to leading order,

\[
\delta_l(r) \xrightarrow{r \to 0} - \frac{V_0 r^{-m}}{k^2} \frac{(kr)^{2l+3}}{(2l + 3 - m)[(2l + 1)!!]^2} \xrightarrow{r \to 0} 0,
\]

(C.31)

and from Eq. C.26

\[
\lim_{r \to \infty} \delta_l(r) = \delta_l(\infty) = \delta_l.
\]

(C.32)

Inserting the definition of \( \delta_l \) into the differential equation for \( t_l \) yields the differential equation

\[
\delta'_l(r) = - \frac{V(r)}{k} \left[ \cos \delta_l(r) j_l(kr) - \sin \delta_l(r) \hat{n}_l(kr) \right]^2.
\]

(C.33)

This last equation is known as the 'phase equation' and the function \( \delta_l(r) \) is known as the 'phase function' for obvious reasons.
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