ELECTRONIC POLARONS

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Abstract

A candidate model for explaining pairing in high- T_c superconductors is studied. When electrons polarize nearby ions, this electronic polarization can follow, and alter its properties. An electron together with its polarization is an electronic polaron. This is described analogously to polarons that instead use phonons. Both a static and a dynamic model are described. Two similar existing models, one for FeAs and one for La₂CuO₄, are discussed and expanded. Both longrange electron-polarization interactions, as well as Coulomb repulsion are added. New parameters in the case of La₂CuO₄ show no bound state, which is needed for superconductivity. The addition of long-range interaction in the case of FeAs can compensate an unscreened Coulomb repulsion. The model is also applied to a new structure, a monolayer of FeSe grown on a $SrTiO_3$ substrate. This structure has achieved critical temperatures of up to 100 K in experiments. For this structure the model shows that long-range interactions are not enough to compensate the Coulomb repulsion, if we do not take into account the $SrTiO_3$ substrate. $SrTiO_3$ has a high dielectric constant and if we introduce this into the model, we do get a bound state for FeSe. Suggestions are made for further research.

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Introduction

In this thesis we examine superconductivity in high temperature superconductors. In particular, we study a candidate model for explaining pairing.

Background

Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes.¹ It is the phenomenon where some materials transition to a state with zero resistivity, and expel magnetic fields. For decades people would try and devise a theory to describe this. The most successful theory was one by Ginzburg and Landau². This was a macroscopic theory, however, and did not describe what individual electrons were doing. This was solved by Bardeen, Cooper, and Schrieffer (known as BCS theory) in 1957.

BCS theory

BCS theory³ was the first microscopic theory of superconductivity. The idea is that two electrons can interact with each other mediated by phonons. The resulting interaction is attractive for those electrons in a small region around the Fermi surface. Such an interaction was shown to give a collective bound state. This collective state could flow without resistance as it would take more energy to create an excited state than the flowing electrons have. In the model an electron with momentum k_1 can emit a phonon with momentum κ , which is then absorbed by another electron with momentum k_2 . The momenta of the electrons before and after the interaction need to lie within a small region around the Fermi surface. As we can see in figure 1, this is more easily done when the two electrons have opposite momenta. If electron a pairs with electron b_2 , they can scatter to anywhere in the green annulus. If it pairs with electron b_1 instead, they can only scatter to a limited subsection. Thus the interaction is greatest for states with total momentum 0.

High- T_c Superconductors

BCS theory and its extension, Migdal-Eliashberg theory can not accurately describe all materials. High- T_c superconductor classes such as cuprates and



Figure 1: Scattering gives greatest interaction for states with opposite momenta. The green annulus is the small region around the Fermi surface that participates in pairing.

pnictides would not be superconducting at such high temperatures according to those models. Since the discovery of the first superconducting cuprates in 1986^4 , numerous theories have been developed, but none have garnered unilateral support. Alexandrov⁵ proposed a model in which the electron-phonon interaction is strong enough that electrons will effectively carry phonons with them. Together the electron and its phonon 'cloud' are called a polaron. Polarons will interact with each other differently than bare electrons.

Polarons

When electrons in crystals interact strongly with phonons, they deform the lattice as they move, which influences its effective mass. An electron with its lattice deformation is called a polaron. Many different theories that describe polarons have been devised. We can treat the crystal as a continuum for large polarons, or as a lattice for small polarons. If we treat the crystal as a lattice, there are two models we can use. One is the Holstein model⁶ where an electron can hop between two sites, interacting with a vibrating ion in between. This can then be extended to an infinite lattice with electrons only interacting with the closest ions. Another model is the Fröhlich model⁷, where the electronphonon interaction (EPI) range is infinite. Because ions are electrically charged, a deformation of the crystal structure induces a polarization, which lowers the energy of the electron. It can also screen the interaction between polarons. If the electron-phonon interaction is strong enough, this screening is stronger than the Coulomb repulsion of two bare electrons. Such an attractive interaction is exactly what is needed to obtain superconductivity. The difference with the typical BCS theory is that this attractive interaction is present in real space, instead of momentum space.

Instead of phonons, electrons can also interact with other electrons by polarizing them. This leads to electronic polarons, which use many of the same methods. An early description of this was done by Toyozawa in 1954.⁸ The polarization wave there was conceived analogous to phonons, replacing the displacement of an ion with the electronic polarization of the ion instead. An important difference is that electrons are much lighter than ions, and as such move much more quickly. Retardation effects are thus reduced. Recently, Berciu et al.⁹ devised an electronic polaron model to describe an iron based superconductor, wherein the carriers that reside on iron polarize arsenic ions. This model was then adapted to cuprate superconductors 10 .

Aim of this Thesis

In this thesis it is the goal to develop a model of pairing that is necessary for the presence of a superconducting state. We aim to use an electronic polaron interaction for this. The theory of (phononic) polaronic superconductivity used by Alexandrov can be altered to use electronic polarons. This thesis compares the model to the static electronic polaron model by Berciu et al.⁹, for both cuprates and iron based superconductors. Recently it was found that a monolayer of FeSe grown on SrTiO₃ is superconducting up to temperatures of $100K^{11}$. Because bulk FeSe is normally superconducting at $8K^{12}$, it is likely that the STO substrate has an effect. SrTiO₃ has a very high dielectric constant, which is related to the polarizability of the constituents. So we can incorporate it into the model as well.

In chapter 1 we will explain quantum mechanical polarization and describe the static model. In chapter 2 we shall look at the dynamic model. In chapter 3 we will then apply the models to some high temperature superconductors.

Chapter 1

Electronic bipolaron theory

Normally, polarons are described by an electron interacting with phonons, where the ions are assumed to move rigidly from an equilibrium position. Ions are not rigid, however, and will deform when there is an electric field present. A simple description of this effect considers the electrons having a constant density sphere of charge, with its center displaced from the nucleus by a certain amount. This displacement can be found by setting the force of the nucleus on the electron cloud equal to the external field. The polarization is then the charge times this displacement, and the polarizability is the ratio between this polarization and the external field. This is easily calculated to be $4\pi\epsilon_0 r^3$, with r being the radius of the electron cloud. Of course this is a extremely simplified classical model, so we want to figure out how to do it quantum mechanically.

1.1 Quantum-mechanical polarization

The quantum-mechanical polarization of an atom can be described with the help of atomic transitions. The Stark effect is an example of this, where degenerate energy levels split in an electric field. This is caused by some superpositions of those states having a lower energy, and others having a higher energy. The way to do this is to take two states, $\psi_a(r)$ and $\psi_b(r)$ and calculate the energy of a superposition of the two in an electric potential:

$$E = -e \int d^3 r (a^* \psi_a^*(r) + b^* \psi_b^*(r)) V(r) (a \psi_a(r) + b \psi_b(r))$$

= $-e |a|^2 \int d^3 r |\psi_a(r)|^2 V(r) - e |b|^2 \int d^3 r |\psi_b(r)|^2 V(r)$
 $- e a^* b \int d^3 r \psi_a^*(r) V(r) \psi_b(r) - e b^* a \int d^3 r \psi_b^*(r) V(r) \psi_a(r).$ (1.1)

Within perturbation theory, we can then expand the potential V(r) to its Taylor series and neglect all but the first two terms:

$$V(r) \approx V(0) + \nabla V(0) \cdot \mathbf{r} = V(0) - \mathbf{F}(\mathbf{0}) \cdot \mathbf{r}, \qquad (1.2)$$

where we have used the fact that the electric field is minus the gradient of the potential. If the states are point symmetric around the origin, as is the case for atomic orbitals, and orthogonal to each other, the energy becomes:

$$E \approx -(|a|^2 + |b|^2)eV(0) + e\mathbf{F} \cdot \left(\int d^3r a^* b\psi_a^*(r)\mathbf{r}\psi_b(r) + b^*a\psi_b^*(r)\mathbf{r}\psi_a(r)\right)$$

= $-eV(0) - \mathbf{F}(\mathbf{0}) \cdot \mathbf{p},$ (1.3)

where we have used $|a|^2 + |b|^2 = 1$, and defined the polarization **p**. Because of the **r** in the integral, the only states we can consider are those that differ exactly \hbar in angular momentum, so an *s* and a *p* state, or a *p* and a *d* state, etc. Other transitions are so called forbidden transitions, for which we need to keep more terms in the Taylor expansion. To keep things simple we use *s* and *p* states, because then there are only 3 transitions, instead of having multiple initial and final states, and needing to keep track of the magnetic spin number as well. We also take only those *s* and *p* states that are closest in energy. Other transitions would also factor in the polarizability, but as we shall see later, they are inversely proportional to the energy difference, thus they give only a small correction. Switching to occupation number formalism, the Hamiltonian for this model then is:

$$H = \epsilon_s s^{\dagger} s + \sum_i \epsilon_p p_i^{\dagger} p_i - e \vec{r} \cdot \vec{F}$$

= $\epsilon_s s^{\dagger} s + \sum_i \epsilon_p p_i^{\dagger} p_i - p_m \sum_i F_i (p_i^{\dagger} s + s^{\dagger} p_i),$ (1.4)

 ϵ_s and ϵ_p are the energies of the s and p states, and p_m is the maximum dipole moment of the transition:

$$p_m = e\langle s | \vec{r} | p_i \rangle \cdot \hat{i}. \tag{1.5}$$

We can see this as the expectation value of the polarization for a state $as + bp_i$:

$$\langle P \rangle = e \langle a^* s^{\dagger} + b^* p_i^{\dagger} | r | as + b p_i \rangle = (a^* b + b^* a) p_m, \qquad (1.6)$$

and finding the maximum, noting that $|b| = \sqrt{1 - |a|^2}$. The maximum is found for $a = b = 1/\sqrt{2}$.

We are assuming that the p states are symmetric, so they each give the same result. We also neglect spin, as we make the approximation that the electrons with different spin do not interact with each other. Therefore, we assume both electrons to behave in the same way, and we just double the expectation values. Now we find the time dependent solution, using the density operator:

$$\rho = \begin{pmatrix} a \\ b \end{pmatrix} \begin{pmatrix} a^* & b^* \end{pmatrix} = \begin{pmatrix} |a|^2 & ab^* \\ a^*b & |b|^2 \end{pmatrix}, \tag{1.7}$$

where we assume the field is applied in one direction only. The a is then the coefficient of the s state, and b the coefficient for the p state that is parallel to

the applied field. The Schrödinger equation gives us the time dependence:

$$i\hbar\partial_t \rho = H \begin{pmatrix} a \\ b \end{pmatrix} \begin{pmatrix} a^* & b^* \end{pmatrix} - \begin{pmatrix} a \\ b \end{pmatrix} \begin{pmatrix} a^* & b^* \end{pmatrix} H = [H, \rho], \qquad (1.8)$$

$$H = \begin{pmatrix} \epsilon_s & -p_m F \\ -p_m F & \epsilon_p \end{pmatrix},\tag{1.9}$$

$$i\hbar\partial_t \rho = \begin{pmatrix} p_m(ab^* - a^*b)F & p_m F(|a|^2 - |b|^2) - \Delta ab^* \\ \Delta a^*b - p_m(|a|^2 - |b|^2)F & p_m(a^*b - ab^*)F \end{pmatrix}.$$
 (1.10)

Here $\Delta = \epsilon_p - \epsilon_s$. We can simplify this by using the following definitions:

$$P_{\pm} = p_m(ab^* \pm a^*b), \tag{1.11}$$
$$Q = |a|^2 - |b|^2 \tag{1.12}$$

$$Q = |a|^2 - |b|^2, (1.12)$$

where P_+ is also the expectation value of the polarization operator. P_+ , P_- and Q can be related by:

$$P_{+}^{2} - P_{-}^{2} = 4p_{m}^{2}|a|^{2}|b|^{2}, \qquad (1.13)$$

$$Q^{2} = |a|^{4} + |b|^{4} - 2|a|^{2}|b|^{2}, \qquad (1.14)$$

$$1 = (|a|^{2} + |b|^{2})^{2} = |a|^{4} + |b|^{4} + 2|a|^{2}|b|^{2},$$
(1.15)

$$\frac{P_{+}^{2} - P_{-}^{2}}{p_{m}^{2}} = 1 - Q^{2}$$
(1.16)

Now we find the equations of motion:

$$i\hbar\partial_t P_+ = -\Delta P_-,\tag{1.17}$$

$$-\hbar^2 \partial_t^2 P_+ = \Delta^2 P_+ - 2\Delta p_m^2 F Q, \qquad (1.18)$$

$$i\hbar\partial_t P_- = -\Delta P_+ + 2p_m^2 FQ, \qquad (1.19)$$

$$-\hbar^2 \partial_t^2 P_- = \Delta^2 P_- + 4p_m^2 F^2 P_- + 2i\hbar p_m^2 Q \partial_t F, \qquad (1.20)$$

$$i\hbar\partial_t Q = 2P_- F,\tag{1.21}$$

$$-\hbar^2 \partial_t^2 Q = -2\Delta F P_+ + 4p_m^2 F^2 Q + 2i\hbar P_- \partial_t F.$$
(1.22)

The simplest situation is where the field is static, and the polarization does not change. Therefore, for the moment, we only have to find the static solution, where all time derivatives are 0:

$$P_{+} = \frac{2p_{m}^{2}Q}{\Delta}F = \frac{\alpha}{2}QF, P_{-} = 0, Q = \frac{1}{\sqrt{1 + \frac{\alpha F^{2}}{\Delta}}},$$
(1.23)

where we have used eq. 1.16. For small fields the ion stays mostly in the ground state, so $Q \approx 1$ and the polarization is proportional to the field with the ratio equal to the polarizability, $\alpha = \frac{4p_m^2}{\Delta}$, where we have used that the polarization is twice P_+ because of spin. Usually α is given in Å³, so we have to divide by $4\pi\epsilon_0$

and get $\alpha = \frac{p_m^2}{\pi \epsilon_0 \Delta}$, but for simplicity we neglect the prefactor unless needed for explicit calculation. The energy relative to the ground state is simply:

$$E = \frac{\Delta}{2}(1-Q) - P_{+} \cdot F = \frac{\Delta}{2} - Q\frac{\Delta + \alpha F^{2}}{2} = \frac{\Delta}{2}\left(1 - \sqrt{1 + \frac{\alpha F^{2}}{\Delta}}\right).$$
 (1.24)

Like the polarization, the energy here is for one electron, but if the ion has two electrons (one with spin down and one with spin up), we need to double the energy. Extending this to p to d transitions, we see that we could have 6 electrons, so if the initial and final states are respectively degenerate, the polarization and energy would be multiplied by 6, and even more for higher transitions. The reverse, d to p transitions, where we have up to 10 initial states, does not multiply the values by 10, because not all transitions are allowed due to conservation of angular momentum in the z direction. For instance an $x^2 - y^2$ orbital only has transitions to x and y states but not to the z state.

If the states are not degenerate, we have to take more care in calculating these values, and likely would have to use a polarizability tensor and keep track of the different level splittings. In the specific case of a cubic lattice, the $x^2 - y^2$ and $3z^2 - r^2$ orbitals are separated in energy from the xy, xz and yz orbitals, while the p states stay degenerate.¹³ With conservation of angular momentum taken into account, this gives us either 2 or 4 transitions for each direction of the field, depending on which states have higher energies. Here we are assuming the splitting is large enough to neglect the lower lying states. We also assume that the electrons that are polarized are at the Γ point of the Brillouin zone (i.e. the momentum is zero), which is appropriate as first order perturbation theory only considers interaction where the momentum of the polaron does not change. For higher order perturbation theory both the energy splitting and the degeneracy change. For an accurate description, the bandstructure must first be calculated.

1.1.1 Application to the electronic polaron model

Now that we know how the energy of an atom or ion changes due to the polarization of an externally applied field, we can apply this to an electronic polaron model. The hole or electron generates a field at the ion, which polarizes it, and reduces the energy, which we calculate with help of eq. 1.24. To find the energy reduction of a bipolaron a certain distance away, we can just add the fields generated by each of the two holes, and insert it in to eq. 1.24 as well. Of course, the single holes also had their energy reduced, so for the binding energy of the bipolaron we take the difference:

$$U_{BP} = E_{12} - E_1 - E_2. (1.25)$$

Here E_{12} is the energy reduction of the ions due to both polarons polarizing them, E_1 and E_2 how much the energy would be reduced if there was only one polaron present. Usually $E_1 = E_2$, but this is not always the case. Meanwhile,

the occupancies of the states are:

$$|a|^{2}, |b|^{2} = \frac{1}{2} \left(1 \pm \frac{1}{\sqrt{1 + \frac{\alpha |F|^{2}}{\Delta}}} \right) = \frac{1}{2} (1 \pm Q),$$
(1.26)

and we can use this later to describe the hopping of electrons or holes. Normally, in a tight binding model, we describe electrons as being mostly in an atomic orbital state, as opposed to the usual Bloch wave. The electrons can then hop from site to site via the overlap between neighboring wavefunctions. In a polaron model, however, the electrons are "dressed" by phonons, or, in this model, polarization clouds. When an electron moves from site to site, it needs to also take the polarization cloud with it. We have to incorporate this into the tight binding model by calculating the overlap of the clouds before and after the hop. We can do this by multiplying the states by this operator:

$$\eta_{i}^{\dagger} = \prod_{n=\langle i \rangle, \sigma} a(F(r_{n} - r_{i}))s_{n\sigma}^{\dagger} - b(F(r_{n} - r_{i}))\frac{F(r_{n} - r_{i}) \cdot p_{n\sigma}^{\dagger}}{|F(r_{n} - r_{i})|}, \qquad (1.27)$$

with n running over nearby ions. Because the states are orthonormal, if the polarization changes, the hopping integral is reduced. To calculate this reduction we find the expectation value of the hopping interaction with the new states (i.e. including the polarization clouds):

$$t_{i,i+\hat{r}} = t \langle c_{i+\hat{r}} \eta_{i+\hat{r}} | c_{i+\hat{r}}^{\dagger} c_i | \eta_i^{\dagger} c_i^{\dagger} \rangle = t \langle \eta_{i+\hat{r}} \eta_i^{\dagger} \rangle = t \prod_{n,\sigma} \left(a_{n1} a_{n2} + b_{n1} b_{n2} \frac{F_{n1} \cdot F_{n2}}{|F_{n1}||F_{n2}|} \right),$$
(1.28)

where the product runs over all the ions where the field changes, and the subscript denotes the field before and after the hop. These overlaps can be easily calculated by finding the fields, and can be extended to ions further away as well. Long range interaction is especially important for calculating mobility, as only part of the polarization needs to change when the electron moves.

When two polarons are nearby, we need to take into account that both will polarize some of the same ions. The calculation then depends on the orientation and distance between the two polarons, before and after the hop. This is easily done, simply by adding the fields produced by both polarons at each ion, instead of just one.

1.2 Band structure

So far we know how an electron or hole interacts with ions to lower its energy and how two such polarons can interact with each other just through polarization. We like to know how they move through the crystal though, as carriers need to be mobile to be useful. The basic model of carriers moving through a crystal

					ψ_i	1/2 F
	ψ_i	ψ_f	-	t'_{a}	$\frac{\tau}{\delta}$	$\frac{\tau}{\delta + (\hat{x} + \hat{y})}$
t_0	δ	$\delta \pm \hat{r}$		ν ₀ +/	ŵ	$0 \pm (x \pm g)$
t_1	0	\hat{r}		$\frac{\iota_1}{\prime}$		g
t_2	\hat{r}	$\hat{x} \pm \hat{y}$		t_2	0	$x \pm y$
t_2	\hat{r}	$2\hat{r}$		t'_3	2r	$x \pm y$
•3 +.	$\hat{x} + \hat{y}$	$\hat{x} + \hat{y} \perp \hat{x}$		t'_4	\hat{r}	$\hat{x} \pm \hat{y} + \hat{r}$
ι_4	$x \perp y$	$\perp g \mid x \perp g \mid r$		t'_5	$\hat{x} \pm \hat{y}$	$2(\hat{x} \pm \hat{y}).$

Table 1.1: Hopping parameters for different transitions (in real space)

for correlated electron systems is the Hubbard model.¹⁴ Therein, every site has two states (one for each spin) and we consider a few different energies for the Hamiltonian. First there is the energy of the state, which is only relevant for models with unequal sites (e.g. a copper or an oxygen site). Then there is the on-site repulsion term for when two carriers are on the same site. A nearest neighbor repulsion is sometimes also used, and in general a repulsion for more distant carriers could also be incorporated. They are usually neglected though, as they are assumed to be heavily screened. Thirdly there is an interaction between nearby sites, by which means a carrier can move from site to site. They are determined by calculating the overlap of the orbitals on different sites. Lastly, for completeness, there is an effective spin-spin interaction caused by an exchange interaction. We will not use this term however.

We can now calculate the band structure of two holes interacting through polarization of nearby ions. The Hubbard Hamiltonian without the effect of polarizing ions is:

$$H = \sum_{i} U_{H} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - t \sum_{i,j=\langle i \rangle} c_{j}^{\dagger} c_{i} - t' \sum_{i,j=\langle \langle i \rangle \rangle} c_{j}^{\dagger} c_{i}, \qquad (1.29)$$

where U_H is on site repulsion, and t and t' are nearest and next-nearest neighbor hopping transfer integrals. The interaction renormalizes the hopping parameters and adds an attraction for nearby holes. If we assume ions are only polarized by the field of the holes, and are static, the energy is simply eq.1.24, which we add for each neighboring ion, although this can easily be extended to ions further away. As before, we take for the energy of two nearby holes:

$$U_{ij} = E_{ij} - E_i - E_j. (1.30)$$

So all we have to do is to take the coordinates of two holes, calculate their individual and combined fields at nearby ions, and put it in to eq. 1.24.

1.3 Hamiltonian

The hopping parameters depend on the overlap of the polarization clouds of the hole before and after the hop. Because another nearby hole also polarizes ions, this affects the effective parameter. We then need the hopping parameters

ψ_i		ψ_j	H_{ij}
k,0 angle	\leftrightarrow	k,0 angle	U_0
$ k,\hat{i} angle$	\leftrightarrow	$ k,\hat{i} angle$	U_1
$ k, \hat{x} \pm \hat{y}\rangle$	\leftrightarrow	$ k, \hat{x} \pm \hat{y} angle$	U_2
$ k,\delta angle$	\leftrightarrow	$ k,\delta\pm\hat{i} angle$	$-2t_0\cos(k_ia/2)$
k,0 angle	\leftrightarrow	$ k,\hat{i} angle$	$-2t_1\cos(k_ia/2)\sqrt{2}$
$ k, \hat{x} \pm \hat{y}\rangle$	\leftrightarrow	$ k,\hat{i} angle$	$-2t_2\cos(k_{i'}a/2)$
$ k,\hat{i} angle$	\leftrightarrow	$ k,2\hat{i} angle$	$-2t_3\cos(k_ia/2)$
$ k, \hat{x} \pm \hat{y}\rangle$	\leftrightarrow	$ k,2\hat{i}\pm\hat{i}' angle$	$-2t_4\cos(k_ia/2)$
$ k,\delta angle$	\leftrightarrow	$ k, \delta \pm (\hat{x} \pm \hat{y})\rangle$	$-2t_0'\cos((k_x\pm k_y)a/2)$
$ k, \hat{x} angle$	\leftrightarrow	$ k,\hat{y} angle$	$-4t_1'\cos(k_xa/2)\cos(k_ya/2)$
k,0 angle	\leftrightarrow	$ k, \hat{x} \pm \hat{y} \rangle$	$-2t_2'\cos((k_x\pm k_y)a/2)\sqrt{2}$
$ k, \hat{x} \pm \hat{y}\rangle$	\leftrightarrow	$ k,2\hat{i} angle$	$-2t_3'\cos((k_x \mp k_y)a/2)$
$ k,\hat{i} angle$	\leftrightarrow	$ k,2\hat{i}\pm\hat{i}' angle$	$-2t_4'\cos((k_x\pm k_y)a/2)$
$ k, \hat{x} \pm \hat{y}\rangle$	\leftrightarrow	$ k,2\hat{x}\pm 2\hat{y} angle$	$-2t_5'\cos((k_x\pm k_y)a/2)$

Table 1.2: Elements of the Hamiltonian (in momentum space)

shown in table 1.1, considering only the effect of the non-hopping hole when it is close by. Left is the initial state, before the hop, while right is the state after the hop. The t stand for nearest neighbor, and t' is the next nearest neighbor. Here t_0 and t'_0 do not include the other transitions, and the reverse transitions should also be taken into account. \hat{r} denotes hopping in either the x- or y-direction. Some transitions depend on geometry, but are averaged out after switching to momentum space:

$$|k,\delta\rangle = \sum_{i} \frac{e^{ik \cdot (R_i + \frac{\delta}{2})}}{\sqrt{N}} |i, i + \delta\rangle.$$
(1.31)

Because of symmetry $|k, -\delta\rangle$ is the same state as $|k, \delta\rangle$, and we only consider states with x = 0, y > 0 or x > 0, y = -n : n. We must then be careful not to overlook any transitions, e.g. the transition $\hat{y} \leftrightarrow -\hat{x} + \hat{y}$ in real space gives rise to a transition of $|k, \hat{y}\rangle \leftrightarrow |k, \hat{x} - \hat{y}\rangle$ in momentum space. We now calculate the hopping interaction in momentum space:

$$\langle k, \delta' | T | k, \delta \rangle = \sum_{i,j} \frac{e^{ik \cdot (R_i - R_j + \frac{\delta - \delta'}{2})}}{N} \langle j, j + \delta' | T | i, i + \delta \rangle, \qquad (1.32)$$

If we take $\delta' = \delta + \hat{r}$, either i = j and we get a factor $e^{-ik\cdot\hat{r}/2}$ or $j = i + \hat{r}$ and we get a factor $e^{ik\cdot\hat{r}/2}$. Together they give a factor $2\cos(k\cdot\hat{r}/2)$. In table 1.2 we see the non-zero elements of the Hamiltonian. The factor $\sqrt{2}$ is obtained because the on site singlet doesn't have the same $\frac{1}{\sqrt{2}}$ factor as the other states. We have only used three terms of the interaction energy U, but this can be easily extended to any distance between holes. The same goes for the hopping parameters,

although as we shall see, these do not change much with the distance, so the usefulness of doing so is marginal.

1.4 Long range electron-ion interactions

For now we have used short range electron-ion interactions. Long range interactions can be used, but are countered by Coulomb repulsion that we have ignored so far. We have also partially ignored screening. Screening has different contributions, including the polarization of nearby ions, which we have used so far. Secondly there is free carrier screening, which is not relevant for insulators such as undoped cuprates, but would be needed as soon as we increase the doping to the levels needed for superconductivity. This screening is restricted to frequencies below the plasma frequency of the carriers, which is $\omega_p = \sqrt{\frac{ne^2}{m^*\epsilon_0}}$, where n is the number density of carriers and m^* is the effective mass. As the doped carriers are polarons here, the effective mass is much increased and the plasma frequency is reduced. Thirdly there is hybridization between states on different ions that depend on the occupancy of the oxygen states. In the FeAs model this hybridization was between As 4p and Fe 4s and 4p states.⁹ The occupation of Fe 3d states changes this mixing and effectively screens the Coulomb repulsion. It was mentioned that this screening was assumed to be included for the value of the on site repulsion U_H , but it would also have an effect on longer range Coulomb repulsion. We can also figure out if a similar screening mechanism is present in cuprates.

It has to be mentioned here that screening does not just affect the Coulomb repulsion between holes, but also the polarization of the ions, so for an accurate description we need to take that also into account. Luckily the frequency at which free carriers screen is much lower than the optical frequencies of the polarization. We will address this further in the next chapter, and ignore screening for the static model.

Chapter 2

Dynamic theory

BCS theory and Migdal-Eliashberg theory relied on phonons mediating the interaction between carriers. When this interaction is strong, these theories fail. The criterion for applicability is the ratio between the electron-phonon energy and the bandwidth of the polarons. $^{5;15}$

Up until now we have assumed that ions are instantly and statically polarized when the field changes. However, in reality an applied field will cause the electrons to oscillate between the ground and the excited states of the ion without the applied field. The time dependent Schrödinger equation shows that the phase of an eigenstate changes proportionally to its energy:

$$i\hbar\partial_t\psi_n = H\psi_n = E_n\psi_n,\tag{2.1}$$

so that the relative phase of the two states changes with the level splitting divided by \hbar , or Ω . This also means that the frequency of the oscillation in polarization is equal to Ω . If the field is constant in time, the ion will relax to the new ground state after a finite amount of time, and remain there until the field changes again. If the ion is by itself, this relaxation comes in the form of dipole radiation or spontaneous emission. The rate of this is:¹⁶

$$A = \frac{\Omega^3 p_m^2}{3\pi\epsilon_0 \hbar c^3} = \frac{\alpha \Omega^4}{3c^3} \tag{2.2}$$

with c equal to the speed of light. Using the parameters from the previous model¹⁰, $\alpha = 6 \text{Å}^3$, $\Omega = 6 \text{eV}/\hbar \approx 2.3 x 10^{16} \text{Hz}$ we find a frequency of about 0.51 GHz. Although the fourth power of Ω means a small difference can give a large change in this frequency, we are well below the 10^{16} hertz range of the oscillating polarization cloud. If the ion is in a lattice, dipole relaxation would suppress the dielectric constant for fields with frequency higher than the relaxation rate. This is because the ions will not oscillate in phase and so the average polarization is canceled out. In a lattice there are also other processes that will relax the polarization. First, there are interactions with impurities. This is especially relevant in high- T_c superconductors because of

the large amount of doping needed to get superconductivity. Secondly, the ion interact with each other through dipole-dipole interactions. This is strongest for similar ions (e.g. one lanthanum ion interacting with another lanthanum ion), because they oscillate with approximately the same frequency, (if the field is not too strong) and thus create a resonance.

2.1 Dynamic solution of a two level system

Using eq. 1.22 we can find a dynamical solution, at first we use a static applied field:

$$\partial_t^2 P_+ = -\frac{\Delta^2}{\hbar^2} (P_+ - \frac{\alpha}{2} FQ), \qquad (2.3a)$$

$$\partial_t^2 Q = \frac{2F}{\Delta} \frac{\Delta^2}{\hbar^2} (P_+ - \frac{\alpha}{2} F Q)$$
(2.3b)

This equation can be solved for t. We assume that at t = 0 the electron hops to a neighboring site and so the ion is in its ground state. This means we can take the values $P_+(0) = 0$, Q(0) = 1, $\partial_t P_+(0) = 0$, $\partial_t Q(0) = 0$. Next we see that a linear combination of 2.3 gives us an equation of only one variable:

$$\partial_t^2 (P_+ - \frac{\alpha}{2} FQ) = -\frac{\Delta^2}{\hbar^2} (1 + \frac{\alpha F^2}{\Delta}) (P_+ - \frac{\alpha}{2} FQ). \tag{2.4}$$

This equation has a simple solution:

$$P_{+} - \frac{\alpha}{2}FQ = A\cos(\omega t + \phi), \qquad (2.5)$$

$$\partial_t^2 (P_+ - \frac{\alpha}{2} FQ) = -\omega^2 (P_+ - \frac{\alpha}{2} FQ) \Rightarrow \omega = \frac{\Delta}{\hbar} \sqrt{1 + \frac{\alpha F^2}{\Delta}}, \qquad (2.6)$$

$$\partial_t (P_+ - \frac{\alpha}{2} FQ)(0) = A\omega \sin(\phi) \Rightarrow \phi = 0,$$
(2.7)

$$(P_+(0) - \frac{\alpha}{2}FQ(0)) = A \Rightarrow A = -\frac{\alpha}{2}F,$$
(2.8)

To find the time dependence of P_+ , we need another equation. A different linear combination of eq. 2.3 gives a trivial equation:

$$\partial_t (P_+ + \frac{\Delta}{2F}Q) = 0 \Rightarrow P_+ + \frac{\Delta}{2F}Q = \frac{\Delta}{2F}.$$
 (2.9)

Combining the two we find the polarization:

$$P_{+} = \frac{\frac{\alpha}{2}F}{1 + \frac{\alpha F^{2}}{\Delta}} (1 - \cos(\omega t)).$$

$$(2.10)$$

We see that the polarization oscillates, so the question is: can we describe the polarization analogously to phonons? To do this we find the energy in terms of P_+ and P_- only:

$$E = \frac{\Delta}{2}(1-Q) - P_{+} \cdot F, \qquad (2.11)$$

$$Q = \pm \sqrt{1 - \frac{P_+^2 - P_-^2}{p_m^2}},$$
(2.12)

$$E = \frac{\Delta}{2} \left(1 - \sqrt{1 - \frac{P_+^2 - P_-^2}{p_m^2}} \right) - F \cdot P_+, \qquad (2.13)$$

$$\approx \frac{P_{+}^{2} - P_{-}^{2}}{\alpha} - F \cdot P_{+},$$
 (2.14)

where we take Q to be positive and close to 1 for small applied fields $(|a|^2 \gg |b|^2)$. (This is valid for $\alpha F^2 \ll \Delta$, and driving frequencies $\hbar \omega \ll \Delta$.) To find the energy for both electrons, we just double this. Now we use the fact that P_{-} is proportional to the time derivative of P_{+} :

$$P_{-} = \frac{-i\hbar}{\Delta}\dot{P}_{+} = -i\frac{\dot{P}_{+}}{\Omega},\qquad(2.15)$$

$$-P_{-}^{2} = \frac{\dot{P}_{+}^{2}}{\Omega^{2}},\tag{2.16}$$

to find the energy in terms of only the polarization and the field:

$$E \approx 2\left(\frac{P_+^2}{\alpha} + \frac{\dot{P}_+^2}{\Omega^2 \alpha} - F \cdot P_+\right).$$
(2.17)

This looks like the energy of a driven harmonic oscillator:

$$E = \frac{m\dot{u}^2}{2} + \frac{m\Omega^2 u^2}{2} - e\mathbf{F} \cdot \mathbf{u}, \qquad (2.18)$$

with $u = \frac{2P_+}{e}$ and mass given by:

$$m = \frac{e^2 \hbar^2}{4\pi\epsilon_0 \Delta^2 \alpha}.$$
(2.19)

For $\alpha = 6 \text{Å}^3$ and $\Delta = 6 \text{eV}$ we find that *m* is approximately half of the electron mass. There is also an amplitude for this harmonic oscillator:

$$\alpha = \frac{2p_m^2}{4\pi\epsilon_0\Delta} = \frac{2e^2}{4\pi\epsilon_0\Delta}L^2,$$
(2.20)

$$L = \sqrt{\frac{2\pi\epsilon_0 \alpha \Delta}{e^2}} = \sqrt{\frac{\hbar}{m\Omega}},$$
(2.21)

which is 1.12Å. Now we take a crystal of N ions coupled through their dipoledipole interactions:

$$H = \sum_{n} \left(\frac{|p_n|^2}{2m} + \frac{m\Omega^2 |u_n|^2}{2} - e\mathbf{u_n} \cdot \mathbf{F}(\mathbf{r_n}) \right)$$
(2.22)

$$=\sum_{n}\left(\frac{|p_{n}|^{2}}{2m}+\frac{m\Omega^{2}|u_{n}|^{2}}{2}-e^{2}\sum_{l}\mathbf{u_{n}}\cdot\hat{\mathbf{S}}(\mathbf{r_{n}}-\mathbf{r_{l}})\cdot\mathbf{u_{l}}\right).$$
(2.23)

We can now apply the same techniques that would be applied to a chain of atoms with harmonic coupling¹⁷, but in three dimensions and a dipole-dipole coupling instead. We transform the Hamiltonian to momentum space:

$$\mathbf{u}_{\mathbf{n}} = \frac{1}{\sqrt{N}} \sum_{q\nu} (U_{q\nu} \cos(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}}) - \frac{1}{m\omega_{q\nu}} P_{q\nu} \sin(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}})) \mathbf{e}_{\mathbf{q}\nu}, \qquad (2.24)$$

$$\mathbf{p}_{\mathbf{n}} = \frac{1}{\sqrt{N}} \sum_{q\nu} (m\omega_{q\nu} U_{q\nu} \sin(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}}) + P_{q\nu} \cos(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}})) \mathbf{e}_{\mathbf{q}\nu}, \qquad (2.25)$$

where ν stands for the mode and $\mathbf{e}_{\mathbf{q}\nu} \cdot \mathbf{e}_{\mathbf{q}\mu} = \delta_{\nu\mu}$.

$$|u_{n}|^{2} = \frac{1}{N} \sum_{q,q',\nu} \left(-\frac{U_{q\nu} P_{q'\nu} + P_{q'\nu} U_{q\nu}}{m\omega_{q'\nu}} \cos(\mathbf{q} \cdot \mathbf{r_{n}}) \sin(\mathbf{q'} \cdot \mathbf{r_{n}}) + U_{q\nu} U_{q'\nu} \cos(\mathbf{q} \cdot \mathbf{r_{n}}) \cos(\mathbf{q'} \cdot \mathbf{r_{n}}) + \frac{P_{q\nu} P_{q'\nu}}{m^{2} \omega_{q\nu} \omega_{q'\nu}} \sin(\mathbf{q} \cdot \mathbf{r_{n}}) \sin(\mathbf{q'} \cdot \mathbf{r_{n}}) \right)$$
(2.26)

$$|p_{n}|^{2} = \frac{1}{N} \sum_{q,q',\nu} (P_{q\nu}P_{q'\nu}\cos(\mathbf{q}\cdot\mathbf{r_{n}})\cos(\mathbf{q'}\cdot\mathbf{r_{n}}) + m^{2}\omega_{q\nu}\omega_{q'\nu}U_{q\nu}U_{q\nu}U_{q'\nu}\sin(\mathbf{q}\cdot\mathbf{r_{n}})\sin(\mathbf{q'}\cdot\mathbf{r_{n}}) + m\omega_{q\nu}(U_{q\nu}P_{q'\nu} + P_{q'\nu}U_{q\nu})\sin(\mathbf{q}\cdot\mathbf{r_{n}})\cos(\mathbf{q'}\cdot\mathbf{r_{n}}))$$
(2.27)

$$\mathbf{u}_{\mathbf{n}} \cdot \hat{\mathbf{S}}_{\mathbf{n}\mathbf{l}} \cdot \mathbf{u}_{\mathbf{l}} = \frac{1}{N} \sum_{q,q',\nu,\nu'} (U_{q\nu} U_{q'\nu'} \cos(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}}) \cos(\mathbf{q}' \cdot \mathbf{r}_{\mathbf{l}})$$

$$- \frac{U_{q\nu} P_{q'\nu'} + P_{q'\nu'} U_{q\nu}}{m\omega_{q'\nu'}} \cos(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}}) \sin(\mathbf{q}' \cdot \mathbf{r}_{\mathbf{l}}))$$

$$+ \frac{P_{q\nu} P_{q'\nu'}}{m^2 \omega_{q\nu} \omega_{q'\nu'}} \sin(\mathbf{q} \cdot \mathbf{r}_{\mathbf{n}}) \sin(\mathbf{q}' \cdot \mathbf{r}_{\mathbf{l}})) \mathbf{e}_{\mathbf{q}\nu} \cdot \hat{\mathbf{S}}_{\mathbf{n}\mathbf{l}} \cdot \mathbf{e}_{\mathbf{q}'\nu'},$$
(2.28)

$$\sum_{n} |u_{n}|^{2} = \frac{1}{2} \sum_{q\nu} \left(U_{q\nu}^{2} + U_{q\nu}U_{-q\nu} + \frac{P_{q\nu}^{2}}{(m\omega_{q\nu})^{2}} - \frac{P_{q\nu}P_{-q\nu}}{m^{2}\omega_{q\nu}\omega_{-q\nu}} \right), \quad (2.29)$$

$$\sum_{n} |p_{n}|^{2} = \frac{1}{2} \sum_{q\nu} \left(P_{q\nu}^{2} + P_{q\nu}P_{-q\nu} + (m\omega_{q\nu})^{2}U_{q\nu}^{2} - m^{2}\omega_{q\nu}\omega_{-q\nu}U_{q\nu}U_{-q\nu} \right), \quad (2.30)$$

$$\sum_{n,l} \mathbf{u}_{n} \cdot \hat{\mathbf{S}}_{nl} \cdot \mathbf{u}_{l} = \frac{1}{2} \sum_{q,\nu,\nu'} (U_{q\nu}^{2} + U_{q\nu}U_{-q\nu}, + \frac{P_{q\nu}^{2}}{(m\omega_{q\nu})^{2}} - \frac{P_{q\nu}P_{-q\nu}}{m^{2}\omega_{q\nu}\omega_{-q\nu}} \right) S_{q\nu}.$$
 (2.31)

Where $S_{q\nu}$ are the eigenvalues of the Fourier transform of $\hat{\mathbf{S}}(\mathbf{r})$:

$$\hat{\mathbf{S}}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{q}\nu} = \sum_{r} \cos(\mathbf{q} \cdot \mathbf{r}) \hat{\mathbf{S}}(\mathbf{r}) \cdot \mathbf{e}_{\mathbf{q}\nu} = S_{q\nu} \mathbf{e}_{\mathbf{q}\nu}$$
(2.32)

Collecting terms we find factors of this form:

$$\frac{1}{2} \left(\frac{m\Omega^2}{2} - \frac{e^2 S_{q\nu}}{2} \pm \frac{m\omega_{q\nu}^2}{2} \right), \tag{2.33}$$

where + stands for coupling terms with the same q, and - stands for coupling terms between positive and negative q. Thus we choose $\omega_{q\nu}$ so that the negative terms cancel:

$$\omega_{q\nu} = \sqrt{\Omega^2 - \frac{e^2 S_{q\nu}}{m}} = \Omega \sqrt{1 - \alpha S_{q\nu}}.$$
(2.34)

At this point we need to mention that we have ignored the dispersion of the electrons we are polarizing. As the ions are in a crystal, the level splitting itself depends on the momentum, as well as the direction in which we are polarizing. This also affects α , so that we have in general:

$$\omega_{q\nu} = \Omega_{q\nu} \sqrt{1 - \hat{\alpha}_q \cdot \mathbf{e}_{q\nu} S_{q\nu}}.$$
(2.35)

This needlessly complicates the model, however, so we ignore this for the following. The Hamiltonian now becomes:

$$H = \sum_{q\nu} \left(\frac{P_{q\nu}^2}{2m} + \frac{m\omega_{q\nu}^2}{2} U_{q\nu}^2 \right).$$
 (2.36)

We can write this using ladder operators:

$$b_{q\nu} = \sqrt{\frac{1}{2m\hbar\omega_{q\nu}}} P_{q\nu} - i\sqrt{\frac{m\omega_{q\nu}}{2\hbar}} U_{q\nu}, \qquad (2.37)$$

$$b_{q\nu}^{\dagger} = \sqrt{\frac{1}{2m\hbar\omega_{q\nu}}}P_{q\nu} + i\sqrt{\frac{m\omega_{q\nu}}{2\hbar}}U_{q\nu}, \qquad (2.38)$$

$$H = \sum_{q\nu} \hbar \omega_{q\nu} (b_{q\nu}^{\dagger} b_{q\nu} + \frac{1}{2}).$$
 (2.39)

For convenience we write u_n and p_n in terms of these operators:

$$\mathbf{u_n} = i \frac{1}{\sqrt{N}} \sum_{q\nu} \sqrt{\frac{\hbar}{2m\omega_{q\nu}}} (b_{q\nu} e^{i\mathbf{q}\cdot\mathbf{r_n}} - b^{\dagger}_{q\nu} e^{-i\mathbf{q}\cdot\mathbf{r_n}}) \mathbf{e_{q\nu}}, \qquad (2.40)$$

$$\mathbf{p}_{\mathbf{n}} = \frac{1}{\sqrt{N}} \sum_{q\nu} \sqrt{\frac{\hbar m \omega_{q\nu}}{2}} (b_{q\nu} e^{i\mathbf{q}\cdot\mathbf{r}_{\mathbf{n}}} + b^{\dagger}_{q\nu} e^{-i\mathbf{q}\cdot\mathbf{r}_{\mathbf{n}}}) \mathbf{e}_{\mathbf{q}\nu}.$$
 (2.41)

Now it is simple to introduce electron-polarization interaction into this, the original Hamiltonian gains an extra term:

$$H = H_0 - e \sum_{n} \mathbf{u_n} \cdot \mathbf{F_{el}}(\mathbf{r_n})$$
(2.42)

The electric field due to electrons (or holes) is a linear combination of terms:

$$\mathbf{F}_{\mathbf{el}}(\mathbf{r}_{\mathbf{n}}) = \sum_{i} \mathbf{F}(\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{i}}) c_{i}^{\dagger} c_{i}, \qquad (2.43)$$

where n is used for polarizable ions and i for electron (hole) states. Transformed to momentum space, this becomes:

$$c_i = \frac{1}{\sqrt{N}} \sum_k c_k e^{i\mathbf{k}\cdot\mathbf{r_i}},\tag{2.44}$$

$$\sum_{n} c_{i}^{\dagger} c_{i} e^{i\mathbf{q}\cdot\mathbf{r_{n}}} = \frac{1}{N} \sum_{k,k',n} c_{k'}^{\dagger} c_{k} e^{i((\mathbf{k'-k})\cdot(\mathbf{r_{n}-r_{i}})+(\mathbf{q}-(\mathbf{k'-k}))\cdot\mathbf{r_{n}})}, \quad (2.45)$$
$$= \sum_{q} c_{k+q}^{\dagger} c_{k} e^{i\mathbf{q}\cdot\mathbf{l}},$$

$$\frac{1}{\sqrt{N}}\sum_{n}\mathbf{F}_{\mathbf{el}}(\mathbf{r}_{\mathbf{n}})e^{i\mathbf{q}\cdot\mathbf{r}_{\mathbf{n}}} = \frac{1}{\sqrt{N}}\sum_{k,l}\mathbf{F}(\mathbf{l})c^{\dagger}_{k+q}c_{k}e^{i\mathbf{q}\cdot\mathbf{l}} \equiv \sum_{k}c^{\dagger}_{k+q}c_{k}\mathbf{F}_{\mathbf{q}},\qquad(2.46)$$

where the sum over l goes over all different $\mathbf{r_n} - \mathbf{r_i}$. The electron-phonon interaction can then be written using a dimensionless parameter:

$$H_{e-ph} = \frac{1}{\sqrt{N}} \sum_{kq\nu} \hbar \omega_{q\nu} (\gamma_{q\nu} c^{\dagger}_{k+q} c_k b_{q\nu} + \gamma^*_{q\nu} c^{\dagger}_k c_{k+q} b^{\dagger}_{q\nu}), \qquad (2.47)$$

$$\gamma_{q\nu} = -i\sqrt{\frac{N}{2\hbar m\omega_{q\nu}^3}} e\mathbf{F}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{q}\nu}.$$
(2.48)

Sometimes it can be convenient to transform this to site representation:

$$H_{e-ph} = \sum_{iq\nu} (\hbar \omega_{q\nu} \hat{n}_i (f_i(q,\nu) b_{q\nu} + f_i^*(q,\nu) b_{q\nu}^{\dagger}), \qquad (2.49)$$

$$f_i(q,\nu) = \frac{-i}{\sqrt{2\hbar m N \omega_{q\nu}^3}} \sum_n \mathbf{e} \mathbf{F}_{\mathbf{el}}(\mathbf{r}_n) \cdot \mathbf{e}_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{r}_n} = \frac{1}{\sqrt{N}} \gamma_{q\nu} e^{i\mathbf{q}\cdot\mathbf{r}_i}.$$
 (2.50)

The total Hamiltonian including electrons and phonons is thus:

$$H = \sum_{ij} (T(r_i - r_j) - \mu \delta_{ij}) c_i^{\dagger} c_j + \frac{1}{2} \sum_{ij} U(r_i - r_j) \hat{n}_i \hat{n}_j$$
(2.51)

$$+\sum_{q\nu} \hbar \omega_{q\nu} (b_{q\nu}^{\dagger} b_{q\nu} + \frac{1}{2}) + \sum_{iq\nu} \hbar \omega_{q\nu} \hat{n}_i (f_i(q,\nu) b_{q\nu} + h.c).$$
(2.52)

Here T(r) is the hopping parameter, which is nonzero only for nearest and next nearest neighbors. μ is the chemical potential, U(r) the Coulomb repulsion, which is equal to the Hubbard repulsion for electrons on the same site. This Hamiltonian is equal to the one Alexandrov⁵ uses in his theory, so that we can follow his derivation. If T is small, we can use a unitary transformation to eliminate some terms:

$$S = \sum_{q\nu i} \hat{n}_i (f_i^*(q,\nu) b_{q\nu}^{\dagger} - f_i(q,\nu) b_{q\nu}), \qquad (2.53)$$

$$\tilde{H} = e^S H e^{-S}, \tag{2.54}$$

$$\tilde{c}_i = e^S c_i e^{-S}, \tag{2.55}$$

$$\tilde{b}_{q\nu} = e^S b_{q\nu} e^{-S}.$$
(2.56)

To calculate the new operators we first scale $f_i \rightarrow \eta f_i$, and differentiate the operators with respect to the scaling factor:

$$\frac{\partial \tilde{c}_i}{\partial \eta} = \sum_{q\nu} e^S[\hat{n}_i, c_i] (f_i^* b_{q\nu}^\dagger - f_i b_{q\nu}) e^{-S}, \qquad (2.57)$$

$$\frac{\partial b_{q\nu}}{\partial \eta} = \sum_{i} e^{S} [b^{\dagger}_{q\nu}, b_{q\nu}] f_{i}^{*} \hat{n}_{i} e^{-S}.$$
(2.58)

Then using $[\hat{n}_i, c_i] = -c_i$ and $[b_{q\nu}^{\dagger}, b_{q\nu}] = -1$ we get:

$$\frac{\partial \tilde{c}_i}{\partial \eta} = -\tilde{c}_i \sum_{q\nu} (f_i^*(q,\nu)\tilde{b}_{q\nu}^\dagger - f_i(q,\nu)\tilde{b}_{q\nu}), \qquad (2.59)$$

$$\frac{\partial \tilde{b}_{q\nu}}{\partial \eta} = -\sum_{i} \hat{n}_{i} f_{i}^{*}(q,\nu).$$
(2.60)

We can integrate this with $\tilde{c}_i = c_i$ and $\tilde{b}_{q\nu} = b_{q\nu}$ at $\eta = 0$ and then set $\eta = 1$:

$$\tilde{c}_i = c_i \exp[\sum_{q\nu} (f_i(q,\nu)b_{q\nu} - f_i^*(q,\nu)b_{q\nu}^{\dagger})], \qquad (2.61)$$

$$\tilde{b}_{q\nu} = b_{q\nu} - \sum_{i} \hat{n}_{i} f_{i}^{*}(q,\nu).$$
(2.62)

Putting this into the old Hamiltonian, eq. 2.52, we get:

$$\tilde{H} = \sum_{ij} (\hat{\sigma}_{ij} - \mu \delta_{ij}) c_i^{\dagger} c_j + \frac{1}{2} \sum_{i \neq j} u_{ij} \hat{n}_i \hat{n}_j$$
(2.63)

$$+\sum_{q\nu} \hbar \omega_{q\nu} (b_{q\nu}^{\dagger} b_{q\nu} + \frac{1}{2}) - E_p \sum_{i} \hat{n}_i$$
(2.64)

$$\hat{\sigma}_{ij} = T(r_i - r_j) \exp[\sum_{q\nu} ((f_j(q,\nu) - f_i(q,\nu))b_{q\nu} - h.c.)]$$
(2.65)

$$u_{ij} = U(r_i - r_j) - \sum_{q\nu} \hbar \omega_{q\nu} f_i^*(q, \nu) f_j(q, \nu)$$
(2.66)

$$= U(r_i - r_j) - \frac{2}{N} \sum_{q\nu} \hbar \omega_{q\nu} |\gamma_{q\nu}|^2 \cos(\mathbf{q} \cdot (\mathbf{r_j} - \mathbf{r_i}))$$
(2.67)

$$E_{p} = \sum_{q\nu} \hbar \omega_{q\nu} |f_{i}(q,\nu)|^{2} = \frac{1}{N} \sum_{q\nu} \hbar \omega_{q\nu} |\gamma_{q\nu}|^{2}$$
(2.68)

We can compare this to the static model. E_p is the energy reduction of each individual polaron, and the interaction energy of two polarons a distance d away from each other is:

$$U_d = -\frac{1}{N} \sum_{q\nu} \hbar \omega_{q\nu} |\gamma_{q\nu}|^2 \cos(\mathbf{q} \cdot \mathbf{d}).$$
 (2.69)

For dispersionless $\omega_{q\nu}$ (i.e. no interaction between ions) these equations reduce to the same value as the static model with $\alpha F^2 \ll \Delta$. Also the hopping parameters are exponentially reduced:

$$t_{i,i+\hat{r}} = t \exp[-\frac{1}{N} \sum_{q\nu} |\gamma_{q\nu}|^2 (1 - \cos(\mathbf{q} \cdot \hat{\mathbf{r}}))].$$
(2.70)

Again this reduces to the value of the static model with weak field if there is no dispersion.

Now that we have a polarization wave analogous to phonons, we can study the effects of retardation on the reduction of the Coulomb repulsion.

2.2 Retardation

For conventional superconductors retardation effects of the electron-phonon interaction reduce the effective strength of the Coulomb repulsion. The relevant parameters here are the frequency of the phonon and the Fermi energy of the electrons. The effective interaction is: 18

$$\mu_c = \frac{\mu}{1 + \mu \ln(\epsilon_F/\omega)},\tag{2.71}$$

where μ is the normal Coulomb repulsion, ϵ_F is the Fermi energy, ω is the phonon frequency (for this calculation the Einstein model was used, in which all

phonons have the same frequency), and μ_c is the effective Coulomb repulsion. As long as the Fermi energy is much bigger than the phonon frequency, the effective Coulomb repulsion is greatly reduced. For our model however, we need to use the polarization wave frequency, which is at least 6 eV for iron based superconductors, much higher than optical phonon frequencies. Meanwhile, the Fermi energy, which is the energy difference between the lowest and highest occupied states, is at most equal to the bandwidth of the polarons, or 8 times the effective nearest neighbor hopping parameter. In cuprates this would be around 5 eV, although this would be much reduced, because only about one sixth of the band will be filled at optimal doping. So retardation effects will not be relevant in this model.

2.3 Dispersion of the polarization

As we saw in eq. 2.34, the frequency of the polarization "wave" is dependent on the momentum, i.e. it has a dispersion. This is similar to the dispersion of phonons. The big difference is that for rigid ions, the restoring force is caused purely by other ions, whereas for electrons the restoring force is partially due to the ion on which they reside. This force is much stronger, so that the dispersion is much weaker. For (acoustic) phonons, the dispersion looks like $\omega_q = \omega_0 \sqrt{1 - \cos(\mathbf{q} \cdot \mathbf{r})}$, i.e. it is zero for q = 0. For polarized electrons it is not. This is relevant because the interaction parameter is proportional to $\omega_a^{-3/2}$.

We can calculate the dispersion for different systems. It is dependent on both polarizability and geometry of the crystal lattice. At first we look at La₂CuO₄, considering only the lanthanum ions. There are lanthanum planes above and below the CuO₂, with a vertical distance¹⁹ of 3.635Å of each other. As this is smaller than the in-plane distance of neighboring ions, it is necessary to include both at the same time. We only consider one layer for now. Because the structure containing just two lanthanum planes is not periodical, we cannot simply take a Fourier transform for the z-direction, as implied by eq. 2.32. Instead we must take the Fourier transform in x and y direction for each layer separately, and then use the interaction between the two layers. This gives a 6 by 6 matrix for each k-point, of which we find the eigenvalues.

Because the dispersion is proportional to $\sqrt{1-\alpha S_{q\nu}}$ (neglecting e^2/ϵ_0), the largest eigenvalue can not be larger than $1/\alpha$. This would correspond to the polarization increasing without bound, implying a phase change of the material. This is not really relevant for lanthanum, as its polarizability is small, but could be an issue for the FeAs system.

Once we have the dispersion we need to couple it to an electron. There are two unequal sites, namely one where the closest lanthanum ions are in the x-direction, and one where they are in the y-direction. We take the Fourier transform of the field on each lanthanum ion, for both sites separately. As these two lattices are translated from each other and the lanthanum ions, they will not have exactly the same momenta, but for a large enough system the mismatch is small. Using eq. 2.69 then gives us the energy, where we take new parameters

(which are obtained in chapter 3), $\alpha = 1.13 \text{\AA}^3$, $\Omega = 22 \text{eV}/\hbar$. If for the moment there is no dispersion, we find for on-site, nearest neighbor and next nearest neighbor the values, -1.86, -0.75 and -0.63 eV respectively. We can compare this with the model we used previously, where the same energies are -1.82, -1.05 and -0.65 eV. These values are reasonably close, although still a bit off, which should not be the case. The on-site interaction can be explained by noting that we assumed the field was weak. If Ω is set to a much larger value, the interaction becomes -1.86 eV, as expected. Turning on the dispersion, we get somewhat different values, -1.85, -0.69 and -0.60 eV, but not significantly so. As such, this model does not improve upon the results of the previous model, at least for La₂CuO₄, and other compounds where the polarizability is low.

Turning to FeAs now, the structure is slightly different, and the polarizability is much higher, so that $\omega_{q\nu}$ has more variability. Again, without dispersion and with the approximation that $\Delta \gg \alpha F^2$, the two models coincide for the onsite energy, at around -12.5 eV. The nearest and next nearest neighbor energies again differ somewhat between the two models, more so now that the energies in general are much higher. This is definitely a flaw that would need to be addressed. Furthermore, the low field approximation is not appropriate, because if we use the more accurate formula for the energy, the on-site energy reduces to -8.5 eV.

We can look at the effect of dispersion and find an increase for the on-site attraction to -13.5 eV, and a decrease for nearest neighbor attraction.

Chapter 3

Application to high- T_c superconductors

Both of the models we have used (chapters 1 and 2) can be applied in general to any compound with a layered structure such as cuprates and pnictides. What is needed is one plane where carriers can move in, and one or more planes of polarizable ions nearby. In-plane ions also have an effect, but it is reduced, because when two electrons are nearby, their fields partially cancel. This reduces the polarization, rather than enhancing it, so that the effective interation becomes repulsive, instead of attractive.

In cuprates the carriers are located on the CuO_2 plane, with various polarizable ions on planes above and below, like barium, lanthanum, and strontium. If we also take into account planes further away, we can include bismuth, mercury, and thallium.

For iron based superconductors the carriers are going through the iron plane, with mostly pnictogens being the polarizable ions. Chalcogens are also possible, in the case of selenium. One important difference between iron based superconductors and cuprates, is that cuprates have more polarizable ions per layer. For La_2CuO_4 , there are 2 lanthanum ions per copper ion, as well as oxygen ions in and out plane, whereas in an iron based superconductor there is only one arsenic (or another pnictogen) ion per iron ion. This is countered by the much higher polarizability of negatively charged ions.

3.1 Cuprates

The very first high- T_c superconductor was a cuprate, $Ba_x La_{5-x} Cu_5 O_{5(3-y)}$, found in 1986⁴. Since then many other cuprates have been found, and models have tried to explain such high critical temperatures. It is natural to apply any theory of high temperature superconductivity to these materials.



Figure 3.1: Top view of La_2CuO_4 . The lanthanum ions are located above and below the CuO₂ plane, and oxygen ions are directly above and below the copper ions. These are called apical oxygen ions. Also we see the p- and dorbitals that interact in the formation of a Zhang-Rice singlet.

3.1.1 Three models

We consider three models below. Firstly there is the previously used model¹⁰ where the states are single holes on oxygen ions. We are mostly comparing results to establish the accuracy of the model, as well as discussing the parameters used in that model.

Secondly, we consider Zhang-Rice singlets²⁰, where the states are a linear combination of holes on the four oxygen ions adjacent to a single copper ion. If we consider an on-site bipolaron then, the first hole has a one in four chance to be on a specific oxygen site, and so does the second hole. The chance that they are both on the same site is then $4 \cdot \frac{1}{4} \cdot \frac{1}{4} = \frac{1}{4}$. The effective repulsion is thus a quarter of the value, as long as we neglect nearest neighbor repulsion. Similarly, nearest neighbor bipolarons now also overlap, so they also get a repulsive term, albeit one sixteenth of the value. This comes at the cost of a smaller interaction with the lanthanum ions.

Thirdly, we can look at a situation where bipolarons are composed of one Zhang-Rice singlet and a hole on the apical oxygen ion above or below the copper ion. An "on-site" bipolaron then has no overlap, so no repulsion, while still having the full interaction with the lanthanum ion. These three models have different geometries, but still the same tetragonal symmetry, which means the same calculation can be performed for each of them, just with different parameters.

3.1.2 Zhang-Rice singlet

Normally in a Hubbard model we consider holes and electrons to be localized on single ions, hopping from site to site. However in cuprates, Zhang and Rice²⁰ showed that it is energetically favorable to put a hole in a superposition of oxygen states surrounding a single copper site, and then combine with the hole on that copper site to create a singlet. We see this in figure 3.1. The energy corresponding to the singlet is

$$E_{ZR} = -\left(\frac{6t_{pd}^2}{\epsilon_p} + \frac{8t_{pd}^2}{U_d - \epsilon_p} + \frac{2t_{pd}^2}{U_p + \epsilon_p}\right),\tag{3.1}$$

where t_{pd} is the hopping between copper and oxygen, ϵ_p is the energy difference between an oxygen p-state and a copper d-state and U_d , U_p are the on

site repulsion energies of copper and oxygen, respectively. (The formula above deviates from the original paper, as Zhang and Rice ignored the oxygen on site repulsion.) We now need to compare this energy to a singlet of a single hole on oxygen and a hole on copper, which is:

$$E_s = -\left(\frac{3t_{pd}^2}{\epsilon_p} + \frac{2t_{pd}^2}{U_d - \epsilon_p} + \frac{2t_{pd}^2}{U_p + \epsilon_p}\right).$$
(3.2)

Barriquand and Sawatzky²¹ calculated these parameters which we enter in eq. 3.2 to find an energy reduction of 3.36 eV. This means that if two single holes attract each other by more than twice 3.36 eV more than two Zhang-Rice singlets, bipolarons will preferentially be bound as single holes. We notice here that the ratios t_{pd}/ϵ_p , $t_{pd}/(U_p + \epsilon_p)$, and $t_{pd}/(U_d - \epsilon_p)$ are quite large, which means that a substantial part of the wavefunction is not a simple combination of a hole on oxygen and a hole on copper²¹ but:

$$\psi_{ZR} \approx \sqrt{0.7} \frac{1}{\sqrt{2}} (\mathrm{Cu}_{\uparrow} \mathrm{L}_{\downarrow} - \mathrm{Cu}_{\downarrow} \mathrm{L}_{\uparrow}) + \sqrt{0.1} \mathrm{Cu}_{\uparrow} \mathrm{Cu}_{\downarrow} + \sqrt{0.2} \mathrm{L}_{\uparrow} \mathrm{L}_{\downarrow}, \qquad (3.3)$$

where Cu stands for a hole on copper, and L stands for a hole in a linear combination of oxygen states. This affects all the energies involved in the model, the question is, how much? Apart from that, a simple combination of states on a copper site and its oxygen neighbors is not orthogonal to a similar state on the next copper site, because they share one oxygen neighbor. This is solved by using Wannier states instead, where we take a superposition of many oxygen states, with the highest occupancy near the copper site it hybridizes with. Again this changes the energies of the state and the interaction with other singlets. We note that Barriquand and Sawatzky did take into account Wannier states in their calculations.

Now we have the Hamiltonian only depending on one variable, the center of mass momentum, so we can diagonalize the matrix at different k and find the dispersion relation of polarons. First, we repeat previous simulations of single holes in figure 3.2, and compare them with simulations of Zhang-Rice singlets in figure 3.3, and apical/Zhang-Rice singlets in 3.4 using the same parameters.

We first find the binding energy, which we take to be the energy difference between the two-polaron continuum and the lowest state, at k = 0. For single holes this energy is 0.47 eV and 0.78 eV for without and with next nearest neighbor hopping, respectively. For Zhang-Rice singlets the energies are 0.093 eV and 0.27 eV instead. These values are much lower, but not enough to break the singlet, which has a binding energy of 6.72 eV. Similarly, we can calculate the binding energy of the apical/Zhang Rice combination, and find 0.027 eV and 0.31 eV. Here we still have one Zhang Rice singlet, so we only have to have half the binding energy, but it still is not enough. Next, we look at the effective mass of the bipolaron relative to free holes. This ratio is equal to the bandwidth of the holes without interaction (i.e. 8t) divided by the bandwidth of the bipolaron. For single holes these values are 2.91 and 5.30, while for Zhang-Rice singlets they are 1.60 and 6.78. Now we see that Zhang-Rice singlet bipolarons are



Figure 3.2: Two-polaron dispersion, as calculated for La₂CuO₄. The carriers are two holes on single in-plane oxygen sites, with the parameters: $\alpha = 6$ Å³, $\Delta = 6$ eV, t = 0.25 eV, $U_H = 5$ eV. We consider the cases with (right) and without (left) next nearest neighbor hopping.



Figure 3.3: Two-polaron dispersion, as calculated for La₂CuO₄. The carriers are two holes that are both Zhang-Rice singlets, with the parameters: $\alpha = 6$ Å³, $\Delta = 6$ eV, t = 0.25 eV, $U_H = 5$ eV. We consider the cases with (right) and without (left) next nearest neighbor hopping.



Figure 3.4: Two-polaron dispersion, as calculated for La₂CuO₄. The carriers are two holes, where one hole is a Zhang-Rice singlet, and the other hole is on an apical oxygen site, with the parameters: $\alpha = 6$ Å³, $\Delta = 6$ eV, t = 0.25 eV, $U_H = 5$ eV. We consider the cases with (right) and without (left) next nearest neighbor hopping.

much lighter than bipolarons made out of single holes, and that they are much less affected by next nearest neighbor hopping. The effective masses of apical hole/Zhang Rice singlet are 6.33 and 11.1, showing that they are much heavier, due to the lower hopping interaction of the apical holes.

In the theory of superconductivity the concept of an order parameter is needed. This order parameter corresponds to the wavefunction of the collective superconductive state. The order parameter has a specific symmetry. The Hamiltonian for a BCS superconductor is:

$$H = \sum_{k,\sigma} \epsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{k,k'} V_{kk'} c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} c_{-k'\downarrow} c_{k'\uparrow}, \qquad (3.4)$$

where $V_{kk'}$ is the (attractive) interaction between electrons, and ϵ_k is the energy dispersion of electrons without the interaction. We also have σ for spin, and $c_{k\sigma}$ as a annihilation operator. This Hamiltonian is then simplified by replacing $\sum_{k'} V_{kk'}c_{-k'\downarrow}c_{k'\uparrow}$ by its expectation value, which is the superconducting gap, Δ_k . For BCS superconductors it is also proportional to the Fourier transform of the order parameter.

All these dispersion relations have minima at the Γ point for the center of mass momentum, just like a BCS type superconductor, which means the order parameter of a condensate will have the same symmetry as the superconducting gap. To find the symmetry of the gap, we need to find the ground state in terms of the relative momentum, or rather, in terms of the difference vectors. We can see this dependence in figures 3.5 and 3.6. Only in the case of single holes with next nearest neighbor hopping is there d-symmetry in the wave function, and thus, in the gap. We also see that the wavefunctions for t' = 0 is more spread out, so the average distance between the polarons is larger, than for the wavefunctions with t' = -t/2.

3.1.3 Applicability parameters

Thus far, the parameters used were replicated from the previous model.¹⁰ However, these parameters might not have been the most appropriate for the model. First of all, hopping transfer integrals have been calculated for cuprates²¹. There the value is 0.65 eV, much higher than the value initially taken (the value was taken from a similar model of a FeAs superconductor⁹). The next nearest neighbor transfer integral is unknown, but we just take its value to be $-\frac{t}{2}$. We also find in this paper the value for hopping of Zhang-Rice singlets, which are 0.56 eV and 0.008 eV for nearest and next nearest neighbor, respectively. For apical oxygen ions the distance is similar to next nearest neighbors in-plane oxygen ions, so we take the same value here. This applies to σ -orientated holes, for π -orientated holes, the value is divided by 4. On-site repulsion is now 6 eV.

The polarizability was formerly chosen to be 6 Å³, which was found in a paper by Shannon²². This corresponds however to the dielectric polarizability, which also includes an ionic component, and is thus not relevant in the current model. Sawatzky et al.²³ suggest taking the ionic radius cubed, which for



Figure 3.5: Coefficients of states by difference vector of the ground state of a bipolaron consisting of single holes. The parameters are: $\alpha = 6$ Å³, $\Delta = 6$ eV, t = 0.25 eV, $U_H = 5$ eV. We see that, for t' = -t/2 the wavefunction changes sign when we rotate over 90 degrees, which corresponds to a d-wave order parameter. For t' = 0 the wavefunction does not change sign as we rotate over 90 degrees, so it has an s-wave order parameter.



Figure 3.6: Coefficients of states by difference vector of the ground state of a bipolaron consisting of Zhang-Rice singlets. The parameters are: $\alpha = 6 \text{ Å}^3$, $\Delta = 6 \text{ eV}$, t = 0.25 eV, $U_H = 5 \text{ eV}$. Both wavefunctions have s-wave symmetry.

lanthanum gives $\alpha = 1.1$ Å³, much lower than before. More accurate calculations²⁴ give a value of 1.13 Å³. The level splitting between the lanthanum 5p and 5d states was roughly estimated to be 6.00-17.7 eV, and was subsequently set to 6 eV. This value is low, however, and should actually be around 15-22 eV.^{19;25} Additionally data from NIST give a free ion level splitting of 19.3-26.8, depending on spin and angular momentum. Of course this is reduced by the crystal field. Taking these values we can redo the calculations and find a much more modest binding energy of 40 meV for single holes with t' = -t/2, while in the other cases all the states lie in the continuum, and so there is no bound state. Of course we said that t' = 0.008 eV, which means there is not a situation where the polarons are bound into a bipolaron. Therefore, we need to expand the model to include long-range electron-ion interactions to increase the interaction energies.

Furthermore, polarization of oxygen ions was previously neglected as its effect was smaller than that of the lanthanum ions for the parameters used. Its polarizability was 2 Å³ before, which was again the dielectric polarizability, so it would have to be revised. However, based on ionic radius alone we already get a polarizability of 2.75 Å³. Obtaining polarizabilities is usually done by measurements on compounds and assuming that the polarizability of the compound is a simple sum of the polarizability of the constituents. For oxygen this assumption is not valid, so we get instead a range of polarizabilities of 0.5-3.5 Å³.²⁶ Even at the low end of this range this is significant, especially considering there are twice as many oxygen ions as there are lanthanum ions, and the in plane ions are closer to the doped holes.

3.1.4 Long range interactions

Incorporating long range interactions without Coulomb repulsion will again give us a definite bound state for all three of the models. Focusing on the Zhang-Rice model The binding energy is quite low, around 0.47 eV. The bipolaron is also quite light, only twice the mass of holes without the interaction with the ions. With Coulomb repulsion we see that a bound state is generally impossible to achieve. The repulsion is many times the attraction due to polarization. To potentially get a bound state, the polarizability has to be increased to at least 6 Å³, which we concluded to be unrealistic. This means that even incorporating more distant planes, or including oxygen ions will most likely not be enough to obtain superconductivity with just this model. A possibility would be to find a way to reduce the Coulomb potential. Nearest neighbor repulsion is about 5 eV, which is comparable to on-site repulsion. As the distance is much larger, this seems unlikely to be the right value. The on-site repulsion is likely to be already reduced.

3.2 Monolayer FeSe on STO

As was stated earlier, the model used here was originally devised to describe bipolarons in iron-based superconductors, specifically those containing an FeAs layer.⁹ Recently¹¹ it was discovered that a monolayer of tetragonal FeSe grown on $SrTiO_3$ is superconducting up to 100 K. Also, $SrTiO_3$ is known to have a very high dielectric constant at low temperatures. Therefore, we expand the model to include a $SrTiO_3$ layer. First, we note that the most extreme values of the dielectric constant in SrTiO₃ occur below 10 K. At 100 K it is closer to 1250, which is still high enough to be notable. Secondly, this dielectric constant is only valid for low frequencies. At higher frequencies, it is much reduced due to dielectric relaxation. To proceed we must understand why SrTiO₃ is highly polarizable. To do so we refer to the theory of dynamical charges.²⁷ The idea is that as an ion displaces from equilibrium, the nearby electrons redistribute themselves, resulting in a polarization greater than just the charge of the ion times the displacement. In $SrTiO_3$ this effect is anomalously large, ²⁷ due to the hybridization of Ti-d and O-p electrons. As a titanium ion is displaced along a O-Ti-O chain, one of the bonds becomes longer, the other shorter. The shorter (longer) bond causes an increase (decrease) in hybridization, so that charge is transferred to (from) the titanium ion. Of course the two effects compensate each other, so that the total charge on each ion does not change, except for the ions at the ends of the chain. This then gives a polarization of the charge transferred times one lattice constant per unit cell.

Because this is partially an ionic effect, the frequencies are much lower than those found for electronic polarization. This means it is easier for carriers to screen the interaction, limiting its range exponentially. For the moment we will use a crude model, where we approximate the dielectric constant as being entirely due to a highly polarizable ion at the location of titanium. We can use the Clausius-Mossotti relation between dielectric constant and polarizability:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha}{3V_c} \tag{3.5}$$

$$\alpha \approx \frac{3V_c}{4\pi}, (\epsilon \gg 1) \tag{3.6}$$

with ϵ the relative dielectric constant, V_c the volume of a unit cell, and α is the polarizability in Å³. For SrTiO₃ we then find a polarizability of 14.2 Å³. For the level splitting we take the bandgap of STO, as that is the energy needed to excite an electron from oxygen to titanium. This is 3.75 eV for the direct bandgap.²⁸

Let us first look at the model applied to FeAs and compare it to FeSe without the SrTiO₃ layer. See figures 3.7 and 3.8. The lattice structure for the FeAs model is cubic with lattice parameter a = 2.8 Å,⁹ whereas FeSe grown on SrTiO₃ has an in-plane lattice parameter of 2.76Å and a distance of 1.40Å (1.41 Å) between the Fe layer and the bottom (top) layer of Se.²⁹ These values are very close and would not give an appreciable difference in result. For the polarizability, As³⁻ has a value much higher than Se²⁻, 9-12 Å³ versus 6-7.5



Figure 3.7: Top down view of FeAs/FeSe. U means above the iron plane, D means below. For FeAS, the iron-iron distance is 2.8 Å, the arsenic ions are 1.4 Å above and below the iron plane. For FeSe on STO the iron-iron distance is 2.76 Å instead, and the selenium ions are respectively 1.41 Å above and 1.40 Å below the iron plane.



Figure 3.8: FeSe on top of $SrTiO_3$. The selenium ions in the bottom layer are directly above the titanium ions at a distance of 3.13 Å, while the selenium ions in the top layer are directly above the strontium ions. The iron ions are directly above the oxygen ions at a distance of 4.43 Å.



Figure 3.9: Two-polaron dispersion, as calculated for FeAs (left) and FeSe, using the parameters: $\Delta = 6$ eV, t = 0.25 eV, $U_H = 10$ eV. Only the nearest neighboring arsenic/selenium ions are polarized, and only on-site Coulomb repulsion is used. We see that both bandstructures show a bound state

Å³. The level splitting Δ was mostly left as a parameter and has a value range of 4-8 eV. Meanwhile, the titanium ions lie directly below the selenium ions, at a distance of 3.13 Å. The oxygen ions lie 0.1 Åbelow the titanium ions.

So far only the polarizability has been significantly altered, which does not give a qualitatively different result, only the binding energy is lowered, and the effective mass is decreased, which is shown in figures 3.9. We also see that the effective bandwidth of single polarons is larger with higher polarizability, which affects how well they screen high frequency interactions. Now we switch to a long range model, and include Coulomb repulsion, neglecting screening for the moment. We see in fig 3.10 that the FeAs will still have a bound state, with an even larger binding energy, despite the Coulomb repulsion. FeSe, however, does not show a bound state at all. Therefore it would not be a superconductor based on this model alone. If we approximate the large dielectric constant of the SrTiO₃ substrate by a highly polarizable ion at the location of the titanium ions, the model shows a different result. As we can see in fig 3.11, now we do have a bound state.



Figure 3.10: Two-polaron dispersion, as calculated for FeAs (left) and FeSe, using the parameters: $\Delta = 6$ eV, t = 0.25 eV, $U_H = 10$ eV. Now all arsenic/selenium ions are polarized, and we use Coulomb repulsion for any distance between the polarons. Only the bandstructure for FeAs shows bound states.



Figure 3.11: Bandstructure as calculated for a monolayer of FeSe deposited on an SrTiO₃ substrate, using the parameters: $\alpha = 6$ Å³, $\Delta = 6$ eV, t = 0.25 eV, $U_H = 10$ eV. Coulomb repulsion is taken in account and both selenium ions and titanium ions are polarized by the polarons. A bound state is present.

Chapter 4

Conclusion & Outlook

We have reassessed a model of superconductivity, using electronic polarons for an attractive interaction, and expanded it to a new situation (a monolayer of FeSe on an SrTiO₃ substrate). To improve upon this static model we have altered another model, the polaronic superconductivity model of Alexandrov, to include dynamical effects.

The dynamical theory reduces to the static one if we calculate it analytically, but only for weak fields. To improve upon that, non-linear theories of polarization must be used. Calculating the results numerically gives deviations however, which are most likely caused by the mismatch of the momenta used in the Fourier transform due to the discreteness of the crystal lattice. As such, in its current form, it cannot give us accurate results.

The static model was reexamined and streamlined. Before, all parameters were calculated analytically for every situation, whereas now they can be calculated numerically simply by inserting coordinates. The parameters that were used in the calculation for cuprates were changed to more realistic values, and it was found that no bound state was present, which is necessary for superconductivity. Long range interactions electron-polarization interactions could create a bound state, but are countered by Coulomb repulsion that are much stronger. Unless a (different) way is found to reduce this repulsion, the model would not predict superconductivity.

Applying the model to FeAs we reproduce the results found by Berciu, and compare it to FeSe, where a weaker but still existing bound state is found. Longrange interaction and Coulomb repulsion cannot destroy superconductivity in FeAs, but will in the case of FeSe. Adding an extra layer of highly polarizable titanium ions can restore the bound state, so that it will be superconducting again.

So far the theories can only predict the existence of a bound state, and its binding energy, but another important parameter in superconductors is the transition temperature. In BCS theory it can be derived from the superconducting gap, but it is to be seen if this is true for high temperature superconductors.

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