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Formulation of Model Problem for Chirality Induced Spin Selectivity Effect

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Abstract

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Spin dependent electron transport in chiral molecules, the so-called chirality induced spin selectivity (CISS) effect, have attracted much attention over the past few years. Experimentally the spin polarization has been detected, and there is a theoretical consensus on the necessity of both spin-orbit coupling and geometrical helicity in order to get a non-vanishing spin polarization. Several model Hamiltonians has been proposed to describe the CISSS effect, and while they can yield spin polarization agreeing with the experimentally observed magnitudes, they are relying on unrealistic values of the spin orbit interaction parameters. In recent years the importance of electron correlation has been emphasized. Thus, this thesis presents the general theory on how to treat the CISS effect as a many body problem, taking electron correlation into account. The Hamiltonian modelling is described and one approach on how to treat the helical structure of the molecule and the spin-orbit coupling is presented. Building on this thesis, further studies will hopefully lead to a first principle understanding of the CISS effect.

Populärvetenskaplig sammanfattning

CISS, kort för chirality induced spin selectivity, är ett fenomen som uppstår när elektroner transporteras genom så kallade kirala molekyler, t.ex. en helix. Elektroner har en inneboende egenskap, spin, som kan vara riktad antingen upp eller ner i någon riktning. I vanliga fall prioriteras ingen av riktningarna över den andra när elektroner transporteras genom något medium, men i fallet med kirala molekyler har man uppmätt att den ena av spinnriktningarna prioriteras över den andra.

Då detta fenomen relativt nyligen upptäcktes har man ännu ingen fulländad förklaring till varför det sker. Forskare världen över är överens om vissa kriterier, så som helicitet och spinn-bankoppling, som måste vara närvarande för att få en spinn-polariserad ström. Ett sätt man tror ska leda till en bättre förklaring är genom att modellera molekylen med en flerkroppsmodell där man tar hänsyn till växelförhållanden mellan flera elektroner samtidigt. Detta är nödvändigt då den ömsesidig påverkan mellan elektroner förändrar elektronernas möjliga energinivåer.

Den här rapporten behandlar CISS fenomenet som ett flerkroppsproblem. Den grundläggande kvantmekaniska teorin för att förstå fenomenet tas upp och ett sätt att modellera molekylen beskrivs. Den här rapporten är inte något färdigt arbete i den mening att fenomenet förklaras till fullo, utan ska snarare betraktas som ett inledande steg i riktningen mot en fullständig teori.

Contents

1 Introduction

1.1 Background

The capability of chiral molecules to spin-polarize electrons has been named chirality induced spin selectivity (CISS). When electrons are transported through chiral molecules, one spin direction is preferred above the other. Which spin direction that is preferred depends on the chirality of the molecule and on the direction of motion. There is a general understanding of what causes the spin polarization, e.g. the necessity of chirality and so-called spin orbit coupling. However, the CISS effect still lacks a first principle understanding.

A chiral molecule is a molecule that can be distinguished from its mirror image. Thus, chiral molecules come in pairs. The only thing separating the two molecules from each other is the three dimensional spatial arrangement of the atoms. One example of a chiral object outside the molecular world is the human hand. One of the hands can never be made to coincide with its own mirror image with translations and rotations alone. But many organic molecules are also chiral, making the CISS effect relevant for many biophysical processes such as electron conduction through helical proteins. Helices can be either left handed or right handed, with the handedness being determined by the right hand rule. Helices are also chiral, with the convention in this thesis being positive (negative) chirality corresponding to right (left) handed helicity.

The ability of chiral molecules to spin-polarize electrons was first reported in 1999 [1]. Since then, numerous experimental studies have been conducted and many theories with model Hamiltonians have been proposed. However, there is not a theoretical consensus on how to explain the phenomenon yet. Although theories based on model Hamiltonians are able to explain the spin polarization qualitatively, they rely on unrealistic values of the spin-orbit interaction parameters. Considering the importance of electron correlations has been suggested as a way to address this problem.

1.2 Project Description

This project aims to study the CISS effect as a many-body problem taking electron correlation into account. One approach on how to model the molecule and the Hamiltonian describing the different interactions is pre-

sented. By doing this a model Hamiltonian for the CISS effect is formulated, from which the equations of motion are calculated. This thesis thus presents a first step towards what eventually is a theoretical first principle understanding of the CISS effect.

The thesis is structured as follows: (i) first, the fundamental theory of quantum physics, as relevant to this paper, is derived and described. (ii) the theory is demonstrated on a simplified Hamiltonian consisting of only two sites. It is important to note that this Hamiltonian is not relevant for the CISS phenomenon since it neither accounts for the chirality nor the spin-orbit interactions. However, it serves a purpose as an illustrative example of how to interpret the model and what it means to solve the system. This is followed up by (iii), a more rigorous description and derivation of the CISS Hamiltonian in the second quantization formalism. Lastly, (iv), the CISS Hamiltonian is expanded in terms of Hubbard operators and and the Heisenberg equation of motion is calculated.

2 Theory

2.1 Postulates of quantum mechanics

In classical mechanics, the total energy of system can be determined by the sum of all kinetic energies $\frac{p^2}{2m}$ plus all potential energies $V(\bar{r})$. If these values are known for every part of the system at all times, one knows how the system will evolve in time. In quantum mechanics on the other hand, the Heisenberg uncertainty principle tells us that both the position and momentum of a particle cannot be determined with certainty at the same time. This forces us to deal with probabilities, and to not consider a particle as a geometric point, but rather as an entity spread out in space. All quantum systems are represented by a wave function, denoted ψ, from which all measurable information about the system can be obtained. The mathematical framework of quantum mechanics is then built around the concept of operators. To get information about a system, so-called operators are used, working on the wave function. The quantum analogue of the classical way of determining the energy of a system is the Hamiltonian operator, $\hat{H}$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\bar{r}, t) \tag{2.1}$$

where $\frac{-\hbar^2}{2m}\nabla^2$ is the kinetic energy and $V(\bar{r}, t)$ can be any potential. In the Dirac formalism of quantum mechanics, the Hamiltonian is an operator in Hilbert space, a complex vector space spanned by the eigenkets, $|\phi\rangle$, of the Hamiltonian. The spectrum of allowed energy levels of the system is given by the set of eigenvalues, E_i, solving the equation,

$$\hat{H}|\phi_i\rangle = E_i|\phi_i\rangle \tag{2.2}$$

One of the postulates of quantum mechanics is that any observable, e.g. any quantity that can be observed in a physical experiment, can be represented by a self-adjoint linear (Hermitian) operator. Hermitian operators always have real eigenvalues, in accordance with them being operators corresponding to observables. Before a measurement has been made, the system is described by its wave function which can be expanded in terms of its eigenstates,

$$|\psi\rangle = \sum_i c_i|\phi_i\rangle \tag{2.3}$$

An operator acting on the wave function, initially a superposition of eigenstates, causes the wave function to collapse into one of its eigenstates. Since the eigenstates are orthonormal, i.e., $\langle\phi_i|\phi_j\rangle = \delta_{i,j}$, the coefficients $c_i = \langle\phi_i|\psi\rangle$ can be found. Hence equation 2.3 can be rewritten,

$$|\psi\rangle = \sum_i \langle\phi_i|\psi\rangle |\phi_i\rangle = \sum_i |\phi_i\rangle\langle\phi_i| |\psi\rangle \tag{2.4}$$

from which one can conclude that,

$$\sum_i |\phi_i\rangle\langle\phi_i| = 1 \tag{2.5}$$

This is known as the completeness relation, implying that a wave function representing any physical system can be expressed as a linear combination of the eigenkets of any observable of the system. The completeness relation can be used to derive matrix representations of any operator. By inserting the completeness twice, for an arbitrary operator $\hat{O}$, the operator can be written as,

$$\hat{O} = \sum_{i,j} |\phi_i\rangle\langle\phi_i| \hat{O} |\phi_j\rangle\langle\phi_j| \tag{2.6}$$

Altogether, there are N^2 numbers of form $\langle\phi_i|\hat{O}|\phi_j\rangle$ where N is the dimensionality of the ket space. By arranging these numbers in a square matrix, with row indices corresponding to i and column indices corresponding to j, the operator $\hat{O}$ can be represented by the matrix

$$\hat{O} \doteq \begin{pmatrix} \langle\phi_1|\hat{O}|\phi_1\rangle & \langle\phi_1|\hat{O}|\phi_2\rangle & \cdots \\ \langle\phi_2|\hat{O}|\phi_1\rangle & \langle\phi_2|\hat{O}|\phi_2\rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{2.7}$$

2.2 Spin and classification of particles

The electron has three intrinsic properties, mass, charge and spin. These properties can be seen as internal states of the electron that does not depend on the position or motion in space. Unlike the scalars mass and charge, spin has a direction. When measuring the spin of an electron in any spatial direction, one always obtain one of two values, $\frac{\hbar}{2}$ or $\frac{-\hbar}{2}$. These values are the eigenvalues of the spin operator $\hat{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ where $\boldsymbol{\sigma}$ is the Pauli matrices σ_x, σ_y and σ_z defined as,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & \text{-}i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.8}$$

The above matrices are only valid for spin $\frac{1}{2}$-particles.

All fundamental particles in nature can be divided into one of two categories, fermions and bosons. Fermions are particles with half integer spin ($\frac{1}{2}, \frac{3}{2}$...) and bosons are particles with integer spin (1, 2...). Thus, electrons, the particle of interest in this study can thus be categorized into the group of fermions. Fermions and bosons behave completely different in many situations. One example being the Pauli exclusion principle which applies to fermions but not to bosons. It states that, in any quantum system, two fermions cannot occupy the same quantum state.

2.3 Identical Particles

Another fundamental property that distinguishes fermions from bosons can be seen when studying systems of many identical particles. In classical physics it is possible to keep track of individual particles even tough they

may look alike. In quantum physics, all the elementary particles, are indistinguishable, meaning they can not even in principle be distinguished from each other. As a consequence of this, for a two electron system where the electrons are restricted to only occupy one of two states, it is impossible to tell if electron 1 is in state $|\phi_i\rangle$ and electron 2 in state $|\phi_j\rangle$ or vice versa. By measurements one can only find out that there is one electron in each state. If the two cases are equally probable, the wave function for the two electrons can be written as,

$$\psi = \frac{1}{\sqrt{2}} \left(|\phi_i\rangle |\phi_j\rangle - |\phi_j\rangle |\phi_i\rangle \right) \tag{2.9}$$

from which one can see that if the states $|\phi_i\rangle$ and $|\phi_2\rangle$ are equal, the wave function is zero. This is the Pauli exclusion principle once again, forcing the negative sign to be present in equation 2.9. This can be understood by the following argument. Suppose that the state of the electrons initially is measured to be electron 1 in state $|\phi_i\rangle$ and electron 2 in state $|\phi_j\rangle$, having the wave function $\psi_{ij} = |\phi_i\rangle |\phi_j\rangle$. At a later measurement, the two electrons states interchange, resulting in a new wave function $\psi_{ji} = |\phi_j\rangle |\phi_i\rangle$. Because the two electrons are indistinguishable, wave functions for the two different possible measurements must be equal, meaning $\psi_{ij} = -\psi_{ji}$. This holds for any fermionic wave function, also for more than two particle systems. All fermionic wave functions must be antisymmetric under the exchange of any two fermions. For bosons on the other, the wave functions are symmetric under such a exchange of identical particles.

2.4   Schrödinger vs Heisenberg picture

The first representation of quantum physics most people learn when first encountering the subject is the Schrödinger picture. In the Schrödinger picture quantum systems evolve in time by time dependence of the state vectors, while operators remain unchanged. Recall the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle \tag{2.10}$$

with the solutions

$$|\psi(t)\rangle = \exp\left\{ -\frac{iH}{\hbar}(t - t_0) \right\} |\psi(t_0)\rangle \tag{2.11}$$

From the solution above, the factor in front of the ket on the right hand side is called the *time evolution operator*, denoted $\mathcal{U}$. It is an unitary operator, meaning

$$\mathcal{U}\mathcal{U}^\dagger = \mathcal{U}^\dagger\mathcal{U} = \mathbb{1} \tag{2.12}$$

The expectation value of an arbitrary operator $\hat{A}_S$ in the Schrödinger picture can be written as

$$\langle\psi(t)\,|\,\hat{A}_S\,|\,\psi(t)\rangle \tag{2.13}$$

which according to equation 2.11 and with the definition of $\mathcal{U}$ is the same as

$$\langle\psi(0)\,|\,\mathcal{U}^\dagger\hat{A}_S\mathcal{U}\,|\,\psi(0)\rangle \tag{2.14}$$

where $t_0 = 0$ has been set. The above equation describes the expectation value of an operator, in a representation where the wave function is stationary. Hence, the Heisenberg operator can be defined, in terms of the corresponding Schrödinger operator as

$$\hat{A}_H = \mathcal{U}^\dagger\hat{A}_S\mathcal{U} \tag{2.15}$$

This is a new representation, the Heisenberg picture, where the time dependence is included in the operators. This picture exists solely thanks to the Schrödinger picture, and does thus not provide any new information. It is simply a new way of thinking about dynamical systems, that often turns out to be quite effective. In both pictures, the eigenvalues are preserved. Using the product rule, one can by differentiating 2.15 and by using the definition of the time evolution operator, derive the Heisenberg equation of motion

$$i\hbar\frac{d\hat{A}_H}{dt} = \left[\hat{A}_H, H\right] + i\hbar\left(\frac{\partial\hat{A}_S}{\partial t}\right)_H \tag{2.16}$$

If the Schrödinger operator has no explicit time dependence, the Heisenberg equation of motion simplifies to

$$i\hbar\frac{d\hat{A}_H}{dt} = \left[\hat{A}_H, H\right] \tag{2.17}$$

which simply states that the time derivative of any Heisenberg operator is the commutator of that operator with the Hamiltonian. Operators commuting with the Hamiltonian, can thus be said to represent constants of motion.

3 Simplified model

Before beginning to describe the simplified Hamiltonian, it is once again important to emphasise that it is not relevant for the CISS phenomenon. It does only consist of two sites and it does not take helicity or SOC into account. The reason it is included is for illustrative purposes alone.

3.1 Hubbard operators

The Hamiltonian is expressed in terms of Hubbard operators. These operators are defined in terms of Dirac bra-ket notation operations in the space of eigenstates of the tight binding Hamiltonian.

$$X_{m,n}^{p,q} = |mp\rangle\langle nq| \tag{3.1}$$

They are in fact transition operators, with initial state $|n,q\rangle$ and final state $|m,p\rangle$. In this thesis, the subscript m,n are the site indices while the superscript p,q specifies the quantum state. Because the Hubbard operators are made of basis states of the Hamiltonian, the Hubbard operators obey orthogonality conditions,

$$X_{m,n}^{p,q} X_{i,j}^{r,s} = \delta_{n,i}\delta_{q,r} X_{m,j}^{p,s} \tag{3.2}$$

3.2 Eigenenergies and transition energies

The simplified Hamiltonian can then be expressed as,

$$\mathcal{H}_s = \sum_{\substack{m=1,2 \\ p=1,2}} E_{mp} X_{mm}^{pp} + \sum_{m=1,2} D\left(X_{mm}^{12} + X_{mm}^{21}\right) + \sum_{p=1,2} t\left(X_{12}^{pp} + X_{21}^{pp}\right) \tag{3.3}$$

where the first sum assigns the energy E_{mp} to electrons in state $|mp\rangle$. The second sum changes the spin state of the electron, while the last sum is the hopping terms, describing tunneling processes occurring with energy t. Using the Heisenberg equation of motion, for an operator $\hat{A}$ with no explicit time dependence, in natural units where $\hbar = 1$,

$$i\frac{\partial \hat{A}}{\partial t} = \left[\hat{A}, \hat{H}\right] \tag{3.4}$$

one can calculate the time evolution for the set of Hubbard operators X_{mn}^{pq}. By defining the vectors,

$$X_{mn} = \begin{pmatrix} X_{mn}^{11} \\ X_{mn}^{12} \\ X_{mn}^{21} \\ X_{mn}^{22} \end{pmatrix} \qquad m, n = 1, 2 \tag{3.5}$$

The resulting expressions can be written as,

$$
\begin{aligned}
i\partial_t X_{11} &= \mathcal{M}_{11} X_{11} + t\left(X_{12} - X_{21}\right) \\
i\partial_t X_{12} &= \mathcal{M}_{12} X_{12} + t\left(X_{11} - X_{22}\right) \\
i\partial_t X_{21} &= \mathcal{M}_{21} X_{21} + t\left(X_{22} - X_{11}\right) \\
i\partial_t X_{22} &= \mathcal{M}_{22} X_{22} + t\left(X_{21} - X_{12}\right)
\end{aligned}
\tag{3.6}
$$

where $\mathcal{M}_{mn}$ are the 4×4 matrices,

$$
\mathcal{M}_{11} = \begin{pmatrix} 0 & D & -D & 0 \\ D & \Delta_1 & 0 & -D \\ -D & 0 & -\Delta_1 & D \\ 0 & -D & D & 0 \end{pmatrix}
\qquad
\mathcal{M}_{12} = \begin{pmatrix} \Delta_3 & D & -D & 0 \\ D & \Delta_4 & 0 & -D \\ -D & 0 & \Delta_5 & D \\ 0 & -D & D & \Delta_6 \end{pmatrix}
$$

$$
\mathcal{M}_{21} = \begin{pmatrix} -\Delta_3 & D & -D & 0 \\ D & -\Delta_5 & 0 & -D \\ -D & 0 & -\Delta_4 & D \\ 0 & -D & D & -\Delta_6 \end{pmatrix}
\qquad
\mathcal{M}_{22} = \begin{pmatrix} 0 & D & -D & 0 \\ D & \Delta_2 & 0 & -D \\ -D & 0 & -\Delta_2 & D \\ 0 & -D & D & 0 \end{pmatrix}
\tag{3.7}
$$

and $\Delta_1 = E_{12} - E_{11}$, $\Delta_2 = E_{22} - E_{21}$, $\Delta_3 = E_{21} - E_{11}$, $\Delta_4 = E_{22} - E_{11}$, $\Delta_5 = E_{21} - E_{12}$ and $\Delta_6 = E_{22} - E_{12}$.

The expressions in equation 3.6 together with the vectors in 3.5 can be rewritten to a 16×16 matrix equation.

$$
\left[i\partial_t - \begin{pmatrix} \mathcal{M}_{11} & \mathbf{t} & -\mathbf{t} & \mathbf{0} \\ \mathbf{t} & \mathcal{M}_{12} & \mathbf{0} & -\mathbf{t} \\ -\mathbf{t} & \mathbf{0} & \mathcal{M}_{21} & \mathbf{t} \\ \mathbf{0} & -\mathbf{t} & \mathbf{t} & \mathcal{M}_{22} \end{pmatrix} \right] \begin{pmatrix} X_{11} \\ X_{12} \\ X_{21} \\ X_{22} \end{pmatrix} = 0 \tag{3.8}
$$

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where the bold $\boldsymbol{t} = t\mathbb{1}_{4\times4}$ and the bold $\boldsymbol{0}$:s are the 4×4 matrix of zeros. The above equation is close to an eigenvalue equation. Performing the Fourier transform $i\partial_t \iff Z$, with $Z \in \mathbb{C}$ obtains get the eigenvalue determinant. In Matlab, these eigenvalues are easily calculated, and they correspond to the energies for transitions between eigenstates. The eigenstate energies themselves are calculated by letting the Hamiltonian in equation 3.3 act on the general state consisting of a linear combination of the basis states. In accordance with equation 2.2, the eigenstates are the states which correspond to the same state, multiplied with a constant.

$$
\begin{aligned}
\hat{H} \left(\alpha_1 \ket{11} + \alpha_2 \ket{12} + \alpha_3 \ket{21} + \alpha_4 \ket{22} \right) = \\
\varepsilon \left(\alpha_1 \ket{11} + \alpha_2 \ket{12} + \alpha_3 \ket{21} + \alpha_4 \ket{22} \right)
\end{aligned}
\tag{3.9}
$$

Computing the state generated by letting the Hamiltonian work on the state above, enables us to write the determinant for determining the eigenenergies,

$$
\begin{vmatrix}
E_{11} - \varepsilon & D & t & 0 \\
D & E_{12} - \varepsilon & 0 & t \\
t & 0 & E_{21} - \varepsilon & D \\
0 & t & D & E_{22} - \varepsilon
\end{vmatrix} = 0
\tag{3.10}
$$

Calculating the transition energies 3.8 and the eigenenergies 3.10, by using Matlab verifies that the matrices are indeed correct. The eigenenergies are split by the exact values of the calculated transition energies. The splitting of the ground state energies E_{mp} is visualized in the energy level diagram below.
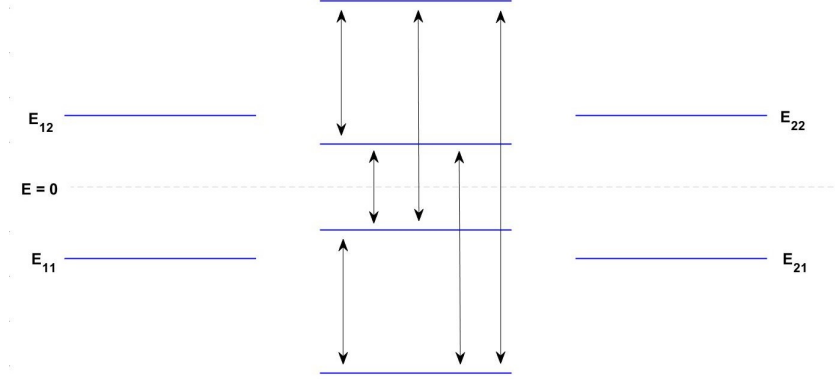
Figure 1: Illustrative spectrum for the simplified model Hamiltonian. The arrows demonstrate the transitions between the eigenstates. The two left- and rightmost energies are the unperturbed energy levels.

The parameter values used for the above figure 1 are in this case chosen such that the unperturbed energies corresponding to the same spin are degenerate. In addition, the unperturbed energies corresponding to different spins are chosen to be centered around zero. This does not necessarily have to be the case. Any set of parameter values, representing any physically possible situation, would result in correct energy calculations.

4   Model Hamiltonian

4.1   Tight Binding model

The molecule is modeled with a helical tight binding model, meaning that the electrons are restricted to fixed sites in a helical geometry. Each site can be represented by a wave function similar to the orbitals of an electron orbiting an atom. For a single isolated atom, the eigenvalues of the Hamiltonian are the atomic orbitals. When the atom is placed in a chain, together with other similar atoms the individual wave functions overlap, leading to coupling of the states. It is sufficient to make the assumption that only one atomic orbital is allowed per electron, and to label the atomic orbital for the electron sitting on atom m as $|m\rangle$. Further, the orbitals are assumed to be orthogonal to each other, e.g. $\langle n|m\rangle = \delta_{nm}$. This allows us to use these states as basis states for the many-body wave function as well.

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The electrons can be scattered by tunneling processes. Since the wave function of an electron stretches over multiple sites, there is a non-zeros probability to find the electron at neighbouring sites. This is allowed for by allowing an electron to tunnel from one orbital of one atom to another orbital of another atom. The energies t which governs this hopping is determined by the overlap of the two wave functions on the pair of atoms. Usually, one only allows hopping between adjacent sites, $t = \langle \phi_i | V | \phi_{i\pm1} \rangle$, since in the tight binding limit, the strength of these hopping integrals die off exponentially in space. Because all ionic sites in the molecule are equidistant, the magnitude of t is the same for all pairs of nearest neighbouring sites.

In addition to the hopping energies, there is on-site energy contribution ε for every electron and U if one site is doubly occupied. These two energies are analogue to the kinetic energy and Coulomb repulsion of electrons orbiting an atom. There are also next-nearest neighbours couplings due to the SOC.

4.2 Necessary conditions for CISS

There are two necessary conditions in order to get a spin polarized current, i.e for the CISS effect to occur. The electrons must be transported through a helical structure, and there must be a spin-orbit coupling (SOC). SOC can be seen as a magnetic field felt by the electrons, changing the energy eigenstates. This interaction can be understood qualitatively by considering the valence electron orbiting a hydrogen-like atom. The electron experiences a screened electric field due to the Coulomb interaction with the nucleus and the inner shell electrons. But whenever a moving charge is subjected to a electric field, it feels an effective magnetic field. This magnetic field is consequently an effect of the relative motion of the nucleus and the orbiting electron. In the rest frame of the electron, the nucleus creates a positive current loop, generating a magnetic field. Due to this magnetic field, the spin magnetic dipole moment of the electron experiences a torque, tending to orient it along the direction of the magnetic field. This changes the energy of the electron. [2] The SOC potential is of the form:

$$V_{SOC} = \frac{\hbar}{4m_0^2 c^2} \overline{\sigma} \cdot (\overline{p} \times \nabla V) \tag{4.1}$$

where σ is the spin operator and $V(\overline{r})$ is a helical potential experienced by the electrons. The quantum momentum operator is $\hat{p} = -i\hbar\nabla$. The energy of an electron in such a potential is eV_{SOC}, which in this thesis will

be modelled by the Hamiltonian $H_{SOC} = \lambda i V \bar{\sigma}$ where λ is the spin orbit interaction parameter. Though the effect of the SOC is small, it is non-negligible in many situations. Especially for the CISS effect, it has proven to play a crucial role. Without the SOC potential, there would be no spin polarized transport [3].

The exact values of the parameters E, U, t and λ, can be complicated to calculate. Usually, they are taken to be free parameters, such that one can adjust them to make them experimentally feasible.

4.3 Second quantization

One can consider a system with the Hamiltonian,

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{h}(\bar{r}_i), \qquad \hat{h}(\bar{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(\bar{r}_i) \tag{4.2}$$

This Hamiltonian consists of terms that each only involves the coordinates of one particle. Thus, the Hamiltonian $\hat{H}_0$ does not describe any interactions between particles, and is called a single-particle operator. This Hamiltonian could for example describe N electrons bound to atoms far apart from each other, such that they don't interact. If placing the atoms closer to each other causing them to interact, these interactions must be incorporated in the Hamiltonian. For example by including the many particle Hamiltonian, $\hat{H}_I$, in equation 4.2

$$\hat{H} = \hat{H}_0 + \hat{H}_I \tag{4.3}$$

where $\hat{H}_I$ is a Hamiltonian depending on more than the coordinates to only one particle and thus describes interactions. It is convenient to work with a basis in which the basis many-particle wave functions are eigenfunctions of the non-interacting Hamiltonian, $\hat{H}_0$. In this thesis, the molecule is modeled with a tight binding model in a helical geometry with the single particle eigenfunctions being the atomic orbitals. The eigenfunctions and the associated eigenvalues for $\hat{h}$ for every site in the molecule can then be written as

$$\hat{h}\phi_i = \varepsilon_i \phi_i \tag{4.4}$$

This provides us with an orthonormal and complete set of eigenvalues and eigenfunctions that can be used to expand the single particle wave functions

and construct many particle wave functions. An advantageous way to do this is to use the formalism of second quantization, or the occupation number formalism.

As mentioned in section 2.3, a many body fermionic wave function must bu antisymmetric under the exchange of any two fermions. In second quantization, this is taken care of by introducing the fermionic annihilation and creation operators, $\hat{c}_\lambda^\dagger$ and $\hat{c}_\lambda$, where λ are the set of all the single particle quantum numbers specifying the state. They are defined in such a way that they can add $(\hat{c}_\lambda^\dagger)$ or remove $(\hat{c}_\lambda)$ an electron from the many body system. These operators follow the anti-commutator relations:

$$\{\hat{c}_\lambda^\dagger, \hat{c}_\nu^\dagger\} = \{\hat{c}_\lambda, \hat{c}_\nu\} = 0, \qquad \{\hat{c}_\lambda, \hat{c}_\nu^\dagger\} = \delta_{\lambda,\nu} \tag{4.5}$$

from which one can see the Pauli exclusion principle in, $\{\hat{c}_\lambda^\dagger, \hat{c}_\lambda^\dagger\} = 2\hat{c}_\lambda^\dagger \hat{c}_\lambda^\dagger = 0$. No state λ can be occupied by more than one fermion.

In the second quantization formalism, the many particle state vector is defined as, $|n_{\lambda_1}, n_{\lambda_2}, ..., n_{\lambda_i}, ...\rangle$, where n_{λ_i} specify the number of particles in the state described by the quantum numbers λ_i. Thus, n_{λ_i} is called the number operator, and is defined as

$$n_{\lambda_i} = \hat{c}_{\lambda_i}^\dagger \hat{c}_{\lambda_i} \tag{4.6}$$

For fermions, each n_λ can because of the Pauli exclusion principle only take on the values 0 or 1. The state vectors are members of the Fock space $\mathcal{F}$. Any state vector in $\mathcal{F}$ can be constructed by letting the creation and annihilation operators work on the vacuum state, $|\mathbf{0}\rangle$, defined as $|\mathbf{0}\rangle = |0, 0, ...0, 0\rangle$. One has to pay attention to the order of operations, since operating in different orders may cause the resulting state vector to differ by a minus sign. For example,

$$\hat{c}_{\lambda_1}^\dagger \hat{c}_{\lambda_2}^\dagger |\mathbf{0}\rangle = \hat{c}_{\lambda_1}^\dagger |0, 1, 0, ...0\rangle = |1, 1, 0, ..., 0\rangle \tag{4.7}$$

while

$$\hat{c}_{\lambda_2}^\dagger \hat{c}_{\lambda_1}^\dagger |\mathbf{0}\rangle = \hat{c}_{\lambda_2}^\dagger |1, 0, ...0\rangle = -|1, 1, 0, ..., 0\rangle \tag{4.8}$$

because of the anticommutator relation in equation 4.5.

4.4 Field operators

Having defined the creation and annihilation operators, enables for converting operators from the first quantized notation to second quantization. This is done by introducing field operators, the analogue of the creation and annihilation operators previously described, but this time in real space. These are operators that can be interpreted as representing a fermionic field, hence the name field operators. For the single particle Hamiltonian with eigenfunctions ϕ_i as in equation 4.4 the field operators are,

$$\psi_\sigma = \sum_i \hat{c}_{i,\sigma} \phi_i \left| \sigma \right\rangle$$
$$\psi_\sigma^\dagger = \sum_i \hat{c}_{i,\sigma}^\dagger \left\langle \sigma \right| \phi_i^* \tag{4.9}$$

These are operators that creates or annihilates electrons with either spin up or spin down at well defined points in space. The field operators contain all eigenvalues and eigenfunctions from the single particle Hamiltonian, allowing us to rewrite the Hamiltonian in terms of these field operators.

$$\hat{H} = \sum_{\sigma,\,\sigma'} \int \psi_\sigma^\dagger(x) \hat{h} \psi_{\sigma'}(x) dx = \sum_{i,j,\sigma,\,\sigma'} \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma'} \int \phi_i^*(x) \hat{h} \phi_j(x) dx \left\langle \sigma | \sigma' \right\rangle \tag{4.10}$$

where i,j are the site indices. From equation 4.4 one can see that $\hat{h}\phi_j = \varepsilon_j \phi_j$. Also, $\left\langle \sigma | \sigma' \right\rangle = \delta_{\sigma,\sigma'}$ allow us to do further simplifications.

$$H = \sum_{i,j,\sigma} \varepsilon_j \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} \int \phi_i^*(x) \phi_j(x) dx \tag{4.11}$$

Assuming properly normalized eigenfunctions ϕ_i and ϕ_j the final expression for the single particle Hamiltonian in second quantization is

$$H = \sum_{i,\sigma} \varepsilon_i \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma} \tag{4.12}$$

This is the on site kinetic energy of the electrons in the final Hamiltonian for the CISS problem. In the next section the other parts of the Hamiltonian will be discussed. They will later be given in the second quantization notation, but the derivation from first to second quantization is done by a similar procedure to the one described above.

5 CISS model

5.1 CISS Hamiltonian

The CISS effect has been detected in chiral helical molecules. In this thesis, the generic molecular geometry is allowed for by ionic sites in a helical structure, in accordance with previous work [4].
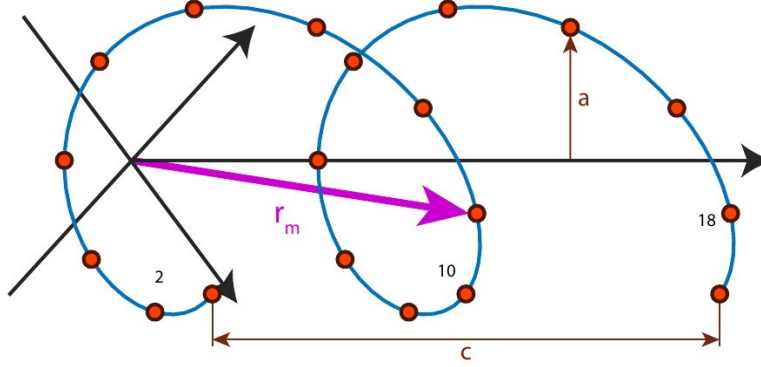

Figure 2: Sketch of the ionic sites in a helical molecule. With the convention used in this study, this molecule has negative chirality (left handed helicity).

The spatial vectors denoting the sites are defined by the following set of cylindrical coordinates,

$$\boldsymbol{r}_m = \left(a \cos \varphi_m, a \sin \varphi_m, (m-1)c/(MN-1)\right),$$
$$\varphi_m = (m-1)2\pi/N, \quad m = 1, ..., MN \tag{5.1}$$

where a is the radius and c is the length of the helix. M is the total number of laps, whereas N is the number of sites per lap, such that $\mathbb{M} = MN$ is the total number of sites. For every site, a pair of unit vectors can be defined, $\hat{\mathbf{d}}_{\mathbf{m+s}} = \left(\mathbf{r_m} - \mathbf{r_{m+s}}\right)/|\mathbf{r_m} - \mathbf{r_{m+s}}|$, for $s = \pm 1$. The vector $\hat{\mathbf{d}}$ is then a vector of length one pointing from the site $m + s$, to the site m. To define the chirality of the molecules, the vector $\mathbf{v_m^{(\pm)}} = \hat{\mathbf{d}}_{\mathbf{m+s}} \times \hat{\mathbf{d}}_{\mathbf{m+2s}}$ is introduced, where the superscript $\pm$ is determined by the chirality of the molecule, and tells what sign to assign s. This vector is used, together with the vector $\overline{\sigma}$ of Pauli matrices, in the SOC part of the CISS Hamiltonian to describe how the helicity influences the spin-orbit coupling in equation 4.1.

The Hamiltonian is defined in terms of the creation and annihilation spinors.

$$\Psi_m = \begin{pmatrix} \hat{c}_{m,\uparrow} \\ \hat{c}_{m,\downarrow} \end{pmatrix}, \qquad \Psi_m^\dagger = \begin{pmatrix} \hat{c}_{m,\uparrow}^\dagger & \hat{c}_{m,\downarrow}^\dagger \end{pmatrix} \tag{5.2}$$

A molecule with positive chirality comprising $\mathbb{M}$ sites can thus be modeled by the Hamiltonian

$$\begin{aligned}
\mathcal{H} = & \sum_{m=1}^{\mathbb{M}} \left(\epsilon_0 \Psi_m^\dagger \Psi_m + U \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} \right) - t \sum_{m=1}^{\mathbb{M}-1} \left(\Psi_m^\dagger \Psi_{m+1} + \mathbf{H.c.} \right) \\
& + \lambda i \sum_{m=1}^{\mathbb{M}-2} \left(\Psi_m^\dagger \boldsymbol{v_m^{(+)}} \cdot \boldsymbol{\sigma} \Psi_{m+2} + \mathbf{H.c} \right)
\end{aligned} \tag{5.3}$$

The first sum describes the on-site energies. The ε_0-term is the kinetic energy of the individual electrons at each site, and the energy U, due to Coulomb interaction between electrons, is added if the site is doubly occupied. Remark, $n_{m,\sigma}$ is the number operator, counting the number of electrons in each state. The second sum describes the electron hopping, with energy t, between nearest neighbouring sites. The term $\boldsymbol{H.c}$ stands for the Hermitian conjugate, and enables hopping to occur in both directions in the molecule. The final sum is the spin orbit coupling, that is picked up between next nearest neighbouring sites.

The dot product $\mathbf{v_m^{(+)}} \cdot \boldsymbol{\sigma}$ is to be interpreted as, dropping the superscript $(+)$ and the subscript m,

$$\mathbf{v_m^{(+)}} \cdot \boldsymbol{\sigma} = \mathbf{v_x}\sigma_{\mathbf{x}} + \mathbf{v_y}\sigma_{\mathbf{y}} + \mathbf{v_z}\sigma_{\mathbf{z}} = \begin{pmatrix} v_z & v_x - iv_y \\ v_x + iv_y & -v_z \end{pmatrix} \tag{5.4}$$

where $v_{x,y,z}$ are the x,y and z components of the vector defining the chirality and $\sigma_{x,y,z}$ are the Pauli spin matrices as in equation 2.8. Denoting $v_x \pm iv_y$ as $v^\pm$ in conformity with the definition of the ladder operators results in,

$$\tilde{V} = \begin{pmatrix} v_z & v^- \\ v^+ & -v_z \end{pmatrix} \tag{5.5}$$

This matrix displays the coupling between spin states, breaking the spin symmetry. The spin $\uparrow$ and spin $\downarrow$ states are coupled by the non-diagonal elements v^+ and v^-. To further analyze this model, reformulation of the Hamiltonian to get a conform way to treat the quantum states is needed.

5.2 Reformulation of Hamiltonian

Using the completeness relation,

$$\sum_p X^{pp} = 1$$

any operator, $\hat{Q}$, in the Hilbert space can be defined in terms of Hubbard operators,

$$\hat{Q} = \sum_{p,q} |p\rangle\langle p| \hat{Q} |q\rangle\langle q| = \langle p| \hat{Q} |q\rangle X^{pq} \tag{5.6}$$

where $\langle p| \hat{Q} |q\rangle$ are matrix elements for transitions from state q to state p. At each site in the molecule, the only four possible states are $|0\rangle, |\uparrow\rangle, |\downarrow\rangle$ or $|2\rangle$. By using a linear combination of these states as ket state $|q\rangle$ one can write the annihilation operator $\hat{c}_\uparrow$ matrix elements as:

$$\langle p| \hat{c}_\uparrow |q\rangle = \langle p| \hat{c}_\uparrow (|0\rangle + |\uparrow\rangle + |\downarrow\rangle + |2\rangle) = \langle p|0\rangle + \langle p| \downarrow\rangle \tag{5.7}$$

where two terms has been cut, $\hat{c}_\uparrow |0\rangle = \hat{c}_\uparrow |\downarrow\rangle = 0$ because of there being no $\uparrow$-electron to annihilate. Thus, only the matrix elements of $\hat{c}_\uparrow$ corresponding to the transitions $|\uparrow\rangle \rightarrow |0\rangle$ and $|2\rangle \rightarrow |\downarrow\rangle$ are non-zero. By similar means the non-zero matrix elements of $\hat{c}_\downarrow$ can be calculated. The Hubbard operator representation of the creation and annihilation operators is then

$$\begin{aligned}
\hat{c}_\uparrow &= X^{0\uparrow} + X^{\downarrow 2} &\implies& \quad \hat{c}_\uparrow^\dagger = X^{\uparrow 0} + X^{2\downarrow} \\
\hat{c}_\downarrow &= X^{0\downarrow} - X^{\uparrow 2} &\implies& \quad \hat{c}_\downarrow^\dagger = X^{\downarrow 0} - X^{2\uparrow}
\end{aligned} \tag{5.8}$$

where the minus sign assures the antisymmetry of the wave function. Consequently, the model can be rewritten in terms of Hubbard operators by expanding the Hamiltonian in 5.3. There are altogether four Hubbard operators of Fermi type in 5.8, and their Hermitian conjugates, making this an expansion to a four dimensional Hilbert space. A new basis for the Hilbert space is defined as,

$$X_m = \begin{pmatrix} X_m^{0\uparrow} \\ X_m^{0\downarrow} \\ X_m^{\downarrow 2} \\ X_m^{\uparrow 2} \end{pmatrix}, \qquad X_m^\dagger = \begin{pmatrix} X_m^{\uparrow 0} & X_m^{\downarrow 0} & X_m^{2\downarrow} & X_m^{2\uparrow} \end{pmatrix} \tag{5.9}$$

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Using the definitions of the number operator in 4.6 and the spinors in 5.2, the on-site ($\hat{H}_0$), tunneling ($\hat{H}_t$) and SOC ($\hat{H}_{SOC}$) parts of the Hamiltonian 5.3 can be expressed in terms of the creation and annihilation operators as

$$\hat{H}_0 = \sum_{m=1}^{\mathbb{M}} \varepsilon_0 \left(\hat{c}^\dagger_{m\uparrow} \hat{c}_{m\uparrow} + \hat{c}^\dagger_{m\downarrow} \hat{c}_{m\downarrow} \right) + U \hat{c}^\dagger_{m\uparrow} \hat{c}_{m\uparrow} \hat{c}^\dagger_{m\downarrow} \hat{c}_{m\downarrow}$$

$$\hat{H}_t = -t \sum_{m=1}^{\mathbb{M}-1} \left(\hat{c}^\dagger_{m\uparrow} \hat{c}_{m+1,\uparrow} + \hat{c}^\dagger_{m\downarrow} \hat{c}_{m+1,\downarrow} \right) + \mathbf{H.c}$$

$$\hat{H}_{SOC} = \lambda i \sum_{m=1}^{\mathbb{M}-2} \left(\hat{c}^\dagger_{m\uparrow} (v_z \hat{c}_{m+1,\uparrow} + v^- \hat{c}_{m+1,\downarrow}) + \hat{c}^\dagger_{m,\downarrow} (v^+ \hat{c}_{m+1,\uparrow} - v_z \hat{c}_{m+1,\downarrow}) \right) + \mathbf{H.c}$$

$$(5.10)$$

From the definition of tin 5.9 the above equations can be written on the form $X^\dagger_m A_{mn} X_n$ where A_{mn} are 4×4 matrix. Carrying out the algebra results in the following expressions

$$\hat{H}_0 = \sum_{m=1}^{\mathbb{M}} X^\dagger_m \mathcal{E} X_m + X^\dagger_m \mathcal{U} X_m$$

$$\hat{H}_t = \sum_{m=1}^{\mathbb{M}-1} X^\dagger_m \mathcal{T} X_{m+1} + X^\dagger_{m+1} \mathcal{T}^\dagger X_m \qquad (5.11)$$

$$\hat{H}_{SOC} = \sum_{m=1}^{\mathbb{M}-2} X^\dagger_m \mathcal{V} X_{m+2} + X^\dagger_{m+2} \mathcal{V}^\dagger X_m$$

where

$$\mathcal{E} = \varepsilon_0 \begin{pmatrix} \sigma_0 & \sigma_z \\ \sigma_z & \sigma_0 \end{pmatrix}, \qquad \mathcal{U} = \frac{U}{2} \begin{pmatrix} 0 & 0 \\ 0 & \sigma_0 \end{pmatrix}$$

$$(5.12)$$

$$\mathcal{T} = -t \begin{pmatrix} \sigma_0 & \sigma_z \\ \sigma_z & \sigma_0 \end{pmatrix}, \qquad \mathcal{V} = \lambda i \begin{pmatrix} \tilde{V} & \tilde{V}\sigma_z \\ \sigma_z\tilde{V} & \sigma_z\tilde{V}\sigma_z \end{pmatrix}$$

where σ_0 is the 2×2 identity matrix and $\tilde{V} = \mathbf{v_m^{(+)}} \cdot \boldsymbol{\sigma}$ as in equation 5.5. Although not explicitly spelled out, $\tilde{V}$ in the matrix above is site dependent, enforcing site dependence on the matrix $\mathcal{V}$ as well. It is also dependent on the direction in which the electrons are moving. Since all matrices are Hermitian,

the Hermitian conjugate on the matrices in 5.11 can be dropped. In the basis defined in equation 5.9 the number operator, $\hat{N}_m$, counting the number of electrons at site m, can be written as

$$\hat{N}_m = \begin{pmatrix} X_m^{\uparrow\uparrow} \\ X_m^{\downarrow\downarrow} \\ X_m^{22} \\ X_m^{22} \end{pmatrix} \tag{5.13}$$

Assuming the molecule consists of at least five sites, one can consider a fixed site i in the middle of the molecule. By keeping the orthogonality of the sites in mind, the equation of motion for the number operator $\hat{N}_i$ using equation 3.4 turns out to be

$$\begin{aligned} i\partial_t \hat{N}_i =& X_i^\dagger \mathcal{T} X_{i+1} + X_i^\dagger \mathcal{T} X_{i-1} - X_{i+1}^\dagger \mathcal{T} X_i - X_{i-1}^\dagger \mathcal{T} X_i \\ &+ X_i^\dagger \mathcal{V}_i^{(+)} X_{i+2} + X_i^\dagger \mathcal{V}_i^{(-)} X_{i-2} - X_{i+2}^\dagger \mathcal{V}_i^{(+)} X_i - X_{i-1}^\dagger \mathcal{V}_i^{(-)} X_i \end{aligned} \tag{5.14}$$

The above equation tells us the time evolution of the number operator at a fixed state is governed by interactions due to tunneling between adjacent sites and SOC between next nearest neighbours. Having formulated the equation of motion in this way enables further work calculating the dynamics of the molecule.

6 Summary

This thesis has described the basic theory and modelling of the CISS phenomenon. Starting from some of the fundamental theory of quantum mechanics, the basic ideas of the tight binding model and second quantization has been explained. This work should not be regarded as the final work, but rather as an entry to further studies. To fully grasp the CISS effect and to calculate an actual magnitude of the spin polarization further work lies ahead.

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