A theoretical model of ferroelectric heterostructures

Searching for superconductivity

A. Heuvel

Delft University of Technology

A theoretical model of ferroelectric heterostructures

Searching for superconductivity

by

A. Heuvel

to obtain the degree of Bachelor of Science
at the Delft University of Technology,
to be defended publicly on Monday February 24, 2025 at 13:00.

Student number:	5619912	
Project duration:	September 2, 2024 – February 24, 2025	
Thesis committee:	Prof. Dr. M. Ali,	TU Delft, supervisor TN faculty
	Dr. P. Visser,	TU Delft, supervisor EWI faculty
	Prof. Dr. Y. Blanter,	TU Delft, second supervisor TN faculty
	Dr. B. Janssens,	TU Delft, second supervisor EWI faculty

TU Delft

Preface

A. Heuvel
Delft, February 2025

Dear reader,

After months of hard work and research, I am happy to present the fruits of my labor, a theoretical model describing electron-electron interactions in a ferroelectric heterostructure. This thesis was written to obtain the degrees of Physics and Mathematics at the Delft University of Technology. The creation of a theoretical, quantum mechanical model that no one had explored before turned out to be a challenge with more ups, downs, and dead ends than I had ever expected. I can safely say that without the guidance of my supervisors, Prof. Dr. Yaroslav Blanter, Dr. Paul Visser, and Prof. Dr Maz Ali, a dead end is where this project would have ended. However, through enlightening weekly discussion where each shared their expertise and experience, they enabled me to find my way through the complicated field of condensed matter physics, and I am very grateful for their help. I would also like to thank Dr. Bas Janssens for taking the time to read and grade this thesis.

Furthermore, I would like to thank my friends and family for always supporting me throughout not just my thesis, but my study in its entirety. In particular I would like to thank Jelle van Kerkhof for listening to many rants about the confusing nature of quantum mechanics, and giving advice on both writing and researching, as well as Amber Pieterse for supporting me through the toughest weeks near the end of my degree, and for baking absolutely delicious cookies for me.

Next, I would like to thank two old teachers of mine. First, my primary school teacher Eric, who from the moment I stepped into his classroom at 6 years olds, challenged me and started my love for Mathematics. Second, my high school teacher Rob Kosman, who reignited my interest in mathematics, and showed me the beauty of doing mathematics for its own sake.

Lastly, I would like to thank my parents and siblings for supporting me and always showing curiosity and interest in my studies, which was not only a great motivator, but also a great tool improve my own ability to explain complex topcis simply.

Abstract

Novel types of superconductivity is a very active area of research. Heterostructures are a promising and recent avenue for finding these. This thesis explores a theoretical model of a ferroelectric heterostructure to investigate whether dipole-mediated electron interactions can induce superconductivity. Two models were analyzed: a static case where the dipole aligns instantaneously with the net electric field and a dynamic case where the dipole has inertia and oscillates. The static model showed that under small lattice constants, dipole mediated interactions can overcome Coulomb repulsion between electrons, though such conditions are challenging to achieve. The dynamic model, analyzed using Floquet theory, revealed resonance effects that amplify electron motion. While definitive superconductivity was not established, experimental validation through pressure-tuned lattice constants and resonance conditions could validate the model's predictions. Future research could extend this framework to quantum mechanical dipoles and more complex materials, enhancing the understanding of superconductivity in engineered heterostructures.

Contents

Nomenclature

An overview of atomic units, together with their standard symbol and value in SI units. These are the units used most prevelantly in this thesis.

Defined Atomic Units

The defined atomic units all have value 1 in this unit system. The values in SI units are given for reference.

Symbol	Definition	Value [SI]
$\hbar$	Reduced Planck constant	1.054571... $\times 10^{-34}$ Js
e^+	Elementary charge	1.602176... $\times 10^{-19}$ C
m_e	Electron rest mass	9.109383... $\times 10^{-31}$ kg
$4\pi\epsilon_0$	Vacuum permittivity	1.112650... $\times 10^{-10}$ Fm^{-1}

Derived Atomic Units

These are the most commonly used derived atomic units in this thesis. Their definition and SI value are given for reference.

Symbol	Name	Definition	Value [SI]
a_0	Bohr radius	$4\pi\epsilon_0\hbar^2/m_e(e^+)^2$	5.291772... $\times 10^{-11}$ m
E_h	Hartree energy	$\hbar^2/m_e a_0^2$	4.359744... $\times 10^{-18}$ J
e^-	Electron charge	$-e^+$	$-1.602176... \times 10^{-19}$ C
$\hbar/\mathrm{a}_0$	Unit of momentum	$\hbar/\mathrm{a}_0$	1.992851... $\times 10^{-24}$ kgms^{-1}
$\hbar/E_h$	Unit of time	$\hbar/E_h$	2.418884... $\times 10^{-17}$ s

1

Introduction

The discovery of superconductivity in 1911 by Heike Kamerlingh Onnes marked a breakthrough in condensed matter physics [1]. Superconducting materials can conduct electricity without any resistance, making them ideal for electronic components. They also exhibit a property called the Meissner effect, whereby magnetic fields are completely expelled from these materials, allowing magnets to float above their surface. Unfortunately, these materials are often complex metallic alloys, and only become superconducting under extremely high pressures and low temperatures. A superconductor that works at room temperature under atmospheric pressure is often called the "Holy Grail" of superconductivity, and would revolutionize the field of electronics. This makes the search for novel kinds of superconductors a very active area of research.

Historically, most superconductors are described by Bardeen-Cooper-Schrieffer (BCS) theory [2]. This framework describes the formation of so-called Cooper pairs: electrons bound through an attraction mediated by lattice vibrations. This attraction is key to superconductivity, and inspires the promising avenue of so-called heterostructures. These are a recent development in material science where two materials are positioned very precisely on top of each other, resulting in structures that can exhibit unique properties quantum mechanical in nature. The interfaces between these layers could cause hitherto unseen interactions, and could be the key to finding new types of superconductors. An example of a heterostructure can be seen in figure 1.1.

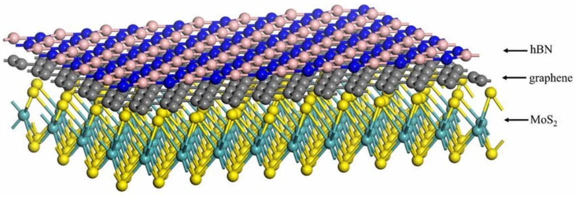


Figure 1.1: A schematic representation of a heterostructure. We see the three materials hexagonal boron nitride (hNB), graphene, and Molybdenum disulfide (MoS_2) positioned atop each other, precise to the atom.

Recent papers on superconducting heterostructures have proved promising. Hua et al. discovered an interesting superconducting state in a heterostructure using a ferromagnetic material [3]. Others have used a superconductor/ferromagnet interface to generate unique phenomena [4]. These developments shows the great potential of heterostructures, and highlights the importance of creating theoretical models to describe them.

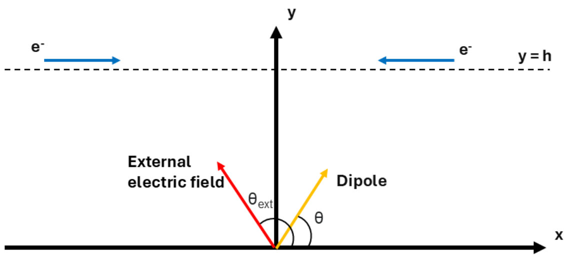


Figure 1.2: A schematic representation of the setup studied in this thesis. We see two electrons restricted to move along a single axis, interacting with each other and with a dipole. An external electric field is applied.

This thesis explores the theoretical background behind one such heterostructure, a conductor positioned on top of a dielectric material. The central model of this heterostructure consists of two electrons restricted to move in one dimension, interacting with each other, and with a single dipole restricted to only rotate, responding to an external electric field and the electric fields caused by the electrons. This setup is shown schematically in figure 1.2. We study two models of this heterostructure. First, we consider a static model, where the dipole responds instantaneously to the net electric field. This allows an exact computation of the energy of the system. Second, we consider a dynamic model, where the dipole oscillates due to an external electric field that dominates the electric field of the electrons. Making an additional assumption on the relative position of the electrons, we can use Floquet theory to explore this system.

This thesis is structured follows: Chapter 2 provides the theoretical background necessary to understand superconducting heterostructures, covering heterostructure physics, dielectric materials, and conventional and unconventional superconductors. Chapter 3 introduces the instant dipole response model, detailing the setup, interaction potentials, and analytical methods used to determine bound states. The results of this model, including parameter dependencies and transitions between different interaction regimes, are discussed in depth. Chapter 4 extends this framework to the case of an oscillating dipole with inertia. This chapter develops a time-dependent Schrödinger equation and employs Floquet theory to analyze the resulting electron dynamics. The implications of these results for superconductivity are explored. Finally, Chapter 5 presents the conclusions of this study and suggests directions for future research, particularly in experimental verification and the possible realization of dipole-mediated superconductivity in practical materials.

By constructing and analyzing these models, this thesis aims to contribute to the understanding of ferroelectric-superconducting heterostructures and their potential role in discovering new superconducting states. The results provide insight into the mechanisms by which dipole interactions might induce electron pairing, offering theoretical groundwork for further investigations into the nature of this heterostructure.

2

Theoretical Background

Before analyzing the ferroelectric heterostructure, it is important give some theoretical background on the materials involved and the standard model of superconductivity. This chapter briefly explains how the standard model of superconductivity works, what heterostructures and dielectrics are, and what electric-field screening is.

2.1. Superconductors

Superconductors are materials that, below a certain critical temperature, exhibit two defining properties: zero electrical resistance and the expulsion of magnetic fields, known as the Meissner effect. Superconductors can be classified into two types. Conventional ones, and unconventional ones. Conventional superconductivity are described by the standard theory of superconductivity, named BCS theory after Bardeen, Cooper, and Schrieffer. BCS theory uses the same basic principles to explain superconductivity as more advanced models. An understanding of BCS theory is therefore crucial for studying more exotic superconductors.

2.1.1. Standard BCS Theory

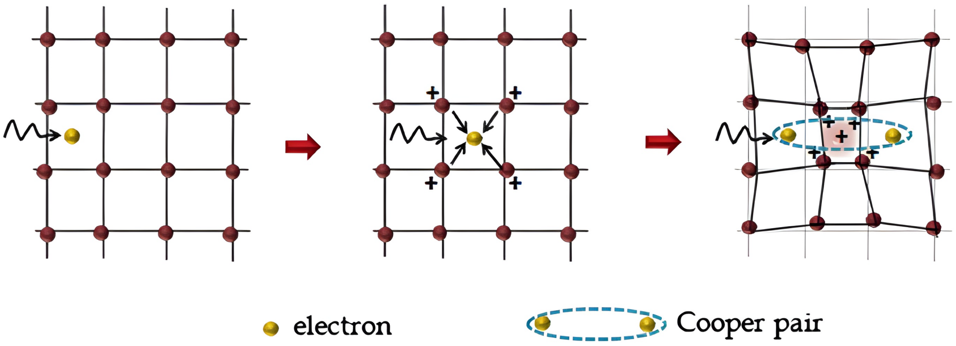


Figure 2.1: Schematic representation of Cooper pairing. An electron induces a phonon in the lattice, which in turns attracts a second electron, giving gives to a net attraction. This pairs the electrons into so-called Cooper pairs

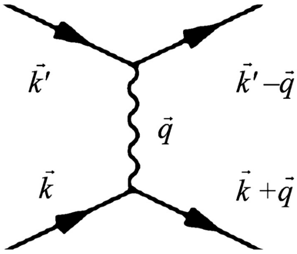


Figure 2.2: Electron-electron interaction mediated by a phonon with momentum $\mathbf{q}$ = **k-k**'. One electron scatters from momentum **k** to **k**' and emits a phonon of momentum **q**, which is in turn absorbed by the other electron.

In standard BCS theory, the theory for describing the formation of bound pairs assumes the following [5]. Two electrons, assumed to be free electrons, are added to a Fermi sea at $T = 0$K. These electrons interact with each other, through both an electric repulsion from a screened Coulomb interaction, and another interaction mediated by phonons through the ions in the crystal lattice. This interaction can gives rise to a net attractive interaction between the electrons, leading to a bound state. This process is shown in figure 2.1. These paired electrons are called Cooper pairs. They are bosonic states, with an energy below the Fermi level. The difference between their energy and the energy at the Fermi level is called the superconducting energy gap 2Δ. To break a Cooper pair, an energy of at least this amount is required, which is what gives rise to the critical temperature T_c. Below this temperature, there isn't enough energy to excite these Cooper pairs, allowing them to flow without resistance through the lattice. Since these pairs form a bosonic state, many of these pairs can form [6]. This is what gives rise to superconductivity. Now that we understand the idea behind BCS theory, we can look at it more quantitatively. First, we need to describe the phonon-mediated interaction. An electron scatters from a momentum **k** to a momentum **k**'. This creates a phonon of momentum **k** - **k**' = **q**, that is carried through the atom core ions in the material. This process is shown schematically in figure 2.2. It is shown by de Gennes [7] using the so-called jellium model that this gives rise to an effective attractive interaction between the two electrons given by

$$V(\mathbf{q},\omega) = \frac{4\pi(e^+)^2}{q^2+\kappa^2}\left(1+\frac{\omega_{\mathbf{q}}^2}{\omega^2-\omega_{\mathbf{q}}^2}\right) \tag{2.1}$$

Here $\frac{1}{\kappa}$ is the screening length, the reciprocal of the screening constant κ. $\omega_{\mathbf{q}}$ is the characteristic frequency of the phonon, and ω is the frequency of the electron, defined using $\hbar\omega = \xi_{\mathbf{k}}$, with $\xi_{\mathbf{k}}$ being the energy of the electron with momentum **k**.

Using a wavefunction ansatz of superpositions of plane waves, we try a wavefunction of electrons with opposite momenta [5] [8]:

$$\psi_0(\mathbf{r_1},\mathbf{r_2}) = \sum_{\mathbf{k}} g_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r_1}-\mathbf{r_2})} \tag{2.2}$$

Here, $g_{\mathbf{k}}$ are coefficients to be determined. We fill this into the expectation value of the energy:

$$E = \frac{\hat{p_1}^2}{2m} + \frac{\hat{p_2}^2}{2m} + V(\mathbf{q}) \tag{2.3}$$

Here, we find by the symmetry of the spatial part of the wavefunction that $E = 2\epsilon_{\mathbf{k}}$ with $\epsilon_{\mathbf{k}} = \frac{p^2}{2m} e^{i\mathbf{k}(\mathbf{r_1}-\mathbf{r_2})}$. We need to find $g_{\mathbf{k}}$ such that all terms in the following equation match.

$$\sum_{\mathbf{k}} E g_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r_1}-\mathbf{r_2})} = 2\sum_{\mathbf{k}} \left(g_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r_1}-\mathbf{r_2})}\right)\left(\epsilon_{\mathbf{k}} + \sum_{\mathbf{k'}} g_{\mathbf{k}} g_{\mathbf{k'}}\right) \tag{2.4}$$

Here, we see that we need $(E - 2\epsilon_{\mathbf{k}}) = \sum_{k'>k_F} V_{\mathbf{k}\mathbf{k}'} g_{\mathbf{k}'}$ for the equation to hold. Since we cannot solve this equation for complicated general V, V is approximated by

$$V_{\mathbf{k}\mathbf{k}'} = \begin{cases} -V & \text{if } |\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}| < \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} \tag{2.5}$$

Here ω_c is a cutoff frequency. Although seemingly a crude approximation, it turns out to give surprisingly accurate and insightful results. It now becomes possible to solve for $g_{\mathbf{k}}$. We find

$$g_{\mathbf{k}} = V \frac{\sum g_{\mathbf{k}'}}{2\epsilon_{\mathbf{k}} - E} \tag{2.6}$$

Summing over $\mathbf{k}$ and simplifying, we find the expression

$$\frac{1}{V} = \sum_{k>k_F} (2\epsilon_{\mathbf{k}} - E)^{-1} \tag{2.7}$$

We can extract an expression for E by turning our sum into an integral. Using the weak coupling approximation results in

$$E \approx 2E_F - 2\hbar\omega_c e^{-2/N(0)V} \tag{2.8}$$

Here $N(0)$ represents the density of states of electrons at the Fermi level. This result allows us to conclude there exists a bound state with energy below the Fermi level, for electrons with kinetic energy greater than the Fermi level. In fact, it is shown that regardless of the strength of the attractive force between these electrons, such a bound state exists. These bound states are what are called Cooper pairs in BCS theory, and they are the critical component of the theory responsible for the superconducting state.

2.1.2. Unconventional superconductors

Unconventional superconductors work similar to standard superconductors, as they also use Cooper pairing [9]. The difference is in the pairing mechanism for the electrons. Instead of electron-phonon coupling as in the jellium model, the necessary attractive interaction can be due to many different sources. This allows for superconductors with higher critical temperatures [10]. Heterostructures are a promising avenue for finding new types of superconductors, as the interfaces between the materials can give rise to new types of interactions. The heterostructure studied in this thesis gives rise to an interaction between electrons mediated by the dipole, with the hope of it being strong enough to cause Cooper pairing, and thereby superconductivity.

2.2. Heterostructures

Heterostructures, also referred to as heterojunctions, are composite materials formed by layering of two or more distinct materials, precise to the atom [11]. This enables unique quantum mechanical properties that are not found in the individual components alone. The interfaces between the layers are key to these emergent behaviors, as they facilitate interactions between different physical phenomena, such as electron transport, magnetism, and superconductivity.

The materials used in heterostructures typically exhibit complementary properties that, when combined, lead to novel functionalities. For example, semiconducting heterostructures have been extensively studied for their role in enabling high electron mobility and quantum well effects, which are critical for the operation of modern electronic and optoelectronic devices [12]. In this study, the focus is on ferroelectric-superconducting heterostructures, where the coupling between ferroelectric polarization and superconducting electron pairs opens up possibilities for novel superconducting states.

2.3. Dielectric Materials

Dielectric materials, or dielectrics, are materials that become polarized in the presence of an electric field. This polarization arises due to a displacement of positive and negative charges within the material, leading to the formation of electric dipoles. The degree to which a material can be polarized is quantified by its permittivity ϵ. Dielectrics consist of many dipoles arranged periodically. The dipoles in dielectric materials will be key to studying the heterostructure studied in this thesis. It is the interaction between the dipoles and the electrons that are hoped to give rise to an attractive interaction between the electrons themselves, which is important to superconductivity. To describe the interaction between dipoles and electrons, we use the equation for the potential between a dipole and an electron [13]

$$V = \frac{-\mathbf{p} \cdot \mathbf{r}}{4\pi\epsilon_0 |\mathbf{r}|^3} \tag{2.9}$$

Here $\mathbf{p}$ is the dipole moment and $\mathbf{r}$ is the vector from pointing from the electron to the dipole. It is important to note that the strength of this interaction goes as $1/r^3$, instead of as $1/r^2$ as between two charges. This makes the distance from the electrons to the dipole an important parameter, and plays an important role in getting a strong enough interaction.

2.4. Screening

In conductors, electric fields behave differently than in a vacuum. The presence of positively charged ions and negatively charged electrons cause electric potentials to drop exponentially with distance, a phenomenon known as screening. Using the Thomas-Fermi approximation [14], a dielectric function can be found that describes the screening of electric fields in a conductor. This function is given by,

$$\epsilon(r) = \epsilon_0 e^{\kappa r} \tag{2.10}$$

Here κ is the screening constant equal to one divided by the screening length. In other words, all electric potentials are multiplied by an $e^{-\kappa r}$ term. This gives rise to the Yukawa potential for the interaction of two charged particles [15]

$$V(r) = \frac{q_1 q_2}{r} e^{-\kappa r} \tag{2.11}$$

Here q_1 and q_2 are the charges of the two interacting particles, and r is the distance between them. The exponential decay of electric fields play an important role in creating an accurate model of the studied heterostructure, and is an important mathematical fact for studying this model by allowing certain approximations for large r.

2.5. Schrödinger Equation

To describe the evolution of a quantum mechanical system, the time-dependent Schrödinger equation [16] is used.

$$i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi \tag{2.12}$$

Here ψ is the wavefunction and $\hat{H}$ the total Hamiltonian. Solving the Schrödinger equation tells us how a system evolves in time, and what energies the system can have. Especially the latter is key showing whether a system can display superconductivity. Often, solving the Schrödinger equation analytically is infeasible or even impossible. In such cases, an ansatz for the wavefunction can be used. An ansatz is a trial wavefunction ψ, often based on heuristic arguments, that can be analyzed to find bounds on energies and explore how the system behaves.

3

Instantaneous dipole response

To analyse the dipole-mediated electron-electron interaction, we begin by analysing a simplified model. We consider the dipole as a classical object that aligns instantaneously with the net electric field. By using a wavefunction ansatz, the possibility of bound states is investigated.

3.1. Model Setup

We consider a system of two localized interacting quantum-mechanical electrons and a classical dipole. For simplicity, the electrons are constrained to move on the x-axis, a fixed distance h apart from the dipole. By making this distance fixed, we can see how important the distance of the electrons from the dipole is. Further, we assume a constant electric field $\mathbf{E}_{\text{ext}}$ at an angle θ_{ext} to the x-axis. The dipole has a dipole moment of $\mathbf{p}$, pointing in the direction of the total electric field, that being the sum of the external electric field and the electric field caused by the two electrons. Figure 3.1 provides a schematic view of this system.

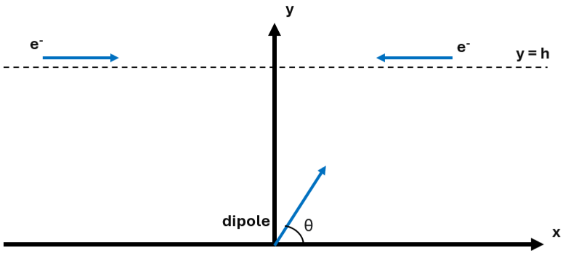


Figure 3.1: Diagram of a system of two interacting electrons and a dipole. The electrons are free to move on the x-axis, and the dipole can freely rotate around the origin. The position of the dipole is fixed at the origin, with the electrons at a constant lateral distance h from the dipole. An external electric field is applied at an angle θ_0 to the x-axis.

The key assumptions are as follows:

Electrons: The electrons are quantum-mechanical particles with a single degree of freedom, constrained to move along the x-axis. They are separated laterally by a fixed distance h

from the dipole and interact directly through a screened Coulomb force.

Dipole: The dipole is a classical object with a dipole moment $\mathbf{p}$ and no inertia. It aligns instantaneously with the total electric field, which is the vector sum of the external field and the fields produced by the electrons. It has a single degree of freedom, defined by its angle to the x-axis.

Electric Fields: All electric fields in the system are screened with screening constant κ. The screening effect is modeled using the Yukawa potential. The external electric field is assumed to be strong, constant, and oriented at an angle θ_{ext} to the x-axis.

System Configuration: The dipole is fixed at the origin, and the electrons are positioned at a constant lateral distance h from it. The electrons interact indirectly via the dipole and directly through the Coulomb force.

These assumptions allow for a tractable analysis of the system, and provides a basis for studying how these interactions can lead to bound states.

3.1.1. Electron and dipole interactions

From this setup, we can derive the interaction between the electrons. This interaction consists of two parts. First, the electrons interact directly through the Coulomb force. This interaction is screened and given by the Yukawa potential

$$V_{\text{C}} = \frac{e^-}{4\pi\epsilon_0|\mathbf{r_1} - \mathbf{r_2}|} e^{-\kappa|\mathbf{r_1}-\mathbf{r_2}|} \tag{3.1}$$

Here $\mathbf{r_1}$ and $\mathbf{r_2}$ are the positions of the electrons and κ is the screening constant. Since the electrons are restricted to move on the x-axis at a lateral distance of h, we can write their position as follows:

$$\mathbf{r_i} = \begin{pmatrix} x_i \\ h \\ 0 \end{pmatrix} \tag{3.2}$$

Here x_i is the position of electron $i \in \{1, 2\}$ on the x-axis. The second part of the interaction is an interaction mediated by the dipole. We assume a constant external electric field

$$\mathbf{E}_{\text{ext}} = \begin{pmatrix} E_{\text{ext}} \cos(\theta_{\text{ext}}) \\ E_{\text{ext}} \sin(\theta_{\text{ext}}) \\ 0 \end{pmatrix} \tag{3.3}$$

As well as an electric field caused by the electrons, again given by the Yukawa potential.

$$V_\kappa(\mathbf{r_i}) = \frac{e^-}{4\pi\epsilon_0 r_i} e^{-\kappa r_i} \tag{3.4}$$

Here, $r_i = \sqrt{x_i^2 + h^2}$ is the distance between electron i and the dipole, and $\mathbf{r_i}$ is the vector pointing from the dipole to electron i. This allows us to calculate the electric field at the dipole. The electric field at the dipole due to an electron at position $\mathbf{r_i}$ is given by

$$\mathbf{E}_i = -\nabla V_\kappa(\mathbf{r_i}) = \frac{e^-}{4\pi\epsilon_0} \frac{e^{-\kappa r_i}}{r_i} \left(\kappa + \frac{1}{r_i}\right) \hat{r_i} \tag{3.5}$$

Since we assume the dipole has no inertia, the dipole will align with the electric field instantaneously. This gives the direction of the dipole moment

$$\hat{p} = \hat{E} = \frac{\mathbf{E}_{\text{ext}} + \mathbf{E_1} + \mathbf{E_2}}{|\mathbf{E}_{\text{ext}} + \mathbf{E_1} + \mathbf{E_2}|} \tag{3.6}$$

Here $\mathbf{E}_{\text{ext}}$ is the externally applied electric field, $\mathbf{E_1}$ is the electric field due to the first electron, and $\mathbf{E_2}$ is the electric field due to the second electron. This gives a dipole moment of

$$\mathbf{p} = p\hat{p} \tag{3.7}$$

Here $p = q\ell$ is the magnitude of the dipole moment, q being the charge of the constituents of the dipole, and ℓ the distance between them. Then we can calculate the potential of the electrons due to the dipole:

$$V_{\text{dp,i}} = \frac{-\mathbf{p} \cdot \mathbf{r}_i}{4\pi\epsilon_0 |\mathbf{r}_i|^3} \tag{3.8}$$

Here the minus sign is due to the negative charge of the electrons. Finally, including screening, we find

$$V_{\text{dp},i} = \frac{-\mathbf{p} \cdot \mathbf{r_i}}{4\pi\epsilon_0 |\mathbf{r_i}|^3} e^{-\kappa|\mathbf{r_i}|} \tag{3.9}$$

This completes the equations for the interaction between the electrons. All that is left is adding the kinetic energy terms. The kinetic energy operator for an electron in one dimension is given by

$$\hat{H}_{\text{kin}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.10}$$

We are now ready to write down the Hamiltonian of the system.

3.1.2. Model Hamiltonian

Now that we have the interaction between electrons mediated by the dipole, we can give the Hamiltonian of the system. This Hamiltonian consists of four parts: The kinetic energies of the electrons, the interaction of the electrons through the Coulomb force, and the interaction mediated by the dipole respectively. This leads to a Hamiltonian $\hat{H} = \hat{H}_{\text{e}_1} + \hat{H}_{\text{e}_2} + \hat{H}_{\text{C}} + \hat{H}_{\text{dp}}$. This gives rise to the Schrödinger equation 2.12 with

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + \frac{1}{x_1}e^{-\kappa x_1} + \frac{1}{x_2}e^{-\kappa x_2} - \frac{d\hat{E}(x_1, x_2)}{x_1^2} - \frac{d\hat{E}(x_1, x_2)}{x_2^2}\right]\psi \tag{3.11}$$

To get a bound state which is interesting for superconductivity, we want a state with electrons that have a net attraction. For maximal interaction between electrons, the dipole should be perpendicular to the axis of movement of the electrons. Because the dipole responds instantaneously to the electric field, the electron velocities do not affect the potential. As a result, only static bound states can be analyzed in this model.

3.1.3. Wavefunction Ansatz

Now that we have the Hamiltonian, we can try to find wavefunctions that have a negative energy. First, we note that we have a time-independent Hamiltonian, so the Schrödinger equation becomes separable. This means finding any state with a negative energy expectation value implies there being an eigenstate with a negative energy. This results from the fact that any wavefunction can be written as a weighted sum of eigenstates:

$$\psi(x_1, x_2) = \sum_{n=1}^{\infty} c_n \psi_n(x_1, x_2) \tag{3.12}$$

Here $\psi_n(x_1, x_2)$ are the eigenstates of the Hamiltonian with eigenvalues E_n. That means that for any wavefunction with negative energy

$$\langle\psi|\hat{H}|\psi\rangle < 0 \implies \sum_{n=1}^{\infty} |c_n|^2 E_n < 0 \tag{3.13}$$

This shows $\exists n \in \mathbb{N} : E_n < 0$. Therefore, there would exist an eigenstate with negative energy, which would also be a bound state. We are now ready to find such a state with negative energy. Due to the Coulomb interaction between electrons, which diverges when the electrons are at the same place, product states of overlapping wavefunctions do not give solutions. Therefore, we try the entangled state

$$\psi(x_1, x_2) = e^{\frac{-(x_1-\mu_1)^2-(x_2-\mu_2)^2}{b}} (x_1 - x_2) \frac{1}{N} \tag{3.14}$$

This does not allow for both electrons to be at the same place. This wavefunction has normalization constant

$$N = \frac{\pi}{4} b(2(\mu_1 - \mu_2)^2 + b) \tag{3.15}$$

. It is shown in figure 3.2b, where it can be see that it indeed does not allow for both electrons to be at the same place. Note that the electrons aren't most likely to be at μ_1 and μ_2 as would be expected with an unmodified product of Gaussians. The $(x_1 - x_2)$ factor makes the expression for the expected location of the electrons slightly more complicated. The expected value of x_i is given by

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_i |\psi(x_1, x_2)|^2 dx_1 dx_2 = \begin{cases} \frac{\pi}{4}(2\mu_1(\mu_1 - \mu_2)^2 - \mu_2) & \text{if } i = 1 \\ \frac{\pi}{4}(2\mu_2(\mu_2 - \mu_1)^2 - \mu_1) & \text{if } i = 2 \end{cases} \tag{3.16}$$

This can also be observed in figure 3.2b. This is an important property, as it allows for μ_1 and μ_2 to be equal, despite the electrons having zero probability of being at the same place.

Relative coordinates

To look at this wavefunction from a different perspective, we express the wavefunction in relative coordinates. This transformation will also turn out to be useful in analyzing this system mathematically. Here, we define

$$\begin{aligned} r &= r_2 - r_1 \\ R &= \frac{r_1 + r_2}{2} \end{aligned} \tag{3.17}$$

Using this transformation, we also get new momentum variables. Defining $q = -i\hbar\frac{\partial}{\partial r}$ and $p = -i\hbar\frac{\partial}{\partial R}$, we find $q = \frac{p_1 - p_2}{2}$ and $p = p_1 + p_2$, where $p_1 = -i\hbar\frac{\partial}{\partial r_1}$ and $p_2 = -i\hbar\frac{\partial}{\partial r_2}$. Performing this transformation, we find a wavefunction in terms of relative coordinates

$$\phi(r, R) = \exp\left\{\frac{-2}{b}(R - \frac{1}{2}(\mu_1 + \mu_2))^2 + \frac{-1}{2b}(r + (\mu_1 - \mu_2))^2 + \frac{-1}{b}(\mu_1 + \mu_2)^2\right\} r \quad (3.18)$$

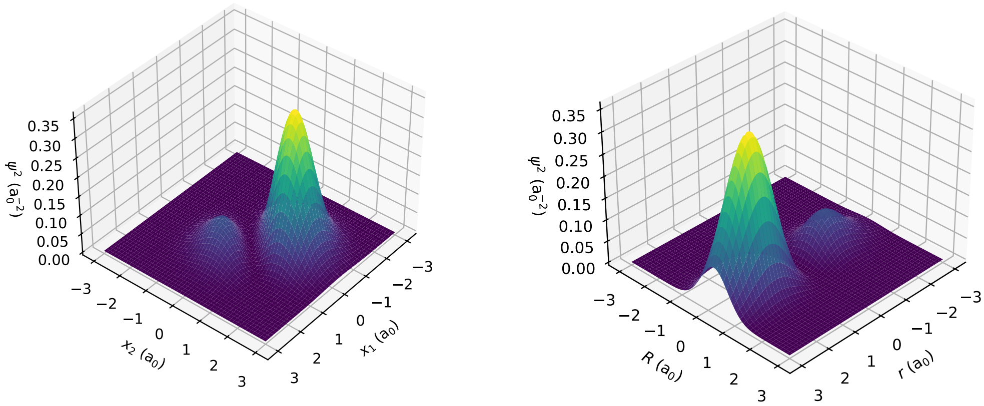
This equation becomes separable into a product of relative and centre-of-mass wavefunctions

$$f(r)g(R) = \exp\left\{\frac{-1}{2b}(r + (\mu_1 - \mu_2))^2\right\} r \exp\left\{\frac{-2}{b}(R - \frac{1}{2}(\mu_1 + \mu_2))^2\right\} \quad (3.19)$$

With normalization constant

$$\frac{1}{4}(2(\mu_2 - \mu_1)^2 + b)\pi b \quad (3.20)$$

Relative coordinates also change the interaction terms: $V_C = \frac{e^-}{4\pi\epsilon_0 r}e^{-\kappa r}$. This results in a wavefunction that can be seen in figure 3.2a. Here it can be clearly seen that at two electrons can't be at a relative distance of zero.



(a) Probability density of one electron being at x_1 and the other at x_2

(b) Probability density of the mean position of the electrons being at R, and their relative position being r

Figure 3.2: Wavefunction squared of two electrons as a function of their positions in figure a), and as a function of their mean position R and their relative position r in figure b), given by the product of two normal distributions and the relative position, with the normal distributions centered at $x_1 = 0$ and $x_2 = 0.5$. It can be seen that the electrons cannot be at the same location

Momentum space

To calculate the kinetic energy terms, as well as gain further insight into the behaviour of the electrons, we look at the wavefunction in momentum space. This is done by taking the Fourier transform of the wavefunction, and using the kinetic energy operator in momentum space. The kinetic energy operator in momentum space is given by $\hat{H}_{e_1} = \frac{p_1^2}{2m}$ and $\hat{H}_{e_2} = \frac{p_2^2}{2m}$. To transform $\psi(x_1, x_2)$ into a function of momenta, $\phi(p_1, p_2)$, we use the Fourier transform:

$$\mathcal{F}\{\psi(x_1, x_2)\}(p_1, p_2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi(x_1, x_2)e^{\frac{-i}{\hbar}(p_1 x_1 + p_2 x_2)}\,\mathrm{d}x_1\,\mathrm{d}x_2 \quad (3.21)$$

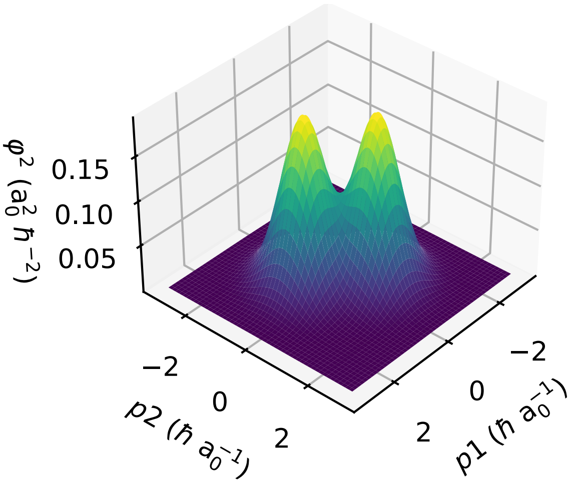


Figure 3.3: Wavefunction squared of two electrons as a function of their momenta, given by the Fourier transform of the wavefunction ansatz. It can be seen the electrons are most likely to have opposite momenta, and thus move away from each other.

Here $p_i = \hbar k_i$ is the quantum mechanical momentum. Filling our wavefunction ansatz into this equation, we find

$$\begin{aligned}\phi(p_1, p_2) = &\int_{-\infty}^{\infty} x_1 e^{-\frac{1}{b}x_1^2 + (\frac{2\mu_1}{b} - \frac{ip_1}{\hbar})x_1 - \frac{\mu_1^2}{b}}\,\mathrm{d}x_1 \int_{-\infty}^{\infty} e^{-\frac{1}{b}x_2^2 + (\frac{2\mu_2}{b} - \frac{ip_2}{\hbar})x_2 - \frac{\mu_2^2}{b}}\,\mathrm{d}x_2 \\ &- \int_{-\infty}^{\infty} x_2 e^{-\frac{1}{b}x_2^2 + (\frac{2\mu_2}{b} - \frac{ip_2}{\hbar})x_2 - \frac{\mu_2^2}{b}}\,\mathrm{d}x_2 \int_{-\infty}^{\infty} e^{-\frac{1}{b}x_1^2 + (\frac{2\mu_1}{b} - \frac{ip_1}{\hbar})x_1 - \frac{\mu_1^2}{b}}\,\mathrm{d}x_1\end{aligned} \tag{3.22}$$

This evaluates to an expression similar to the wavefunction ansatz, being in the form of the product of two Gaussians and a term linear in p_1 and p_2. This wavefunction is given by

$$\phi(p_1, p_2) = \frac{1}{4} b\left(2\mu_1 - 2\mu_2 + ib(p_1 - p_2)\right) e^{i\mu_1 p_1 + i\mu_2 p_2 - \frac{b}{4}(p_1^2 + p_2^2)} \tag{3.23}$$

Now, to use this to calculate the potential energy, we need to take its absolute value squared to get the probability density. We find

$$|\phi(p_1, p_2)|^2 = e^{-\frac{b}{2}(p_1^2 + p_2^2)}(4(\mu_1 - \mu_2)^2 + b^2(p_1 - p_2)^2)\frac{1}{N} \tag{3.24}$$

This has the following normalization constant:

$$N = \frac{4(2(\mu_1 - \mu_2)^2 + b)}{b}\pi \tag{3.25}$$

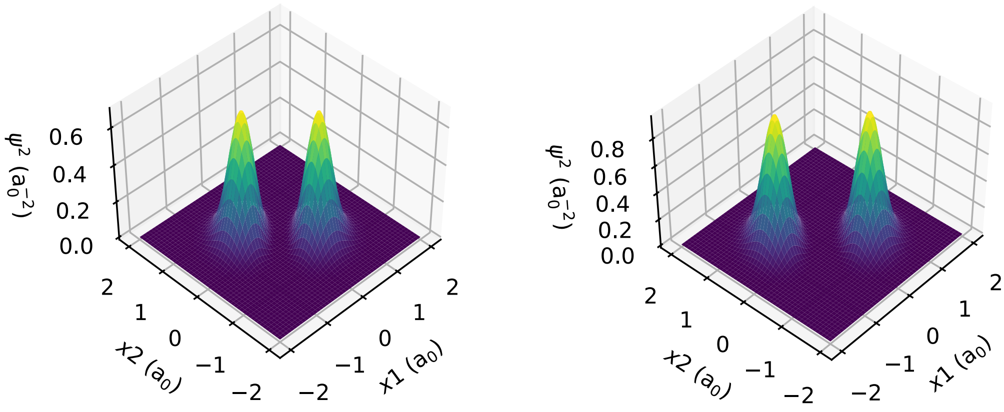
This function is shown in figure 3.3 for $\mu_1 = \mu_2 = 0$. It can be seen that the electrons are most likely to have opposite momenta, and thus move away from each other. This is a result of the $(x_1 - x_2)$ term in the wavefunction ansatz.

Other wavefunctions

Other wavefunctions of the form

$$\psi(x_1, x_2) = e^{\frac{-(x_1-\mu_1)^2-(x_2-\mu_2)^2}{b}}(x_1 - x_2)^n \tag{3.26}$$

For $n \in \mathbb{N}$ have been considered. For non-integer values of n, the wavefunction becomes discontinuous at 0, causing problems for finding their energy. For values of $n > 1$, the two electrons are more distinctly separate, as can be seen in figure 3.4. This causes a higher energy, and therefore gives no information on the ground-state energy.



(a) Case where the polynomial factor is given by $(x_1 - x_2)^2$.

(b) Case where the polynomial factor is given by $(x_1 - x_2)^3$.

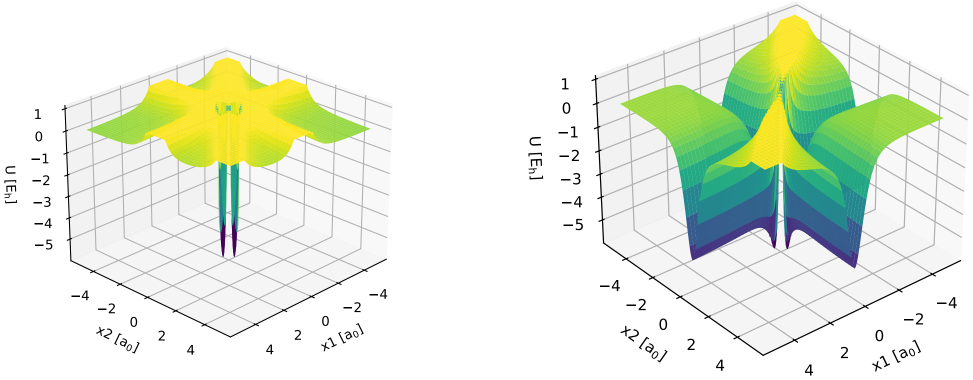
Figure 3.4: Wavefunction squared of two electrons as a function of their positions, given by the product of two normal distributions and a polynomial factor.

3.2. Results

Now that we have an ansatz for the wavefunction to try, it is possible to see how the system reacts to these wavefunctions. First, in order to get an intuition for how the particles interact near a freely rotating dipole, the Hamiltonian described by equation 3.11 has been evaluated as a classical potential. Furthermore, the wavefunction ansatz given by equation 3.14 has been evaluated for many values of μ_1 and μ_2, to explore the possibility of a bound state.

3.2.1. Attractive interaction

Now it is possible to look for situations in which the electrons feel a net attractive interaction. With the dipole pointing down, that is, the negative side closer to the electrons, we find there is a small region in which the dipole-mediated force gives rise to an attractive interaction, as shown in figure 3.5a. On the line $x_1 = x_2$, we see the repulsion between the two electrons, and on the lines $x_1 = 0$ and $x_2 = 0$ we see the dipole's repulsion. At $x_1 \approx -2$, $x_2 \approx 2$, as well as at $x_1 \approx 2$, $x_2 \approx -2$, a strong attractive potential appears. At this point, the electric field of the electrons overcomes the external electric field and flips the dipole the other way around. The dipole can just barely overcome the repulsion of the electrons, leading to an attractive potential, and giving rise to the possibility of a bound state. With the dipole pointing up, the region of attractive interaction is a lot larger, as shown in figure 3.5b. This is because the dipole will now always be attracting the electrons. This larger region of attractive interaction makes it more likely to find a bound state.



(a) External electric field pointing from the axis of movement of the electrons to the dipole

(b) External electric field pointing from the dipole towards the axis of movement of the electrons

Figure 3.5: The sum of the potentials given by the Coulombic repulsion and a dipole-mediated interaction between two electrons as a function of the positions of the electrons. The dipole has its positive side towards the electrons, with the electrons always at least a lateral distance of $\frac{5}{8}$ Bohr radii removed from the dipole. It can be seen that at very specific positions, the electrons experience an attractive interaction mediated by the dipole. In this figure, the electrons are considered classical.

3.2.2. States with high lattice constant

Now that there is an understanding of the attractive interaction, we can look for bound states. Using the wavefunction ansatz it is possible to try find a bounded state, that is, one with a negative energy. First, we need some estimates for the parameters in the model. Typical screening lengths are on the order of about $1/20\mathrm{a}_0$. Further, a dipole moment of

$2 \times 10^{-31}\text{Cm} \approx 2e^{+}a_0$ is common for dielectrics. For the lateral distance h between the dipole and electrons, we can expect this to be on the order of a lattice constant in metals, which for cobalt is around $4.72a_0$ [17]. Numerically trying out wavefunctions of this form and calculating $\langle\psi|\hat{H}|\psi\rangle$, we find bound states are impossible. Since the Coulombic repulsion between the electrons falls of as $1/r^2$, while the field from the dipole decreases as $1/r^3$, at large distances it becomes impossible for the dipole-mediated interaction to overcome the Coulombic repulsion, as can be seen in figure 3.6

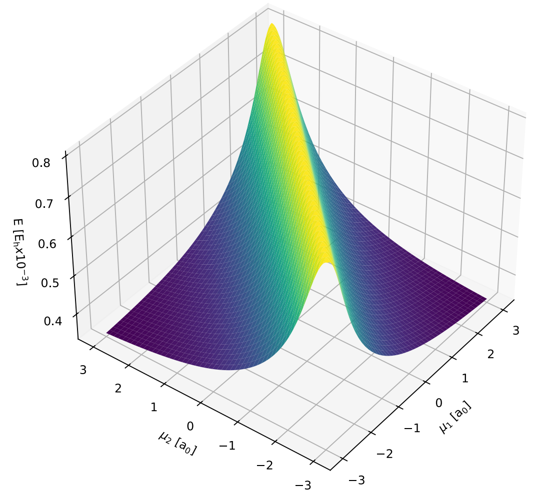
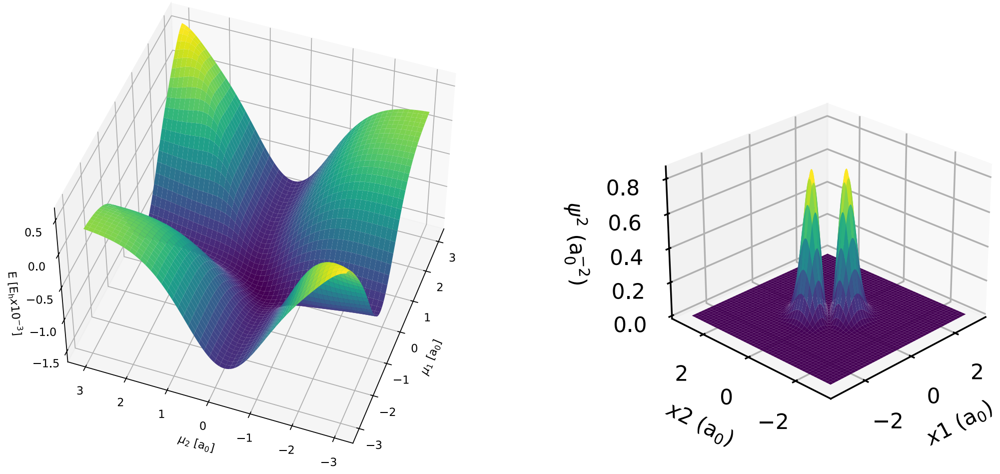


Figure 3.6: Sum of kinetic and potential energy of a system of two electrons interacting directly through the Coulombic force, and indirectly through a dipole, as a function of the parameters μ_1 and μ_2 in the wavefunction given by equation 3.14. Here, the dipole has a dipole moment of $2e^{+}a_0$, the electrons are at a lateral distance of $4.72a_0$ from the dipole, the external electric field is $3.5E_h$, and the screening constant is 0.05.

3.2.3. States with low lattice constant

The most important parameter in this model is the distance of the axis of movement of the electrons to the dipole. Since a dipole's electric field decreases as $1/r^3$, and the repulsion between electrons only as $1/r^2$, having this distance small is crucial for overcoming the Coulombic repulsion. Under extremely high pressures, it becomes possible to attain lattice constants on the order of 0.4a_0. We take this distance $h = 0.625\text{a}_0$, $\text{E}_{\text{ext}} = 3.5\text{E}_\text{h}$, $\kappa = 0.05\text{a}_0$, $\text{d} = 2e^{+}\text{a}_0$. To find a bound state, first the width of the Gaussians given by equation 3.14 was optimized numerically. A value of $b = 0.552\text{a}_0^2$ was found. Then, the energy of states was calculated for parameters $\mu_1 \in [-2, 2]$ and $\mu_2 \in [-2, 2]$ using the Hamiltonian in equation 3.11. The energy of the states was calculated using the Hamiltonian, and the results are shown in figure 3.7a. We see the energy has two different local minima with the electrons slightly off-center. This shows it is theoretically possible to get bound states.

An example of such a bound state is given in figure 3.7b.



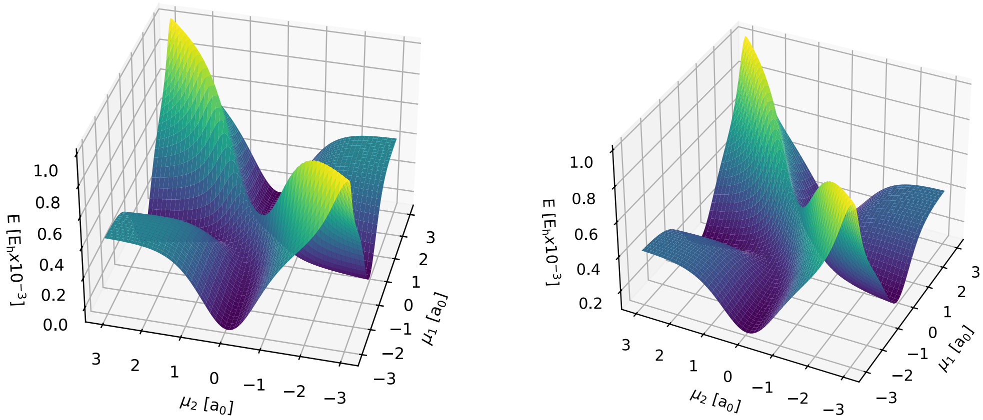
(a) Sum of kinetic and potential energy of a system of two electrons interacting directly through the Coulombic force, and indirectly through a dipole, as a function of the parameters μ_1 and μ_2.

(b) A bound state of a system of two electrons interacting directly through the coulombic force, and indirectly through a dipole. It can be seen the electrons prefer to be on opposite sides of the dipole

Figure 3.7: Wavefunction given by equation 3.14 of two electrons, illustrating how the potential of the system changes with the parameters μ_1 and μ_2 in figure a), and showing a bound state in figure b). Here, the dipole has a dipole moment of $2e^+$a$_0$, the electrons are at a lateral distance of 0.625a$_0$ from the dipole, the external electric field is 3.5E$_\mathrm{h}$, and the screening constant is 0.05a$_0$.

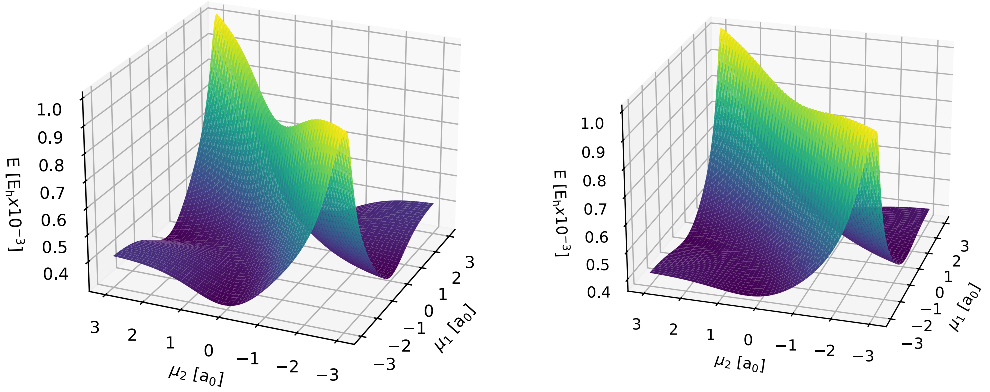
3.2.4. Transition between states

To experimentally test for these bound states, it is important to find at what lattice constants the systems transition from bound to unbound states. To this end, we show the energy landscape for values of $h = 0.8$, 1, 1.5, and 2a$_0$, shown in figure 3.8. We see that the attractive dipole-mediated gradually decreases in strength, making the bound state disappear, and creating a saddle point in the energy landscape, where the coulombic repulsion and the dipole-mediated attraction oppose each other. By observing this heterostructure under varying pressures, which changes the lattice constants, this effect should be experimentally observable. Such an observation would support the validity of this model.



(a) Distance of dipole to the electron's axis of movement $h = 0.8\mathrm{a}_0$

(b) Distance of dipole to the electron's axis of movement $h = 1\mathrm{a}_0$



(c) Distance of dipole to the electron's axis of movement $h = 1.5\mathrm{a}_0$

(d) Distance of dipole to the electron's axis of movement $h = 2\mathrm{a}_0$

Figure 3.8: Sum of kinetic and potential energy of a system of two electrons interacting directly through the Coulombic force, and indirectly through a dipole, as a function of the parameters μ_1 and μ_2 in the wavefunction given by equation 3.14. Here, the dipole has a dipole moment of $2e^{+}\mathrm{a}_0$, the external electric field is $3.5\mathrm{E}_\mathrm{h}$, and the screening constant is $0.05\mathrm{a}_0$.

4

Electric dipole with inertia

4.1. Setup

We have found bound states, but as current is a non-static phenomenon, we want free electrons to describe (super)conductivity. To have a dynamic description solutions, we need to allow the dipole to oscillate. To get this working, we need to consider the inertia of the dipole. This changes the Schrödinger equation by adding time-dependence, and adds equations for the motion of the dipole. We will first consider the motion of the dipole. We still restrict the electrons to move along the x-axis at a fixed lateral distance h from the dipole. This means the positions of the electrons, $\mathbf{r_1}$ and $\mathbf{r_2}$, are of the form

$$\begin{aligned}\mathbf{r_1} &= x_1\hat{x} + h\hat{y}\\ \mathbf{r_2} &= x_2\hat{x} + h\hat{y}\end{aligned} \tag{4.1}$$

Here x_1 and x_2 are the positions of the electrons along the axis, with the dipole being at $x = 0$. Furthermore, we give the dipole an inertia $I = \frac{m\ell^2}{2}$, which allows it to oscillate. This is in contrast with the model of chapter 3, where the dipole follows the electric field without delay. Next, the externally applied electric field is assumed to dominate the electric field of the electrons, allowing a simplified treatment of the dipole's movement. The electrons are also assumed to be a lateral distance $h \gg x_i$ from the dipole. We are now ready to treat a dipole with inertia.

4.1.1. Dipole Motion

Consider the dipole as two oppositely charged point charges with mass $m = m_e$ and charge magnitude $q = e^+$, separated by a vector $\mathbf{d}$ centered at the origin, with $|d| = \ell$. We define $\mathbf{p} = q\mathbf{d}$. Since the moment of inertia of an object is given by $I = \sum_{i=1}^{N} m_i {r_i}^2$ the dipole has a moment of inertia

$$I = \frac{m}{2}|d|^2 \tag{4.2}$$

To find how the dipole reacts to the electric field, we first need the torque. The force on the positively charged particle is given by $q\mathbf{E}$, and the force on the negatively charged particle is $-q\mathbf{E}$. This gives a torque of $q\mathbf{E} \times \frac{\mathbf{d}}{2}$ caused by the positive charge, and a torque of $-q\mathbf{E}\times\frac{-\mathbf{d}}{2}$ caused by the negative charge. This amounts to a total torque of [13]

$$\boldsymbol{\tau}=\mathbf{p}\times\mathbf{E} \tag{4.3}$$

Next, we consider the angular momentum $\mathbf{J}=m(\mathbf{d}\times\dot{\mathbf{d}})$. We know $\dot{\mathbf{J}}=\boldsymbol{\tau}$ [18]. From this, we find an equation of motion for the dipole in terms of the electric field.

$$\dot{\mathbf{J}}=m(\mathbf{d}\times\ddot{\mathbf{d}})=q\mathbf{d}\times\mathbf{E} \tag{4.4}$$

The external electric field is composed of an external electric field $\mathbf{E}_{\text{ext}}$ and the electric fields caused by two electrons described by the wavefunction $\psi(\mathbf{r_1},\mathbf{r_2},t)$. Filling this out, the total electric field at the dipole ($\mathbf{r}=0$) is given by

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_{\text{ext}}+\iint \mathrm{d}\mathbf{r_1}\,\mathrm{d}\mathbf{r_2}|\psi(\mathbf{r_1},\mathbf{r_2},t)|^2\left(\frac{\mathbf{r}-\mathbf{r_1}}{|\mathbf{r}-\mathbf{r_1}|^3}e^{-\kappa|\mathbf{r}-\mathbf{r_1}|}+\frac{\mathbf{r}-\mathbf{r_2}}{|\mathbf{r}-\mathbf{r_2}|^3}e^{-\kappa|\mathbf{r}-\mathbf{r_2}|}\right)e^- \tag{4.5}$$

Here we average the electric field over the probability density of the electrons since we consider the dipole to behave classically. This leads to

$$m\mathbf{d}\times\ddot{\mathbf{d}}=q\mathbf{d}\times\left[\mathbf{E}_{\text{ext}}+2\iiint d\mathbf{r_1}d\mathbf{r_2}|\psi(\mathbf{r_1},\mathbf{r_2},t)|^2\frac{-\mathbf{r_1}}{|\mathbf{r_1}|^3}e^{-\kappa|\mathbf{r_1}|}e^-\right] \tag{4.6}$$

Here we have used the fact that electrons have antisymmetric wavefunctions to find $|\psi(\mathbf{r_1},\mathbf{r_2},t)|^2=|\psi(\mathbf{r_2},\mathbf{r_1},t)|^2$ to eliminate $\frac{\mathbf{r}-\mathbf{r_2}}{|\mathbf{r}-\mathbf{r_2}|^3}$ from the integral. Together with the restriction that $\frac{d}{dt}(\mathbf{d}\cdot\mathbf{d})=0$, so $\dot{\mathbf{d}}\cdot\mathbf{d}=0$, since the two particles in a dipole are assumed to be at a fixed distance, we can find the equations of motion for the dipole. First, we calculate $\mathbf{J}\times\mathbf{d}=m(\mathbf{d}\times\dot{\mathbf{d}})\times\mathbf{d}=m\dot{\mathbf{d}}(\mathbf{d}\cdot\mathbf{d})=I\dot{\mathbf{d}}$, where we have used the vector triple products

$$\begin{aligned}\mathbf{a}\times(\mathbf{b}\times\mathbf{c})&=(\mathbf{a}\cdot\mathbf{c})\mathbf{b}-(\mathbf{a}\cdot\mathbf{b})\mathbf{c}\\(\mathbf{a}\times\mathbf{b})\times\mathbf{c}&=(\mathbf{a}\cdot\mathbf{c})\mathbf{b}-(\mathbf{b}\cdot\mathbf{c})\mathbf{a}\end{aligned} \tag{4.7}$$

For any three vectors $\mathbf{a},\mathbf{b},\mathbf{c}\in\mathbb{R}^3$. This leads to the equations of motion

$$\begin{aligned}\dot{\mathbf{J}}&=q\mathbf{d}\times\mathbf{E}\\I\dot{\mathbf{d}}&=\mathbf{J}\times\mathbf{d}\end{aligned} \tag{4.8}$$

Taking the time derivative of the second equation and using the vector triple product 4.7, we find the non-coupled equation of motion

$$I\ddot{\mathbf{d}}=-q(\mathbf{E}\cdot\mathbf{d})\mathbf{d}+q\ell^2\mathbf{E}-m(\dot{\mathbf{d}}\cdot\dot{\mathbf{d}})\mathbf{d} \tag{4.9}$$

Using $I=\frac{m\ell^2}{2}$, we rewrite above equation as

$$\frac{m\ell^2}{2}\ddot{\mathbf{d}}=-q(\mathbf{E}\cdot\mathbf{d})\mathbf{d}+q\ell^2\mathbf{E}-m(\dot{\mathbf{d}}\cdot\dot{\mathbf{d}})\mathbf{d} \tag{4.10}$$

By using small angle approximations, we show that $|\ddot{\mathbf{d}}|\propto\sin(\omega t)$. We first write $\mathbf{d}=\mathbf{d_0}+\sin(\theta)\mathbf{d}_\perp$, where $\mathbf{d_0}\parallel\mathbf{E}_{\text{ext}}$ with $|\mathbf{d_0}|=\ell$, and $\mathbf{d}_\perp\perp\mathbf{E}_{\text{ext}}$, with $|\mathbf{d}_\perp|=1$. Then $\ddot{\mathbf{d}}=[-\sin(\theta)\dot{\theta}^2+\cos(\theta)\ddot{\theta}]\mathbf{d}_\perp$. For the three terms on the right of equation 4.10 we get

$$[-qE\ell\sin(\theta)-2m\dot{\theta}^2\cos^2(\theta)\sin(\theta)]\mathbf{d}_\perp \tag{4.11}$$

for the perpendicular part, and

$$[-qE\ell^2 + qE\ell^2 - 2m\dot{\theta}^2\cos^2(\theta)]\mathbf{d}_{\parallel} \tag{4.12}$$

for the parallel part. Using the small angle approximations $\sin(\theta) \approx \theta$ and $\cos(\theta) \approx 1$, as well as dropping all terms quadratic in θ and $\dot{\theta}$, we find

$$\begin{aligned} \frac{m\ell^2}{2}\ddot{\mathbf{d}}_{\perp} &= -qE\ell\theta \\ \frac{m\ell^2}{2}\ddot{\mathbf{d}}_{\parallel} &= 0 \end{aligned} \tag{4.13}$$

So we find $\ddot{\theta} = -2\frac{qE}{ml}\theta$, which is a simple harmonic oscillator with $\omega = \sqrt{\frac{2qE}{m\ell}}$. This gives us the solution

$$\theta(t) = \theta_0 \sin(\omega t) \tag{4.14}$$

Here θ_0 is the initial angle between $\mathbf{d}$ and $\mathbf{E}$, and ω is the characteristic frequency of the dipole, given by

$$\omega = \sqrt{\frac{2qE}{m\ell}} \tag{4.15}$$

Assuming the electrons move parallel to the x-axis, and the external electric field points parallel to the y-axis, we find that $\mathbf{r} = x\hat{x} + h\hat{y}$ and $\mathbf{E}_{\text{ext}} = E_{\text{ext}}\hat{y}$. We then find $\mathbf{r} \cdot \mathbf{d} = x\theta_0 \sin(\omega t) + h\ell$

4.1.2. Time-dependent Schrödinger equation

We are now ready to write down the Schrödinger equation for this system. We use the potential for a dipole interacting with an electron given by equation 3.9 and the Yukawa potential given by equation 3.1. Furthermore, we use $\frac{\hbar}{2m}\frac{\partial^2}{\partial x_i^2}$ as the kinetic energy of electron i. This leads to the following time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(\mathbf{r_1}, \mathbf{r_2}, t) = \begin{bmatrix} \dfrac{-\mathbf{p}\cdot\mathbf{r_1}}{|\mathbf{r_1}|^3}e^{-\kappa|\mathbf{r_1}|} + \dfrac{-\mathbf{p}\cdot\mathbf{r_2}}{|\mathbf{r_2}|^3}e^{-\kappa|\mathbf{r_2}|} \\ + \dfrac{1}{|\mathbf{r_1}-\mathbf{r_2}|}e^{-\kappa|\mathbf{r_1}-\mathbf{r_2}|} - \dfrac{\hbar^2}{2m}\nabla_1^2 - \dfrac{\hbar^2}{2m}\nabla_2^2 \end{bmatrix} \psi(\mathbf{r_1}, \mathbf{r_2}, t) \tag{4.16}$$

Here we leave out $\frac{e^+}{4\pi\epsilon_0}$ terms, to keep the notation compact. Equation 4.16 and 4.8 are a set of coupled differential equations that describe this system. To find a solution to these equations, we assume a strong external electric field, making the contributions of the electrons negligible. This leads to small oscillations of the dipole with respect to the applied electric field. This can be described by $\mathbf{d} = \mathbf{d_0} + \sin(\omega t)\mathbf{d}_{\perp}$ using equation 4.14. To simplify the Hamiltonian in equation 4.16, we assume $h \gg x_i$ for $i = 1, 2$. This allows for the approximation $|\mathbf{r_i}| = \sqrt{x_i^2 + h^2} \approx h + \frac{x_i^2}{2h}$, which allows us to write the dipole electron interaction as

$$-q\left(\frac{x_i\theta_0\sin(\omega t)}{h^3} + \frac{\ell}{h^2}\right)e^{-\kappa h}e^{-\kappa\frac{x_i^2}{2h^2}} \tag{4.17}$$

Furthermore, $|\mathbf{r_1} - \mathbf{r_2}| = |x_1 - x_2|$. This allows us to write the Hamiltonian in equation 4.16 as

$$\begin{aligned}\hat{H}(t) \approx &- q\left(\frac{x_1\theta_0 \sin(\omega t)}{h^3} + \frac{\ell}{h^2}\right) e^{-\kappa h} e^{-\kappa\frac{x_1^2}{2h}} - q\left(\frac{x_2\theta_0 \sin(\omega t)}{h^3} + \frac{\ell}{h^2}\right) e^{-\kappa h} e^{-\kappa\frac{x_2^2}{2h}} \\ &+ \frac{1}{|x_1 - x_2|} e^{-\kappa|x_1-x_2|} - \frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2\end{aligned} \tag{4.18}$$

Using a Taylor approximation of the exponential function, we can reduce this to an equation quadratic in x_1, x_2. We take a first-order approximation and assume $x_i \ll \sqrt{h/\kappa}$ to find

$$e^{-\kappa\frac{x_i^2}{2h}} \approx 1 - \kappa\frac{x_i^2}{2h} \tag{4.19}$$

By discarding terms higher than second order, we can write the Hamiltonian in equation 4.18 as

$$\begin{aligned}\hat{H}(t) \approx &\, q e^{-\kappa h}\left(\frac{\ell\kappa(x_1^2 + x_2^2)}{2h^3} - \frac{2\ell}{h^2} - \frac{(x_1 + x_2)\theta_0 \sin(\omega t)}{h^3}\right) \\ &+ \frac{1}{|x_1 - x_2|} e^{-\kappa|x_1-x_2|} - \frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\end{aligned} \tag{4.20}$$

Now, using relative coordinates $r = x_1 - x_2$ and $R = \frac{x_1+x_2}{2}$, we can rewrite this Hamiltonian using $x_1^2 + x_2^2 = 2R^2 + \frac{r^2}{2}$. This gives us a Hamiltonian with separate centre of mass and relative position terms

$$\begin{aligned}\hat{H}(t) \approx &\, q e^{-\kappa h}\left(\frac{\ell\kappa R^2}{h^3} - \frac{2R\theta_0 \sin(\omega t)}{h^3}\right) - \frac{\hbar^2}{4m}\frac{\partial^2}{\partial R^2} \\ &+ \frac{q\ell\kappa r^2}{4h^3} + \frac{1}{|r|}e^{-\kappa|r|} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial r^2} - \frac{2\ell}{h^3}e^{-\kappa h}\end{aligned} \tag{4.21}$$

This gives us a separable equation! Here we have used

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{2}\nabla_R^2 + 2\nabla_r^2 \tag{4.22}$$

This we can see from the fact that

$$\begin{aligned}&\frac{\partial^2}{\partial^2 x_1} f(x_1, x_2) + \frac{\partial^2}{\partial^2 x_2} f(x_1, x_2) \\ =&\frac{\partial}{\partial x_1}\left(\frac{\partial R}{\partial x_1}\frac{\partial}{\partial R} f(R, r) + \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r} f(R, r)\right) + \frac{\partial}{\partial x_2}\left(\frac{\partial R}{\partial x_2}\frac{\partial}{\partial R} f(R, r) + \frac{\partial r}{\partial x_2}\frac{\partial}{\partial r} f(R, r)\right) \\ =&\frac{1}{2}\frac{\partial^2}{\partial R^2} f(R, r) + 2\frac{\partial^2}{\partial r^2} f(R, r)\end{aligned} \tag{4.23}$$

We can neglect the constant term in the Hamiltonian, since this at most introduces a phase shift. This can be seen as follows. Let $\hat{H}' = \hat{H} + c$. Here $c \in \mathbb{C}$. Then the Schrödinger equation becomes

$$i\hbar\dot{\psi} = \hat{H}'\psi = (\hat{H} + c)\psi = \hat{H}\psi + c\psi \tag{4.24}$$

Letting $\phi = \psi e^{\frac{ict}{\hbar}}$ we see

$$i\hbar\dot{\phi} = i\hbar\dot{\psi}e^{\frac{ict}{\hbar}} + i\hbar\psi\frac{c}{\hbar}e^{\frac{ict}{\hbar}} = \hat{H}\psi e^{\frac{ict}{\hbar}} + c\psi e^{\frac{ict}{\hbar}} = \hat{H}'\phi \tag{4.25}$$

So when the Hamiltonian is shifted by a constant, the solutions remain unchanged up to an overall phase factor. This leaves us with the Schrödinger equation for this system:

$$i\frac{\partial}{\partial t}\psi = \left[\begin{array}{l} \quad qe^{-\kappa h}\left(\frac{\ell\kappa R^2}{h^3} - \frac{2R\theta_0\sin(\omega t)}{h^3}\right) - \frac{\hbar^2}{4m}\frac{\partial^2}{\partial R^2} \\ + \frac{q\ell\kappa r^2}{4h^3} + \frac{1}{|r|}e^{-\kappa|r|} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial r^2} - \frac{2\ell}{h^3}e^{-\kappa h} \end{array}\right]\psi \tag{4.26}$$

4.2. Floquet Theory

The dynamics of quantum mechanical systems with time-periodic Hamiltonians can be analyzed using Floquet theory [19]. It will allow us to see how the electrons behave under the influence of the oscillating dipole. Floquet theory deals with a given periodic Hamiltonian $\hat{H}(t) = \hat{H}(t+T)$ and the linear first-order differential equation $\dot{\phi} = \hat{H}\phi$. It states that for all fundamental matrix solutions $\Psi(t)$, that is, a matrix whose columns are linearly independent solutions of the differential equation, we have [20]

$$\Psi(t+T) = \Psi(t)\Psi^{-1}(0)\Psi(T) \tag{4.27}$$

Here $\Psi^{-1}(0)\Psi(T)$ is called the monodromy matrix, denoted as $M(t_0)$. This means that the solution to the differential equation is periodic with period T up to a complex, time-dependent phase factor. This is useful for solving the time-dependent Schrödinger equation, since we can write the solution as a linear combination of Floquet modes. We write $\Psi(t, t_0)$ for the principal matrix solution at t_0. Floquet's theorem states that

$$\Psi(t, t_0) = \Phi(t, t_0)e^{(t-t_0)Q(t_0)} \tag{4.28}$$

Here $\Phi(t, t_0)$ is periodic with period T, $\Phi(t_0, t_0) = \mathbb{I}$, and $Q(t_0)$ is a matrix such that $M(t_0) = \exp\{TQ(t_0)\}$ and $Q(t_0 + T) = Q(t_0)$ [20]. This means that for any solution $\Psi_\alpha(t)$

$$\Psi_\alpha(t+T) = \Psi_\alpha(t)e^{-i\epsilon_\alpha T} \tag{4.29}$$

Here Φ_α is a function periodic in time with period T called a Floquet mode, ϵ_α is a real parameter called the quasi-energy, and α an index labelling the solutions. These quasi-energy are analogous to the quasi-momenta $\mathbf{k}$ in Bloch theory.

4.2.1. Unitary Transformations

An important step in solving this quantum system is performing a unitary transformation on the Hamiltonian. A unitary transformation is a transformation of the statevector ψ by a so-called unitary operator $U(t)$, given by $\psi \to U\psi$. A unitary operator is an operator which satisfies $UU^\dagger = U^\dagger U = \mathbb{I}$. If we let $\psi' = U\psi$, where $i\hbar\dot{\psi} = H\psi$, then $i\hbar\dot{\psi}' = H'\psi'$, where $H' = UHU^\dagger + i\hbar\dot{U}U^\dagger$ [21]. Below is a derivation of this property.
Starting with the Schrödinger equation

$$i\hbar\dot{\psi} = H(t)\psi \tag{4.30}$$

We multiply by U on both sides, and insert $UU^\dagger$ to find

$$i\hbar U\dot{\psi} = UHU^\dagger U\psi \tag{4.31}$$

Next, using the product rule on the time derivative of $U\psi$, we find

$$\frac{d}{dt}(U\psi) = U\dot{\psi} + \dot{U}\psi \tag{4.32}$$

Combining the two equations above, we find

$$i\hbar\frac{d}{dt}(U\psi) = UHU^\dagger U\psi + i\hbar\dot{U}\psi \tag{4.33}$$

This finally leads to

$$i\hbar\frac{d}{dt}(U\psi) = (UHU^\dagger + i\hbar\dot{U}U^\dagger)(U\psi) \tag{4.34}$$

So the evolution of the new state $\psi' = U\psi$ is governed by the new Hamiltonian

$$H' = UHU^\dagger + i\hbar\dot{U}U^\dagger \tag{4.35}$$

These unitary transformations will be useful for solving our Schrödinger equation 4.36.

4.2.2. Solution to the Schrödinger equation

We solve equation 4.26 in two parts. Since its Hamiltonian $H(R,r,t) = H_R(R,t) + H_r(r)$, we have a separable differential equation. Letting the solution $\psi(R,r,t) = \xi(R,t)\chi(r)$, we first solve for $\xi(R,t)$.

Time-dependent part

We solve for ξ using Floquet theory. We have the time-dependent Schrödinger equation, shown in figure 4.1.

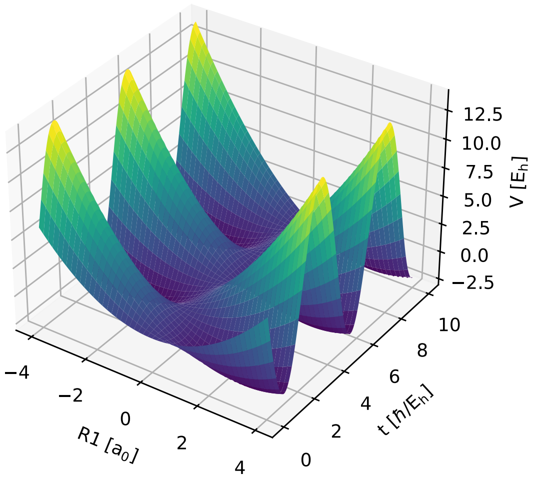


Figure 4.1: The potential for the centre of mass of two electrons interacting with a dipole. It can be seen that the potential oscillates with a time corresponding to the characteristic frequency of the dipole.

$$i\hbar\dot{\xi}(R,t) = \left[qe^{-\kappa h}\left(\frac{\ell\kappa R^2}{h^3} - \frac{2R\theta_0\sin(\omega t)}{h^3}\right) - \frac{\hbar^2}{4m}\nabla_R^2\right]\xi(R,t) \tag{4.36}$$

This system is actually exactly solvable, as shown by Hänggi [22]. To solve it, we start with the coordinate transformation

$$R \to y = R - \zeta(t) \tag{4.37}$$

Here, $\zeta(t)$ is a function that will be determined later. First, we apply this transformation to our equation by noting that

$$\dot{\xi}(R,t) = \frac{\partial}{\partial t}\xi(y,t) + \frac{\mathrm{d}y}{\mathrm{d}t}\frac{\partial}{\partial y}\xi(y,t) = \dot{\xi}(y,t) - \dot{\zeta}\frac{\partial}{\partial y}\xi(y,t) \tag{4.38}$$

This allows to find the transformed equation

$$i\hbar\dot{\xi}(y,t) = \left[i\hbar\dot{\zeta}\frac{\partial\xi}{\partial y} + qe^{-\kappa h}\left(\frac{\ell\kappa(y+\zeta)^2}{h^3} - \frac{2(y+\zeta)\theta_0\sin(\omega t)}{h^3}\right) - \frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2}\right]\xi(y,t) \tag{4.39}$$

We now apply the unitary transformation using equation 4.34

$$\phi(y,t) = e^{-2im\dot{\zeta}y/\hbar}\xi(y,t) \tag{4.40}$$

Approaching each term in the Hamiltonian separately, we find

$$i\hbar\dot{\zeta}\frac{\partial\xi}{\partial y} \to \left(i\hbar\dot{\zeta}\frac{\partial}{\partial y} - 2m\dot{\zeta}^2\right)\phi \tag{4.41}$$

The next terms remains unchanged, since functions commute with other functions.

$$-\frac{\hbar^2}{4m}\frac{\partial^2\xi}{\partial y^2} \to -\frac{\hbar^2}{4m}\left(\frac{\partial^2}{\partial y^2} + \frac{4im\dot{\zeta}}{\hbar}\frac{\partial}{\partial y} - \frac{m^2\dot{\zeta}^2}{\hbar^2}\right)\phi \tag{4.42}$$

This, when collecting terms, gives us

$$-\frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2} - m\dot{\zeta}^2 \tag{4.43}$$

Next, we look at the LHS of equation 4.39. The time-derivative becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}(e^{2im\dot{\zeta}y/\hbar}\phi(y,t)) = e^{2im\dot{\zeta}y/\hbar}\left[\frac{2im}{\hbar}\ddot{\zeta}y + \frac{\mathrm{d}}{\mathrm{d}t}\right]\phi(y,t) \tag{4.44}$$

We are left with the transformed equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\phi(y,t) = \left[\begin{array}{l} 2m\ddot{\zeta}y - \frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2} - m\dot{\zeta}^2 + e^{-\kappa h}\frac{2\ell\kappa}{h^3}y\zeta + e^{-\kappa h}\frac{\ell\kappa}{h^3}y^2 \\ + qe^{-\kappa h}\left(\frac{\ell\kappa}{h^3}\zeta^2 - \frac{2\theta_0\sin(\omega t)}{h^3}y - \frac{2\theta_0\sin(\omega t)}{h^3}\zeta\right) \end{array}\right]\phi(y,t) \tag{4.45}$$

We let ζ obey the equation of motion

$$2m\ddot{\zeta} + qe^{-\kappa h}\frac{2\ell\kappa}{h^3}\zeta = qe^{-\kappa h}\frac{2\theta_0\sin(\omega t)}{h^3} \tag{4.46}$$

This is the equation of motion for a classical harmonic oscillator. We fill this into the Schrödinger equation, and are left with

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\phi(y,t) = \left[-\frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2} - m\dot{\zeta}^2 + qe^{-\kappa h}\left(\frac{\ell\kappa}{h^3}y^2 + \frac{\ell\kappa}{h^3}\zeta^2 - \frac{2\theta_0\sin(\omega t)}{h^3}\zeta\right)\right]\phi(y,t) \quad (4.47)$$

Now we define the Lagrangian similar to the Lagrangian for a classical harmonic oscillator.

$$L(\zeta,\dot{\zeta},t) = -m\dot{\zeta}^2 + qe^{-\kappa h}\left(\frac{\ell\kappa}{h^3}\zeta^2 - \frac{2\theta_0\sin(\omega t)}{h^3}\zeta\right) \quad (4.48)$$

Using the Lagrangian to simplify equation 4.47, our differential equation reduces to

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\phi(y,t) = \left[-\frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2} + qe^{-\kappa h}\frac{\ell\kappa}{h^3}y^2 + L(\zeta,\dot{\zeta},t)\right]\phi(y,t) \quad (4.49)$$

Now we apply one more unitary transformation

$$\chi(y,t) = e^{i\int_0^t L(\zeta,\dot{\zeta},t')dt'}\phi(y,t) \quad (4.50)$$

Since this transformation is independent of y, we end up with the Schrödinger equation for a quantum-mechanical harmonic oscillator!

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\chi(y,t) = \left[-\frac{\hbar^2}{4m}\frac{\partial^2}{\partial y^2} + qe^{-\kappa h}\frac{\ell\kappa}{h^3}y^2\right]\chi(y,t) \quad (4.51)$$

The solutions are well-known. They are the Hermite polynomials times an exponential factor. The Hermite polynomials are an orthogonal set of functions on $\mathbb{R}$ [16]. They are given by

$$H_n(x) = (-1)^n e^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2} \quad (4.52)$$

This makes our solution to the harmonic oscillator

$$\phi_n(R-\zeta(t)) = H_n\left(2\sqrt{\frac{m\omega_R}{\hbar}}[R-\zeta(t)]\right)\exp\left\{-2m\omega_R[R-\zeta(t)]^2/\hbar\right\} \quad (4.53)$$

The eigenvalues of the harmonic oscillator given by equation 4.51 are given by

$$E_n = \hbar\omega_R(n+\frac{1}{2}) \quad (4.54)$$

Here

$$\omega_R = 2\sqrt{qe^{-\kappa h}\frac{\kappa\ell}{mh^3}} \quad (4.55)$$

Is the characteristic frequency of the centre of mass of the electrons. Now we need to solve for $\zeta(t)$. We had ζ satisfy equation 4.46. We find solutions of the form

$$\zeta_\varphi(t) = \frac{\theta_0 qe^{-\kappa h}}{mh^3(\omega_R^2-\omega^2)}\sin(\omega t+\varphi) \quad (4.56)$$

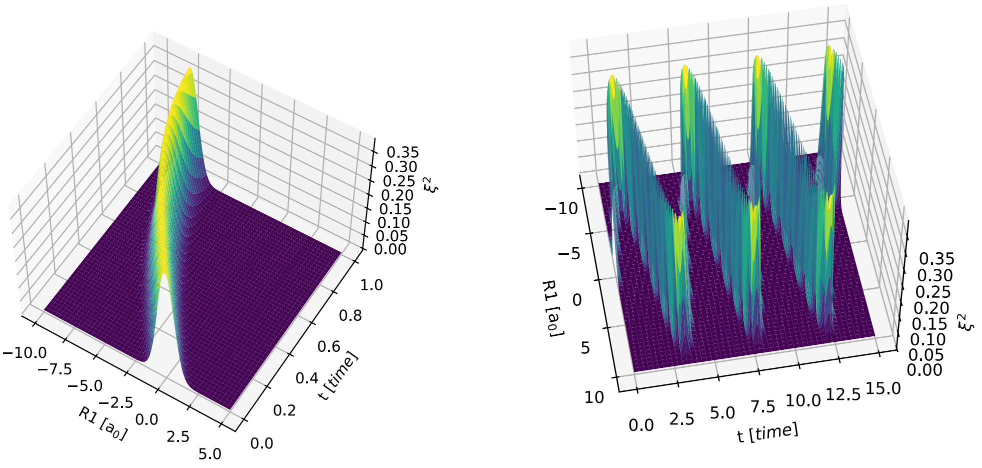
This is a solution $\forall \varphi \in \mathbb{R}$. Now all that rests is calculating the integral over the Lagrangian.

$$\begin{aligned}\int_0^t L(\zeta,\dot{\zeta},t')dt' &= \int_0^t \left[-\frac{m}{4}\dot{\zeta}^2 + qe^{-\kappa h}\left(\frac{\ell\kappa}{h^3}\zeta^2 - \frac{2\theta_0\sin(\omega t')}{h^3}\zeta\right)\right]dt' \\ &= \int_0^t \frac{3\theta_0^2 q^2 e^{-2\kappa h}}{mh^6(\omega_R^2-\omega^2)^2}\left(3\omega^2\sin^2(\omega t') - \omega^2 + \omega_R\sin^2(\omega t)\right)dt' \\ &= \frac{3\theta_0^2 q^2 e^{-2\kappa h}}{4mh^6(\omega_R^2-\omega^2)}\left(2t - \frac{3\omega^2+\omega_R\sin(2\omega t)}{\omega(\omega_R^2-\omega^2)}\right)\end{aligned} \tag{4.57}$$

Here $T = \frac{2\pi}{\omega}$ is the period of the oscillation of the dipole. We can now read off our quasi-energies to be $\epsilon_\alpha = \hbar\omega_R(\alpha+\frac{1}{2}) - \frac{3\theta_0^2 q^2 e^{-2\kappa h}}{4mh^6(\omega_R^2-\omega^2)}$. Reversing all the unitary transformations, we finally get the wavefunction that solves our Schrödinger equation.

$$\xi(R,t)_n = H_n(R-\zeta(t))\exp\left\{\frac{i}{\hbar}\left[m\dot{\zeta}(t)(R-\zeta(t)) + \left(\int_0^t Ldt' - \frac{t}{T}\int_0^T Ldt'\right)\right]\right\} \tag{4.58}$$

The magnitude squared of the wavefunction can be seen in figure 4.2. It is important to note that, while ω_R is an important frequency in determining the amplitude of the oscillation of the electrons, the electrons still oscillate with the characteristic frequency of the dipole ω.



(a) Close-up view of the wavefunction on a timescale smaller than a single dipole oscillation

(b) View of the wavefunction on a timescale on the order of several dipole oscillations

Figure 4.2: Wavefunction of the centre of mass of two electrons interacting with a dipole. The wavefunction oscillates with the dipole, and the amplitude of the oscillations increases with time.

Relative electron motion

The spatial part $\chi(r)$ can be treated as a perturbed harmonic oscillator. For $\chi(r)$ we have the differential equation

$$\left(\frac{\ell\kappa r^2}{4h^3} + \frac{1}{|r|}e^{-\kappa|r|} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial r^2}\chi(r)\right) = E\chi(r) \tag{4.59}$$

The potential term in this equation is shown in figure 4.3

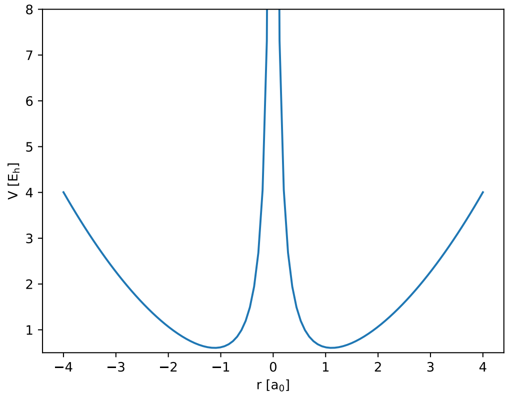
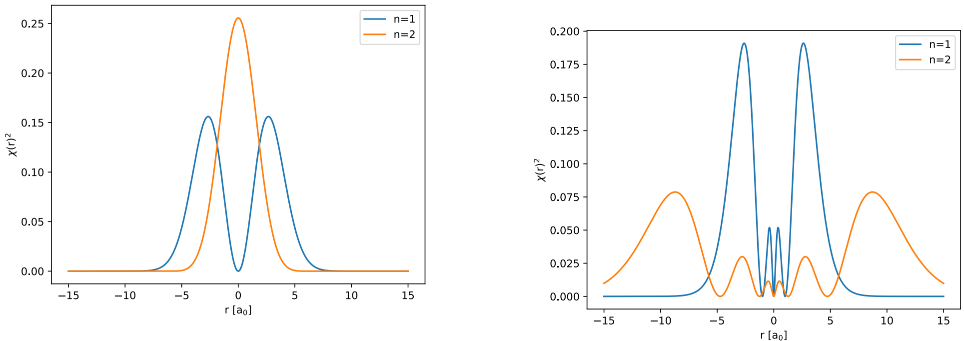


Figure 4.3: The potential for a particle in a harmonic oscillator potential with a Coulombic repulsion. This is equivalent to the 1-dimensional Hydrogen atom in a harmonic oscillator. It can be seen the repulsion dominates for small r, and the harmonic oscillator potential dominates for large r.

For small r, the $\frac{1}{|r|}$ term dominates. For large r, the $\frac{\ell\kappa r^2}{4h^3}$ term dominates. To find a solution to this equation, we consider the limits $r \to 0$ and $r \to \infty$. For $r \to 0$, we find the equation

$$\left(\frac{1}{|r|} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial r^2}\right)\chi(r) = E\chi(r) \tag{4.60}$$

This is equivalent to the model of the 1-Dimensional Hydrogen atom, and can be solved



(a) For large r, the harmonic oscillator term dominates, leading to the wavefunction displayed here

(b) r small

Figure 4.4: For small r, the Coulombic repulsion dominates, leading to the wavefunction displayed here, where it is impossible for the electrons to have the same position.

exactly, as shown by Loudon [23]. This leads to wavefunctions of the form

$$\exp\left(\frac{-|r|}{na_0}\right)L_n^1\left(\frac{2|r|}{na_0}\right)|r| \tag{4.61}$$

Here L_n^1 are the generalized Laguerre polynomials. For an explanation of these polynomials, see appendix A For $r \to \infty$, we find the equation

$$\left(\frac{\ell\kappa r^2}{4h^3} - \frac{\hbar^2}{m}\frac{\partial^2}{\partial r^2}\right)\chi(r) = E\chi(r) \tag{4.62}$$

Which is a simple harmonic oscillator again. The solutions to this are the Hermite polynomials times an exponential decay factor. This gives

$$\chi(r) = H_n\left(r\sqrt{\frac{m\omega_r}{\hbar}}\right)e^{-m\omega_r r^2/2\hbar} \tag{4.63}$$

This wavefunction is displayed in figure 4.4.Here the characteristic frequency ω_r is given by the following expression:

$$\omega_r = \sqrt{\frac{\ell\kappa}{mh^3}} \tag{4.64}$$

This completes the picture of the relative position of the electrons. The most important takeaway is the in this situation, the electrons still can't be at the same place, and their relative position is time-independent.

Full solution

We end up with a full wavefunction $\psi(R, r, t) = \xi(R, t)\chi(r)$. Here $\xi(R, t)$ is a Floquet mode, and $\chi(r)$ is a perturbed harmonic oscillator. We see that under our assumptions, the centre of mass of the electrons change through time, while the relative position of the electrons is static.

In our solution, we have two important characteristic frequencies. ω, the characteristic frequency of the dipole, represents how quickly the dipole oscillates back and forth due to the external electric field. It depends on the strength of the external electric field as well as the dipole's properties. ω_R is the natural frequency of the centre of mass of the electrons. This represents at what frequencies we would expect effects characteristic of resonance to occur, and depends on properties of the solid the electrons are in, such as the screening constant κ and the lateral distance to the dipole h, as well as the dipole's properties. From equation 4.57, it can be seen that the closer these frequencies, the stronger they resonate and the stronger the effect of the dipole is on the electrons. To get an idea of the timescales of these frequencies, and to see whether they can be brought close to each other, we fill in some common values for the parameters. We take $h = 10\mathrm{a}_0$, $\mathrm{E}_{\mathrm{ext}} = 10^{-9}\mathrm{E}_\mathrm{h}/e^+\mathrm{a}_0$, $\kappa = 1\mathrm{a}_0^{-1}$, $\ell = 0.5\mathrm{a}_0$, and $m = m_e$. We find

$$\begin{aligned} \omega_R &\approx 3.013 \cdot 10^{-4}\mathrm{E}_\mathrm{h}\hbar^{-1} = 12.46\mathrm{THz} \\ \omega &\approx 6.325 \cdot 10^{-5}\mathrm{E}_\mathrm{h}\hbar^{-1} = 2.615\mathrm{THz} \end{aligned} \tag{4.65}$$

The large difference in these values shows we don't expect resonance between to occur under these conditions. However, upon inspection of equations 4.15 and 4.55, it is apparent that the dipole's frequency has a dependence on the strength of the external electric field that does not appear in that of the electrons. This would mean that by using an electric field strength of approximately $2.27\dot{1}0^{-8}\mathrm{E_h}/e^{+}\mathrm{a_0}$, resonance would occur. In general, resonance should occur when

$$\omega_R = \omega \implies \mathrm{E_{ext}} = 2e^{-\kappa h}\frac{\kappa \ell^2}{h^3} \tag{4.66}$$

This should be experimentally verifiable, as it has a significant effect on the behaviour of the electrons.

4.3. Discussion

We have found a solution to the Schrödinger equation for a system of two electrons interacting near a dipole. We have made the assumptions that the electrons are far from the dipole relative to their distance from each other. Furthermore, we have assumed that the influence of the electron's electric field on the dipole is negligible, except for causing a tiny perturbation resulting in the dipole oscillating. Under these assumptions, we can see that the electrons don't move relative to each other, and their centre of mass follows a Floquet state, oscillating around the dipole. This is interesting behaviour, but further research is needed to determine whether this could lead to superconductivity.

Experimental research into the response to an electric field applied to this structure could be used to verify this theory and show whether the assumptions made are valid. Further theoretical research could be done to determine the behaviour of the electrons under different conditions. Dropping the restriction of movement along one axis could lead to interesting results. To more accurately describe the environment the electrons would be in in practice, a model of a periodic lattice of dipoles could be used.

Another important note to make is that despite the assumption that $h \gg x_i$, the resulting wavefunctions has the electrons most commonly at places with $x_i \gg h$. This might point to a flaw in the model, and should be explored further. This could be done by dropping this assumption. By experimentally testing what happens at electric field strengths matching resonance, it should be possible to check the validity of this model.

5

Conclusion

This thesis set out to explore whether ferroelectric heterostructures can mediate an electron-electron interaction strong enough to induce superconductivity. A theoretical model was constructed to describe such a heterostructure, focusing on the interactions between two electrons and a dipole. Two different approaches were analyzed: a static model in which the dipole responds instantaneously to the local electric field, and a dynamic model where the dipole exhibits inertia and oscillates in response to an external driving field.

In the static case, it was found that the dipole-mediated interaction can, under specific conditions, generate an attractive force between electrons. However, achieving bound states required the electrons to be sufficiently close to the dipole, necessitating small lattice constants that are typically only attainable under extreme pressures. These results suggest that dipole interactions alone may be insufficient to induce superconductivity under standard conditions but could play a role in exotic condensed matter systems.

The dynamic model introduced a time-dependent Schrödinger equation, which was solved using Floquet theory. The analysis demonstrated that electron motion in such a system follows a Floquet state, where the center of mass oscillates due to the dipole's periodic motion. Importantly, it was shown that resonance effects can amplify these oscillations when the dipole's natural frequency matches that of the electron system. This suggests a possible mechanism by which dipole interactions could influence electron pairing dynamics, though further work is needed to establish whether this effect could lead to superconducting behavior.

The findings of this thesis open several avenues for future research. Experimentally, direct observation of the predicted dipole-mediated interactions and their dependence on lattice constants would be crucial to validating the model. Additionally, extending the theoretical framework to include more complex many-body interactions and realistic material parameters could provide a clearer picture of whether these interactions can contribute to unconventional superconductivity. Another promising direction is the exploration of heterostructures where the dipole itself is quantum mechanical rather than classical, potentially leading to enhanced coupling effects.

While the results do not provide definitive evidence for superconductivity in these systems, they contribute to the broader understanding of how ferroelectric and superconducting properties can interplay. As material synthesis techniques continue to advance, heterostructures with tunable dipole-electron interactions could become an important platform for engineering novel quantum phases, including possible new routes to superconductivity.

A

Appendix: Orthogonal polynomials

In this appendix, a summary of orthogonal sets of polynomials is given. Orthogonal polynomials are a special class of polynomials that form a basis for function spaces and have the property of being mutually perpendicular under a given inner product. This property makes them useful in many areas of mathematical physics, numerical analysis, and engineering. They occur in many quantum mechanical problems as solutions for wave equations.

A.1. Definition and Key Properties

A set of polynomials $\{P_n(x)\}$ is said to be orthogonal with respect to a weight function $w(x)$ over an interval $[a, b]$ if they satisfy the condition

$$\int_a^b P_n(x)P_m(x)w(x)dx = \delta_{nm} \tag{A.1}$$

Here δ_{nm} is the Kronecker delta function. These polynomials often appear as solutions to simple quantum mechanical systems, and are useful in solving more complicated systems.

A.2. Examples

The best-known sets of orthogonal polynomials are the Legendre, Hermite, Laguerre, and Chebyshev polynomials. In this thesis, the Laguerre and Hermite polynomials are of particular importance.

A.2.1. Hermite polynomials

The Hermite polynomials, denoted $H_n(x)$ are an important as of orthogonal polynomials, as they appear in the solution of one of the most fundamental quantum mechanical systems, the quantum harmonic oscillator [16]. They are orthogonal with respect to the weight function $w(x) = e^{-x^2}$ over the interval $(-\infty, \infty)$. The first few Hermite polynomials are.

$$H_0(x) = 1 \tag{A.2}$$
$$H_1(x) = 2x \tag{A.3}$$
$$H_2(x) = 4x^2 - 2 \tag{A.4}$$
$$H_3(x) = 8x^3 - 12x \tag{A.5}$$

They are used to define Hermite functions, which are the solutions to the quantum harmonic oscillator. These are given by

$$\phi_n(x) = (2^n n! \sqrt{\pi})^{-1/2} e^{-x^2/2} H_n(x) \tag{A.6}$$

These also appear in the solution for the electron-dipole system discussed in this thesis, as Floquet theory was used to reduce that system to a quantum harmonic oscillator.

A.2.2. Laguerre polynomials

The Laguerre polynomials, denoted $L_n(x)$ are another important set of orthogonal polynomials. They are orthogonal with respect to the weight function $w(x) = e^{-x}$ over the interval $[0, \infty)$. They are defined recursively from $L_0(x) = 1$ and $L_1(x) = 1 - x$. The Laguerre polynomials can be generalized by defining $L_1^\alpha(x) = 1 + \alpha - x$. The first few generalized Laguerre polynomials are

$$L_0^\alpha(x) = 1 \tag{A.7}$$
$$L_1^\alpha(x) = 1 + \alpha - x \tag{A.8}$$
$$L_2^\alpha(x) = \frac{1}{2}(x^2 - 2(\alpha + 2)x + (\alpha + 1)(\alpha + 2)) \tag{A.9}$$
$$\tag{A.10}$$

The generalized Laguerre polynomials appear as a solution to the one-dimensional Hydrogen atom [23], with $\alpha = 1$. This solution appears in this thesis for the behaviour of the relative motion of the electron in chapter 4.

References

[1] H.K. Onnes. “The Superconductivity of Mercury”. In: *Comm. Phys. Lab. Univ., Leiden* (1911), pp. 122–124.

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. “Theory of Superconductivity”. In: *Phys. Rev.* 108 (5 Dec. 1957), pp. 1175–1204. DOI: `10.1103/PhysRev.108.1175`. URL: `https://link.aps.org/doi/10.1103/PhysRev.108.1175`.

[3] Xiangyu Hua et al. *Superconducting stripes induced by ferromagnetic proximity in an oxide heterostructure.* 2024. arXiv: `2402.16022 [cond-mat.supr-con]`. URL: `https://arxiv.org/abs/2402.16022`.

[4] Ranran Cai, Igor Žutić, and Wei Han. “Superconductor/Ferromagnet Heterostructures: A Platform for Superconducting Spintronics and Quantum Computation”. In: *Advanced Quantum Technologies* 6.1 (2023), p. 2200080. DOI: `https://doi.org/10.1002/qute.202200080`. eprint: `https://onlinelibrary.wiley.com/doi/pdf/10.1002/qute.202200080`. URL: `https://onlinelibrary.wiley.com/doi/abs/10.1002/qute.202200080`.

[5] M. Tinkham. *Introduction to Superconductivity.* 2nd ed. Dover, 1996.

[6] Richard P Feynman, Robert B Leighton, and Matthew Sands. *The Feynman lectures on physics, vol. III.* London, England: Basic Books, Oct. 2011.

[7] P.G. de Gennes. *Superconductivity in metals and alloys.* 1st ed. Westview press, 1966.

[8] R. Parks. *Superconductivity.* 1st ed. Marcel Dekker, 1969.

[9] Manfred Sigrist. “Introduction to Unconventional Superconductivity”. In: *AIP Conference Proceedings* 789 (Sept. 2005). DOI: `10.1063/1.2080350`.

[10] Yassine Slimani and Essia Hannachi, eds. *Superconducting materials.* en. 2022nd ed. Singapore, Singapore: Springer, May 2022.

[11] Songqing Zhang et al. “Two-dimensional heterostructures and their device applications: progress, challenges and opportunities—review”. In: *Journal of Physics D: Applied Physics* 54 (Aug. 2021), p. 433001. DOI: `10.1088/1361-6463/ac16a4`.

[12] C G Smith. “Low-dimensional quantum devices”. In: *Reports on Progress in Physics* 59.2 (Feb. 1996), p. 235. DOI: `10.1088/0034-4885/59/2/003`. URL: `https://dx.doi.org/10.1088/0034-4885/59/2/003`.

[13] D.J. Griffiths. *Introduction to Electrodynamics.* 4th ed. Pearson Education, 2017.

[14] N.W. Ashcroft and N.D. Mermin. *Solid state physics.* 2003.

[15] Hideki Yukawa. “On the Interaction of Elementary Particles. I”. In: *Progress of Theoretical Physics Supplement* 1 (Jan. 1955), pp. 1–10. ISSN: 0375-9687.

[16] D.J. Griffiths and D.F. Schroeter. *Introduction to Quantum Mechanics*. 3rd ed. Pearson Education, 2018.

[17] *ElementData*. Wolfram Research. 2014. URL: `https://reference.wolfram.com/language/ref/ElementData.html` (visited on 11/19/2024).

[18] J.R. Taylor. *Classical Mechanics*. 1st ed. University Science Books, 2005.

[19] K. Viebahn. *Introduction to Floquet theory*. Nov. 2020.

[20] G. Teschl. *Ordinary Differential Equations and Dynamical Systems*. 1st ed. American Mathematical Society, 2012.

[21] C. Axline. *Building Blocks for Modular Circuit QED Quantum Computing*. 2018.

[22] Thomas Dittrich et al. *Quantum Transport and Dissipation*. Jan. 1998. Chap. 5.

[23] Rodney Loudon. "One-dimensional hydrogen atom". In: *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 472.2185 (Jan. 2016), p. 20150534. DOI: `10.1098/rspa.2015.0534`.