

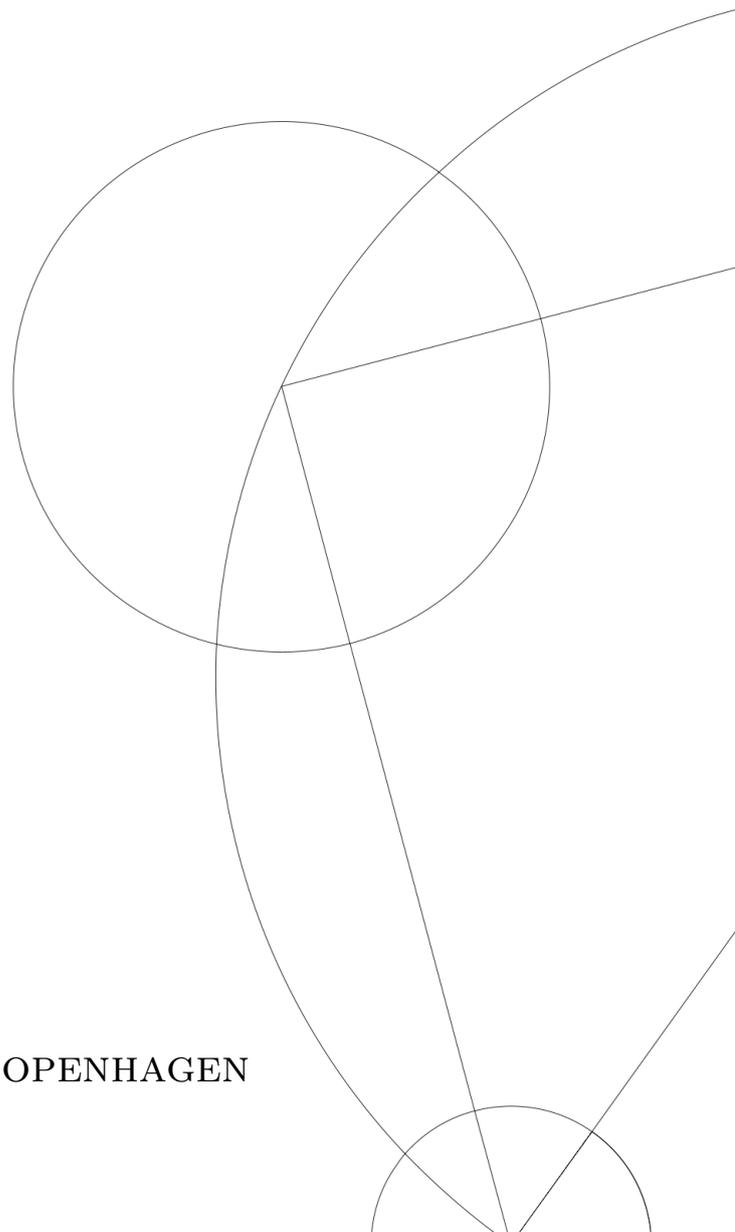


# POLARON EFFECTS IN LAO/STO INTERFACES

Written by *Bjarke Geza Solyom Høgdall*  
February 2, 2021

Supervised by  
Jens Paaske

UNIVERSITY OF COPENHAGEN





UNIVERSITY OF  
COPENHAGEN

NAME OF INSTITUTE: Niels Bohr Institute  
NAME OF DEPARTMENT: Faculty of Science  
AUTHOR(S): Bjarke Geza Solyom Høgdall  
EMAIL: ldw760@ku.alumni.dk  
TITLE AND SUBTITLE: Polaron effects in LAO/STO interfaces  
-  
SUPERVISOR(S): Jens Paaske  
HANDED IN: 20.01.2021  
DEFENDED: 01.02.2021

NAME \_\_\_\_\_

SIGNATURE \_\_\_\_\_

DATE \_\_\_\_\_

# Contents

## Abstract

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Quantum dot in LAO/STO</b>	<b>1</b>
<b>3</b>	<b>Intraband electron-phonon coupling</b>	<b>5</b>
3.1	Perturbation theory . . . . .	6
3.2	Lang-Firsov method . . . . .	7
<b>4</b>	<b>Interband electron-phonon coupling</b>	<b>9</b>
4.1	Perturbation theory . . . . .	10
4.2	Transformation of the interband Hamiltonian . . . . .	11
4.2.1	Averaging over the phonons . . . . .	13
4.2.2	Strong coupling regime . . . . .	14
4.2.3	Weak coupling regime . . . . .	15
<b>5</b>	<b>Spin-Orbit coupling</b>	<b>15</b>
5.1	Spin-orbit effects on electron-phonon coupling . . . . .	17
<b>6</b>	<b>Generalization of electron-phonon couplings to <math>N</math> quantum dot levels</b>	<b>18</b>
<b>7</b>	<b>Conclusion and discussion</b>	<b>19</b>
<b>A</b>	<b>Unitary transformation of the interband Hamiltonian</b>	<b>22</b>
<b>B</b>	<b>Evaluating <math>\langle e^{\pm\alpha(b^\dagger-b)} \rangle</math></b>	<b>25</b>
<b>C</b>	<b>Anderson-Holstein model</b>	<b>27</b>
<b>D</b>	<b>Constant interaction model</b>	<b>28</b>
<b>E</b>	<b>LAO/STO Band structure</b>	<b>30</b>
<b>F</b>	<b>Spin-orbit coupling for d-orbitals and angular momentum basis change</b>	<b>31</b>

# Abstract

When transport experiments are done on quantum dots in LAO/STO interfaces, electron pairing is found to occur. This thesis investigates the effect that intraband and interband electron-phonon coupling can have on electron pairing in a quantum dot in an LAO/STO interface. Initially the orbital structure of the energy levels in the quantum dot are examined and orbital mixing is found in the quantum dot. This is done using a particle in a box model and the band structure of the LAO/STO interface. The effects of intraband, interband and spin-orbit orbit coupling are studied using a two level Anderson-Holstein model of a quantum dot. With intraband coupling, a Lang-Firsov transformation is used and the local electron-electron potential  $U$  becomes negative for strong coupling. With interband coupling, the approach of [13] is followed and a modified Lang-Firsov transformation is used. A positive contribution to the  $U$  is found. When averaging out the phonons, degenerate polaron states with lowered energies are found. The effects of spin-orbit coupling is not found to affect pairing, but spin-orbit coupling giving rise to interband coupling will give a positive contribution to the  $U$ . Finally a generalized Lang-Firsov transformation applied to a quantum dot with  $N$  levels is studied, finding and a general negative contribution to the  $U$  from intraband coupling, and a positive contribution to the  $U$  from interband coupling.

# 1 Introduction

SrTiO<sub>3</sub> (Strontium Titanate, STO) and LaAlO<sub>3</sub> (Lathanum Aluminate, LAO) by themselves are two non-magnetic insulators, but when sandwiched together they form an interface that shows interesting properties. STO when doped with high electron densities becomes superconducting at 0.35K and was the first insulator and oxide discovered to become superconducting. [9] The LAO/STO interface shows properties like superconductivity, ferromagnetism, strong atomic spin-orbit coupling and more. In 2004, it was shown that metallic conduction occurs at the LAO/STO interface. Then in 2007 superconductivity was reported in the 2D electron gas (2DEG) forming in the interface with a transition temperature of  $\sim 200\text{mK}$  [11] In 2012 an experimental study on the interface between LAO/STO [8] found that a Lifshitz transition between d-orbitals of different symmetries lies at the core of the superconductivity, ferromagnetism and magnetotransport phenomena occuring in the interface. They found that the maximum superconducting critical temperature occurs at the Liftshitz transition. The behavior observed follows from only a small number of bands, coming from the  $xy/xz/yz$  *d*-orbitals, but a simple relation between the specific energy bands and transport phenomena is still missing. It was then shown experimentally from transport measurements that electron-pairing was occurring in an electrostatically gated quantum dot on a nano-wire in the LAO/STO interace, without superconductivity, having a higher critical magnetic field and temperature than the superconducting electron pairs [3]. The conductance peaks in the transport measurements would split into two peaks at high enough magnetic fields, suggesting paired electrons. The phenomena can be described with a negative U Anderson-Holstein model with a local attractive potential between electrons on the same site but no explanation for the negative U center is found from the experiment. The experiment is performed again with a different quantum dot [10] where the same tunneling effects are observed and compared with a negative-U Anderson model.

Cheng et al [4] observed in 2016 that at lower chemical potential the electron–electron interaction is attractive and the pairing local. As the chemical potential is raised by increasing the gate-voltage, the interaction becomes repulsive and non-local. Cheng et al proposed that the interaction changes sign when the  $xz/yz$  bands become populated, which is at the Lifshitz-point. In [2] it was found that the charge carriers in the 2DEG, forming in the STO close to the interface, were polarons, electrons coupled to the lattice vibrations in the STO.

Polaronic effects in which electrons couple to phonons could be a reason for the negative U-center creating locally paired electrons [1]. With the population of the  $xz/yz$  bands at the Lifshitz transition, interband electron-phonon coupling could play a role in explaining the local electron pairing in the quantum dots in LAO/STO.

The aim of this thesis is to study the polaronic effects on electron pairing in a quantum dot in LAO/STO, by using a one-site Anderson-Holstein model with two energy levels and with electron-phonon coupling terms added to the Hamiltonian. First a model will be examined where the electrons in each level couple to a phonon. Later interband electron-phonon coupling will be studied where electrons scatter between levels due to a phonon. Second, the effects of atomic spin-orbit coupling on the local interaction potential will be examined too. Before going to the polaronic effects we will examine the orbital structure of the energy levels in a quantum dot made in the LAO/STO 2DEG.

## 2 Quantum dot in LAO/STO

In a quantum dot electrons are confined with zero degrees of freedom as they are enclosed in all directions. This can be thought of as a particle in a box and we will therefore use the solutions to the simple particle in a box problem and compare them to the band structure of the LAO/STO 2DEG,

from which the electrons come from. By doing this we will be able to examine the orbital structure of the energy levels in a quantum dot defined in an LAO/STO interface.

We model our quantum dot in the 2DEG as an infinite potential well lying in the  $xy$ -plane with sides of length  $L_x$  and  $L_y$ . Due to the quantum confinement the electron wave vector  $k$ , will be quantized in the  $x$  and  $y$ -direction in levels of  $\frac{\pi n_i}{L_i}$  with  $n_i \in \mathbb{N}$  and  $i = x, y$ . The energy is proportional to  $k^2$  and therefore the lowest energy-level that will be filled first will be from an electron with  $n_x = n_y = 1$ . The next energy level then depends on the symmetry of the quantum dot. For a symmetric dot with  $L_x = L_y = L$  it would be degenerate with either  $n_x = 1$  and  $n_y = 2$  or  $n_x = 2$  and  $n_y = 1$ . With an asymmetric dot, like a dot defined on a nano-wire as in [3], we will expect one dimension to be more confined such that the first energy levels would be e.g.  $n_y = 1$  and then  $n_x$  increasing if  $L_y \ll L_x$  due to the quantum confinement. With the gate voltage controlling the electro-chemical level in the quantum dot, an electron will be added to the quantum dot when the electro-chemical level is lowered by the addition energy, which is the general energy required to go from  $N$  to  $N - 1$  electrons. In the constant interaction model, which is derived in appendix D, the addition energy required to add another electron to the quantum dot is the sum of the charging energy coming from the capacitance and the "orbital energy" coming from the quantization of the energy levels in the quantum dot.

We will work with the band structure of the LAO/STO interface found in [8]. The numerical values and form are found in appendix E. The conduction band is made up of electrons in the  $t_{2g}$  band containing the  $xy$ ,  $xz$  and  $yz$  orbitals, and the band structure is therefore written in the basis of these orbitals. The energy of the  $xy$  orbital that lie in the  $xy$ -plane is lower than the other two orbitals that lie out of the  $xy$ -plane. The Hamiltonian for the band structure in the LAO/STO interface is:

$$H_0 = \begin{pmatrix} \frac{\hbar^2 k_x^2}{2m_h} + \frac{\hbar^2 k_y^2}{2m_l} & \Delta_d \hbar^2 k_x k_y & 0 \\ \Delta_d \hbar^2 k_x k_y & \frac{\hbar^2 k_x^2}{2m_l} + \frac{\hbar^2 k_y^2}{2m_h} & 0 \\ 0 & 0 & \frac{\hbar^2 k_x^2}{2m_l} + \frac{\hbar^2 k_y^2}{2m_l} - \Delta_E \end{pmatrix} \begin{cases} |yz\rangle \\ |xz\rangle \\ |xy\rangle \end{cases}. \quad (2.1)$$

When adding spin-orbit coupling we get the full Hamiltonian,  $H$ :

$$H = H_0 \otimes \sigma_0 + \Delta_{SO} \sum_i^3 L_i \otimes \sigma_i. \quad (2.2)$$

The addition of spin-orbit coupling to the Hamiltonian is worked out in appendix F. We want to find solutions to the Hamiltonian for the allowed values of  $k$  in the infinite 2D quantum well, and we use the solution to the single particle Schrödinger equation for an electron in the 2D quantum well to find the allowed  $k$  [6]. As the  $k$ 's are quantized in levels of  $\Delta k_i = \frac{\pi}{L_i}$ , we know which electronic states, from each band in the LAO/STO interface, that can occupy the quantum dot. First we can figure out how many states will be available in the quantum dot from each band. As the electrons in the LAO/STO interface have wave vectors in the first Brillouin zone with  $k_i$  between  $-\pi/a$  to  $\pi/a$ , we get that the number of available states in 2D is  $N = (\frac{2L_x}{a})(\frac{2L_y}{a})$ , and is thus proportional to the size of the quantum dot. For a 10nm by 10nm dot we have  $N = 4 \frac{100^2}{3.9^2} \approx 2630$ , with 3.9Å being the lattice constant of STO, and for a constant  $n_y$  we will then have  $\sim 51$  levels in  $k_x$ . Thus by solving the Hamiltonian for  $\Delta k_x n_x$  for each of the 51 electrons with  $k_y = 0$  in LAO/STO we get a plot of the energy levels shown in figure 1:

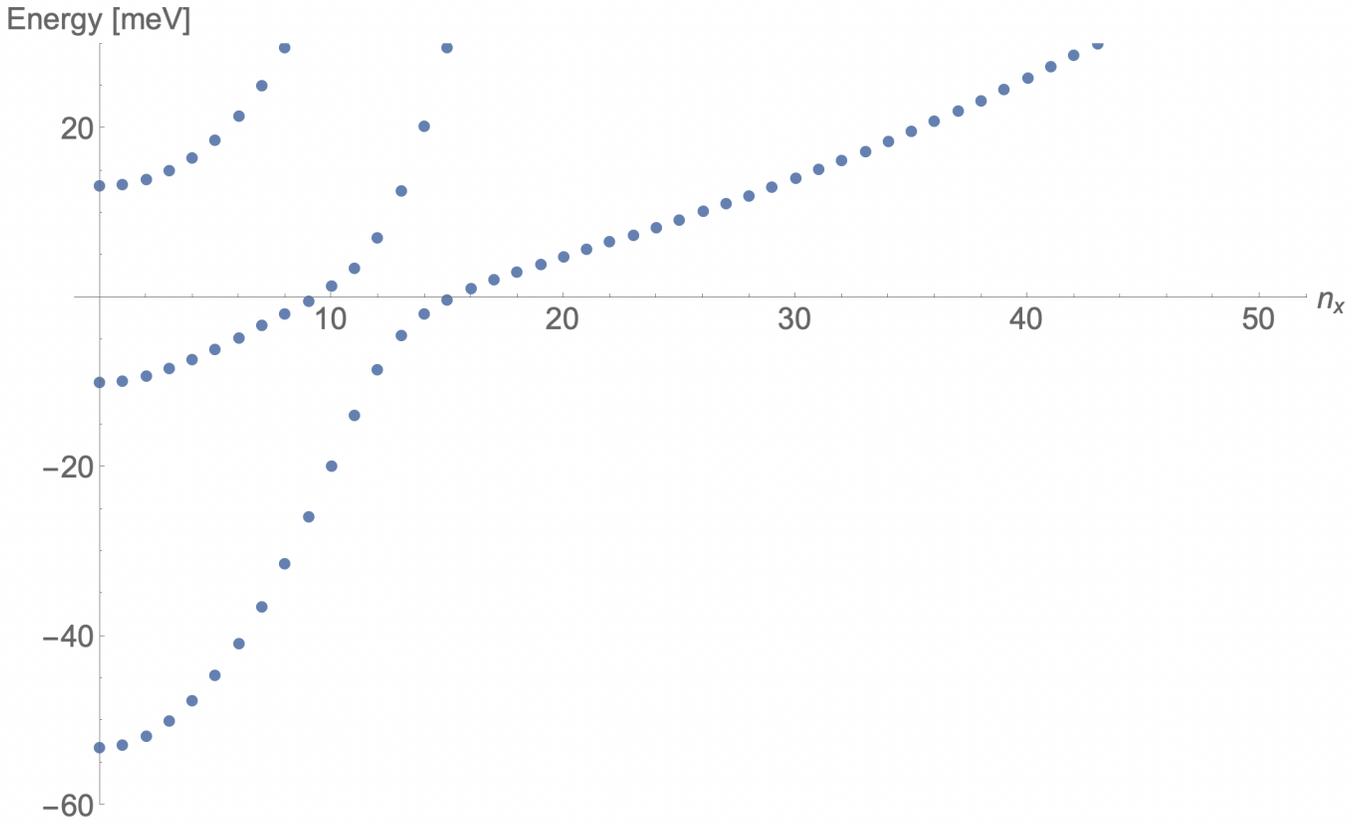


Figure 1: Quantum well energy plot along  $n_x$

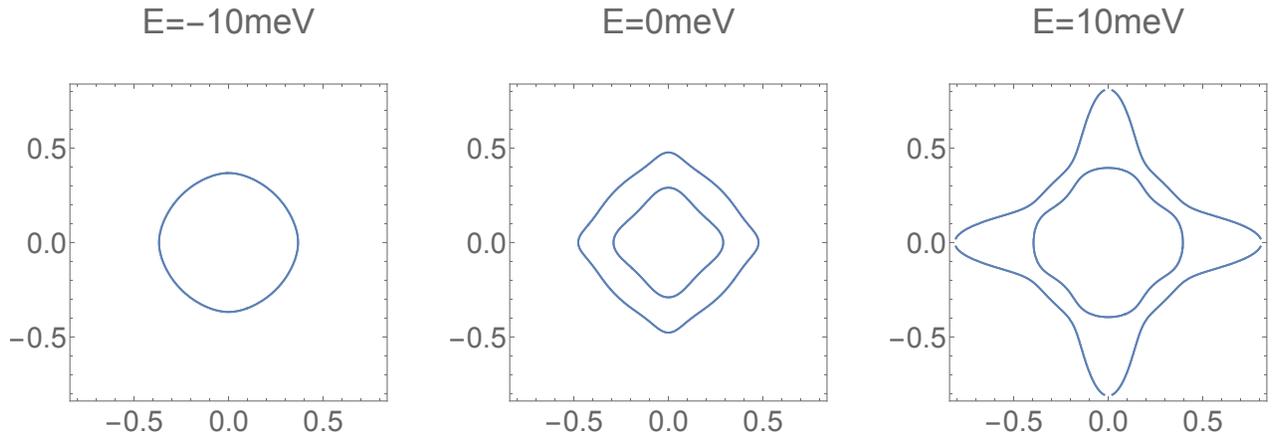


Figure 2: Contour plots of bands in LAO/STO in the  $k_x k_y$ -plane

As electrons from the LAO/STO 2DEG fill the quantum dot with quantized momenta, we see that at low energies only electrons from the  $xy$ -orbitals are available due to their lowered energies, but at higher energies also  $xz/yz$ -orbitals can fill the dot. In figure 2, contour plots of the energy bands in the LAO/STO 2DEG show that only one band is populated at low energies. By looking at the eigenstates from the numerical solutions to the Hamiltonian for each allowed  $k$ , we can examine which orbitals make up the electronic states in the quantum dot.

For each allowed  $k$ , we find the eigenstates of the Hamiltonian in (2.2), and from that we know the orbital contribution to each quantum dot level, as the eigenstate will be a linear combination of the  $xy$ ,  $xz$  and  $yz$ -orbitals. By restricting ourselves to a constant  $n_y$  we can calculate the orbital probabilities at each allowed  $k_x$ , which is for  $n_x$  up to  $\sim 51$  in a 10nm by 10nm quantum well. From normalizing the eigenvectors and then calculating the contribution from each orbital we see in figure 3 that the highest lying band is mostly made up of  $xz$ -states, whereas the electrons in the lowest band is mostly made up of  $xy$ -states until the Lifshitz point, around  $n_x = 13$  for a quantum dot of this size, where the band shifts to being mostly made up of  $yz$ -states. We see that the quantum dot states are mixed the most around the Lifshitz point where different types of orbitals will make up the quantum dot state, depending on the direction of  $k$ . The Lifshitz point is where a transition of the symmetry of the bands happen.

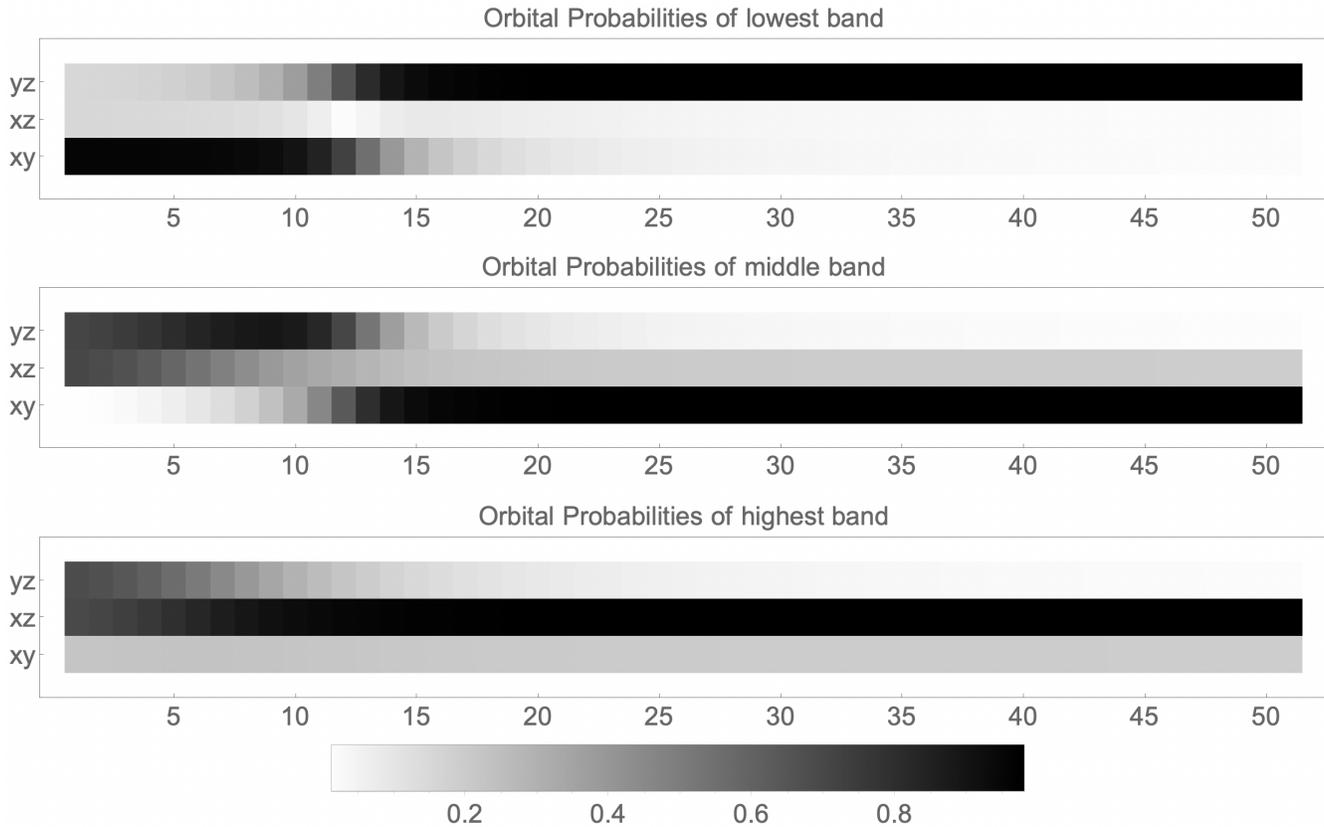


Figure 3: Orbital probabilities along  $k_x$  for the  $n_x$ 'th level

Figure 4 shows the same plot but with constant  $n_x$ , where it is shifted such that at the Lifshitz point the bands are made up of  $xz$  and  $xy$  states instead of  $yz$  and  $xy$ . As the quantum dot levels with lower energy are from states with low  $n_x$  and  $n_y$ , and since we see the same pattern for a constant  $n_x$  we expect in general to not see much mixing of the  $d$ -orbitals in the quantum dot states before we get to the Lifshitz point. Due to the band structure in figure 1 and the orbital probabilities of the bands in figures 3 and 4, we see that the density of states of the  $xz/yz$  is going to be higher than the density of states of the  $xy$  electrons above the Lifshitz point, and we therefore expect a high density of mixed  $xz/yz$  states past the Lifshitz point.

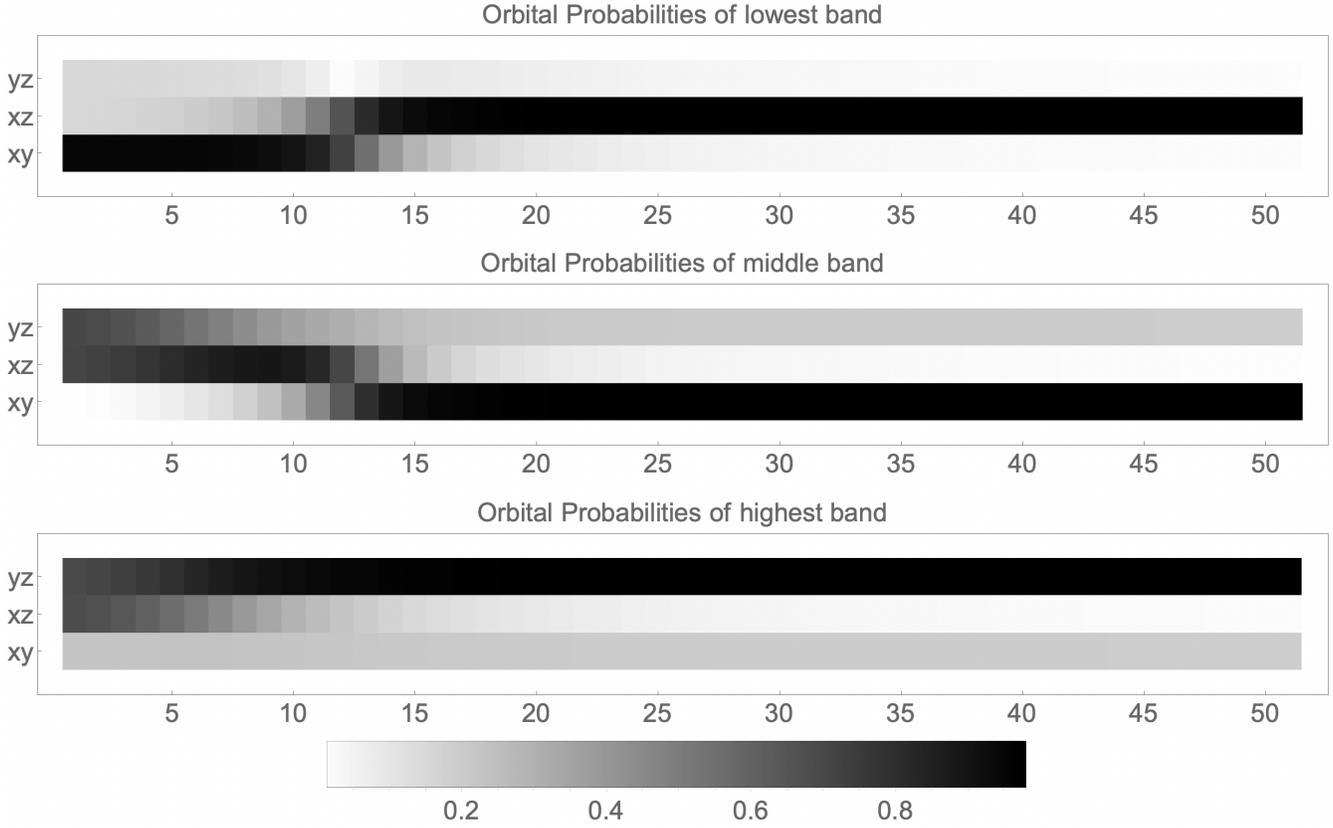


Figure 4: Orbital probabilities along  $k_y$  for the  $n_y$ 'th level

We note that changing the size of the quantum dot, by changing the side lengths  $L_i$ , should only result in a change of  $\Delta k_i$ , changing the number of electrons in the quantum dot and their energy level spacing. The quantum dots used in the experiments discussed in the introduction have larger dimensions and are also not symmetric, but the same mixing of orbitals should still occur. The mixing of orbitals in the quantum dot could change the types of electron-phonon couplings present, possibly creating or destroying the electron pairs seen in an LAO/STO quantum dot.

### 3 Intraband electron-phonon coupling

Considering that the charge carriers in the LAO/STO interface are polarons, electrons coupling to the lattice vibrations in the solid, we are motivated to work with a Hamiltonian that incorporates electron-phonon coupling. As stated in the first aim of this thesis, we want to study the effect of electron-phonon interaction with multiple bands available, and we will do that by using a one-site two level Anderson-Holstein model to describe a quantum dot with electrons localized on the same site and with an energy difference between the two levels due to the addition energy in the quantum dot. When we have two electrons on the same site we will have a repulsive potential and we want to study the effect that electron-phonon coupling will have on that interaction. In this section, we will examine the effect of intraband electron-phonon coupling where electrons in the two energy levels couple to the same phonon but no scattering between levels occur. We work with the following Hamiltonian

$$H = \epsilon c^\dagger c + (\epsilon + \Delta) d^\dagger d + U n_d n_c + \omega_0 b^\dagger b + \lambda (d^\dagger d + \alpha c^\dagger c) (b^\dagger + b), \quad (3.1)$$

where  $c^\dagger$  and  $d^\dagger$  are the creation operators for the electrons in the  $c$  and  $d$  quantum dot energy level.  $b^\dagger$  is a phonon creation operator.  $U > 0$  is the repulsive electrostatic potential between the two electrons on the same site.  $\omega_0$  is the phonon frequency and  $\lambda$  is the electron-phonon coupling constant with the dimension of energy. The energy of the  $d$ -level electron is shifted by  $\Delta$  due to the energy cost of adding an electron to the quantum dot.  $\alpha$  is a dimensionless constant creating a difference in the coupling strength for the  $d$  and  $c$ -level electrons. Especially for higher energy levels in the quantum dot with mixed orbitals, we could imagine that the electrons in different levels couple differently to the phonon. The second quantization electron operators in the two levels follow standard anti-commutation, whereas the phonon operators follow bosonic commutation relations. This model is a modified Anderson-Holstein model with only one site  $i$ , being the quantum dot. We work with two levels representing two different energy levels in the quantum dot coming from the energy spectrum discussed in section 2.

The Hamiltonian then consists of a part diagonal in the space of zero, one or two electrons and  $n$  phonons,  $H_0 = H_e + H_{ph}$ :

$$H_0 = \epsilon c^\dagger c + (\epsilon + \Delta) d^\dagger d + U n_d n_c + \omega_0 b^\dagger b. \quad (3.2)$$

$H_0$  describes the energies of creating the electrons in the  $c$  and  $d$ -levels, the phonons and the energy,  $U$ , of the two electrons repelling each other, when both electrons are located on the quantum dot. Then we have

$$H_{e-ph} = \lambda(d^\dagger d + \alpha c^\dagger c)(b^\dagger + b), \quad (3.3)$$

which is the coupling between the phonons and electrons in both levels. Both energy levels in the quantum dot couple to the same phonon. We thus have the total system  $H = H_e + H_{ph} + H_{e-ph}$ . We want to see how the electron-phonon interaction term affects the energy levels of the system, and if it will result in a negative effective interaction potential,  $U < 0$ , giving attractive electron-electron interaction.

The electronic part,  $H_e$  has eigenstates in the 4-dimensional Hilbertspace consisting of either no electrons (vacuum state), an electron in the  $c$ -level, an electron in the  $d$ -level and electrons in both levels. The states will be represented in same order as

$$|0\rangle, \quad |c\rangle = c^\dagger |0\rangle, \quad |d\rangle = d^\dagger |0\rangle, \quad |cd\rangle = d^\dagger c^\dagger |0\rangle. \quad (3.4)$$

In this basis  $H_e$  is diagonal and will have energies  $0, \epsilon, \epsilon + \Delta$  and  $2\epsilon + \Delta + U$ . The phonon Hamiltonian with eigenstates  $|n\rangle$  and energies  $n\omega_0$  is infinitely dimensional. We can now have electrons in either or both levels and phonons which gives us the Hilbert space spanned by  $|i\rangle \otimes |n\rangle$  with  $i \in \{0, c, d, cd\}$  and  $n \in \mathbb{N}$ , with kets  $|i, n\rangle$ . Only with the addition of  $H_{e-ph}$  do we end up with  $H$  not diagonal in the  $|i, n\rangle$  basis.

### 3.1 Perturbation theory

To extract information about the electrons in the system with electron-phonon coupling, we look towards perturbation theory where we will stay in the basis of uncoupled electrons and phonons.  $H_0$  has non-degenerate eigenstates so we will use non-degenerate perturbation theory up to second order in  $\lambda$  and we will treat  $H_{e-ph}$  as the perturbation. We already know the solutions to the unperturbed Hamiltonian and their energies. Up to second order we have

$$E_n \approx E_n^0 + H_{nn}^{e-ph} + \sum_{m \neq n} \frac{|H_{mn}^{e-ph}|^2}{E_n^0 - E_m^0}. \quad (3.5)$$

As the perturbation has a bosonic creation and annihilation operator, the first order correction will be zero.

We will use a notation where a state in the Hilbert space is  $|cdn\rangle = |c\rangle \otimes |d\rangle \otimes |n\rangle$ , with  $c$  and  $d$  being 0 or 1, as they are fermions and  $n \in \mathbb{N}$  representing the phonons. This will give us a second order correction. We are only interested in the terms where the phonon numbers differ by one as all other terms will be zero. This will then give an energy correction to the states only one or two electrons. We will begin by calculating the second order correction. First we will do it for the state  $|10n\rangle$ :

$$E_{10n}^{(2)} = \sum_{m'n'o' \neq mno} \frac{|\langle m'n'o' | H^{e-ph} | mno \rangle|^2}{E_{mno}^0 - E_{m'n'o'}^0}, \quad (3.6)$$

but knowing that the perturbation,  $H^{e-ph}$ , contains electronic number operators and bosonic annihilation and creation operators, we have that  $n = n'$ ,  $m = m'$  and  $o' = o \pm 1$ . Also we will use that  $b^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$  and  $b |n\rangle = \sqrt{n} |n-1\rangle$ . From this we can find the energy correction to the state  $|10n\rangle$ :

$$\begin{aligned} E_{10n}^{(2)} &= \frac{|\langle 10(n+1) | H' | 10n \rangle|^2}{(\varepsilon + \omega_0 n) - (\varepsilon + \omega_0(n+1))} + \frac{|\langle 10(n-1) | H' | 10n \rangle|^2}{(\varepsilon + \omega_0 n) - [\varepsilon + \omega_0(n-1)]} \\ &= \frac{|\langle 10(n+1) | (\lambda\alpha\sqrt{n+1}) | 10(n+1) \rangle|^2}{-\omega_0} + \frac{|\langle 10(n-1) | (\lambda\alpha\sqrt{n}) | 10(n-1) \rangle|^2}{\omega_0} \\ &= -\frac{\lambda^2}{\omega_0} \alpha^2. \end{aligned} \quad (3.7)$$

We get that the correction lowers the energy of the state. It is also easy to see now that for the state  $|00n\rangle$  we will get no correction, for the state  $|01n\rangle$  we will get the correction  $E_{01n}^{(2)} = -\frac{\lambda^2}{\omega_0}$  and lastly for the  $|11n\rangle$  we get:

$$E_{11n}^{(2)} = \frac{|\langle 11(n+1) | (\lambda\omega_0(1+\alpha)b^\dagger) | 11n \rangle|^2}{-\omega_0} + \frac{|\langle 11(n-1) | (\lambda\omega_0(1+\alpha)b) | 11n \rangle|^2}{\omega_0} = -\frac{\lambda^2}{\omega_0} (1+\alpha)^2. \quad (3.8)$$

We see that the energy correction to the state with both levels occupied is lowered more than the states with only one level occupied. From the perturbation theory, we have that for strong enough coupling,  $\lambda$ , the energy of having two electrons will become lower than having one electron in the quantum dot resulting in electron pairs.

## 3.2 Lang-Firsov method

Now we will attempt at solving the Hamiltonian exactly by doing a unitary Lang-Firsov transformation to get rid of the coupling term, in the hopes that we can exactly solve the transformed Hamiltonian. This will give us new eigenstates  $U |\psi\rangle$ , not necessarily pure electronic states, but we can still analyze the energy levels. We do a unitary transformation of the Hamiltonian using the unitary operator  $U = e^{iS_p}$  with

$$iS_p = \frac{\lambda}{\omega_0} (b^\dagger - b)(n_d + \alpha n_c), \quad (3.9)$$

where  $n_c = c^\dagger c$  and  $n_d = d^\dagger d$ . To ease notation we will use  $n_t(\alpha) = n_d + \alpha n_c$ , with  $n_t(\alpha = 0)$  being the total number of electrons. We will need the factor  $\frac{\lambda}{\omega_0}$  in  $iS_p$  for the coupling term to cancel out in

the transformed Hamiltonian. We do the transformation  $H' = UHU^\dagger$  which means the eigenstates to the transformed Hamiltonian are  $|\psi'\rangle = U|\psi\rangle$ , with  $|\psi\rangle$  the original eigenstates. We only transform the annihilation operators since  $(A')^\dagger = (UAU^\dagger)^\dagger = UA^\dagger U^\dagger = (A^\dagger)'$ . Also we will transform each operator independently, as it is possible to insert the identity  $UU^\dagger$  between operators. We will make use of the Baker-Campbell-Hausdorff formula:

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2}[A[A, B]] + \dots = \sum_{n=0} \frac{1}{n!} [A, B]_n, \quad (3.10)$$

and to that we will use that  $[cA, B]_n = c^n [A, B]_n$ . First we will transform  $c$  and from that  $d$  will follow:

$$c' = UcU^\dagger = \sum_{n=0} \frac{1}{n!} \left[ \frac{\lambda}{\omega_0} (b^\dagger - b) n_t(\alpha), c \right]_n = \sum_{n=0} \frac{\left[ \frac{\lambda}{\omega_0} (b^\dagger - b) \right]^n}{n!} [n_t(\alpha), c]_n. \quad (3.11)$$

We need to calculate the commutation between  $n_t(\alpha)$  and  $c$ , and we get

$$\begin{aligned} [n_t(\alpha), c] &= [n_d + \alpha n_c, c] = \alpha [c^\dagger c, c] = \alpha (c^\dagger c c - c c^\dagger c) = -\alpha (1 - c^\dagger c) c \\ &= -\alpha c, \end{aligned} \quad (3.12)$$

by using that  $c^2 = (c^\dagger)^2 = 0$ , and that  $[n_d, c] = 0$ . This gives us that

$$c' = \sum_{n=0} \frac{\left[ \frac{\lambda}{\omega_0} (b^\dagger - b) (-\alpha) \right]^n}{n!} c = e^{\alpha \frac{\lambda}{\omega_0} (b - b^\dagger)} c. \quad (3.13)$$

When letting  $\alpha = 1$  we get that  $d' = e^{\frac{\lambda}{\omega_0} (b - b^\dagger)} d$ . We then see that

$$n'_c = (c^\dagger c)' = (c^\dagger)' c' = \left( e^{\alpha \frac{\lambda}{\omega_0} (b - b^\dagger)} c \right)^\dagger e^{\alpha \frac{\lambda}{\omega_0} (b - b^\dagger)} c = c^\dagger e^{-\alpha \frac{\lambda}{\omega_0} (b - b^\dagger)} e^{\alpha \frac{\lambda}{\omega_0} (b - b^\dagger)} c = n_c, \quad (3.14)$$

and likewise  $n'_d = n_d$ . The transformation of  $b$  follows:

$$b' = \sum_{n=0} \frac{\left[ \frac{\lambda}{\omega_0} n_t(\alpha) \right]^n}{n!} [(b^\dagger - b), b]_n, \quad (3.15)$$

where we have that  $[(b^\dagger - b), b] = [b^\dagger, b] = -1$ , giving

$$[(b^\dagger - b), [(b^\dagger - b), b]] = [(b^\dagger - b), -1] = 0, \quad (3.16)$$

such that according to equation 3.10:

$$b' = b - \frac{\lambda}{\omega_0} n_t(\alpha). \quad (3.17)$$

From equation (3.14) we see that  $H_e$  does not change during the Lang-Firsov transformation as  $n_c$  and  $n_d$  do not change so we only have to work out the transformation of  $H_{ph} + H_{e-ph}$ :

$$\begin{aligned} H'_{ph} + H'_{e-ph} &= \lambda(n_d + \alpha n_c) \left[ b^\dagger + b - 2 \frac{\lambda}{\omega_0} n_t(\alpha) \right] + \omega_0 \left[ b^\dagger - \frac{\lambda}{\omega_0} n_t(\alpha) \right] \left[ b - \frac{\lambda}{\omega_0} n_t(\alpha) \right] \\ &= \lambda n_t(\alpha) (b^\dagger + b) - 2 \frac{\lambda^2}{\omega_0} n_t(\alpha)^2 + \omega_0 b^\dagger b - \lambda n_t(\alpha) (b^\dagger + b) + \frac{\lambda^2}{\omega_0} n_t(\alpha)^2 \\ &= \omega_0 b^\dagger b - \frac{\lambda^2}{\omega_0} (\alpha^2 n_c + n_d + 2\alpha n_c n_d). \end{aligned} \quad (3.18)$$

Putting the transformed terms back in the full Hamiltonian and collecting terms we end up with the total Hamiltonian:

$$H' = \epsilon_c c^\dagger c + (\epsilon_d + \Delta) d^\dagger d + U' n_c n_d + \omega_0 b^\dagger b, \quad (3.19)$$

where the energies are now shifted to

$$\epsilon_c = \epsilon - \alpha^2 \frac{\lambda^2}{\omega_0}, \quad \epsilon_d = \epsilon - \frac{\lambda^2}{\omega_0}, \quad U' = U - 2\alpha \frac{\lambda^2}{\omega_0}. \quad (3.20)$$

We can then easily find the eigenstates after the transformation. The transformed Hamiltonian is diagonal in the basis  $\{|00n\rangle, |10n\rangle, |01n\rangle, |11n\rangle\}$  with the eigenenergies:

$$\begin{aligned} E_{|00n\rangle} &= n\omega_0, & E_{|10n\rangle} &= \epsilon - \alpha^2 \frac{\lambda^2}{\omega_0} + n\omega_0, \\ E_{|01n\rangle} &= \epsilon + \Delta - \frac{\lambda^2}{\omega_0} + n\omega_0, & E_{|11n\rangle} &= 2\epsilon + \Delta + U - \frac{\lambda^2}{\omega_0} (1 + \alpha)^2 + n\omega_0, \end{aligned} \quad (3.21)$$

corresponding to zero particles, one particle in the  $c$ -level, one particle in the  $d$ -level and two particles in the system, along with  $n$  phonons. To get the eigenstates of the untransformed Hamiltonian, we know that the solutions to the transformed Hamiltonian are  $U|i\rangle$ , with  $|i\rangle$  being the eigenstates to the untransformed Hamiltonian, so we just apply  $U^\dagger$  to the new eigenstates to retrieve the old ones. We then see that  $|i\rangle = U^\dagger |cdn\rangle = e^{-\frac{\lambda}{\omega_0}(b^\dagger - b)(n_d + \alpha n_c)} |cdn\rangle$ , and in the electron and phonon basis the state will be electrons coupled with phonons, which we see when Taylor expanding the exponential function. This new polaronic eigenstate will have a lowered energy compared to the electron energies in the uncoupled system. We also see that the energy of the state with two polarons is lowered faster as a function of  $\lambda$  than the energy to the states with only one polaron, similar to the result found from perturbation theory. We note that at strong enough coupling and  $\alpha < 1$  the energy of the polaron in the  $d$ -level will become lower than the energy of an electron in the  $c$ -level. We can also conclude that the energy gap between the levels does not give rise to any resonant effects so the coupling will only result in electron-pairing if we have a large enough  $\lambda$  or the phonon mode becomes soft and  $\omega_0 \rightarrow 0$ .

## 4 Interband electron-phonon coupling

Following the results of section 2, and the change in orbital population of the quantum dot energy levels at the Lifshitz transition discussed in the introduction, we imagine different types of polaronic effects could be in play at different points in the energy spectrum of the quantum dot. One such polaronic effect could be the intraband electron-phonon coupling discussed in section 3, another effect could be interband electron-phonon coupling. This leads us to studying a Hamiltonian which allows electrons to scatter between levels due to interband electron-phonon interaction and we want to examine the contribution to the  $U$  that this type of coupling can give. We could imagine that around the Lifshitz point, where the bands with  $xz/yz$  orbitals starts to be populated, some coupling between orbitals could occur where an electron could be scattered from a level comprised mostly of one type of orbital to a level comprised of another type of orbital. If the scattering occurs between orbitals we could imagine that this type of coupling only could be possible around and after the Lifshitz point. We could also have made the other guess, that interband transition is only allowed until the Lifshitz point, where scattering between levels would not be possible anymore due to the levels having different orbital symmetries. If the interband coupling turns out to create a repulsive potential, and interband coupling occur after the Lifshitz point, it could be interesting due to [4]

where local electron pairing occurred only up until the Lifshitz point when the  $xz/yz$ -orbitals become populated. This brings us to the following model:

$$H = \epsilon c^\dagger c + (\epsilon + \Delta) d^\dagger d + U n_c n_d + \omega b^\dagger b + \lambda (b^\dagger + b)(d^\dagger c + c^\dagger d), \quad (4.1)$$

where we divide it into  $H = H_e + H_{ph} + H_{e-e} + H_{e-ph}$ . The electron-phonon interaction is understood as an electron in the initial  $c$ -level being scattered into the  $d$ -level by either absorption or emission of a phonon or similarly from  $d$ -level to  $c$ -level. We have also again used that the  $\frac{1}{2}\hbar\omega$  from the zero-point mode of the phonon will only add a constant to the total energy so we have ignored it. Again by treating the electron-phonon term as a perturbation, we can easily find the unperturbed energy levels from having an electron in either level, both levels filled or no electrons denoted as  $|cdn\rangle = |c\rangle \otimes |d\rangle \otimes |n\rangle$  with the first being the  $c$ -level, then  $d$ -level and lastly the phonon number. This gives us the energies  $0, \epsilon, \epsilon + \Delta, 2\epsilon + \Delta + U$ , plus the phonon energy, for the system without electron-phonon coupling, same as in the intraband model.

## 4.1 Perturbation theory

We again start by using perturbation theory where we work with the electron-phonon coupling as perturbation to the Hamiltonian  $H_0 = H_e + H_{ph} + H_{e-e}$ . With this model we can then apply perturbation theory to find corrections to the energy levels due to the interband electron-phonon interaction. We quickly see that the first order corrections are going to be zero due to  $H_{e-ph}$  either raising or lowering the phonon level, so we go to second order. At second order we note that the corrections to the highest and lowest energy level will be zero, as both levels are either empty or full such that a phonon can't scatter an electron between levels. We then have for the  $|10n\rangle$  state which is the state with an electron in the  $c$ -level and the phonon mode excited to the  $n$ 'th level:

$$E_{|10n\rangle}^{(2)} = \sum_{m \neq |10n\rangle} \frac{|\langle m | \lambda(b^\dagger + b)(d^\dagger c + c^\dagger d) | 10n \rangle|^2}{\epsilon + n\omega - E_m^{(0)}}. \quad (4.2)$$

We see that the  $m$ -state can only be either  $|01(n+1)\rangle$  or  $|01(n-1)\rangle$  for the correction to be non-zero so we get:

$$E_{|10n\rangle}^{(2)} = \lambda^2 \left( \frac{n+1}{-\Delta - \omega} + \frac{n}{-\Delta + \omega} \right) = -\lambda^2 \left( \frac{n+1}{\Delta + \omega} + \frac{n}{\Delta - \omega} \right), \quad (4.3)$$

with the right most term coming from absorbing a phonon, and we see that there is no correction from absorbing a phonon if there are no phonons in the system, since  $n = 0$ . We also get from the other initial state the same correction but with a sign difference on the  $\Delta$ :

$$E_{|01n\rangle}^{(2)} = -\lambda^2 \left( \frac{n+1}{-\Delta + \omega} + \frac{n}{-\Delta - \omega} \right). \quad (4.4)$$

We see that we get divergences around the point where the energy gap between the quantum dot levels is equal to the phonon energy. At this point we have that  $E_{|10n\rangle}^{(0)} = E_{|01(n-1)\rangle}^{(0)}$ , and we get degeneracies in the system resulting in the perturbation theory breaking down. It could look as if resonant coupling might be possible around the point where the energy gap and the phonon energy is close to the same energy. This resonant energy would then depend on the addition energy,  $\Delta$ , in the quantum dot which depends on the charging energy that we assume is constant and the difference in orbital energies which depends on the size. In [3] it was found experimentally for their quantum dot that the addition energy varied, but was at energies in the orders of  $100\mu\text{eV}$  whereas the phonon

energies in LAO/STO are in the order 10meV [2]. With  $\omega \gg \Delta$  we have from equations (4.4) and (4.3) that

$$E_{|10n\rangle}^{(2)} = -\frac{\lambda^2}{\omega} \left( \frac{n+1}{\frac{\Delta}{\omega} + 1} + \frac{n}{\frac{\Delta}{\omega} - 1} \right) \rightarrow -\frac{\lambda^2}{\omega}, \quad (4.5)$$

$$E_{|01n\rangle}^{(2)} = -\frac{\lambda^2}{\omega} \left( \frac{n+1}{-\frac{\Delta}{\omega} + 1} + \frac{n}{-\frac{\Delta}{\omega} - 1} \right) \rightarrow -\frac{\lambda^2}{\omega}, \quad (4.6)$$

which are the energy corrections we expect for the states with one electron, with phonon energies in the range of 10meV. Since we saw from perturbation theory that the  $|11n\rangle$  is unchanged we would expect that  $U \rightarrow U + 2\frac{\lambda^2}{\omega}$  to second order such that  $E_{|11n\rangle}^{(0)} = E_c + E_d + U$  doesn't change.

## 4.2 Transformation of the interband Hamiltonian

We will now use a unitary transformation on the Hamiltonian to solve for the states and energies of the full system without the use of perturbation theory. From the perturbation theory we expect to find a positive contribution to the  $U$  from the interband electron-phonon coupling. Again, we will use a Lang-Firsov type transformation. If we use the same unitary operator  $U = e^{\frac{\lambda}{\omega}(b^\dagger - b)(n_c + n_d)}$  to transform the system so that  $H' = UHU^\dagger$ , it will give the same transformed operators as earlier where the operators  $n_c, n_d, c^\dagger d$  and  $d^\dagger c$  don't change under transformation. This transformation will help cancel out intraband coupling but not interband coupling. Since we only have an interband coupling now we will instead make use of a modified Lang-Firsov transformation. To get a Hamiltonian without an interband electron-phonon coupling term we will use a transformation with  $U_2 = e^{S_2}$  where

$$S_2 = \frac{\lambda}{\omega}(b^\dagger - b)(c^\dagger d + d^\dagger c). \quad (4.7)$$

We then work out the transformation  $\bar{H} = U_2 H U_2^\dagger$ , following the approach of [13]. We will start by transforming the operators in the new Hamiltonian. When doing this we keep the Baker-Campbell-Hausdorff formula used earlier in mind. Beginning with the phonon creation and annihilation operators we get:

$$\begin{aligned} \bar{b} &= e^{\frac{\lambda}{\omega}(b^\dagger - b)(c^\dagger d + d^\dagger c)} b e^{-\frac{\lambda}{\omega}(b^\dagger - b)(c^\dagger d + d^\dagger c)} \\ &= b + \frac{\lambda}{\omega}(c^\dagger d + d^\dagger c)[b^\dagger - b, b] + \dots = b - \frac{\lambda}{\omega}(c^\dagger d + d^\dagger c), \end{aligned} \quad (4.8)$$

similar to how we did when dealing with intraband coupling. Now to the electron creation and annihilation operators:

$$\begin{aligned} \bar{c} &= e^{S_2} c e^{-S_2} \\ &= c + \frac{\lambda}{\omega}(b^\dagger - b)[c^\dagger d + d^\dagger c, c] + \frac{1}{2} \frac{\lambda^2}{\omega^2} (b^\dagger - b)^2 [c^\dagger d + d^\dagger c [c^\dagger d + d^\dagger c, c]] + \dots \end{aligned} \quad (4.9)$$

We start by calculating the commutators. To do this we use that the electrons in the  $c$  and  $d$ -levels are fermions so that their operators obey the normal anticommutation relations,  $\{c_a^\dagger, c_b^\dagger\} = \{c_a, c_b\} = 0$  and  $\{c_a, c_b^\dagger\} = \delta_{ab}$ :

$$\begin{aligned}
[c^\dagger d + d^\dagger c, c] &= [c^\dagger d, c] + [d^\dagger c, c] = c^\dagger dc - cc^\dagger d + d^\dagger cc - cd^\dagger c \\
&= -d\{c, c^\dagger\} = -d.
\end{aligned} \tag{4.10}$$

Now we can calculate the third term in the Bakers-Hausdorff-Campbell formula:

$$\begin{aligned}
[c^\dagger d + d^\dagger c, [c^\dagger d + d^\dagger c, c]] &= [c^\dagger d + d^\dagger c, -d] = -[d^\dagger c, d] \\
&= -d^\dagger cd + dd^\dagger c = d^\dagger dc + dd^\dagger c \\
&= \{d^\dagger, d\}c = c.
\end{aligned} \tag{4.11}$$

From this we know that the uneven terms give  $-d$  and the even terms give  $c$ . This gives us the transformation of  $c$  as:

$$\begin{aligned}
\bar{c} &= \sum_{n=0} \frac{\left[\frac{\lambda}{\omega}(b^\dagger - b)\right]^{2n}}{(2n)!} c - \sum_{n=0} \frac{\left[\frac{\lambda}{\omega}(b^\dagger - b)\right]^{2n+1}}{(2n+1)!} d \\
&= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c - \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d,
\end{aligned} \tag{4.12}$$

where we used that  $\sinh(x) = \sum_n \frac{x^{2n+1}}{(2n+1)!}$  and  $\cosh(x) = \sum_n \frac{x^{2n}}{(2n)!}$ . Then we also know that:

$$\begin{aligned}
\bar{c}^\dagger &= \cosh\left[-\frac{\lambda}{\omega}(b^\dagger - b)\right] c^\dagger - \sinh\left[-\frac{\lambda}{\omega}(b^\dagger - b)\right] d^\dagger \\
&= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c^\dagger + \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d^\dagger.
\end{aligned} \tag{4.13}$$

Similarly for  $\bar{d}$  we use the same procedure and find that  $[c^\dagger d + d^\dagger c, d] = -c$  giving us that  $[c^\dagger d + d^\dagger c, [c^\dagger d + d^\dagger c, d]] = [c^\dagger d + d^\dagger c, -d] = c$ , so we find that we just exchange the  $c$  and  $d$  to get  $\bar{d}$ . We now have the transformed operators as:

$$\begin{aligned}
\bar{b} &= b - \frac{\lambda}{\omega}(c^\dagger d + d^\dagger c), & \bar{b}^\dagger &= b^\dagger - \frac{\lambda}{\omega}(c^\dagger d + d^\dagger c), \\
\bar{c} &= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c - \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d, & \bar{c}^\dagger &= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c^\dagger + \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d^\dagger, \\
\bar{d} &= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d - \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c, & \bar{d}^\dagger &= \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] d^\dagger + \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] c^\dagger.
\end{aligned} \tag{4.14}$$

We can now work on transforming the Hamiltonian. The transformation of the Hamiltonian requires a bit more work in the interband case, since the number operators after this transformation contain multiple terms so the calculation have been moved to Appendix A. To transform the Hamiltonian we transform it one term at a time and introduce the notation:

$$A_1 = \cosh^2\left[\frac{\lambda}{\omega}(b^\dagger - b)\right], \quad A_2 = \sinh^2\left[\frac{\lambda}{\omega}(b^\dagger - b)\right], \quad A_3 = \cosh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right] \sinh\left[\frac{\lambda}{\omega}(b^\dagger - b)\right]. \tag{4.15}$$

From this we get that  $A_4 = A_1^2$ ,  $A_5 = A_2^2$ ,  $A_6 = A_3^2$ ,  $A_7 = A_1 A_3$  and  $A_8 = A_3 A_2$ . We then end up with a transformed Hamiltonian on the form:

$$\bar{H} = \bar{E}_c n_c + \bar{E}_d n_d + \bar{U} n_c n_d + V_1 d^\dagger c + V_2 c^\dagger d + \omega b^\dagger b, \quad (4.16)$$

with the transformed energies:

$$\begin{aligned} \bar{E}_c &= \epsilon - \Delta A_2 - \frac{\lambda^2}{\omega}, & \bar{E}_d &= \epsilon + \Delta A_1 - \frac{\lambda^2}{\omega}, & \bar{U} &= U + 2\frac{\lambda^2}{\omega}, \\ V_1 &= -\Delta A_3 - 2U A_8, & V_2 &= \Delta A_3 - 2U A_7. \end{aligned} \quad (4.17)$$

This gives us a Hamiltonian without the coupling term, but we have instead ended up with the exponential factors containing the phonon creation/annihilation operators, and therefore the result from the unitary transformation is not as clear cut as it was with the Lang-Firsov transformation in section 3. We do already see that the  $U \rightarrow U + 2\frac{\lambda^2}{\omega}$ , which works to create a repulsive potential. We also get similarly to the Lang-Firsov result that the energies for a single particle on the quantum dot,  $\bar{E}_c$  and  $\bar{E}_d$  are again lowered by  $\frac{\lambda^2}{\omega}$ . These two results are the same as we got from perturbation theory to second order in  $\lambda$  for  $\omega \gg \Delta$ . We also get two new terms from the transformation, the  $V_1$  and  $V_2$  that give an on-site hybridization that mixes the orbitals. The transformation has thus gotten rid of the electron-phonon coupling term but by expanding out the  $A$ 's we get infinitely many terms with both electron and phonon operators. We have achieved the goal of removing the electron-phonon coupling term but that didn't diagonalize the Hamiltonian. To study this new Hamiltonian further we will try averaging over the phonons.

#### 4.2.1 Averaging over the phonons

We will trace out the exponential function with the bosonic operators. We do this by assuming that we are in a thermal equilibrium at a low temperature, and then trace over the unperturbed phonon states with the density operator  $\rho = \frac{e^{-\beta H_{ph}}}{\text{Tr}[e^{-\beta H_{ph}}]}$ , and  $H_{ph} = \omega b^\dagger b$ . We use the result,  $\langle e^{\pm\alpha(b^\dagger - b)} \rangle = e^{-\frac{1}{2}\alpha^2 \coth(\frac{\beta\omega}{2})}$ , from appendix D, and for low temperatures where  $\lim_{x \rightarrow \infty} \coth(x) = \lim_{x \rightarrow \infty} \frac{e^{2x} + 1}{e^{2x} - 1} = 1$ , we have that:

$$\frac{1}{Z} \text{Tr} \left[ \rho e^{\pm\alpha(b^\dagger - b)} \right] = e^{-\frac{1}{2}\alpha^2 \coth(\frac{\beta\omega}{2})} \approx e^{-\frac{1}{2}\alpha^2}. \quad (4.18)$$

We can now easily calculate the reduced Hamiltonian by using that the trace is a linear mapping. As an example:

$$\begin{aligned} \frac{1}{Z} \text{Tr} (\rho A_5) &= \frac{1}{Z} \text{Tr} \left\{ \rho \sinh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} = \text{Tr} \left\{ \rho \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} \\ &= \frac{1}{Z} \text{Tr} \left[ \rho \frac{1}{2^4} \left( e^{\frac{\lambda}{\omega} (b^\dagger - b)} - e^{-\frac{\lambda}{\omega} (b^\dagger - b)} \right) \left( e^{\frac{\lambda}{\omega} (b^\dagger - b)} - e^{-\frac{\lambda}{\omega} (b^\dagger - b)} \right) \right] \\ &= \frac{1}{Z} \text{Tr} \left( \rho \frac{1}{16} (6 + e^{4\frac{\lambda}{\omega} (b^\dagger - b)} - 4e^{2\frac{\lambda}{\omega} (b^\dagger - b)} + e^{-4\frac{\lambda}{\omega} (b^\dagger - b)} - 4e^{-2\frac{\lambda}{\omega} (b^\dagger - b)}) \right) \\ &\approx \frac{1}{8} \left( e^{-8\frac{\lambda^2}{\omega^2}} + 3 - 4e^{-2\frac{\lambda^2}{\omega^2}} \right). \end{aligned} \quad (4.19)$$

Having averaged the Hamiltonian over the phonons, we now have a completely fermionic Hamiltonian. We can then examine the eigenstates of the Hamiltonian in the limit of weak and strong coupling.

### 4.2.2 Strong coupling regime

In the strong-coupling regime  $\frac{\lambda}{\omega} \gg 1$ , we see that  $\text{Tr}(\rho A_5) \approx \frac{3}{8}$ . We calculate the rest of the averages over the  $A$ 's in the same way as in (4.19) and get the same result as in [13]. In the strong coupling regime, where the exponential functions go to zero, we get:

$$\begin{aligned} \text{Tr}(\rho A_1) &\approx \frac{1}{2}, & \text{Tr}(\rho A_2) &\approx -\frac{1}{2}, \\ \text{Tr}(\rho A_3) = \text{Tr}(\rho A_7) = \text{Tr}(\rho A_8) &\approx 0, & \text{Tr}(\rho A_4) = \text{Tr}(\rho A_5) &\approx \frac{3}{8}, & \text{Tr}(\rho A_6) &\approx -\frac{1}{8}. \end{aligned} \quad (4.20)$$

At last we have the term  $\omega \langle b^\dagger b \rangle = \omega \frac{\exp\{-\beta\omega\}}{1 - \exp\{-\beta\omega\}} = \omega n_B(\omega)$ . These are boson operators and it will give us the Bose-function that goes to zero for  $T$  going to zero with a constant phonon energy. So we can safely neglect the phonon energy for low enough temperature. For  $T = 1\text{K}$  and  $\hbar\omega \approx 20\text{meV}$ , an LAO/STO phonon energy from a phonon possibly involved in the electron pairing [2], we get  $\beta\hbar\omega > 200$ . This limit then gives the totally fermionic reduced Hamiltonian,  $H_F$ :

$$H_F = \bar{E}n_c + \bar{E}n_d + \bar{U}n_cn_d, \quad (4.21)$$

with the transformed energies

$$\bar{E} = \epsilon + \frac{\Delta}{2} - \frac{\lambda^2}{\omega}, \quad \bar{U} = U + 2\frac{\lambda^2}{\omega}. \quad (4.22)$$

We thus have two degenerate states, as the states with one particle in the  $c$  or  $d$ -level now have the same energy. With our new  $\bar{U} > 0$ , the energies of the system are:

$$\begin{aligned} E_{00} &= 0, \\ E_{10} = E_{01} &= \epsilon + \frac{\Delta}{2} - \frac{\lambda^2}{\omega}, \\ E_{11} &= 2\epsilon + \Delta + U. \end{aligned} \quad (4.23)$$

We see that the energy of having a particle pair does not change, just like the model predicts, as it doesn't allow jumping between levels with both levels already occupied, but it still allows for polaron modes with lowered energy, favoring single particle states over particle pairs. We note the main result of this calculation, that the interband electron-phonon coupling results in a positive addition to the electron-electron potential  $U$ , and thus works against electron-pairing as the energy of single particle states was lowered compared to the two-particle state. We now understand that in a system with both intraband and interband coupling mechanisms, we would have a competition between pairing up electrons and breaking up those pairs. Since we have not studied the actual form of electron-phonon coupling in LAO/STO, but only worked with made up toy-models for intraband and interband electron-phonon coupling in an Anderson-Holstein model we can not know if this exact pairing mechanism is present in the interface. We do know however that there are polarons and if these types of couplings exist, then an intraband coupling between the  $xy$ -orbital energy levels below the Lifshitz point and an interband coupling between the mixed levels above the Lifshitz point, could encourage electron-electron paring below the Lifshitz point, and discourage the pairing above it, and thus be in line with the experimental findings in [4]. We also note that this coupling requires the electrons to coupling to the same phonon.

### 4.2.3 Weak coupling regime

In the weak coupling regime with  $\frac{\lambda}{\omega} \rightarrow 0$  we expect to recover the non-perturbed eigenenergies in the low-temperature regime with  $\langle n \rangle = 0$ . For weak coupling we can expand the exponential functions, that we get after averaging the  $A$ 's, to second order in  $\lambda$  and we get that  $\text{Tr}[\rho A_1] \approx 1 - \frac{\lambda^2}{\omega^2}$ ,  $\text{Tr}[\rho A_2] \approx -\frac{\lambda^2}{\omega^2}$ , while  $\text{Tr}[\rho A_3] = \text{Tr}[\rho A_7] = \text{Tr}[\rho A_8] \rightarrow 0$  this will gives us

$$E_c \rightarrow \epsilon + \frac{\lambda^2}{\omega} \left( \frac{\Delta}{\omega} - 1 \right) \quad , \quad E_d \rightarrow \epsilon + \Delta - \frac{\lambda^2}{\omega} \left( \frac{\Delta}{\omega} + 1 \right) \quad , \quad U \rightarrow U + 2 \frac{\lambda^2}{\omega} \quad , \quad (4.24)$$

where we see that we recover the perturbation result from equation (4.5) and (4.6) in the limit of  $\omega \gg \Delta$ .

## 5 Spin-Orbit coupling

We now introduce spin and spin-orbit coupling to the system. This expands the Hilbert space to 16 dimensions. We now have the Hamiltonian:

$$H = H_e + H_{ph} + H_{SO} + H_{e-e} + H_{e-ph}. \quad (5.1)$$

The angular momentum matrices in the  $\{yz, xz, xy\}$  basis are:

$$L_z = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, \quad L_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}. \quad \begin{cases} |yz\rangle \\ |xz\rangle \\ |xy\rangle \end{cases} \quad (5.2)$$

They are worked out in appendix F. The terms  $H_e + H_{SO}$  in the Hamiltonian with spin is then:

$$H = H_0 \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \Delta_{SO} \sum_{\alpha} L_{\alpha} \otimes \sigma_{\alpha}, \quad \alpha = x, y, z \quad (5.3)$$

which in the basis of  $\{yz \uparrow, yz \downarrow, xz \uparrow, xz \downarrow, xy \uparrow, xy \downarrow\}$  turns out to be

$$H = H_0 + \Delta_{SO} \begin{pmatrix} 0 & i\sigma_z & -i\sigma_y \\ -i\sigma_z & 0 & i\sigma_x \\ i\sigma_y & -i\sigma_x & 0 \end{pmatrix}. \quad (5.4)$$

We see that  $H_{SO}$  is zero on the diagonal and the second quantization Hamiltonian will then have terms like  $c_{yz\uparrow}^{\dagger} c_{xz\downarrow}$ . So with  $i, j \in \{yz \uparrow, yz \downarrow, xz \uparrow, xz \downarrow, xy \uparrow, xy \downarrow\}$ , we have:

$$\mathcal{H}_{SO} = \sum_{ij} c_j^{\dagger} \langle j | H_{SO} | i \rangle c_i, \quad (5.5)$$

$$H_{SO} = \Delta_{SO} \begin{pmatrix} 0 & 0 & i & 0 & 0 & -1 \\ 0 & 0 & 0 & -i & 1 & 0 \\ -i & 0 & 0 & 0 & 0 & i \\ 0 & i & 0 & 0 & i & 0 \\ 0 & 1 & 0 & -i & 0 & 0 \\ -1 & 0 & -i & 0 & 0 & 0 \end{pmatrix} \begin{cases} |yz, \uparrow\rangle \\ |yz, \downarrow\rangle \\ |xz, \uparrow\rangle \\ |xz, \downarrow\rangle \\ |xy, \uparrow\rangle \\ |xy, \downarrow\rangle \end{cases}. \quad (5.6)$$

The goal is now to examine the effect of spin-orbit coupling in the two-level one-site Anderson-Holstein model. We will work the special case were  $d_{\sigma}^{\dagger} |0\rangle = |yz, \sigma\rangle$  and  $c_{\sigma}^{\dagger} |0\rangle = |xy, \sigma\rangle$ . We imagine

that this could be for a quantum dot where  $L_x \ll L_y$  such that the orbital contributions to the quantum dot states resemble those in figure 4, combined with being around the Lifshitz point to allow for energy levels containing different orbitals. We work out  $H_{SO}$  in the basis  $\{|yz, \sigma\rangle, |xy, \sigma\rangle\}$ , and the only non-zero elements in our second quantization Hamiltonian,  $H_{SO}$ , are

$$\langle yz \downarrow | H_{SO} | xy \uparrow \rangle = \Delta_{SO} \quad \& \quad \langle yz \uparrow | H_{SO} | xy \downarrow \rangle = -\Delta_{SO}, \quad (5.7)$$

and their complex conjugates. We now have in second quantization that:

$$H_{SO} = \Delta_{SO}(c_{\uparrow}^{\dagger}d_{\downarrow} - c_{\downarrow}^{\dagger}d_{\uparrow} - d_{\uparrow}^{\dagger}c_{\downarrow} + d_{\downarrow}^{\dagger}c_{\uparrow}). \quad (5.8)$$

In more compact notation we get for the  $t_{2g}$  band the entire spin-orbit coupling Hamiltonian in second quantization as:

$$\begin{aligned} H_{SO} &= i\Delta_{SO}c_{yz,\alpha}^{\dagger}\sigma_{\alpha\beta}^z c_{xz,\beta} + H.c \\ &+ i\Delta_{SO}c_{xz,\alpha}^{\dagger}\sigma_{\alpha\beta}^x c_{xy,\beta} + H.c \\ &+ i\Delta_{SO}c_{xy,\alpha}^{\dagger}\sigma_{\alpha\beta}^y c_{yz,\beta} + H.c. \end{aligned} \quad (5.9)$$

With  $\sigma_{\alpha\beta}^i$  being the matrix element between spin  $\alpha$  and  $\beta$  for the  $i$ -th pauli matrix. We get this from equation (5.3) by multiplying the matrix element in orbital space first and leaving the spin space matrix element. This notation gives (5.8) and is general for the spin-orbit coupling of  $t_{2g}$ -electrons. We know that the Lang-Firsov transform will not affect this Hamiltonian as  $c_{\sigma}$  and  $d_{\sigma}$  acquire the same factor  $e^{\lambda(b^{\dagger}-b)}$  so that  $\tilde{c}_{\sigma}^{\dagger}\tilde{d}_{\sigma} = c_{\sigma}^{\dagger}d_{\sigma}$ . We instead transform it with the transformation used for the interband electron-phonon coupling. This gives:

$$\tilde{c}_{\uparrow}^{\dagger}\tilde{d}_{\downarrow} = \left\{ c_{\uparrow}^{\dagger}\cosh[\lambda(b^{\dagger}-b)] + d_{\uparrow}^{\dagger}\sinh[\lambda(b^{\dagger}-b)] \right\} \left\{ d_{\downarrow}\cosh[\lambda(b^{\dagger}-b)] - c_{\downarrow}\sinh[\lambda(b^{\dagger}-b)] \right\}. \quad (5.10)$$

We multiply this out and rewrite it in terms of the matrices  $A_i$ . By permuting  $c$  and  $d$  and taking the conjugate transpose (or permuting spins) we find all the transformed terms:

$$\begin{aligned} \tilde{c}_{\uparrow}^{\dagger}\tilde{d}_{\downarrow} &= c_{\uparrow}^{\dagger}d_{\downarrow}A_1 + (d_{\uparrow}^{\dagger}d_{\downarrow} - c_{\uparrow}^{\dagger}c_{\downarrow})A_3 - d_{\uparrow}^{\dagger}c_{\downarrow}A_2 \quad , \quad \tilde{d}_{\uparrow}^{\dagger}\tilde{c}_{\downarrow} = d_{\uparrow}^{\dagger}c_{\downarrow}A_1 + (c_{\uparrow}^{\dagger}c_{\downarrow} - d_{\uparrow}^{\dagger}d_{\downarrow})A_3 - c_{\uparrow}^{\dagger}d_{\downarrow}A_2, \\ \tilde{c}_{\downarrow}^{\dagger}\tilde{d}_{\uparrow} &= c_{\downarrow}^{\dagger}d_{\uparrow}A_1 + (d_{\downarrow}^{\dagger}d_{\uparrow} - c_{\downarrow}^{\dagger}c_{\uparrow})A_3 - d_{\downarrow}^{\dagger}c_{\uparrow}A_2 \quad , \quad \tilde{d}_{\downarrow}^{\dagger}\tilde{c}_{\uparrow} = d_{\downarrow}^{\dagger}c_{\uparrow}A_1 + (c_{\downarrow}^{\dagger}c_{\uparrow} - d_{\downarrow}^{\dagger}d_{\uparrow})A_3 - c_{\downarrow}^{\dagger}d_{\uparrow}A_2, \end{aligned} \quad (5.11)$$

which gives the full  $\tilde{H}_{SO}$  and we get:

$$\begin{aligned} \tilde{H}_{SO} &= \Delta_{SO}(\tilde{c}_{\uparrow}^{\dagger}\tilde{d}_{\downarrow} - \tilde{d}_{\uparrow}^{\dagger}\tilde{c}_{\downarrow} - \tilde{c}_{\downarrow}^{\dagger}\tilde{d}_{\uparrow} + \tilde{d}_{\downarrow}^{\dagger}\tilde{c}_{\uparrow}) \\ &= \Delta_{SO}(c_{\uparrow}^{\dagger}d_{\downarrow}A_1 + d_{\uparrow}^{\dagger}d_{\downarrow}A_3 - c_{\uparrow}^{\dagger}c_{\downarrow}A_3 - d_{\uparrow}^{\dagger}c_{\downarrow}A_2 - d_{\uparrow}^{\dagger}c_{\downarrow}A_1 - c_{\uparrow}^{\dagger}c_{\downarrow}A_3 + d_{\uparrow}^{\dagger}d_{\downarrow}A_3 + c_{\uparrow}^{\dagger}d_{\downarrow}A_2 \\ &\quad - c_{\downarrow}^{\dagger}d_{\uparrow}A_1 - d_{\downarrow}^{\dagger}d_{\uparrow}A_3 + c_{\downarrow}^{\dagger}c_{\uparrow}A_3 + d_{\downarrow}^{\dagger}c_{\uparrow}A_2 + d_{\downarrow}^{\dagger}c_{\uparrow}A_1 + c_{\downarrow}^{\dagger}c_{\uparrow}A_3 - d_{\downarrow}^{\dagger}d_{\uparrow}A_3 - c_{\downarrow}^{\dagger}d_{\uparrow}A_2). \end{aligned} \quad (5.12)$$

We are now left with:

$$\tilde{H}_{SO} = \Delta_{SO}\{(A_1 + A_2)(c_{\uparrow}^{\dagger}d_{\downarrow} - d_{\uparrow}^{\dagger}c_{\downarrow} - c_{\downarrow}^{\dagger}d_{\uparrow} + d_{\downarrow}^{\dagger}c_{\uparrow}) + 2A_3(c_{\downarrow}^{\dagger}c_{\uparrow} + d_{\uparrow}^{\dagger}d_{\downarrow} - d_{\downarrow}^{\dagger}d_{\uparrow} - c_{\uparrow}^{\dagger}c_{\downarrow})\} \quad (5.13)$$

From earlier we know that in the strong coupling limit,  $\langle A_1 \rangle = -\langle A_2 \rangle = \frac{1}{2}$  and that  $\langle A_3 \rangle = 0$  which will give that  $\langle \tilde{H}_{SO} \rangle = 0$  for  $T \rightarrow 0$ .

If we instead chose that  $d_\sigma^\dagger$  represents the  $xz, \sigma$  state, we arrive at:

$$H_{SO}^{xz,xy} = i\Delta_{SO}(d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow - c_\uparrow^\dagger d_\downarrow - c_\downarrow^\dagger d_\uparrow), \quad (5.14)$$

which under the unitary transformed used earlier transforms like:

$$\bar{H}_{SO}^{xz,xy} = H_{SO}^{xz,xy}(A_1 + A_2), \quad (5.15)$$

which when averaged over the phonons is zero, at  $T \rightarrow 0$  and goes back to  $H_{SO}^{xz,xy}$  at  $T \rightarrow \infty$ . We see from this result that when working with interband and intraband electron-phonon coupling the spin-orbit coupling of the electrons will not affect the  $U$  in the Anderson-Holstein model and change the result from sections 3 and 4.

## 5.1 Spin-orbit effects on electron-phonon coupling

We could imagine that the spin-orbit coupling could affect the electron-phonon coupling term in the Hamiltonian and only allow certain interband scattering terms depending in the symmetry of the phonon. Here we work with an electron-phonon coupling term only allowing scattering between levels with different spins:

$$H_{e-ph} = \lambda(b^\dagger + b)(d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow + c_\uparrow^\dagger d_\downarrow + c_\downarrow^\dagger d_\uparrow). \quad (5.16)$$

This leads us to use a non-spin conserving unitary transformation,  $U = e^{iS}$  with the anti-hermitian operator  $iS$ :

$$iS = \frac{\lambda}{\omega} (b^\dagger - b) \left( d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow + c_\uparrow^\dagger d_\downarrow + c_\downarrow^\dagger d_\uparrow \right). \quad (5.17)$$

For ease of notation in this section we'll use  $S = \frac{\lambda}{\omega} (b^\dagger - b) \hat{E}$ , with the electronic part  $\hat{E} = d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow + c_\uparrow^\dagger d_\downarrow + c_\downarrow^\dagger d_\uparrow$ . Then we can find the transformed operators in the same was as we have done before, only now with spins:

$$UbU^\dagger = e^S b e^{-S} = b + \frac{\lambda}{\omega} \hat{E} [(b^\dagger - b), b] + \dots = b - \frac{\lambda}{\omega} \hat{E}, \quad (5.18)$$

and for the fermionic operators with spin:

$$Uc_\sigma U^\dagger = e^S c_\sigma e^{-S} = \sum_{n=0} \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right]^n \frac{[\hat{E}, c_\sigma]_n}{n!}. \quad (5.19)$$

To evaluate this we use that

$$\begin{aligned} [AB, C] &= ABC - CAB = ABC + ACB - ACB - CAB \\ &= A\{B, C\} - \{A, C\}B. \end{aligned} \quad (5.20)$$

We then have

$$[\hat{E}, c_\sigma] = [d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow + c_\uparrow^\dagger d_\downarrow + c_\downarrow^\dagger d_\uparrow, c_\sigma] = -d_\sigma, \quad (5.21)$$

where we used that  $[d_\sigma^\dagger c_{\sigma'}, c_{\sigma''}] = 0$ , and that  $[c_\sigma^\dagger d_{-\sigma}, c_{\sigma'}] = -\{c_\sigma^\dagger, c_{\sigma'}\} d_{-\sigma} = \delta_{\sigma, \sigma'} d_{-\sigma}$ . Then we evaluate the next term in the sum

$$[\hat{E}, c_\sigma]_2 = [\hat{E}, -d_{-\sigma}] = -[d_\uparrow^\dagger c_\downarrow + d_\downarrow^\dagger c_\uparrow, d_{-\sigma}] = -(-c_\sigma). \quad (5.22)$$

We can now evaluate the entire transformed operator, as all even terms of the commutator evaluates to  $c_\sigma$  and the uneven terms to  $-d_{-\sigma}$ :

$$\begin{aligned} U c_\sigma U^\dagger &= c_\sigma \sum_{n=0} \frac{\left[\frac{\lambda}{\omega} (b^\dagger - b)\right]^{2n}}{(2n)!} - d_{-\sigma} \sum_{n=0} \frac{\left[\frac{\lambda}{\omega} (b^\dagger - b)\right]^{2n+1}}{(2n+1)!} \\ &= c_\sigma \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] - d_{-\sigma} \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right]. \end{aligned} \quad (5.23)$$

From this we have all the transformed operators and it is then only a matter of transforming the Hamiltonian following the same approach as used before. We get that:

$$\tilde{d}_\sigma^\dagger \tilde{c}_{\sigma'} = d_\sigma^\dagger c_{\sigma'} A_1 + (c_{-\sigma}^\dagger c_{\sigma'} - d_\sigma^\dagger d_{-\sigma'}) A_3 - c_{-\sigma}^\dagger d_{-\sigma'} A_2, \quad (5.24)$$

and with this we have that  $U \hat{E} U^\dagger = \hat{E}$ . We can now transform the electron-phonon coupling term and the phonon term in the Hamiltonian:

$$\tilde{H}_{e-ph} = \lambda \left[ (b^\dagger + b) - 2 \frac{\lambda}{\omega} \hat{E} \right] \hat{E} = \lambda (b^\dagger + b) \hat{E} - 2 \frac{\lambda^2}{\omega} \hat{E}^2, \quad (5.25)$$

$$\tilde{H}_{ph} = \omega b^\dagger b - \lambda (b^\dagger + b) \hat{E} + \frac{\lambda^2}{\omega} \hat{E}^2, \quad (5.26)$$

giving us that the coupling term cancels out again. To understand the effect of the contribution  $-\frac{\lambda^2}{\omega} \hat{E}^2$  we look at the term  $\hat{E}^2$  which will give some terms proportional to  $n_\sigma^c$  and  $n_\sigma^d$ , some terms proportional to  $n_\sigma^c n_{-\sigma}^d$  and then some orbital mixing terms:

$$\begin{aligned} \hat{E}^2 &= d_\uparrow^\dagger c_\downarrow d_\downarrow^\dagger c_\uparrow + d_\uparrow^\dagger c_\downarrow c_\uparrow^\dagger d_\downarrow + d_\uparrow^\dagger c_\downarrow c_\downarrow^\dagger d_\uparrow + d_\uparrow^\dagger c_\uparrow d_\uparrow^\dagger c_\downarrow + d_\uparrow^\dagger c_\uparrow c_\uparrow^\dagger d_\downarrow + d_\downarrow^\dagger c_\uparrow d_\downarrow^\dagger c_\uparrow \\ &\quad + c_\uparrow^\dagger d_\downarrow d_\uparrow^\dagger c_\downarrow + c_\uparrow^\dagger d_\downarrow d_\downarrow^\dagger c_\uparrow + c_\uparrow^\dagger d_\downarrow c_\downarrow^\dagger d_\uparrow + c_\downarrow^\dagger d_\uparrow d_\uparrow^\dagger c_\downarrow + c_\downarrow^\dagger d_\uparrow d_\downarrow^\dagger c_\uparrow + c_\downarrow^\dagger d_\uparrow c_\uparrow^\dagger d_\downarrow \\ &= \sum_{\sigma, \gamma} n_\sigma^\gamma - 2 \sum_{\sigma} n_\sigma^c n_{-\sigma}^d + 2 d_\downarrow^\dagger d_\uparrow^\dagger c_\uparrow c_\downarrow + 2 c_\downarrow^\dagger c_\uparrow^\dagger d_\uparrow d_\downarrow + 2 \sum_{\sigma} c_\sigma^\dagger d_\sigma^\dagger c_{-\sigma} d_{-\sigma}, \end{aligned} \quad (5.27)$$

with  $\gamma$  representing the quantum dot levels  $c$  and  $d$ . We see that the term contributing to the on-site potential proportional to  $n_\sigma^c n_{-\sigma}^d$  is negative and will give then a positive contribution to the interaction term from the transformation of the phonon and electron-phonon term in the Hamiltonian, and we see that this potential electron-phonon coupling will also contribute towards a repulsive potential just like we had it for the interband case. An electron-phonon term like this could work to break up local pairs. With the spin-orbit coupling allowing interband electron-phonon interaction terms, only when a mixing of orbitals is available, it would then only contribute to breaking up electron pairs around and above the Lifshitz point.

## 6 Generalization of electron-phonon couplings to $N$ quantum dot levels

With these previous sections in mind we have an understanding of the contribution that electron-phonon coupling can give to the potential between two electrons on the same site in a two-level Anderson-Holstein model. Now we can briefly discuss the more general effect of electron-phonon

coupling for an  $N$ -level quantum dot with interband and intraband electron-phonon coupling. We use a general electronic contribution :

$$\hat{E} = \sum_{ij} \alpha_{ij} c_i^\dagger c_j, \quad (6.1)$$

with an electron phonon coupling on the form

$$H_{e-ph} = \lambda (b^\dagger + b) \hat{E}, \quad (6.2)$$

so that we can use a unitary transformation on the form  $e^{iS}$ , with  $iS = \frac{\lambda}{\omega} (b^\dagger - b) \hat{E}$ , as we see from the Baker-Hausdorf-Campbell formula (3.10) that  $\hat{E}$  will transform to itself, while  $b^\dagger + b$  transforms to  $b^\dagger + b - 2\frac{\lambda}{\omega} \hat{E}$ . We will then always end up with  $H_{ph} + H_{e-ph}$  transforming to  $\omega b^\dagger b - \frac{\lambda^2}{\omega} \hat{E}^2$ . We then examine the effect of the  $\hat{E}^2$  on the  $U$  in the Anderson-Holstein model and we have:

$$\hat{E}^2 = \sum_{ijkl} \alpha_{ij} \alpha_{kl} c_i^\dagger c_j c_k^\dagger c_l. \quad (6.3)$$

Terms with  $i = j = k = l$  will contribute to lowering the energy of the polaron on the quantum dot. Terms with  $i = j$  and  $k = l$  but  $i \neq k$ , which corresponds to intraband coupling, will recover the result from section 3, where  $U_{ij} \rightarrow U_{ij} - 2\frac{\lambda^2}{\omega} \alpha_{ii} \alpha_{jj}$ . We also get two interband terms with  $i = l$  and  $j = k$  but  $i \neq j$  which will give contributions like  $\alpha_{ij} \alpha_{ji} c_i^\dagger c_j c_j^\dagger c_i = \alpha_{ij} \alpha_{ji} n_i (1 - n_j)$  which will give that  $U_{ij} \rightarrow U_{ij} + 2\frac{\lambda^2}{\omega} \alpha_{ij} \alpha_{ji}$ , which recovers the result of section 4 and section 5 which works against local electron pairing. If we could have an interband type electron phonon coupling where the sign of  $\alpha_{ij}$  is opposite of the sign of  $\alpha_{ji}$  it would result in a negative contribution of  $U$ , but we do not know if a phonon that couples to the electrons in LAO/STO like that exists.

## 7 Conclusion and discussion

The effects of electron-phonon coupling on the electron pairing in a quantum dot in LAO/STO has been investigated. First we used the band structure of the LAO/STO interface to examine the orbital structure of the energy levels in the quantum dot, and orbital mixing was found to occur after the Lifshitz transition. The effects of electron phonon coupling were studied using a two level Anderson-Holstein model of a quantum dot, and both interband and intraband electron-phonon coupling was examined. In the intraband case a unitary Lang-Firsov transformation was used, and it was found that the eigenstates are polaronic states with a lowered energy. It is also found that the local pairing potential  $U$  becomes negative for strong electron-coupling strength giving rise to local electron pairing. In the interband case the approach of [13] was followed. A new unitary transformation was used, and it was found that the interband electron phonon coupling resulted in a positive addition to the  $U$  in the Anderson-Holstein model. After averaging over the phonons in the system, degenerate polaron states were found with lowered energies. A two-electron state was not affected by the interband electron-phonon coupling. In the end, a possible electron-phonon pairing coming from spin-orbit coupling was examined and had the same result as the interband electron-phonon coupling.

For the results in this thesis to align with the experimental results from [4], we could expect that if polaronic effects are the explanation for local electron pairing in an LAO/STO quantum dot, then the energy levels below the Lifshitz point would have dominant intraband electron-phonon coupling. Thus, resulting in electron pairs, whereas above the Lifshitz point interband coupling would be dominant. This could be due to the spin-orbit coupling affecting the electron-phonon

coupling term. To further examine if intra and interband coupling is the reason for electron pairing an investigation of the possibility of interband coupling would be needed. Then also the strength of the possible intraband and interband coupling below and above the Lifshitz point would have to be found. Studying the electron-phonon coupling between  $xz/yz$  states could be interesting due to their mixing and high density of states above the Lifshitz point. The possibility of electron-phonon coupling affected by spin-orbit coupling in LAO/STO could be studied, as phonons with different symmetries might interact differently with electrons in different orbitals, that also have different symmetries. The effect of the electron phonon couplings on a physical observable would be a way to extract quantitative results and it would avoid possible problems of changing the basis since the expectation value is independent on the basis.

## References

- [1] P. W. Anderson. “Model for the Electronic Structure of Amorphous Semiconductors”. In: *Phys. Rev. Lett.* 34 (15 Apr. 1975), pp. 953–955. DOI: 10.1103/PhysRevLett.34.953. URL: <https://link.aps.org/doi/10.1103/PhysRevLett.34.953>.
- [2] C. Cancellieri et al. “Polaronic metal state at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface”. In: *Nature Communications* 7.1 (Jan. 2016). ISSN: 2041-1723. DOI: 10.1038/ncomms10386. URL: <http://dx.doi.org/10.1038/ncomms10386>.
- [3] Guanglei Cheng et al. “Electron pairing without superconductivity”. In: *Nature* 521.7551 (2015), pp. 196–199. DOI: 10.1038/nature14398.
- [4] Guanglei Cheng et al. “Tunable Electron-Electron Interactions in LaAlO<sub>3</sub>/SrTiO<sub>3</sub> Nanostructures”. In: *Physical Review X* 6.4 (Dec. 2016). ISSN: 2160-3308. DOI: 10.1103/physrevx.6.041042. URL: <http://dx.doi.org/10.1103/PhysRevX.6.041042>.
- [5] Andreas Fuhrer and Carina Fasth. URL: [http://www.ftf.lth.se/fileadmin/ftf/Course\\_pages/FFF042/cb\\_lecture07.pdf](http://www.ftf.lth.se/fileadmin/ftf/Course_pages/FFF042/cb_lecture07.pdf).
- [6] David Jeffrey Griffiths and Darrell F. Schroeter. In: *Introduction to quantum mechanics*. Cambridge University Press, 2019.
- [7] R. Hanson et al. “Spins in few-electron quantum dots”. In: *Reviews of Modern Physics* 79.4 (Oct. 2007), pp. 1217–1265. ISSN: 1539-0756. DOI: 10.1103/revmodphys.79.1217. URL: <http://dx.doi.org/10.1103/RevModPhys.79.1217>.
- [8] Arjun Joshua et al. “A universal critical density underlying the physics of electrons at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface”. In: *Nature communications* 3 (Oct. 2012), p. 1129. DOI: 10.1038/ncomms2116.
- [9] C. S. Koonce et al. “Superconducting Transition Temperatures of Semiconducting SrTiO<sub>3</sub>”. In: *Phys. Rev.* 163 (2 Nov. 1967), pp. 380–390. DOI: 10.1103/PhysRev.163.380. URL: <https://link.aps.org/doi/10.1103/PhysRev.163.380>.
- [10] Guenevere E. D. K. Prawiroatmodjo et al. “Transport and excitations in a negative-U quantum dot at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface”. In: *Nature Communications* 8.1 (2017). DOI: 10.1038/s41467-017-00495-7.
- [11] N. Reyren et al. “Superconducting Interfaces Between Insulating Oxides”. In: *Science* 317.5842 (Aug. 2007), p. 1196. DOI: 10.1126/science.1146006.
- [12] Jai Singh and Koichi Shimakawa. “Chapter 6.3”. In: *Advances in amorphous semiconductors*. Taylor amp; Francis, 2003.

- [13] P. Tarasewicz. “The Intra- and Interband Phonon-Electron Potentials in a Two-Band Model of Interacting Lattice Fermions”. In: *Journal of Superconductivity and Novel Magnetism* 28.8 (2015), pp. 2307–2320. DOI: 10.1007/s10948-015-3039-0.

# A Unitary transformation of the interband Hamiltonian

To transform the Hamiltonian the number operators are no longer the same as with the Lang-Firsov, so lets start by transforming the Hamiltonian one term at a time:

$$\bar{H} = \epsilon \bar{c}^\dagger \bar{c} + (\epsilon + \Delta) \bar{d}^\dagger \bar{d} + U \bar{c}^\dagger \bar{c} \bar{d}^\dagger \bar{d} + \omega \bar{b}^\dagger \bar{b} + \lambda (\bar{b}^\dagger + \bar{b}) (\bar{d}^\dagger \bar{c} + \bar{c}^\dagger \bar{d}). \quad (\text{A.1})$$

Starting with the number operators:

$$\begin{aligned} \bar{c}^\dagger \bar{c} &= (\cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger + \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger) (\cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c - \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d) \\ &= \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_c - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_d + \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (d^\dagger c - c^\dagger d). \end{aligned} \quad (\text{A.2})$$

Likewise we get:

$$\bar{d}^\dagger \bar{d} = \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_d - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_c + \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (c^\dagger d - d^\dagger c). \quad (\text{A.3})$$

Now on to the electrostatic interaction term with  $U n_c n_d$ . Here we use that  $n_c (c^\dagger d + d^\dagger c) = c^\dagger d$  as  $n_c c = c^\dagger c c = 0$  and also  $n_d (c^\dagger d + d^\dagger c) = d^\dagger c$ . Also we use that

$$\begin{aligned} (d^\dagger c - c^\dagger d)(c^\dagger d - d^\dagger c) &= d^\dagger d c c^\dagger + d d^\dagger c^\dagger c \\ &= d^\dagger d (1 - c^\dagger c) + (1 - d^\dagger d) c^\dagger c \\ &= n_c + n_d - 2 n_c n_d \\ &= (n_c - n_d)^2. \end{aligned}$$

$$\begin{aligned}
\bar{n}_c \bar{n}_d &= \bar{c}^\dagger \bar{c} \bar{d}^\dagger \bar{d} \\
&= \left\{ \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_c - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_d + \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (d^\dagger c - c^\dagger d) \right\} \\
&\times \left\{ \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_d - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] n_c + \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (c^\dagger d - d^\dagger c) \right\} \\
&= \left\{ \cosh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] + \sinh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} n_c n_d \\
&- \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] [n_c + n_d - (d^\dagger c - c^\dagger d)(c^\dagger d - d^\dagger c)] \\
&- \cosh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] [n_c (c^\dagger d - d^\dagger c) + (d^\dagger c - c^\dagger d) n_d] \\
&- \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] [n_d (c^\dagger d - d^\dagger c) + (d^\dagger c - c^\dagger d) n_c] \\
&= \left( \cosh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] + \sinh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right) n_c n_d \\
&- \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (n_c + n_d - n_c - n_d + 2n_c n_d) \\
&- \cosh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (c^\dagger d + c^\dagger d) - \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (d^\dagger c + d^\dagger c) \\
&= \left\{ \cosh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] + \sinh^4 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] - 2\cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} n_c n_d \\
&- 2\cosh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger d - 2\cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh^3 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger c.
\end{aligned} \tag{A.4}$$

We have for the bosonic operators that:

$$\begin{aligned}
\bar{b}^\dagger \bar{b} &= \left[ b^\dagger - \frac{\lambda}{\omega} (c^\dagger d + d^\dagger c) \right] \left[ b - \frac{\lambda}{\omega} (c^\dagger d + d^\dagger c) \right] \\
&= b^\dagger b + \left[ \frac{\lambda}{\omega} (c^\dagger d + d^\dagger c) \right]^2 - \frac{\lambda}{\omega} (b^\dagger + b) (c^\dagger d + d^\dagger c) \\
&= b^\dagger b + \frac{\lambda^2}{\omega^2} (n_c + n_d - 2n_c n_d) - \frac{\lambda}{\omega} (b^\dagger + b) (c^\dagger d + d^\dagger c).
\end{aligned} \tag{A.5}$$

Now we find:

$$\begin{aligned}
\bar{c}^\dagger \bar{d} &= \left( \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger + \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger \right) \left( \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d - \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c \right) \\
&= \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger d - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger c - \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (n_c - n_d),
\end{aligned} \tag{A.6}$$

$$\begin{aligned}
\bar{d}^\dagger \bar{c} &= \left( \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger + \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger \right) \left( \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c - \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d \right) \\
&= \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] d^\dagger c - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] c^\dagger d + \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] (n_c - n_d),
\end{aligned} \tag{A.7}$$

which gives us:

$$\bar{c}^\dagger \bar{d} + \bar{d}^\dagger \bar{c} = \left\{ \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] - \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} (c^\dagger d + d^\dagger c). \tag{A.8}$$

Now we have with  $(c^\dagger d + d^\dagger c)^2 = n_c + n_d - 2n_c n_d$ , that:

$$\begin{aligned}
(\bar{b}^\dagger + \bar{b})(\bar{c}^\dagger \bar{d} + \bar{d}^\dagger \bar{c}) &= \left[ b^\dagger + b - 2\frac{\lambda}{\omega} (c^\dagger d + d^\dagger c) \left\{ \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} \right] (c^\dagger d + d^\dagger c) \\
&= \left[ (b^\dagger + b)(c^\dagger d + d^\dagger c) - 2\frac{\lambda}{\omega} (n_c + n_d - 2n_c n_d) \right] \left\{ \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] - \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \right\} \\
&= (b^\dagger + b) (c^\dagger d + d^\dagger c) - 2\frac{\lambda}{\omega} (n_c + n_d - 2n_c n_d).
\end{aligned} \tag{A.9}$$

This gives us that the coupling term in the Hamiltonian cancels out:

$$\begin{aligned}
\omega \bar{b}^\dagger \bar{b} + \lambda (\bar{b}^\dagger + \bar{b})(\bar{d}^\dagger \bar{c} + \bar{c}^\dagger \bar{d}) &= \omega b^\dagger b + \frac{\lambda^2}{\omega} (n_c + n_d - 2n_c n_d) - \lambda (b^\dagger + b)(c^\dagger d + d^\dagger c) \\
&\quad + \lambda (b^\dagger + b)(c^\dagger d + d^\dagger c) - 2\frac{\lambda^2}{\omega} (n_c + n_d - 2n_c n_d) \\
&= \omega b^\dagger b - \frac{\lambda^2}{\omega} (n_c + n_d - 2n_c n_d).
\end{aligned} \tag{A.10}$$

We have now removed the coupling term in the Hamiltonian. We simplify notation and use:

$$A_1 = \cosh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right], \quad A_2 = \sinh^2 \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right], \quad A_3 = \cosh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right] \sinh \left[ \frac{\lambda}{\omega} (b^\dagger - b) \right]. \tag{A.11}$$

Then it follows that  $A_4 = A_1^2$ ,  $A_5 = A_2^2$ ,  $A_6 = A_3^2$ ,  $A_7 = A_1 A_3$  and  $A_8 = A_3 A_2$ . This gives that:

$$\begin{aligned}
\bar{H} &= \epsilon [A_1 n_c - A_2 n_d + A_3 (d^\dagger c - c^\dagger d)] + (\epsilon + \Delta) [A_1 n_d - A_2 n_c - A_3 (d^\dagger c - c^\dagger d)] \\
&\quad + U [(A_4 + A_5 - 2A_6) n_c n_d - 2A_7 c^\dagger d - 2A_8 d^\dagger c] + \omega b^\dagger b - \frac{\lambda^2}{\omega} (n_c + n_d - 2n_c n_d) \\
&= \left( \epsilon (A_1 - A_2) - \Delta A_2 - \frac{\lambda^2}{\omega} \right) n_c + \left( \epsilon (A_1 - A_2) + \Delta A_1 - \frac{\lambda^2}{\omega} \right) n_d \\
&\quad + \left( U (A_1 - A_2)^2 + 2\frac{\lambda^2}{\omega} \right) n_c n_d - (\Delta A_3 + 2U A_8) d^\dagger c + (\Delta A_3 - 2U A_7) c^\dagger d + \omega b^\dagger b.
\end{aligned} \tag{A.12}$$

Then using that  $A_4 + A_5 - 2A_6 = (A_1 - A_2)^2$ , and that  $A_1 - A_2 = 1$ , we arrive at:

$$\bar{H} = \bar{E}_c n_c + \bar{E}_d n_d + \bar{U} n_c n_d + V_1 d^\dagger c + V_2 c^\dagger d + \omega b^\dagger b, \quad (\text{A.13})$$

with the transformed energies:

$$\bar{E}_c = \epsilon - \Delta A_2 - \frac{\lambda^2}{\omega}$$

$$\bar{E}_d = \epsilon + \Delta A_1 - \frac{\lambda^2}{\omega}$$

$$\bar{U} = U + 2\frac{\lambda^2}{\omega}$$

$$V_1 = -\Delta A_3 - 2UA_8$$

$$V_2 = \Delta A_3 - 2UA_7.$$

## B Evaluating $\left\langle e^{\pm\alpha(b^\dagger - b)} \right\rangle$

In this appendix we will show that

$$\left\langle e^{\pm\alpha(b^\dagger - b)} \right\rangle = e^{-\frac{1}{2}\alpha^2 \coth\left(\frac{\beta\omega}{2}\right)}. \quad (\text{B.1})$$

This is done by working out the trace  $\text{Tr} \left[ \rho e^{\pm\alpha(b^\dagger - b)} \right]$ . We will be using boson annihilation and creation operators  $b|n\rangle = \sqrt{n}|n-1\rangle$  and  $b^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$  with  $[b, b^\dagger] = 1$ . First, we use the Baker-Hausdorff-Campbell formula where  $e^X e^Y = e^Z$ , with

$$Z = X + \frac{1}{2}[Y, X] + \frac{1}{12}[X, [X, Y]] - \frac{1}{12}[Y, [X, Y]] + \dots \quad (\text{B.2})$$

As the boson annihilation and creation operators commute to a constant we have that:

$$e^{\alpha b^\dagger} e^{-\alpha b} e^{-\frac{1}{2}\alpha^2} = e^{\alpha(b^\dagger - b)}. \quad (\text{B.3})$$

We now calculate:

$$\begin{aligned} \langle n | e^{\alpha(b^\dagger - b)} | n \rangle &= e^{-\frac{1}{2}\alpha^2} \langle n | e^{\alpha b^\dagger} e^{-\alpha b} | n \rangle \\ &= e^{-\frac{1}{2}} \sum_{m, m'} \frac{\alpha^m}{m!} \frac{(-\alpha)^{m'}}{(m')!} \sqrt{n} \sqrt{n-1} \dots \sqrt{n-(m+1)} \sqrt{n} \dots \sqrt{n-(m'+1)} \langle n-m | n-m' \rangle. \end{aligned} \quad (\text{B.4})$$

The square roots come from applying the annihilation and creation operators to the bra and ket. We will use that  $\langle n-m | n-m' \rangle = \delta_{m, m'}$ , and that  $\sqrt{n} \sqrt{n-1} \dots \sqrt{n-(m+1)} = \frac{\sqrt{n!}}{\sqrt{(n-m)!}}$  giving:

$$\langle n | e^{\alpha(b^\dagger - b)} | n \rangle = e^{-\frac{1}{2}} \sum_m \frac{(-\alpha^2)^m}{(m!)^2} \frac{n!}{(n-m)!}. \quad (\text{B.5})$$

Upon using that  $\frac{n!}{m!(n-m)!} = \binom{n}{m}$ , we arrive at:

$$\langle n | e^{\alpha(b^\dagger - b)} | n \rangle = e^{-\frac{\alpha^2}{2}} \sum_m \frac{(-\alpha^2)^m}{m!} \binom{n}{m}. \quad (\text{B.6})$$

We then have that

$$\begin{aligned}
\frac{d^2}{dx^2}x^2 &= \frac{d}{dx}n x^{n-1} = n(n-1)x^{n-2} \\
\Rightarrow \frac{d^m}{dx^m}x^n &\stackrel{(m \leq n)}{=} n(n-1)\dots(n-(m+1))x^{n-m} = m! \binom{n}{m} x^{n-m} \\
\Rightarrow \binom{n}{m} x^n &= \frac{x^m}{m!} \frac{d^m}{dx^m}(x^n).
\end{aligned} \tag{B.7}$$

Now using  $\rho_{ph} = e^{-\beta\omega(\hat{n}-\frac{1}{2})}$ , we get with B.6 and B.7 that

$$\begin{aligned}
\text{Tr} \left[ \rho_{ph} e^{\alpha(b^\dagger-b)} \right] &= e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_{n,m} (e^{-\beta\omega})^n \sum_m \frac{(-\alpha^2)^m}{m!} \binom{n}{m} \\
&= e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_{m \leq n} \frac{(-\alpha^2)^m}{(m!)^2} x^n \binom{n}{m} \\
&= e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_{n,m} \frac{(-\alpha^2)^m x^m}{(m!)^2} \frac{d^m}{dx^m}(x^n),
\end{aligned} \tag{B.8}$$

where we defined  $x = e^{-\beta\omega}$ . In the second line the sum is only for  $m \leq n$  because of the derivation of B.7, but since  $\frac{d^m}{dx^m}(x^n) = 0$  for  $m > n$  anyways we can sum over  $m$  going to infinity. We will now use that  $0 < x < 1$  so that we can perform the sum over  $n$ ,  $\sum_n x^n = \frac{1}{1-x}$ , and we get:

$$\begin{aligned}
\text{Tr} \left[ \rho_{ph} e^{\alpha(b^\dagger-b)} \right] &= e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_m \frac{(-\alpha^2)^m x^m}{(m!)^2} \frac{d^m}{dx^m} \left( \sum_n x^n \right) \\
&= e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_m \frac{(-\alpha^2)^m x^m}{(m!)^2} \frac{d^m}{dx^m} \left( \frac{1}{1-x} \right).
\end{aligned} \tag{B.9}$$

We now evaluate the differentiation:

$$\begin{aligned}
\frac{d^m}{dx^m} \left( \frac{1}{1-x} \right) &= \frac{d^{m-1}}{dx^{m-1}} 1(1-x)^{-2} = \frac{d^{m-2}}{dx^{m-2}} 1 \cdot 2(1-x)^{-3} = \frac{d^{m-k}}{dx^{m-k}} k!(1-x)^{-1-k} \dots \\
&= m!(1-x)^{-1-m},
\end{aligned} \tag{B.10}$$

and using this we get that:

$$\text{Tr} \left[ \rho_{ph} e^{\alpha(b^\dagger-b)} \right] = e^{-\frac{\alpha^2}{2}} e^{-\frac{\beta\omega}{2}} \sum_m \frac{(-\alpha^2)^m x^m}{(m!)^2} m!(1-x)^{-1-m}. \tag{B.11}$$

We then use that:

$$\begin{aligned}
Z = \text{Tr}[\rho_{ph}] &= e^{-\frac{\beta\omega}{2}} \sum_n (e^{-\beta\omega})^n \\
&= \frac{e^{-\frac{\beta\omega}{2}}}{1 - e^{-\beta\omega}} \\
&= \frac{e^{-\frac{\beta\omega}{2}}}{1 - x},
\end{aligned} \tag{B.12}$$

so that we get:

$$\begin{aligned}
\text{Tr} \left[ \rho_{\text{ph}} e^{\alpha(b^\dagger - b)} \right] &= e^{-\frac{\alpha^2}{2}} \frac{e^{-\frac{\beta\omega}{2}}}{1-x} \sum_m \frac{(-\alpha^2)^m x^m}{m!} (1-x)^{-m} \\
&= Z e^{-\frac{\alpha^2}{2}} \sum_m \frac{1}{m!} \left( \frac{-\alpha^2 x}{(1-x)} \right) \\
&= Z e^{-\frac{\alpha^2}{2}} e^{-\alpha^2 \frac{e^{-\beta\omega}}{1-e^{-\beta\omega}}} \\
&= Z \exp \left\{ -\frac{\alpha^2}{2} \left( 1 - 2 \frac{e^{-\beta\omega}}{1-e^{-\beta\omega}} \right) \right\} \\
&= Z \exp \left\{ -\frac{\alpha^2}{2} \frac{1+e^{-\beta\omega}}{1-e^{-\beta\omega}} \right\} \\
&= Z e^{-\frac{\alpha^2}{2} \coth\left(\frac{\beta\omega}{2}\right)}.
\end{aligned} \tag{B.13}$$

We now have that:

$$\left\langle e^{\alpha(b^\dagger - b)} \right\rangle = e^{-\frac{\alpha^2}{2} \coth\left(\frac{\beta\omega}{2}\right)} \tag{B.14}$$

## C Anderson-Holstein model

P. W. Anderson proposed a model for amorphous diamagnetic semi-conductors, preferring paired electrons. Anderson assumed a potential between a pair of localized electrons of opposite spin on a covalent bond. The potential,  $V$ , included the electrons interacting with lattice vibrations in addition to the repulsive Coulomb potential,  $U$ , between the electrons:

$$V = \sum_i \left[ \frac{1}{2} c x_i^2 - \lambda x_i (n_{i\uparrow} + n_{i\downarrow}) \right], \tag{C.1}$$

where  $x_i$  is the vibrating bond length between a pair of atoms with a covalent bond.  $c$  is a bond force constant and  $\lambda$  an electron-phonon coupling constant. The electron number operator is  $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$  for spin  $\sigma$  at bond site  $i$ . The Hamiltonian considered by Anderson is then:

$$H^{\text{tot}} = \sum_{i\sigma} E_i n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{ij\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i \frac{1}{2} M \dot{x}_i^2 + V, \tag{C.2}$$

where  $E_i$  is the energy of an electron localized at site  $i$ ,  $U$  the repulsive electrostatic potential of two electrons localized at the same site and  $T_{ij}$  the electron hopping energy from site  $i$  to site  $j$ .  $M$  being the mass of the vibrating pair of atoms on the covalent bond and  $\dot{x}_i$  being the linear velocity of vibrating atoms. This is simply the kinetic energy of the vibrating atoms on the bond. Then by minimizing the potential energy of the bond:  $\frac{\partial V}{\partial x_i} = 0$  we can eliminate  $x_i$  and get a minimum potential energy, with our new equilibrium  $x_0 = \frac{\lambda}{c} (n_{\uparrow} + n_{\downarrow})$  which upon substitution back into  $V$  gives:

$$V^{\text{min}} = -\frac{\lambda}{2c} \sum_i (n_{i\uparrow} + n_{i\downarrow}). \tag{C.3}$$

Now substituting  $V^{\text{min}}$  into the Hamiltonian we get:

$$H^{min} = \sum_{i\sigma} \left( E_i - \frac{\lambda}{2c} \right) n_{i\sigma} + \left( U - \frac{\lambda}{c} \right) \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{ij\sigma} T'_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i \frac{1}{2} M \dot{x}_i^2 + V. \quad (C.4)$$

Since we have used the minimized potential, which corresponds to a static case with  $x_0$  we ignore the kinetic term. This is valid for very low frequencies with  $\omega \ll \omega_0$  with  $\omega_0 = \sqrt{\frac{c}{m}}$ , occurring at very low temperatures. We now see that we have the effective potential

$$U^{eff} = U - \frac{\lambda}{c}, \quad (C.5)$$

which for strong enough coupling constants or weak bond force constant can become negative, referred to as Anderson's negative- $U$  which tells us that a pair of like charges can be localized on the same bond. This should also tell us that all covalent bonded materials with two electrons on the same bond must have a strong electron-phonon coupling strength.

We also have that the energy of an electron localized on site  $i$  is lowered. The hopping integral  $T'_{ij}$  is also lowered by a lot giving strongly localized states. If we then neglect the weak hopping term we are left with, for very low frequencies:

$$H^{eff} = \sum_{i\sigma} E_i^{eff} n_{i\sigma} + U^{eff} \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (C.6)$$

where  $E_i^{eff} = E_i - \frac{\lambda}{2c}$ . This gives us the energy spectrum:

$$\begin{aligned} n_i = 0 : & \quad E = 0 \\ n_i = 1 : & \quad E = E^{eff} \\ n_i = 2 : & \quad E = 2E^{eff} + U^{eff}. \end{aligned} \quad (C.7)$$

We see that the system will always prefer either zero or two electron states. For  $2E_i^{eff} < -U^{eff}$  we have that the state with  $n_i = 2$  will have negative energy and will be preferred while for  $2E_i^{eff} > -U^{eff}$  the states with  $n_i = 1$  and  $n_i = 2$  will have  $E > 0$  and thus the state with zero electrons is preferred, given here that we are a temperature of  $k_B T \ll U^{eff}$  such that around  $E_i^{eff} \approx \frac{1}{2} U^{eff}$  the energy gap up to the state of  $n_i = 1$  is very large. This now gives us that the Fermi level  $\epsilon_F = 0$  as the state with  $n_i = 2$  is only occupied if  $E < 0$ . [12] [1]

## D Constant interaction model

The constant of proportionality between the charge and potential difference is called the capacitance and is defined as  $C = \frac{Q}{V}$ . As we have that  $W = Q[V(b) - V(a)]$  is the work required to bring a charge from  $a$  to  $b$  in a potential independent of path, then we will have that bringing another charge from the the negative conductor to the positive is  $dW = V_{a \rightarrow b} dQ' = \frac{Q'}{C} dQ' \Rightarrow W = \frac{Q^2}{2C}$  which gives the work required to bring  $Q$  charge onto a capacitor. The constant interaction model builds upon two assumptions

1. The coulomb interaction between electrons in the dot and between electrons in the dot and outside is described by a constant capacitance parameter,  $C$ , which is the sum of capacitances between the dot and source, gate and drain and other sources of capacitance:  $C = C_S + C_G + C_D$ . This means that we assume that the capacitance of the quantum dot doesn't depend on the number of electrons, bias or gate voltages or anything but is constant. We have a Thomas-Fermi wavevector of  $k_0 \approx 0.25 \text{ nm}^{-1}$

2. The single particle energy spectrum is independent of the coulomb interactions from the voltage sources around the quantum dot

We will use that for  $N$  electrons  $Q = -|e|N = CV$  and  $U = \frac{Q^2}{2C}$ , with  $U$  being the electrostatic energy required to add  $Q$  electrons to the capacitor, then the electrostatic energy of a quantum dot with capacitance  $C$  with  $N$  electrons, with voltages  $V_S$ ,  $V_D$  and  $V_G$  is given by:

$$U(N) = \frac{(-|e|(N - N_0) + C_S V_S + C_D V_D + C_G V_G)^2}{2C}, \quad (\text{D.1})$$

where  $-|e|$  is the electron charge, the term  $N_0|e|$  is the charge in the quantum dot compensating for a positive background.  $N_0|e|$  is then the number of electrons on the dot with all voltages zero. The total energy of the quantum dot with  $N$  electrons is then given by the electrostatic energy plus the sum the  $N$  single particle energies:

$$E(N) = \frac{(-|e|(N - N_0) + C_S V_S + C_D V_D + C_G V_G)^2}{2C} + \sum_{n=1}^N E_n. \quad (\text{D.2})$$

The last term is a sum of the occupied energy levels that depend on the confinement potential. The electrochemical potential is defined as the energy required to add the  $N$ 'th electron to the system, and is then:

$$\mu(N) = E(N) - E(N - 1). \quad (\text{D.3})$$

We will then work out  $E(N - 1)$  as follows, where we will shorthand  $C_S V_S + C_D V_D + C_G V_G = Q_{S,D,G}$ :

$$\begin{aligned} E(N - 1) &= \frac{(-|e|(N - 1 - N_0) + C_S Q_{S,D,G})^2}{2C} + \sum_{n=1}^{N-1} E_n \\ &= \frac{-|e|^2(N - N_0)^2 - 2|e|(N - N_0)Q_{S,D,G} - 2Q_{S,D,G}|e| - 2|e|^2(N - N_0) + Q_{S,D,G}^2 + |e|^2}{2C} \\ &\quad + \sum_{n=1}^N E_n - E_N \\ &= \frac{(-|e|(N - N_0) + Q)^2}{2C} + \sum_{n=1}^N E_n - \frac{2|e|^2(N - N_0) - |e|^2 - 2|e|Q_{S,D,G} - E_N}{2C} \\ &= E(N) - E_C \left( N - N_0 - \frac{1}{2} - \frac{Q_{S,D,G}}{|e|} \right) - E_N, \end{aligned} \quad (\text{D.4})$$

where we introduced the constant energy  $E_C = \frac{|e|^2}{C}$ . We can now easily find the energy required to add the  $N$ 'th electron to the system:

$$\mu(N) = E_C \left( N - N_0 - \frac{1}{2} - \frac{C_S V_S + C_D V_D + C_G V_G}{|e|} \right) + E_N. \quad (\text{D.5})$$

We can finally find the addition energy which is the general energy required to go from  $N$  to  $N + 1$  electrons on the quantum dot:

$$E_{\text{add}} = \mu(N + 1) - \mu(N) = E_C + E_{\Delta}. \quad (\text{D.6})$$

We now have that the energy from adding one more electron only depends on the constant term energy term  $E_C$  and the energy difference between the  $N$ 'th and  $(N + 1)$ 'th energy level in the dot as  $\Delta E = E_{N+1} - E_N$ .  $\Delta E$  between two levels can be zero in a system with degeneracies due to spin or symmetries. In a quantum dot modeled as a particle in a 2D box we will necessarily have degenerate energy levels as we can rotate the momentum vector  $\frac{\pi}{2}$  and have the same energy. [7] [5]

## E LAO/STO Band structure

In STO the electrons are confined to the d-orbitals  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  [8]. The 2DEG is located on the STO side of the LAO/STO interface [2]. The band structure is described by the Hamiltonian:

$$H_0 = \begin{pmatrix} \frac{\hbar^2 k_x^2}{2m_h} + \frac{\hbar^2 k_y^2}{2m_l} & \Delta_d \hbar^2 k_x k_y & 0 \\ \Delta_d \hbar^2 k_x k_y & \frac{\hbar^2 k_x^2}{2m_l} + \frac{\hbar^2 k_y^2}{2m_h} & 0 \\ 0 & 0 & \frac{\hbar^2 k_x^2}{2m_l} + \frac{\hbar^2 k_y^2}{2m_l} - \Delta_E \end{pmatrix} \quad (\text{E.1})$$

It is easy to see that along  $\Gamma X(k_y = 0)$  and  $\Gamma Y(k_x = 0)$  the Hamiltonian is diagonalized with the eigenvalues along the diagonal. We first make the Hamiltonian dimensionless by factoring out the dimension of energy  $\frac{\hbar^2}{a^2 m_e} (6.24 \text{E}18 \frac{\text{eV}}{\text{J}})$  in eV. We get that  $\frac{\hbar^2}{a^2 m_e} = 0.4997 \text{eV}$ . Then for every  $k_x$  that we choose, we solve the Hamiltonian. We use some dimensionless values for all the values in the Hamiltonian, we use:

$$m_l = 0.7$$

$$m_h = 15$$

$$\Delta_E = 50$$

$$\Delta_d = 0.28$$

$$k_x, k_y \in \left\{ -\frac{\pi}{3}, \frac{\pi}{3} \right\}$$

Giving us the band structure without any spin-orbit coupling as:

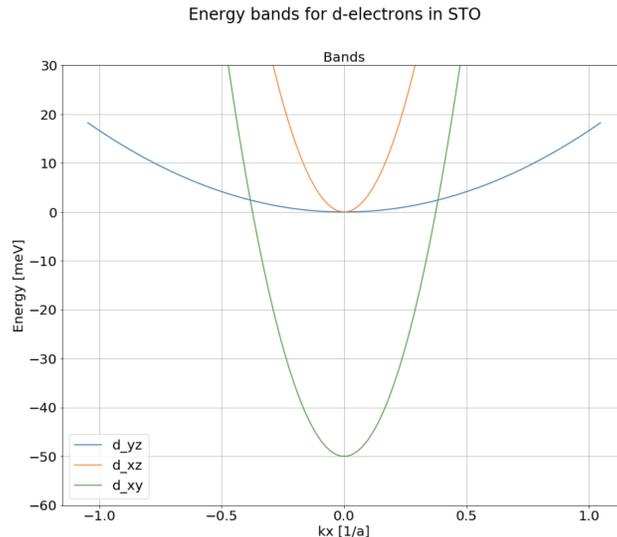


Figure 5: Bands along the  $[1, 0, 0]$  direction ( $k_y = 0$ )

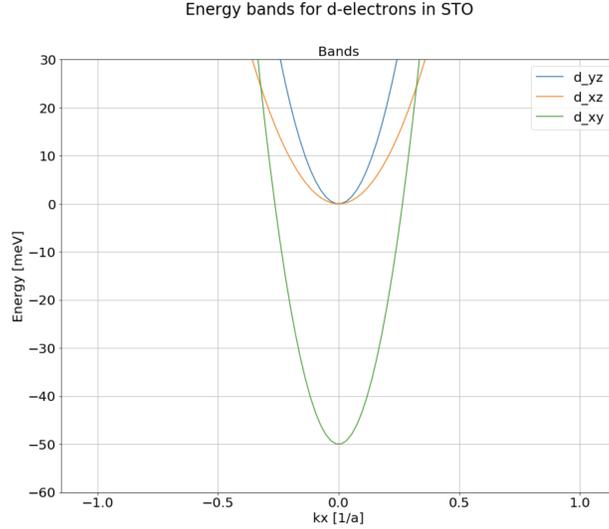


Figure 6: Bands along the  $[1, 1, 0]$  direction ( $k_y = k_x$ )

## F Spin-orbit coupling for d-orbitals and angular momentum basis change

To add atomic spin orbit coupling to the electrons in the bands we want to add the spin orbit term  $\Delta_{SO} \mathbf{L} \cdot \mathbf{S}$ . First we put spin on the original Hamiltonian written in the basis of the  $d$ -orbitals, by taking the tensor product with the 2 by 2 identity matrix so that  $H = H_0 \otimes \sigma_0$  which takes us to the 6-dimensional space spanned by  $\{|d_{yz}\rangle \otimes |\uparrow\rangle, |d_{yz}\rangle \otimes |\downarrow\rangle, |d_{xz}\rangle \otimes |\uparrow\rangle, \dots\}$ . To add the spin-orbit term to the Hamiltonian we must change the basis of the angular momentum matrix to the basis of  $H_0$ . The Hamiltonian  $H_0$  is written in the basis of the real  $d$ -orbitals that are superpositions of eigenstates to the angular momentum operator:

$$\begin{aligned}
 |d_{xy}\rangle &= \frac{i}{\sqrt{2}} (|m_l = -2\rangle - |m_l = 2\rangle), \\
 |d_{xz}\rangle &= \frac{1}{\sqrt{2}} (|m_l = -1\rangle - |m_l = 1\rangle), \\
 |d_{yz}\rangle &= \frac{i}{\sqrt{2}} (|m_l = 1\rangle + |m_l = -1\rangle).
 \end{aligned} \tag{F.1}$$

The electrons are in states that are solutions to angular momentum operators. As we know from quantum mechanics that the Hydrogen atom commutes with the total angular momentum operator and the angular momentum operator,  $[H, L^2] = [H, L_z] = 0$ , we choose eigenstates that are eigenstates to all the operators with different eigenvalues,  $n, l$  and  $m_l$ . The eigenfunctions to the square of the orbital angular momentum operator  $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$  are the spherical harmonics  $Y_l^{m_l}(\mathbf{r})$ . We can choose them to also be eigenfunctions to the orbital angular momentum operator  $L_z$  but then not to  $L_x, L_y$  as they do not commute, and as is standard they are chosen to be eigenfunctions to just  $L_z$ . The  $t_{2g}$  orbitals,  $d_{yz}, d_{xz}$  and  $d_{xy}$ , are by convention written as real orbitals so that they have direction and are easily plottable. They are thus written as linear combinations of the complex  $Y_2^{\pm 1}$  and  $Y_2^{\pm 2}$  spherical harmonics.

$$Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \sin(\theta) \cos(\theta) = \mp \sqrt{\frac{15}{8\pi}} \sin(\theta) \cos(\theta) [\cos(\phi) \pm i \sin(\phi)], \tag{F.2}$$

and with  $x = r \sin(\theta)\cos(\phi)$ ,  $y = r \sin(\theta)\sin(\phi)$  and  $z = r \cos(\theta)$  we get that:

$$Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \frac{z}{r^2} (x \pm iy) \quad (\text{F.3})$$

$$\Rightarrow \frac{i}{\sqrt{2}} (Y_2^1 + Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2} = \frac{i}{\sqrt{2}} \langle \mathbf{r} | (|m_l = 1\rangle + |m_l = -1\rangle) = \langle \mathbf{r} | d_{yz} \rangle \quad (\text{F.4})$$

$$\Rightarrow \frac{1}{\sqrt{2}} (-Y_2^1 + Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2} = \frac{1}{\sqrt{2}} \langle \mathbf{r} | (-|m_l = 1\rangle + |m_l = -1\rangle) = \langle \mathbf{r} | d_{xz} \rangle. \quad (\text{F.5})$$

For the last one we have:

$$Y_2^{\pm 2} = \mp \sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} \sin^2(\theta) = \mp \sqrt{\frac{15}{32\pi}} [\cos(2\phi) + i\sin(2\phi)] \sin^2(\theta) \quad (\text{F.6})$$

$$\Rightarrow \frac{i}{\sqrt{2}} (Y_2^{-2} - Y_2^2) = \frac{i}{\sqrt{2}} \sqrt{\frac{15}{32\pi}} \sin(\theta)^2 (-2i\sin(2\phi)), \quad (\text{F.7})$$

but  $\sin(2x) = \frac{e^{2ix} - e^{-2ix}}{2i} = \frac{(e^{ix} + e^{-ix})(e^{ix} - e^{-ix})}{2i} = 2\cos(x)\sin(x)$  we get that:

$$= \frac{1}{\sqrt{2}} \sqrt{\frac{15}{32\pi}} \sin^2(\theta) [4\sin(\phi)\cos(\phi)] = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2} = \frac{i}{\sqrt{2}} \langle \mathbf{r} | (|-2\rangle - |2\rangle) = \langle \mathbf{r} | d_{xy} \rangle. \quad (\text{F.8})$$

By writing our orbitals as real orbitals they are no longer eigenstates to  $L_z$  angular momentum operator and thus don't have a momentum around the chosen z-axis.

We can now change the basis of the orbital angular momentum operators from  $\{|m_l = \alpha\rangle\}$  with  $\alpha = -2, -1, 0, 1, 2$  to the basis of  $\{d_{yz}, d_{xz}, d_{xy}\}$  by calculating the matrix elements  $\langle i | L_j | k \rangle$  with  $i, k = d_{yz}, d_{xy}, d_{xz}$  and  $j = x, y, z$ . This is straight forward matrix multiplication when we have the matrices  $L_x, L_y$  and  $L_z$  in the  $L_z$  basis, so that:

$$L_z = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{pmatrix}, L_+(L_-) = \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ (2) & 0 & \sqrt{6} & 0 & 0 \\ 0 & (\sqrt{6}) & 0 & \sqrt{6} & 0 \\ 0 & 0 & (\sqrt{6}) & 0 & 2 \\ 0 & 0 & 0 & (2) & 0 \end{pmatrix}, \begin{cases} |m_l = 2\rangle \\ |m_l = 1\rangle \\ |m_l = 0\rangle \\ |m_l = -1\rangle \\ |m_l = -2\rangle \end{cases} \quad (\text{F.9})$$

The last vector in brackets indicates the basis. We also have that  $L_x = \frac{L_+L_-}{2}$  and  $L_y = \frac{L_-L_+}{2i}$ . In the  $L_z$  basis we then have that:

$$d_{yz} = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, d_{xz} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ -1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, d_{xy} = \frac{i}{\sqrt{2}} \begin{pmatrix} -1 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \quad (\text{F.10})$$

We now get from calculating each matrix element, that:

$$L_z = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}, L_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}. \begin{cases} |d_{yz}\rangle \\ |d_{xz}\rangle \\ |d_{xy}\rangle \end{cases} \quad (\text{F.11})$$

From this we can now numerically compute the eigenvalues of the Hamiltonian

$$H = H_0 \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \Delta_{SO} \sum_{\alpha} L_{\alpha} \otimes \sigma_{\alpha}, \quad \alpha = x, y, z \quad (\text{F.12})$$

which gives us plots on the form:

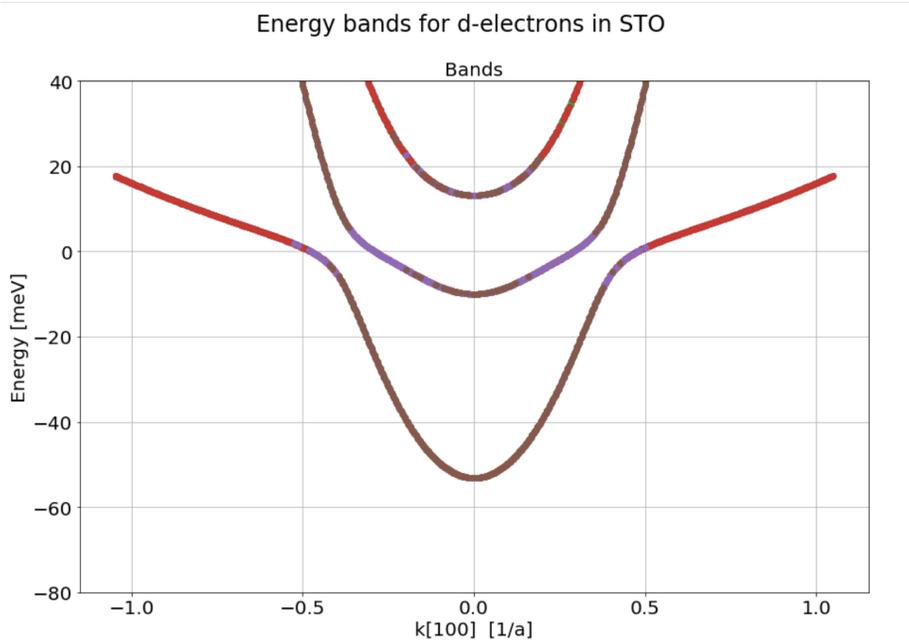


Figure 7: Bands along the  $[1, 0, 0]$  direction ( $k_y = 0$ ),  $\Delta_{so} = 10\text{meV}$

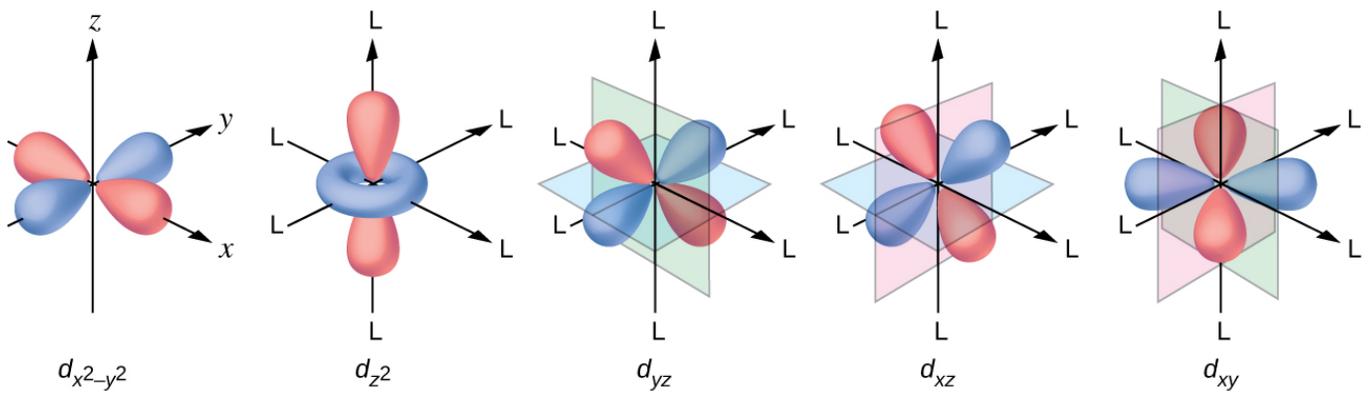


Figure 8: Real d-orbitals with ligands. From chem.libretexts.org