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Spin Transport Hamiltonians on Molecular Helices: Derivations from symmetry

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Resumen

Experimentos recientes han encontrado actividad de espín en moléculas quirales, sugiriendo procesos activos de espín debido a la interacción espín-órbita en los átomos. Algunos modelos actuales suelen ser incompletos y omiten características de las moléculas helicoidales. Este trabajo estudia los efectos de espín analizando el grupo de simetría discreta de un sistema helicoidal para obtener una comprensión más general de los acoplamientos permitidos en la molécula. Se revisó la literatura sobre grupos de línea para identificar el grupo adecuado que describe la simetría de hélices simples y dobles acopladas. Con esta metodología, se derivó un Hamiltoniano en el espacio real que permite identificar los canales de transporte de espín. Nuestro análisis muestra que la ausencia de simetría de inversión espacial genera un campo eléctrico interno que induce un término de tipo Rashba, además del acoplamiento espín-órbita intrínseco. También identificamos los canales activos de espín que operan entre cadenas helicoidales.

Abstract

Recent experiments have revealed spin activity in chiral molecules, suggesting spin-active processes arising from spin-orbit interaction at the atomic level. Current models are often incomplete and overlook key features of helical molecules. This work investigates spin effects by analyzing the discrete symmetry group of a helical system to gain a more general understanding of the couplings allowed in the molecule. A review of the literature on line groups was conducted to identify the appropriate group describing the symmetry of single and coupled double helices. Using this methodology, a real-space Hamiltonian was derived to identify spin transport channels. Our analysis shows that the lack of spatial inversion symmetry generates an internal electric field that induces a Rashba-type term, in addition to intrinsic spin-orbit coupling. We also identified spin-active channels operating between helical strands.

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Chapter 1

Introduction

Spintronics is a field of study in solid-state physics that has emerged and gained popularity in the last 30 years. It takes into consideration the spin degree of freedom in the electron motion. It was first studied in inorganic materials, but later, organic molecules were considered in this field of study [1]. Some experiments have been carried out, showing the effects of spin transport through chiral organic molecules such as DNA [2, 3]. Those works suggest that spin activity is likely to happen in DNA because the geometry of those molecules has a defined chirality.

Most of the theoretical work tries to explain this effect by means of Spin-orbit coupling between the different bases of DNA. Some of them are based on scattering that involves an electrostatic potential caused by the geometry of a helix [4, 5]. Other works in the field studied the phenomenon of quantum transport, such as [6, 7, 8, 9]. The main characteristic of some of the theoretical works is that spin transport may be explained by a Spin-orbit coupling, which for chiral molecules includes a Rashba-type interaction caused by the break of space-inversion in these kinds of molecules.

The tight-binding model can be used to find spin transport effects for organic molecules caused by SOC. The traditional approach is based on choosing certain orbitals by intuition to see the different interactions. Varela et al. [9] apply this model to a double helix as the one considered in this work, taking each base as a hydrogenoid atom and considering only the orbitals s, p_x, p_y, and p_z. However, this approach may omit certain processes. For example, in the works of Konschun et al. and Gmitra et al. [10, 11], it is shown that for graphene, the interactions with the highest magnitude involve orbitals d.

To avoid these problems, it has been proposed to study the spin-orbit interaction processes, taking the orbital where the free electrons are located and then applying symmetry operations to find the different paths by which processes involving spin can occur, as seen in the work of Kochan et al. [12] for graphene. Interestingly, this approach uses the symmetry operations to simplify the spin-orbit Hamiltonian in the direct space to later transform the Hamiltonian to reciprocal space. This approach is also useful because we can find from symmetry principles which processes involving spin transport are allowed and which are prohibited.

Another treatment using group theory found in the literature is directly applying symmetry operations in the reciprocal space. Using this approach, one can consider the theory of invariants, such as the work of Winkler [13] for graphene, or the study of spin-orbit for MoS2 nanotubes carried out by in [14], to find the energy levels of SOC.

In this work, the spin-orbit effect for a double-helix system will be studied using derivations from the symmetry of the system. To do this, we first introduce line groups since they are used to represent the symmetry of low-dimensional structures such as nanotubes or helices. Then, with the group operators defined, we look for the action they perform on p_z orbitals with spin in a double helix arrangement. With this and the properties of invariance of Hamiltonians in symmetry operations, we are able to construct a SOC Hamiltonian in direct space using symmetry arguments only. Later on, we construct the Hamiltonian in reciprocal space to find the energy levels for this system. Then, we briefly analyze the spin-orbit interaction processes, taking into account the geometry of a single and double helix, which explains the processes previously studied, where we show the relevance of the Rashba effect caused by the lack of space-inversion symmetry in our system.

Chapter 2

Line groups

If we wish to describe the symmetries of a system that can be placed along a line, such as a nanotube, a polymer, or a helicoidal molecule, we must use a line groups formalism. In our case, we want to describe a double helix, so we must find the proper line group that describes this system. In this work, we are using reference [15] to analyze and describe a double helix system.

First, we must understand some useful concepts that clarify the structure of a line group. We begin with the factorization of line groups, having generalized translations and axial point groups as the subgroups of a line group, so we should explain their nature. Then we are able to construct a proper line group that describes a double helix and find the way they act on orbitals with spin.

2.1 Construction of Line Groups

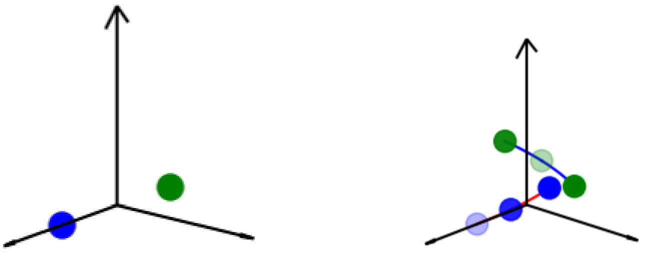
2.1.1 Generalized translations

We denote the axis where we place our system as the z axis. Generalized translations are those transformations that we can build our whole system by applying them to a monomer. In our double-helix case, a monomer is each pair of DNA bases. We will omit the complexity of a DNA base molecule and represent them just as single atoms. Those generalized translations can be described with the Koster-Seitz notation, which is written as $Z = (X|\vec{f})$ and transforms under the definition:

$$(X|\vec{f})\vec{r} = X\vec{r} + \vec{f}. \tag{2.1}$$

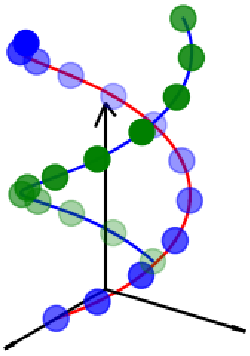
Here, X is an orthogonal transformation and $\vec{f}$ defines a translation vector. Due to the helical symmetry of the system, we must orient the helix along the z axis, so the translation vectors will always be of the form $\vec{f} = f\hat{z}$. Due to this, from now on we will ignore the vector notation and simply write f for a translation on the z axis, omitting the vector notation. We now note that the X transformation must leave the z axis invariant, which limits the possibilities. Due to the chirality present in our system, we cannot allow any reflection, leaving us only the option $X = C_Q$ (rotation of $\frac{2\pi}{Q}$ around the z axis). Then, the subgroup corresponding to the generalized translations corresponds to $\mathbf{T}_Q$, generated by $(C_Q|f)$. For commensurable systems, Q is a rational number $Q = \frac{q}{r}$. For cases $r = 1$, a complete loop is completed after applying $q = Q$ times the generalized translation operation, obtaining a pure translation, that is, $(C_Q|f)^q = (E|qf)$, corresponding to a translation of qf along the z axis.

From now on, we will call one helix A and the other B. Using cylindrical coordinates, we can place our first pair of basis in the $z = 0$ plane. We assume that one base is just in front of the other, so we can place them in the positions described by $\vec{r}_0^A = (\rho, 0, 0)$ and $\vec{r}_0^B = (\rho, \pi, 0)$. We now apply the elements of the subgroup of generalized translations $\mathbf{T}_Q$, which $(C_Q|f)^t$, with $t = \pm1, \pm2, \ldots$, obtaining the double helix. This is shown in Figure 2.1 for $t = 1, 2$ and $t = 1, \ldots, 11$. The points



(a) Monomer

(b) Monomer after one applies $(C_Q|f)^t$ for $t = 1, 2$



(c) Monomer after one applies $(C_Q|f)^t$ for $t = 1, \ldots, 11$

Figure 2.1: Double helix formed with generalized translations.

of our double-helix system then are those formed by $(C_Q|f)^t\vec{r}_0^{A,B}$, and thus will have the following form for the first elementary cell

$$\begin{aligned}
r_0^A &= (\rho, 0, 0), \\
r_1^A &= (\rho, 1 \cdot \frac{2\pi}{Q}, 1 \cdot \frac{b}{Q}), \\
r_2^A &= (\rho, 2 \cdot \frac{2\pi}{Q}, 2 \cdot \frac{b}{Q}), \\
&\vdots \\
r_Q^A &= (\rho, Q \cdot \frac{2\pi}{Q}, Q \cdot \frac{b}{Q}),
\end{aligned} \tag{2.2}$$

$$\begin{aligned}
r_0^B &= (\rho, 0, 0), \\
r_1^B &= (\rho, 1 \cdot \frac{2\pi}{Q} + \pi, 1 \cdot \frac{b}{Q}), \\
r_2^B &= (\rho, 2 \cdot \frac{2\pi}{Q} + \pi, 2 \cdot \frac{b}{Q}), \\
&\vdots \\
r_Q^B &= (\rho, Q \cdot \frac{2\pi}{Q} + \pi, Q \cdot \frac{b}{Q}),
\end{aligned} \tag{2.3}$$

It is important to note that with these definitions, we define the parameters of the helix, namely ρ the radius, $b = fQ$ the pitch of the helix, Q the number of atoms in each helix in a complete turn, and f the vertical distance between two atoms in the same strand.

2.1.2 Axial point groups

The subgroup that corresponds to the internal symmetry of the monomer is described by a point group. It must respect the characteristics of the whole system,

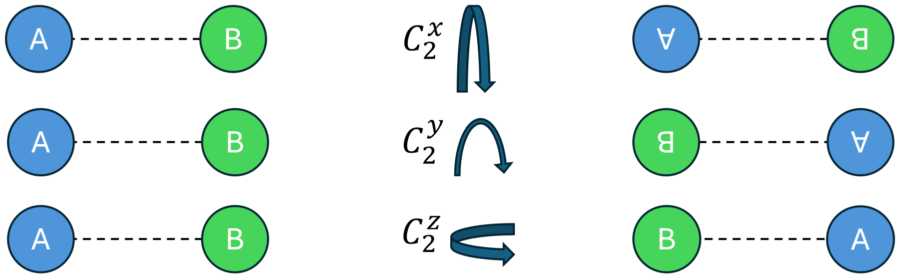


Figure 2.2: Operations from point group $\mathbf{D}_2$

such as preserving the z axis and maintaining the chirality. As we stated before, the monomer in the double-helix system is each pair of bases, which we consider to be a pair of equivalent atoms. A more complicated and realistic description should consider each base as a collection of atoms, and then we would have what is called a "multi-orbit" system in reference [15]. An example of this description can be found in [16].

Our consideration of a basis as a pair of atoms forming a double helix limits the internal symmetries of the monomer. Chirality does not allow certain symmetries, such as space-inversion and mirror-plane reflections. However, as we will see later, this leads to spin-active processes caused by the Rashba effect, and this will allow several spin-active processes that make chiral molecules really good candidates for spintronics. The operations that do not affect chirality and leave the z axis are rotations with respect to the fixed axes of our system. In particular, if we consider all bases to be the same, the internal symmetry of our monomer corresponds to the point group $\mathbf{D}_2 = \{E, C_2^x, C_2^y, C_2^z\}$. If we consider that the bases are not equivalent to each other, this symmetry is broken since we cannot have helix changes, obtaining the subgroup $\mathbf{D}_1 = \{E, C_2^x\}$. The operations of those groups can be seen in figure 2.2

2.1.3 Line group $\mathbf{T}_Q\mathbf{D}_2$

With the previous subgroups defined, we can now build the line group $\mathbf{T}_Q^1\mathbf{D}_2$ as the semidirect product of the previously discussed groups, so we have $\mathbf{T}_Q\mathbf{D}_2 = \mathbf{T}_Q \wedge \mathbf{D}_2$. It belongs to the fifth family of line groups in the description of [15], this being one of the families that allow defined chirality. It is important to specify the order that defines the semidirect product since the elements of the two subgroups do not commute with each other. To observe how the elements operate on the atoms of the system, let us first notice their individual actions:

- $E : EA_n$,
- C_x: $C_xA_n = A_{-n}$,
- C_z: $C_zA_n = B_n$,
- C_y: $C_yA_n = B_{-n}$,
- $(C_Q|f) : (C_Q|f)^tA_n = A_{n+t}$,

so the elements of $\mathbf{T}_Q\mathbf{D}_2$ act like:

$$\begin{aligned}
(C_Q|f)^tEA_p &= A_{p+t} & (C_Q|f)^tEB_p &= B_{p+t},\\
(C_Q|f)^tC_xA_p &= A_{-p+t} & (C_Q|f)^tC_xB_p &= B_{-p+t},\\
(C_Q|f)^tC_yA_p &= B_{-p+t} & (C_Q|f)^tC_yB_p &= A_{-p+t},\\
(C_Q|f)^tC_zA_p &= B_{p+t} & (C_Q|f)^tC_zB_p &= A_{p+t}s.
\end{aligned} \tag{2.4}$$

We can also express the operation with the use of three parameters which we call t, s, and p by using the equation 2.5, where $t = 0, \pm 1, \pm 2, \ldots$, $s = 0, 1$, $p = 0, 1$.

$$l_{t,s,p} = (C_Q|f)^t (C_2^z)^s (C_2^x)^p. \tag{2.5}$$

2.2 Operations of the line group in systems with spin

By increasing the degree of freedom of the spin, we add an additional symmetry to our system, caused by the time reversal operation $\mathcal{T}$. A more detailed and formal treatment for the addition of this operation in Line groups can be found in [17, 14]. For further development, we can simply consider the group $\mathbf{T}_q^1\mathbf{D}_2 \otimes \{E, \tau\}$, similar to the approach developed by Kochan in [12] for the case of graphene.

Following this approach, we can find that the symmetry operations on an arbitrary orbital X in the site m with spin σ, i.e. $|X_m\sigma\rangle$ act as:

$$|X_m\sigma\rangle \xrightarrow{(C_Q|f)} e^{-i\sigma\frac{\pi}{Q}} \left|X_{(C_Q|f)m}\sigma\right\rangle, \tag{2.6a}$$

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{x}}} -i \left|X_{C_2^{\hat{x}}m}(-\sigma)\right\rangle, \tag{2.6b}$$

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{y}}} (-1)^{\frac{1-\sigma}{2}} \left|X_{C_2^{\hat{y}}m}(-\sigma)\right\rangle, \tag{2.6c}$$

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{z}}} i(-1)^{\frac{1+\sigma}{2}} \left|X_{C_2^{\hat{z}}m}\sigma\right\rangle, \tag{2.6d}$$

$$|X_m\sigma\rangle \xrightarrow{\mathcal{T}} (-1)^{\frac{1-\sigma}{2}} |X_m(-\sigma)\rangle, \tag{2.6e}$$

These expressions can be obtained through the operations obtained by Kochan in [12], where he details how the rotations with respect to the mentioned axes could be obtained using the reflection operations that are valid for graphene. Its different combinations allow us to investigate the relations involving rotations:

$$\begin{aligned} C_x \left| X_m \sigma \right\rangle &= \Sigma_d \Sigma_h \left| X_m \sigma \right\rangle , \\ &= i(-1)^{\frac{1+\sigma}{2}} \Sigma_d \left| X'_m \sigma \right\rangle , \\ &= i(-1)^{\frac{1+\sigma}{2}} (-1)^{\frac{1+\sigma}{2}} \left| X''_m (-\sigma) \right\rangle , \\ &= i \left| X''_m (-\sigma) \right\rangle , \end{aligned} \tag{2.7}$$

$$\begin{aligned} C_y \left| X_m \sigma \right\rangle &= \Sigma_h \Sigma_v \left| X_m \sigma \right\rangle , \\ &= i \Sigma_h \left| X'_m (-\sigma) \right\rangle , \\ &= -(-1)^{\frac{1+\sigma}{2}} \left| X''_m (-\sigma) \right\rangle , \\ &= (-1)^{\frac{3+\sigma}{2}} \left| X''_m (-\sigma) \right\rangle , \\ C_y \left| X_m \sigma \right\rangle &= (-1)^{\frac{1-\sigma}{2}} \left| X''_m (-\sigma) \right\rangle , \end{aligned} \tag{2.8}$$

$$\begin{aligned} C_z \left| X_m \sigma \right\rangle &= \Sigma_v \Sigma_d \left| X_m \sigma \right\rangle , \\ &= (-1)^{\frac{1+\sigma}{2}} \left| X'^m (-\sigma) \right\rangle , \\ &= i(-1)^{\frac{1+\sigma}{2}} \left| X''^m (-\sigma) \right\rangle . \end{aligned} \tag{2.9}$$

. We could get the same expressions by using the rotation generator for the spin in an axis given by a unitary vector $\hat{n}$ [18].

$$\hat{R}(\theta, \vec{n}) = e^{i \frac{\theta}{2} \vec{\mathbf{n}} \cdot \vec{\sigma}} = I \cos \frac{\theta}{2} + i \left(\vec{n} \cdot \vec{\sigma} \right) \sin \frac{\theta}{2} . \tag{2.10}$$

We are working with rotations of the type C_2, so we have that $\theta = \pi$. The rotations only for the spinor will be given by:

$$C_2^x = i\sigma_x \ ; \quad C_2^y = i\sigma_y \ ; \quad C_2^z = i\sigma_z. \tag{2.11}$$

Here, the Pauli matrices are given by:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{2.12}$$

so we have, by asigning $|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$C_2^x \left|\uparrow\right\rangle = \sigma_x \left|\uparrow\right\rangle = i \left|\downarrow\right\rangle \qquad C_2^x \left|\downarrow\right\rangle = \sigma_x \left|\downarrow\right\rangle = i \left|\uparrow\right\rangle \tag{2.13}$$

$$C_2^y \left|\uparrow\right\rangle = \sigma_y \left|\uparrow\right\rangle = -\left|\downarrow\right\rangle \qquad C_2^y \left|\downarrow\right\rangle = \sigma_y \left|\downarrow\right\rangle = \left|\uparrow\right\rangle \tag{2.14}$$

$$C_2^z \left|\uparrow\right\rangle = \sigma_z \left|\uparrow\right\rangle = \left|\uparrow\right\rangle \qquad C_2^z \left|\downarrow\right\rangle = \sigma_z \left|\downarrow\right\rangle = -\left|\downarrow\right\rangle, \tag{2.15}$$

and then assigning $|\uparrow\rangle$ to $\sigma = 1$ and $|\downarrow\rangle$ with $\sigma = -1$, we arrive at the expressions given before.

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{x}}} -i \left|X_{C_2^{\hat{x}}m}(-\sigma)\right\rangle, \tag{2.16}$$

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{y}}} (-1)^{\frac{1-\sigma}{2}} \left|X_{C_2^{\hat{y}}m}(-\sigma)\right\rangle, \tag{2.17}$$

$$|X_m\sigma\rangle \xrightarrow{C_2^{\hat{z}}} i(-1)^{\frac{1+\sigma}{2}} \left|X_{C_2^{\hat{z}}m}\sigma\right\rangle, \tag{2.18}$$

Chapter 3

Hamiltonian in direct space

3.1 Intra-helix Hamiltonian

With the methods previously studied, we are able to construct our Hamiltonian of spin-orbit interaction in direct space. Here, we should notice that we do not know the exact form of the Hamiltonian; however, we know that the operations of the line group described in the previous sections do preserve the potential V and the orientation of the orbitals. So, if we describe our systems with orbitals at the site m with spin σ as $|X_m\sigma\rangle$, we can follow the procedure found in [12] and find which matrix elements $\langle X_m\sigma|\hat{H}|X_n\sigma'\rangle$ are non-zero and also find the relations between them. Because of the preservation of the potential V with any symmetry $\mathcal{S}$ of the system, the Hamiltonian will commute with the space symmetries $\mathcal{S}V = V\mathcal{S}$. The fact that the space symmetries that we are considering are unitary, so they preserve the inner product, we may write:

$$\langle \mathcal{S}(X_m\sigma)|\hat{H}|\mathcal{S}(X_n\sigma')\rangle = \left\langle \mathcal{S}(X_m\sigma)\middle|\mathcal{S}(\hat{H}X_n\sigma')\right\rangle = \langle X_m\sigma|\hat{H}|X_n\sigma\rangle\,. \tag{3.1}$$

Other useful relations are derived in [12] using the antiunitary property of time-reversal symmetry and will be useful for our procedure, so we summarize them:

$$\langle X_m\sigma|\hat{H}|X_n\sigma'\rangle = -(-1)^{\frac{\sigma+\sigma'}{2}}\langle X_n(-\sigma')|\hat{H}|X_m(-\sigma)\rangle \tag{3.2}$$

$$\langle X_m\sigma|\hat{H}|X_n\sigma'\rangle = -\langle X_m(-\sigma)|\hat{H}|X_n(-\sigma')\rangle \tag{3.3}$$

3.1.1 Helix A

For a single strand, we may first look at the cases where we have spin-flipping. If we consider first neighbors, we may see that our most general Hamiltonian will have the following form:

$$H_A^{\text{flip}} = \sum_{\sigma\neq\sigma'}\sum_n \left[\Lambda^\sigma_{n,n+1}|A_n\sigma\rangle\langle A_{n+1}\sigma'| + \Lambda^\sigma_{n+1,n}|A_{n+1}\sigma\rangle\langle A_n\sigma'|\right]. \tag{3.4}$$

Here we have called $\Lambda^\sigma_{n,n+1} = \langle A_n\sigma|\hat{H}|A_{n+1}\sigma'\rangle$. We can use equation 3.2 and the fact that $\sigma \neq \sigma'$ to write:

$$\langle A_n\sigma|\hat{H}|A_{n+1}\sigma'\rangle \overset{3.2}{=} -\langle A_{n+1}(-\sigma')|\hat{H}|A_n(-\sigma)\rangle = -\langle A_{n+1}\sigma|\hat{H}|A_n\sigma'\rangle\,, \tag{3.5}$$

so $\Lambda^{\sigma}_{n+1,n} = -\Lambda^{\sigma}_{n,n+1}$, and we can write our Hamiltonian as

$$H_A^{\text{flip}} = \sum_{\sigma\neq\sigma'}\sum_n \Lambda^{\sigma}_{n,n+1}\left[|A_n\sigma\rangle\langle A_{n+1}\sigma'| - |A_{n+1}\sigma\rangle\langle A_n\sigma'|\right]. \tag{3.6}$$

We now use relations 2.6a and 3.1 to write:

$$\begin{aligned}\langle A_n\sigma|\hat{H}|A_{n+1}\sigma'\rangle &\overset{2.6a}{=} \left\langle e^{i\sigma\frac{\pi}{Q}n}(T_Q|f)^n A_0\sigma\middle|\hat{H}\middle|e^{i\sigma'\frac{\pi}{Q}n}(T_Q|f)^n A_0\sigma'\right\rangle\\ &\overset{3.1}{=} e^{i(\sigma'-\sigma)\frac{\pi}{Q}n}\,\langle A_0\sigma|\hat{H}|A_1\sigma'\rangle\,.\end{aligned} \tag{3.7}$$

So, our Hamiltonian simplifies even further, and it can be written in the form:

$$H_A^{\text{flip}} = \sum_{\sigma\neq\sigma'}\sum_n e^{i(\sigma'-\sigma)\frac{\pi}{Q}}\Lambda^{\sigma}_{0,1}\left[|A_n\sigma\rangle\langle A_{n+1}\sigma'| - |A_{n+1}\sigma\rangle\langle A_n\sigma'|\right] \tag{3.8}$$

The last useful relation is 3.2, which allows us to write:

$$\langle A_0\uparrow|\hat{H}|A_1\downarrow\rangle \overset{3.2}{=} -\langle A_1\uparrow|\hat{H}|A_0\downarrow\rangle = -\overline{\langle A_0\downarrow|\hat{H}|A_1\uparrow\rangle}. \tag{3.9}$$

So, if we define $\Lambda^{\downarrow}_{0,1} \equiv \frac{\Lambda}{2i}$, where Λ is a complex number, our Hamiltonian takes the form:

$$\begin{aligned}H_A^{\text{flip}} &= \frac{\Lambda}{2i}\sum_n e^{i\frac{2\pi}{Q}n}\left[|A_n\downarrow\rangle\langle A_{n+1}\uparrow| - |A_{n+1}\downarrow\rangle\langle A_n\uparrow|\right]\\ &-\left(\frac{\Lambda}{2i}\right)^*\sum_n e^{-i\frac{2\pi}{Q}n}\left[|A_n\uparrow\rangle\langle A_{n+1}\downarrow| - |A_{n+1}\uparrow\rangle\langle A_n\downarrow|\right].\end{aligned} \tag{3.10}$$

For the spin-conserving processes, we again start from a general Hamiltonian.

$$H_A^{\text{no-flip}} = \sum_{\sigma}\sum_n\left[\lambda^{\sigma}_{n,n+1}|A_n\sigma\rangle\langle A_{n+1}\sigma| + \lambda^{\sigma}_{n+1,n}|A_{n+1}\sigma\rangle\langle A_n\sigma|\right], \tag{3.11}$$

and again, we have called $\lambda^{\sigma}_{n,n+1} = \langle A_n\sigma|\hat{H}|A_{n+1}\sigma\rangle$.

We now use the expressions 3.2 and 3.3 and can write:

$$\langle A_n\sigma|\hat{H}|A_{n+1}\sigma\rangle = \langle A_{n+1}(-\sigma)|\hat{H}|A_n(-\sigma)\rangle = -\overline{\langle A_{n+1}\sigma|\hat{H}|A_n\sigma\rangle} \tag{3.12}$$

So $\lambda^{\sigma}_{n,n+1} = -\overline{\lambda^{\sigma}_{n+1,n}}$. Using the relation obtained in 3.7, we note that for spin-conserving processes, we have $\langle A_n\sigma|\hat{H}|A_{n+1}\sigma\rangle = \langle A_0\sigma|\hat{H}|A_1\sigma\rangle$, and so $\lambda^{\sigma}_{n,n+1} = \lambda^{\sigma}_{0,1}$. Note also that equation 3.3 tells us that $\langle A_0\downarrow|\hat{H}|A_1\downarrow\rangle = -\overline{\langle A_0\uparrow|\hat{H}|A_1\uparrow\rangle}$, so $\lambda^{\downarrow}_{0,1} = -\overline{\lambda^{\uparrow}_{0,1}}$. Finally, by means of equation 3.12, we can see that $\langle A_0\sigma|\hat{H}|A_1\sigma\rangle = -\overline{\langle A_0\sigma|\hat{H}|A_1\sigma\rangle}$, so $\lambda^{\uparrow}_{0,1}$ is purely imaginary, and we can call $\lambda^{\uparrow}_{0,1} = \frac{\lambda}{2i}$, with λ real. We can now write our Hamiltonian for spin-conserving processes related to spin-orbit coupling.

$$H^{\text{no-flip}}_A = i\lambda\sum_{\sigma}\sum_{n}\sigma\left[|A_n\sigma\rangle\langle A_{n+1}\sigma| - |A_{n+1}\sigma\rangle\langle A_n\sigma|\right] \tag{3.13}$$

Finally, we must also consider the orbital kinetic Hamiltonian, which couples the p_z orbital with the same spin but is unrelated to the spin-orbit coupling. It has the usual form, having the real hopping parameter t, which for convenience, we write as $\frac{t}{2}$.

$$H^{\text{orb}}_A = -\frac{t}{2}\sum_{\sigma}\sum_{n}\left[|A_n\sigma\rangle\langle A_{n+1}\sigma| + |A_{n+1}\sigma\rangle\langle A_n\sigma|\right] \tag{3.14}$$

3.1.2 Helix B

Following the same procedure, we obtain the same result for helix B, only changing the parameters Λ, λ and t for the parameters of helix B, so we have:

$$\begin{aligned} H_B^{\text{flip}} &= \frac{\Lambda_B}{2i} \sum_n e^{i\frac{2\pi}{Q}n} \left[|B_n \downarrow\rangle\langle B_{n+1} \uparrow| - |B_{n+1} \downarrow\rangle\langle B_n \uparrow| \right] \\ &- \left(\frac{\Lambda_B}{2i}\right)^* \sum_n e^{-i\frac{2\pi}{Q}n} \left[|B_n \uparrow\rangle\langle B_{n+1} \downarrow| - |B_{n+1} \uparrow\rangle\langle B_n \downarrow| \right] \end{aligned} \tag{3.15}$$

$$H_B^{\text{no-flip}} = i\lambda_B \sum_\sigma \sum_n \sigma \left[|B_n\sigma\rangle\langle B_{n+1}\sigma| - |B_{n+1}\sigma\rangle\langle B_n\sigma| \right] \tag{3.16}$$

$$H_B^{\text{orb}} = -t \sum_\sigma \sum_n \left[|B_n\sigma\rangle\langle B_{n+1}\sigma| + |B_{n+1}\sigma\rangle\langle B_n\sigma| \right] \tag{3.17}$$

However, if the strands are equivalent, we may use the expression 2.6d and write:

$$\begin{aligned} \langle B_n\sigma|\hat{H}|B_{n+1}\rangle &\overset{2.6d}{=} \left\langle i(-1)^{\frac{1-\sigma}{2}} C_2^{\hat{z}} A_n\sigma \middle| \hat{H} \middle| i(-1)^{\frac{1-\sigma}{2}} C_2^{\hat{z}} A_{n+1}\sigma' \right\rangle \\ &= -(-1)^{\frac{\sigma+\sigma'}{2}} \langle A_n\sigma|\hat{H}|A_{n+1}\sigma'\rangle \end{aligned} \tag{3.18}$$

So, for spin-flipping and spin-conserving when the strands are equivalent, we have the following:

$$\Lambda_B = -\Lambda \quad \lambda_B = \lambda \quad t_B = t \tag{3.19}$$

3.2 Inter-helix Hamiltonian

We now focus on the interaction between the bases of each pair so that they are on the same plane. First, note that:

$$\begin{aligned}\langle A_n\sigma|\hat{H}_{so}|B_n\sigma'\rangle &\overset{2.6d}{=} \left\langle i(-1)^{\frac{1-\sigma}{2}}C_2^{\hat{z}}B_n\sigma\middle|\hat{H}_{so}\middle|i(-1)^{\frac{1-\sigma'}{2}}C_2^{\hat{z}}A_n\sigma'\right\rangle \\ &\overset{3.1}{=} -(-1)^{\frac{\sigma+\sigma'}{2}}\langle B_n\sigma|\hat{H}_{so}|A_n\sigma'\rangle \\ &\overset{3.2}{=} \langle A_n(-\sigma')|\hat{H}_{so}|B_n(-\sigma)\rangle\end{aligned} \tag{3.20}$$

If we want a spin-conserving process, i.e., $\sigma' = \sigma$, we use equation 3.3, so we have eq. 3.20:

$$\langle A_n\sigma|\hat{H}_{so}|B_n\sigma\rangle = \langle A_n(-\sigma)|\hat{H}_{so}|B_n(-\sigma)\rangle = -\langle A_n\sigma|\hat{H}_{so}|B_n\sigma\rangle \tag{3.21}$$

Thus, spin-conserving processes are not allowed for a pair of bases on the same plane. This is a NO-GO rule, as stated in reference [12].

Note that it is not possible to find a NO-GO rule for spin flipping on the pair of bases. However, if our system had allowed space-inversion symmetry $\mathcal{I}$, then it would have operated in an orbital as given in [12]: $|X_m\sigma\rangle \xrightarrow{\mathcal{I}} |-X_{\mathcal{I}m}\sigma\rangle$. Then we would have for spin-flipping:

$$\begin{aligned}\langle A_n\sigma|\hat{H}|B_n\sigma'\rangle &= \langle -\mathcal{I}B_n\sigma|\hat{H}|-\mathcal{I}A_n\sigma\rangle \\ &\overset{3.1}{=} \langle B_n\sigma|\hat{H}|A_n\sigma'\rangle \\ &\overset{3.2}{=} -\langle A_n(-\sigma')|\hat{H}|B_n(-\sigma)\rangle \\ &= -\langle A_n(-\sigma)|\hat{H}|B_n(-\sigma')\rangle\,,\end{aligned} \tag{3.22}$$

and we would have a NO-GO rule. However, as we want to emphasize, space inversion is not allowed by the chirality of the system. This is one of the main reasons chiral molecules are good for spin transport and allow processes we could not have without chirality. In this case, we will have spin-flipping processes for a pair of bases on the same plane. Before analyzing the process that allows it, let us write the Hamiltonian.

We start as before, writing a general Hamiltonian of the form:

$$H_{AB}^{\text{flip}} = \sum_{\sigma\neq\sigma'}\sum_{n}\left[\Lambda_{A\perp,n}^{\sigma}\left|A_n\sigma\right\rangle\!\left\langle B_n\sigma'\right| + \Lambda_{B\perp,n}^{\sigma}\left|B_n\sigma\right\rangle\!\left\langle A_n\sigma'\right|\right] \tag{3.23}$$

Here we have called $\Lambda_{A\perp,n}^{\sigma} = \langle A_n\sigma|\hat{H}|B_n\sigma'\rangle$ and $\Lambda_{B\perp,n}^{\sigma} = \langle B_n\sigma|\hat{H}|A_n\sigma'\rangle$. Note from equation 3.20, that $\langle B_n\sigma|\hat{H}|A_n\sigma'\rangle = -\langle A_n\sigma|\hat{H}|B_n\sigma'\rangle$, so $\Lambda_{B\perp,n}^{\sigma} = -\Lambda_{A\perp,n}^{\sigma}$, so the Hamiltonian is now:

$$H_{AB}^{\text{flip}} = \sum_{\sigma\neq\sigma'}\sum_{n}\Lambda_{A\perp,n}^{\sigma}\left[\left|A_n\sigma\right\rangle\!\left\langle B_n\sigma'\right| - \left|B_n\sigma\right\rangle\!\left\langle A_n\sigma'\right|\right] \tag{3.24}$$

We now use equation 2.6a:

$$\begin{aligned}
&\langle A_n\sigma|\hat{H}_{so}|B_n\sigma'\rangle\\
&\overset{2.6a}{=}\left\langle e^{i\sigma\frac{\pi}{Q}n}(C_Q|f)^n A_0\sigma\middle|\hat{H}_{so}\middle|e^{i\sigma'\frac{\pi}{Q}n}(C_Q|f)^n B_0\sigma'\right\rangle\\
&\overset{3.1}{=}e^{i(\sigma'-\sigma)\frac{\pi}{Q}n}\langle A_0\sigma|\hat{H}_{so}|B_0\sigma'\rangle
\end{aligned} \tag{3.25}$$

So $\Lambda^{\sigma}_{A\perp,n} = e^{i(\sigma'-\sigma)\frac{\pi}{Q}n}\Lambda^{\sigma}_{A\perp,0}$, and the Hamiltonian now is:

$$H^{\text{flip}}_{AB} = \sum_{\sigma\neq\sigma'}\sum_{n}\Lambda^{\sigma}_{A\perp,0}e^{i(\sigma'-\sigma)\frac{\pi}{Q}n}\left[|A_n\sigma\rangle\langle B_n\sigma'| - |B_n\sigma\rangle\langle A_n\sigma'|\right]. \tag{3.26}$$

Finally, note that by means of equation 3.2, we have $\langle A_0\uparrow|\hat{H}|B_0\downarrow\rangle = -\langle B_0\uparrow|\hat{H}|A_0\downarrow\rangle = -\overline{\langle A_0\downarrow|\hat{H}|B_0\uparrow\rangle}$. So $\Lambda^{\uparrow}_{A\perp,0} = \left(\Lambda^{\downarrow}_{A\perp,0}\right)^{*}$. We define $\Lambda^{\downarrow}_{A\perp,0} \equiv \frac{\Lambda_\perp}{2i}$, with Λ being a complex number, so the inter-helix Hamiltonian reads:

$$\begin{aligned} H^{\text{flip}}_{AB} = \frac{\Lambda_\perp}{2i}\sum_{n}e^{i\frac{2\pi}{Q}n}\left[|A_n\downarrow\rangle\langle B_n\uparrow| - |B_n\downarrow\rangle\langle A_n\uparrow|\right] \\ -\left(\frac{\Lambda_\perp}{2i}\right)^{*}\sum_{n}e^{-i\frac{2\pi}{Q}n}\left[|A_n\uparrow\rangle\langle B_n\downarrow| - |B_n\uparrow\rangle\langle A_n\downarrow|\right] \end{aligned} \tag{3.27}$$

We finally must include the kinetic Hamiltonian that couples the orbitals with the same spin and will have the form:

$$H^{\text{orb}}_{AB} = -t_\perp\sum_{\sigma}\sum_{n}\left[|B_n\sigma\rangle\langle B_{n+1}\sigma| + |B_{n+1}\sigma\rangle\langle B_n\sigma|\right] \tag{3.28}$$

Chapter 4

Hamiltonian in reciprocal space

To find the energy values, we must transform our Hamiltonian to reciprocal space. We do this by using a Bloch sum, so we may write:

$$|A_n\rangle = \frac{1}{\sqrt{2N+1}} \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}_n^A} |A_{\vec{q}}\rangle \tag{4.1}$$

$$|B_n\rangle = \frac{1}{\sqrt{2N+1}} \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}_n^B} |B_{\vec{q}}\rangle \tag{4.2}$$

We add the spin of each orbital, and we also define the quantum numbers k and m as the conjugated momenta of vertical displacements and rotations, respectively. We do not include the radial momentum because it will not play any role since the radius will be the same for all the atoms. We can write then:

$$|A_{\vec{q}}\rangle \otimes |\sigma\rangle \to |A_{k,m}\sigma\rangle \tag{4.3}$$

$$|B_{\vec{q}}\rangle \otimes |\sigma\rangle \to |B_{k,m}\sigma\rangle \tag{4.4}$$

4.1 Intra-helix Hamiltonian

Let us calculate:

$$\sum_n e^{i\frac{2\pi}{Q}n} \left[|A_n \downarrow\rangle\langle A_{n+1} \uparrow| - |A_{n+1} \downarrow\rangle\langle A_n \uparrow| \right] =$$
$$\frac{1}{2N+1} \sum_n e^{i\frac{2\pi}{Q}n} \Big[\sum_{\vec{q}} \sum_{\vec{q}'} e^{-i\vec{q}\cdot\vec{r}_n} e^{i\vec{q}'\cdot\vec{r}_{n+1}} |A_{\vec{q}}\rangle\langle A_{\vec{q}'}| - \sum_{\vec{q}} \sum_{\vec{q}'} e^{-i\vec{q}\cdot\vec{r}_{n+1}} e^{i\vec{q}'\cdot\vec{r}_n} |A_{\vec{q}}\rangle\langle A_{\vec{q}'}| \Big] \tag{4.5}$$

If we use cylindrical coordinates and we omit the radial coordinate because it is a constant and it will eventually vanish, we may write:

$$\vec{r}_n = \frac{2\pi}{Q} n \hat{\phi} + f_n \hat{z} \tag{4.6}$$

$$\vec{r}_{n+1} = \vec{r}_n + \frac{2\pi}{Q} \hat{\phi} + f \hat{z}, \tag{4.7}$$

and if we denote by k and m the components of the momentum conjugated to the coordinates z and ϕ, we can write:

$$\vec{q} \cdot \vec{r}_n = k f_n + m \frac{2\pi}{Q} n. \tag{4.8}$$

So we can now write equation 4.5 as follows, where the sum in $\vec{q}$ denotes a sum in k and m, and the sum in $\vec{q}'$ a sum in k' and m'

$$\begin{aligned}&\sum_n e^{i\frac{2\pi}{Q}n}\left[|A_n \downarrow\rangle\langle A_{n+1}\uparrow| - |A_{n+1}\downarrow\rangle\langle A_n \uparrow|\right] = \\ &\qquad \frac{1}{2N+1}\sum_n \sum_{\vec{q},\vec{q}'} \Big[e^{i\frac{2\pi}{Q}n} e^{-i(kf_n+m\frac{2\pi}{Q}n)} e^{i(k'f_n+m'\frac{2\pi}{Q}n+k'f+m'\frac{2\pi}{Q})} \\ &\qquad - e^{i\frac{2\pi}{Q}n} e^{i(kf_n+m\frac{2\pi}{Q}n+kf+m\frac{2\pi}{Q})} e^{-i(k'f_n+m'\frac{2\pi}{Q}n)}\Big] \,|A_{k,m}\downarrow\rangle\langle A_{k',m'}\uparrow| = \\ &\qquad \frac{1}{2N+1}\sum_n \sum_{\vec{q},\vec{q}'} e^{-i(k-k')f_n} e^{-i(m-1+m')\frac{2\pi}{Q}n} \big[e^{i(k'f+m'\frac{2\pi}{Q}} - e^{-i(kf+m\frac{2\pi}{Q}})\big] \\ &\qquad |A_{k,m}\downarrow\rangle\langle A_{k',m'}\uparrow|\end{aligned} \tag{4.9}$$

The usual relation for a system with N atoms:

$$\sum_n e^{-i(\vec{q}-\vec{q}')\cdot r_n} = N\delta_{\vec{q},\vec{q}'} \tag{4.10}$$

For our system with $2N+1$ atoms in each strand and in cylindrical coordinates, it reads:

$$\sum_n e^{-i(k-k')f_n} e^{-i(m-m')\frac{2\pi}{Q}n} = (2N+1)\delta_{k,k'}\delta_{m,m'} \tag{4.11}$$

So, equation 4.9 can be written as:

$$\begin{aligned}&\sum_n e^{i\frac{2\pi}{Q}n}\left[|A_n \downarrow\rangle\langle A_{n+1}\uparrow| - |A_{n+1}\downarrow\rangle\langle A_n \uparrow|\right] = \\ &\sum_{k,m} \big[e^{i(kf+(m-1)\frac{2\pi}{Q}} - e^{-i(kf+m\frac{2\pi}{Q}})\big] \,|A_{k,m}\downarrow\rangle\langle A_{k,m-1}\uparrow| = \\ &\sum_{k,m} e^{-\frac{\pi}{Q}} \left[e^{i(kf+(m-\frac{1}{2})\frac{2\pi}{Q}} - e^{-i(kf+(m-\frac{1}{2})\frac{2\pi}{Q}}\right] |A_{k,m}\downarrow\rangle\langle A_{k,m-1}\uparrow|\end{aligned} \tag{4.12}$$

Following the same procedure, we obtain the following result.

$$\begin{aligned}&\sum_n e^{-i\frac{2\pi}{Q}n}\left[|A_n\downarrow\rangle\langle A_{n+1}\uparrow| - |A_{n+1}\downarrow\rangle\langle A_n\uparrow|\right] = \\ &\sum_{k,m} e^{\frac{\pi}{Q}}\left[e^{i(kf+(m-\frac{1}{2})\frac{2\pi}{Q}} - e^{-i(kf+(m-\frac{1}{2})\frac{2\pi}{Q}}\right]|A_{k,m-1}\uparrow\rangle\langle A_{k,m}\downarrow|\end{aligned} \tag{4.13}$$

So, replacing these equations in the Hamiltonian H_A^{flip}, obtained in equation 3.10, we transform our Hamiltonian from direct space to reciprocal space. The Hamiltonian now reads:

$$\begin{aligned}H_A^{\mathrm{flip}} = \Lambda e^{-\frac{\pi}{Q}}\sin\left(kf+\left(m-\frac{1}{2}\right)\frac{2\pi}{Q}\right)|A_{k,m}\downarrow\rangle\langle A_{k,m-1}\uparrow| + \\ \Lambda^* e^{\frac{\pi}{Q}}\sin\left(kf+\left(m-\frac{1}{2}\right)\frac{2\pi}{Q}\right)|A_{k,m-1}\uparrow\rangle\langle A_{k,m}\downarrow|\end{aligned} \tag{4.14}$$

So we should choose $\{|A_{k,m}\downarrow\rangle, |A_{k,m-1}\uparrow\rangle\}$ as our basis for the subhamiltonian H_A. We now focus on the diagonal terms of this Hamiltonian, given by $H_A^{no-flip}$ and H_A^{orb} given by equations 3.13 3.14. Let us calculate:

$$\begin{aligned}&\sum_n\left[|A_n\downarrow\rangle\langle A_{n+1}\downarrow| - |A_{n+1}\downarrow\rangle\langle A_n\downarrow|\right] = \\ &\sum_n\sum_{\vec{q},\vec{q}'} e^{-i\vec{q}\cdot\vec{r}_n}e^{i\vec{q}'\cdot\vec{r}_{n+1}}|A_{\vec{q}}\downarrow\rangle\langle A_{\vec{q}'}\downarrow| - \\ &e^{-i\vec{q}\cdot\vec{r}_{n+1}}e^{i\vec{q}'\cdot\vec{r}_n}|A_{\vec{q}}\downarrow\rangle\langle A_{\vec{q}'}\downarrow|,\end{aligned} \tag{4.15}$$

and, as before, we only consider the terms k and m of the momentum, so we assign $\vec{q} = k\hat{z} + m\hat{\phi}$ and omit the radial part. Using again sums in $\vec{q}$ and $\vec{q}'$ as sums in

k, m and k', m':

$$\begin{gathered}\sum_n \left[|A_n \downarrow\rangle\langle A_{n+1} \downarrow| - |A_{n+1} \downarrow\rangle\langle A_n \downarrow| \right] = \\ \sum_n \sum_{\vec{q}} \sum_{\vec{q}'} \big[e^{-ikf_n} e^{-im\frac{2\pi}{Q}n} e^{ik'(f_n+f)} e^{im'(\frac{2\pi}{Q}n+\frac{2\pi}{Q})} \\ -e^{-ik(f_n+f)} e^{-im(\frac{2\pi}{Q}n+\frac{2\pi}{Q})} e^{ik'f_n} e^{im'\frac{2\pi}{Q}} \big] \, |A_{\vec{q}} \downarrow\rangle\langle A_{\vec{q}'} \downarrow| = \\ \sum_{k,m} \left[e^{i(kf+m\frac{2\pi}{Q})} - e^{-i(kf+im\frac{2\pi}{Q})} \right] |A_{k,m} \downarrow\rangle\langle A_{k,m} \downarrow| \end{gathered} \tag{4.16}$$

and with the same procedure:

$$\begin{gathered}\sum_n \left[|A_n \uparrow\rangle\langle A_{n+1} \uparrow| - |A_{n+1} \uparrow\rangle\langle A_n \uparrow| \right] = \\ \sum_{k,m} \left[e^{i(kf+m\frac{2\pi}{Q})} - e^{-i(kf+im\frac{2\pi}{Q})} \right] |A_{k,m} \uparrow\rangle\langle A_{k,m} \uparrow| \\ \sum_{k,m} \left[e^{i(kf+(m-1)\frac{2\pi}{Q})} - e^{-i(kf+i(m-1)\frac{2\pi}{Q})} \right] |A_{k,m-1} \uparrow\rangle\langle A_{k,m-1} \uparrow| \end{gathered} \tag{4.17}$$

Replacing in equation 3.13 for no-flipping, we obtain:

$$\begin{gathered} H_A^{\text{no-flip}} = \lambda \sin\left(kf + m\frac{2\pi}{Q} \right) |A_{k,m} \downarrow\rangle\langle A_{k,m} \downarrow| \\ -\lambda \sin\left(kf + (m-1)\frac{2\pi}{Q} \right) |A_{k,m-1} \uparrow\rangle\langle A_{k,m-1} \uparrow| , \end{gathered} \tag{4.18}$$

and replacing in H_A^{orb}, we have:

$$\begin{gathered} H_A^{\text{orb}} = -t \cos\left(kf + m\frac{2\pi}{Q} \right) |A_{k,m} \downarrow\rangle\langle A_{k,m} \downarrow| \\ -t \cos\left(kf + (m-1)\frac{2\pi}{Q} \right) |A_{k,m-1} \uparrow\rangle\langle A_{k,m-1} \uparrow| \end{gathered} \tag{4.19}$$

So we have obtained our sub-hamiltonian H_{AA}, which in the basis $(|A_{k,m} \downarrow\rangle,$

$|A_{k,m-1}\uparrow\rangle$) will be written as:

$$H_{AA} = \begin{pmatrix} -tf(k,m) + \lambda g(k,m) & \Lambda e^{-\frac{\pi}{Q}} h(k,m) \\ \Lambda^* e^{\frac{\pi}{Q}} h(k,m) & -tf(k,m-1) - \lambda g(k,m-1) \end{pmatrix} \tag{4.20}$$

With

$$f(k,m) = \cos\left(kf + m\frac{2\pi}{Q}\right) \tag{4.21}$$

$$g(k,m) = \sin\left(kf + m\frac{2\pi}{Q}\right) \tag{4.22}$$

$$h(k,m) = \sin\left(kf + \left(m - \frac{1}{2}\right)\frac{2\pi}{Q}\right) \tag{4.23}$$

With the relations of the Hamiltonian H_{BB} stated in equations 3.15, this matrix will be:

$$H_{BB} = \begin{pmatrix} -tf(k,m) + \lambda g(k,m) & -\Lambda e^{-\frac{\pi}{Q}} h(k,m) \\ -\Lambda^* e^{\frac{\pi}{Q}} h(k,m) & -tf(k,m-1) - \lambda g(k,m-1) \end{pmatrix} \tag{4.24}$$

4.2 Inter-helix Hamiltonian

We now calculate with the same procedure as before:

$$\begin{gathered}\sum_n e^{i\frac{2\pi}{Q}n}\left[|A_n\downarrow\rangle\langle B_n\uparrow| - |B_n\downarrow\rangle\langle A_n\uparrow|\right] = \\ \sum_n e^{i\frac{2\pi}{Q}n}\frac{1}{\sqrt{2N+1}}\sum_{\vec{q},\vec{q}'}\Big[e^{-i\vec{q}\cdot\vec{r}_n^A}e^{i\vec{q}'\cdot\vec{r}_n^B}\,|A_{\vec{q}}\downarrow\rangle\langle B_{\vec{q}'}\uparrow| - e^{-i\vec{q}\cdot\vec{r}_n^B}e^{i\vec{q}'\cdot\vec{r}_n^A}\,|B_{\vec{q}}\downarrow\rangle\langle A_{\vec{q}'}\uparrow|\Big] = \\ \vdots \\ \sum_{k,m}\left[e^{i(m-1)\pi}\,|A_{k,m}\downarrow\rangle\langle B_{k,m-1}\uparrow| - e^{-im\pi}\,|B_{k,m}\downarrow\rangle\langle A_{k,m-1}\uparrow|\right]\end{gathered} \tag{4.25}$$

And for the orbital part, again as we did before:

$$\begin{gathered}\sum_n\left[|A_n\downarrow\rangle\langle B_n\downarrow| - |B_n\downarrow\rangle\langle A_n\downarrow|\right] = \\ \sum_{k,m}\left[e^{im\pi}\,|A_{k,m}\downarrow\rangle\langle B_{k,m}\downarrow| - e^{-im\pi}\,|B_{k,m}\downarrow\rangle\langle A_{k,m}\downarrow|\right]\end{gathered} \tag{4.26}$$

$$\begin{gathered}\sum_n\left[|A_n\uparrow\rangle\langle B_n\uparrow| - |B_n\uparrow\rangle\langle A_n\uparrow|\right] = \\ \sum_{k,m}\left[e^{i(m-1)\pi}\,|A_{k,m}\uparrow\rangle\langle B_{k,m-1}\uparrow| - e^{-i(m-1)\pi}\,|B_{k,m-1}\uparrow\rangle\langle A_{k,m}\uparrow|\right]\end{gathered} \tag{4.27}$$

So, replacing these expressions with direct Hamiltonians, which we calculated in equations 3.27 and 3.28, the off-diagonal Hamiltonian H_{AB} is:

$$H_{AB} = \begin{pmatrix} -t_\perp e^{im\pi} & i\Lambda_\perp e^{i(m-1)\pi} \\ -i\Lambda_\perp e^{-im\pi} & -t_\perp e^{i(m-1)\pi} \end{pmatrix} \tag{4.28}$$

So, our final Hamiltonian is written in the basis: $(\left|A_{k,m}\downarrow\right\rangle, \left|A_{k,m-1}\uparrow\right\rangle, \left|B_{k,m}\downarrow\right\rangle,$ $\left|B_{k,m-1}\uparrow\right\rangle)$ as:

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ (H_{AB})^* & H_{BB} \end{pmatrix} \tag{4.29}$$

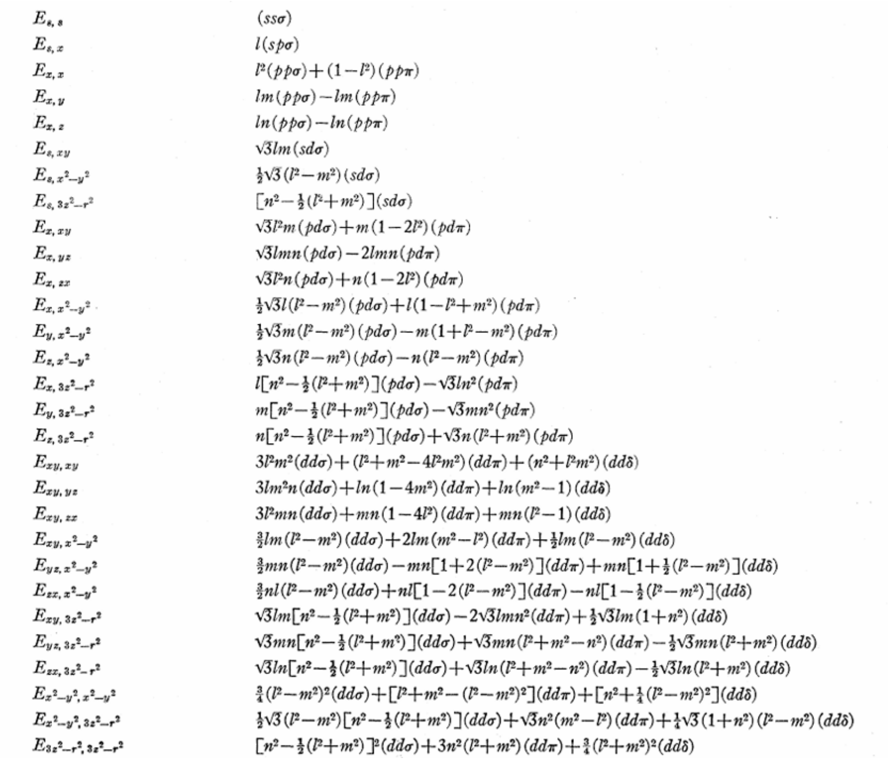
Chapter 5

Nature of the interactions

After obtaining the Hamiltonian, we may ask about the nature of the interactions. Why are there only spin-flipping and no spin-conserving interactions in atoms on the same plane? How do both spin-flipping and conserving processes occur in first-neighbor atoms in the same strand? To answer those questions, we must investigate the spin-active process.

5.1 Slater-Koster

The two-center Slater-Koster approximation is a method used to find band structures. It describes the matrix elements of the interaction between two different sites, considering the orbitals involved by using the direction cosines between the two sites. The original paper of Slater and Koster [19] contains the values of the



$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

Figure 5.1: Slater-Koster values [19].

integrals for orbitals s, p, and d, which we will use to calculate the overlap elements between the different atoms. The table found in the paper of Slater and Koster can be found in figure 5.1, where l, m, and n denote the direction cosines in the x, y, and z directions, respectively. For the interactions of the atoms, A_0 and B_0, i.e., the atoms in the same plane, the vector between them is $\vec{r}_{A_0,B_0} = 2a\hat{x}$. So, the direction cosines are $l = 1$, $m = n = 0$. We only look for processes involving p orbitals, assuming that our mobile electrons are located in p_z orbitals. So, these interactions are:

$$\begin{gathered} E_{s,p_x} = V_{ss\sigma} \quad E_{p_x,p_x} = V_{pp\sigma} \quad E_{p_y,p_y} = V_{pp\pi} \quad E_{p_z,p_z} = V_{pp\pi} \\ E_{p_z,d_{xz}} = V_{pd\pi} \quad E_{p_y,d_{xy}} = V_{pd\pi} \quad E_{p_x,d_{x^2-y^2}} = \frac{\sqrt{3}}{2}V_{pd\sigma} \quad E_{p_x,d_{z^2}} = -\frac{1}{2}V_{pd\sigma} \end{gathered} \tag{5.1}$$

For the interaction between the atoms A_0 and A_1 it will be more tedious to calculate the terms; however, we notice that the vector $\vec{r}_{A_0,A_1}$ has components in the three directions, so $l \neq 0$, $m \neq 0$ and $n \neq 0$, so we will have terms involving all the orbitals p with orbitals s, p and d.

5.2 Spin-orbit coupling

The spin-orbit Hamiltonian, without any consideration of breaking space-inversion symmetry, has the form:

$$H_{so} = \xi \vec{L} \cdot \vec{s}, \tag{5.2}$$

where $\vec{L}$ is the angular momentum operator and $\vec{s}$ is the vector of Pauli matrices. The matrix elements of $\vec{L} \cdot \vec{s}$ in the basis of s, p and d orbitals is calculated in [10], and has the following form:

Orbital	s	p_x	p_y	p_z
s	0	0	0	0
p_x	0	0	$-is_z$	is_y
p_y	0	is_z	0	$-is_x$
p_z	0	$-is_y$	is_x	0

Orbital	d_{xy}	$d_{x^2-y^2}$	d_{xz}	d_{yz}	d_{z^2}
d_{xy}	0	$2is_z$	$-is_x$	is_y	0
$d_{x^2-y^2}$	$-2is_z$	0	is_y	is_x	0
d_{xz}	is_x	$-is_y$	0	$-is_z$	$i\sqrt{3}s_y$
d_{yz}	$-is_y$	$-is_x$	is_z	0	$-i\sqrt{3}s_x$
d_{z2}	0	0	$-i\sqrt{3}s_y$	$i\sqrt{3}s_x$	$0.$

(5.3)

The matrix elements will also have an energy ξ associated with this type of orbital. For example, an interaction between p_x and p_z will be $is_y\xi_p$.

5.3 Rashba effect

The Rashba effect was discovered in 1959 by the scientist who gave its name to the effect. It is a phenomenon that occurs in systems lacking space-inversion symmetry, and it allows spin-active processes. This led to new investigations of spin-orbit interactions in systems lacking space-inversion symmetry, as seen in [20], where the authors reviewed the work studying the Rashba effect. The lack of space-inversion symmetry can be considered using the electric field caused by a helical structure.

For simplicity, to analyze the Rashba effect in a double helix, focus on the electric field caused by a single helix. We may consider then point charges located in 2.2. We will resume the process made by Eremko and Loktev in [21], where they calculate the electric field of a distribution of charges placed along a helix.

We can define the helix with cylindrical coordinates parametrized with some parameter τ:

$$\rho(\tau) = \rho, \quad \phi(\tau) = 2\pi\tau, \quad z(\tau) = b\tau. \tag{5.4}$$

Notice that $b = Qf$ is the pitch of the helix, so it is the same description as the helix of section 2.1.1. The potential $V(\vec{r})$ is invariant under displacements of $\tau = \frac{1}{Q}$. We can define a Frenet frame that describes the helical curve at each point. For the helix described by the curve 5.4, those unit vectors are [21]:

$$\begin{aligned}
\hat{e}_t &= -\frac{2\pi\rho}{a(\rho)}\sin\phi\hat{e}_x + \frac{2\pi\rho}{a(\rho)}\cos\phi\hat{e}_y + \frac{b}{a(\rho)}\hat{e}_z, \\
\hat{e}_b &= \frac{b}{a(\rho)}\sin\phi\hat{e}_x - \frac{b}{a(\rho)}\cos\phi\hat{e}_y + \frac{2\pi\rho}{a(\rho)}\hat{e}_z, \\
\hat{e}_\rho &= \cos\phi\hat{e}_x + \sin\phi\hat{e}_y,
\end{aligned} \tag{5.5}$$

with t, b and ρ denoting the tangential, binormal, and normal directions, and $a(\rho) = \sqrt{b^2 + (2\pi\rho)^2}$ the arc length of one turn of the helix. Eremko and Loktev calculated the electric field caused by this helicoidal distribution of charges using the Fourier transformation. A more detailed procedure may be found in their work

[21]. Here, we only summarize the form of the field, which is:

$$\vec{E'} = \boldsymbol{\nabla} V = \left|\vec{E'}\right|(\cos\theta \hat{e}_\rho + \sin\theta \hat{e}_b), \tag{5.6}$$

where $\left|\vec{E'}\right| = \sqrt{E'^2_\rho + E'^2_b}$, $\tan\theta = \frac{E'_b}{E'_\rho}$, $E'_\rho = \frac{\partial V}{\partial \rho}$, and $E'_b = -\frac{a(\rho)}{b\rho}\frac{\partial V}{\partial \phi}$. So, the electric field caused by the helical potential has radial and binormal components. Then, it is convenient to place the p_z orbital in the binormal direction and the p_x orbital in the radial component to maintain the Slater-Koster terms for the A_0 and B_0 atoms as calculated. This electric field will open up the possibility to connect the p_z orbital with the s, d_{xz} and d_{z^2}, and the p_x orbital with the s, d_{xz} and $d_{x^2-y^2}$ orbitals.

These couplings are proportional to the electron's charge and the electric field in the direction needed to make the interaction. For example, the Hamiltonian term describing the interaction between the orbital p_x (placed in the radial direction) and the orbital s will be proportional to the radial component of the field:

$$\langle p_x|H|s\rangle = eE'^{\rho}_{sp} \tag{5.7}$$

Another useful example is the Hamiltonian term describing the interaction between the p_z and d_{xz} orbitals, which requires both components of the field so that it will have the following form:

$$\langle p_z|H|d_{xz}\rangle = eE'^{\rho b}_{pd} \tag{5.8}$$

Considering this, we can find the terms involving the coupling caused by the electric field. We can then write again an intra-atom Hamiltonian of orbitals, as we did in 5.3 with the basis of $(s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{xz}, d_{yz}, d_{z^2})$:

$$H = \begin{pmatrix} \varepsilon_s & eE^{\prime\rho}_{sp} & 0 & eE^{\prime b}_{sp} & 0 & 0 & 0 & 0 & 0 \\ eE^{\prime\rho}_{sp} & \varepsilon_p & -is_z\xi_p & is_y\xi_p & 0 & eE^{\prime\rho}_{pd} & eE^{\prime\rho b}_{pd} & 0 & 0 \\ 0 & is_z\xi_p & \varepsilon_p & -is_x\xi_p & 0 & 0 & 0 & 0 & 0 \\ eE^{\prime b}_{sp} & -is_y\xi_p & is_x\xi_p & \varepsilon_p & 0 & 0 & eE^{\prime\rho b}_{pd} & 0 & eE^{\prime b}_{pd} \\ 0 & 0 & 0 & 0 & \varepsilon_d & 2is_z\xi_d & -is_x\xi_d & is_y\xi_d & 0 \\ 0 & eE^{\prime\rho}_{pd} & 0 & 0 & -2is_z\xi_d & \varepsilon_d & is_y\xi_d & is_x\xi_d & 0 \\ 0 & eE^{\prime\rho b}_{pd} & 0 & eE^{\prime\rho b}_{pd} & is_x\xi_d & -is_y\xi_d & \varepsilon_d & -is_z\xi_d & i\sqrt{3}s_y\xi_d \\ 0 & 0 & 0 & 0 & -is_y\xi_d & -is_x\xi_d & is_z\xi_d & \varepsilon_d & -i\sqrt{3}s_x\xi_d \\ 0 & 0 & 0 & eE^{\prime b}_{pd} & 0 & 0 & -i\sqrt{3}s_y\xi_d & i\sqrt{3}s_x\xi_d & \varepsilon_d \end{pmatrix} \tag{5.9}$$

5.4 Inter-helix interaction

As we stated in the construction of the Hamiltonian, we obtain terms that allow spin flipping between pairs of bases. We noticed that it was because of the absence of space-inversion symmetry that a Rashba-type interaction should be present.

As we consider a first-order Hamiltonian of spin-orbit interaction and assume our orbitals to be p_z orbitals, we expect hopping paths of the form:

$$\left|p_z^A\sigma\right\rangle \xrightarrow{I_1} \left|\right\rangle \xrightarrow{I_2} \left|\right\rangle \xrightarrow{I_3} \left|p_z^B(-\sigma)\right\rangle, \tag{5.10}$$

where I_1, I_2, and I_3 are a spin-orbit interaction in the intra-atomic, a coupling between p and s, or p and d orbitals caused by the electric field, and an inter-atomic energy value given by Slater-Koster terms (not necessary in this order). Note that the mix of spin-orbit and the coupling caused by the field is the Rashba effect.

In fact, we know that it has to be of this form by the absence of space-inversion, but we can also see it from the fact that it cannot be only due to intrinsic SO coupling because it will need an interaction of orbitals p_x from one atom to p_z of the other. As they are on the same plane and the p_x are oriented in the radial direction, the p_x and p_z are orthogonal, and no Slater-Koster term allows their overlap. This would be the case in a system where space inversion is allowed. We need this extra Rashba term to find the process.

We will find some possible paths in this three-step process and will consider the s, p, and d orbitals by using the terms found in equation 5.9 and the Slater-Koster terms of equation 5.1. Now we have the tools to find a three-way path from $\left|p_z^A\right\rangle$ to $\left|p_z^B\right\rangle$. Let us return to the path given in 5.10.

We can consider two cases. The first one is that either I_1 or I_3 is the Slater-Koster term. That means that it should be either E_{p_z,p_z} or $E_{p_z,d_{xz}}$. Notice that the first one is a direct path and is, in fact, the kinetic orbital term. It does not depend on spin, so we discard it. The other option is $E_{p_z,d_{xz}}$. The orbital d_{xz} can couple with the orbital p_x by the electric field. It can also happen with the p_z orbital, but it will not have a SOC, so we discard it. In the first scenario, the p_x orbital can be coupled with the p_z orbital of atom B, with spin-orbit completing the process. So, it will be:

$$\left|p_z^A\sigma\right\rangle \xrightarrow{V_{pd\pi}} \left|d_{xz}^B\sigma\right\rangle \xrightarrow{\vec{E}} \left|p_x^B(-\sigma)\right\rangle \xrightarrow{SOC} \left|p_z^B(-\sigma)\right\rangle \tag{5.11}$$

Another option would be first to have the SOC term and then the coupling using the electric field. We need that in the end we have the p_z orbital, so the orbital mediating the process should be d_{z^2}, and then the process would be:

$$\left|p_z^A\sigma\right\rangle \xrightarrow{V_{pd\pi}} \left|d_{xz}^B\sigma\right\rangle \xrightarrow{SOC} \left|d_{z^2}^B(-\sigma)\right\rangle \xrightarrow{\vec{E}} \left|p_z^B(-\sigma)\right\rangle \tag{5.12}$$

Notice that in those processes, we may exchange the processes, so the Rashba effect happens in the A atom, but it will have the same elements:

$$\begin{gathered}\left|p_z^A\sigma\right\rangle \xrightarrow{SOC} \left|p_x^B(-\sigma)\right\rangle \xrightarrow{\vec{E}} \left|d_{xz}^A(-\sigma)\right\rangle \xrightarrow{V_{pd\pi}} \left|p_z^B(-\sigma)\right\rangle \\ \left|p_z^A\sigma\right\rangle \xrightarrow{\vec{E}} \left|d_{z^2}^A\sigma\right\rangle \xrightarrow{SOC} \left|d_{xz}^A(-\sigma)\right\rangle \xrightarrow{V_{pd\pi}} \left|p_z^B(-\sigma)\right\rangle\end{gathered} \tag{5.13}$$

Those processes will have energies that will be given by the functions:

$$\left\langle p_z^A\sigma\middle|H\middle|p_z^B(-\sigma)\right\rangle = f(V_{pd\pi}, \xi_p i s_y, E_{pd}^{\rho b}) \tag{5.14}$$

$$\left\langle p_z^A\sigma\middle|H\middle|p_z^B(-\sigma)\right\rangle = f(V_{pd\pi}, \xi_d i\sqrt{3}s_y, E_{pd}^{b}) \tag{5.15}$$

Notice that s_y is responsible for the flip spin, which makes this a spin-flip process.

The other possible scenario is that I_2 is given by the Slater-Koster term, which means that I_1 or I_3 should be a SOC. The possible mediating orbitals should then be p_x or p_y. We then need processes like:

$$\begin{gathered}\left|p_z^A\sigma\right\rangle \xrightarrow{SOC} \left|p_{x,y}^A(-\sigma)\right\rangle \xrightarrow{V} |\rangle \xrightarrow{\vec{E}} \left|p_z^B(-\sigma)\right\rangle \\ \left|p_z^A\sigma\right\rangle \xrightarrow{\vec{E}} |\rangle \xrightarrow{V} \left|p_{x,y}^B(\sigma)\right\rangle \xrightarrow{SOC} \left|p_z^B(-\sigma)\right\rangle\end{gathered} \tag{5.16}$$

So, the blank state should be either s, d_{xz}, or d_{z^2} orbital. The only orbital that couples with p_y by Slater-Koster is d_{yz}, but it does not couple with p_z, so the mediating p orbital should be p_x. These processes would then have the following form:

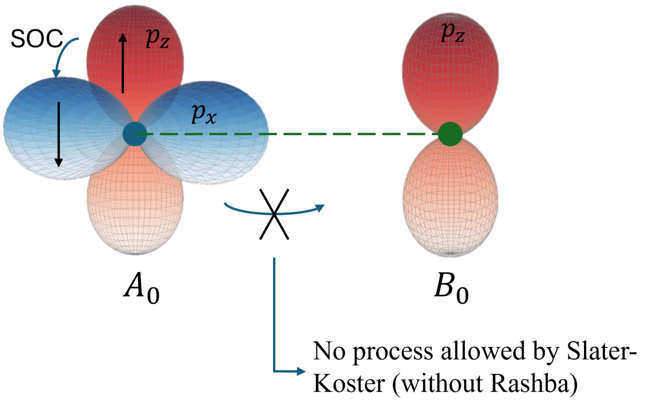
$$\begin{gathered}\left|p_z^A\sigma\right\rangle \xrightarrow{SOC} \left|p_x^A(-\sigma)\right\rangle \xrightarrow{V_{sp\sigma}} \left|s^B(-\sigma)\right\rangle \xrightarrow{\vec{E}} \left|p_z^B(-\sigma)\right\rangle \\ \left|p_z^A\sigma\right\rangle \xrightarrow{SOC} \left|p_x^A(-\sigma)\right\rangle \xrightarrow{-\frac{1}{2}V_{pd\sigma}} \left|d_{z^2}^B(-\sigma)\right\rangle \xrightarrow{\vec{E}} \left|p_z^B(-\sigma)\right\rangle \\ \left|p_z^A\sigma\right\rangle \xrightarrow{\vec{E}} \left|s^A\sigma\right\rangle \xrightarrow{V_{sp\sigma}} \left|p_x^B(\sigma)\right\rangle \xrightarrow{SOC} \left|p_z^B(-\sigma)\right\rangle \\ \left|p_z^A\sigma\right\rangle \xrightarrow{\vec{E}} \left|d_{z^2}^A\sigma\right\rangle \xrightarrow{V_{pd\sigma}} \left|p_x^B(\sigma)\right\rangle \xrightarrow{SOC} \left|p_z^B(-\sigma)\right\rangle\end{gathered} \tag{5.17}$$

The Hamiltonians then will be given by functions of the form:

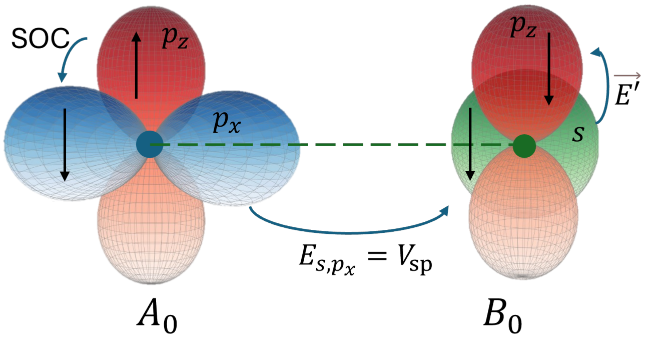
$$\left\langle p_z^A\sigma\middle|H\middle|p_z^B(-\sigma)\right\rangle = f(V_{pd\sigma}, \xi_p i s_y, E_{sp}^{\rho b}) \tag{5.18}$$

$$\left\langle p_z^A\sigma\middle|H\middle|p_z^B(-\sigma)\right\rangle = f(V_{pd\sigma}, \xi_p i s_y, E_{pd}^{b}) \tag{5.19}$$

We should emphasize that we did not restrict this to processes involving spin-flipping. In fact, we just calculated the possible paths that led to these interactions. This result was natural from the Slater-Koster overlaps and the Rashba effect. Notice that the symmetry consideration was, in fact, a good prediction because it predicted that we have only spin-flipping but not spin-conserving processes. In figure 5.2, we plot the not-account of interactions without an electric field and a spin-flipping process involving a s orbital (the first path of 5.17).



(a) No interaction possible without an Electric field



(b) Interaction allowing spin-flipping with Rashba effect involving s orbital

Figure 5.2: Interactions of atoms in the same xy plane

5.5 Intra-helix interactions

Here, we have interactions involving spin-flipping and spin-conserving. The terms of SOC and Rashba are the same as before. As we stated before, the Slater-Koster terms are more complicated because neither of the direct cosines is equal to zero, so we will have a lot of overlap terms involving p orbitals. We will not perform a deep analysis of these processes because of their complexity. We summarize some of the paths allowing the spin-flipping and spin-conserving processes.

The spin-flipping processes may not even include the electric field. There are terms involving p_x and p_y orbitals of the atom A_0 directly with the p_z orbital of the first neighbor of the same strand A_1. Those Slater-Koster terms will be E_{p_x,p_z}, and E_{p_y,p_z} from the figure 5.1. They include both π and σ bondings, but we will not calculate the explicit form involving the direction cosines. These processes will have the form:

$$\left|p_z^{A_0}\sigma\right\rangle \xrightarrow{SOC} \left|p_{x,y}^{A_0}(-\sigma)\right\rangle \xrightarrow{E_{(p_x,p_y),p_z}} \left|p_z^{A_1}(-\sigma)\right\rangle \tag{5.20}$$

This matrix element will be defined by some function f:

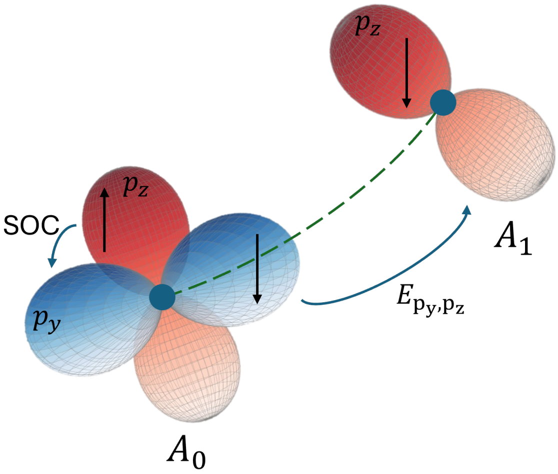
$$\langle A_0\sigma|H|A_1(-\sigma)\rangle = f(i\xi_p s_y, E_{p_x,p_z}) \quad \text{or} \quad f(i\xi_p s_x, E_{p_y,p_z}) \tag{5.21}$$

With $E_{p_x,p_z} = E_{p_x,p_z}(V_{pp\sigma}, V_{pp\pi})$ and $E_{p_y,p_z} = E_{p_y,p_z}(V_{pp\sigma}, V_{pp\pi})$, due to the form of the Slater-Koster terms. We can also have some paths involving the electric field, which may include the s and d orbitals. We do not include them, but they will have an extra term that includes the terms $E_{sp,pd}^{\prime b,\rho,\rho b}$ of the interaction of orbitals due to the field.

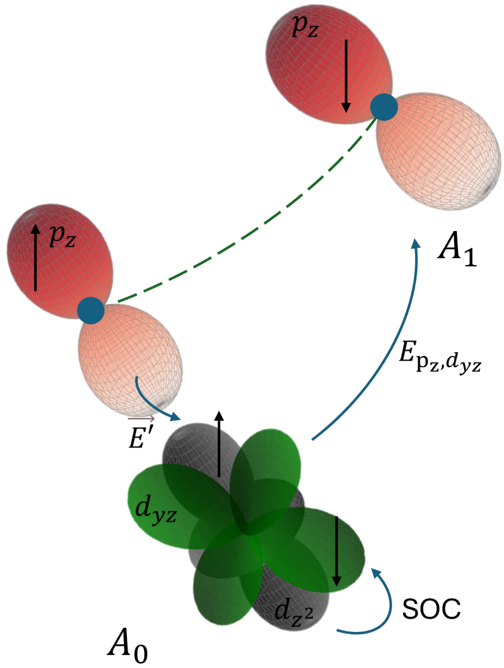
The spin-conserving paths need the Rashba effect. Recall that we are looking for first-order operations and that we are considering the electrons in the p_z orbitals. The SOC terms that involve the orbital p_z flip the spin, as they involve the s_x and s_y Pauli matrices, so a term only involving the orbitals p will need a second-order SOC interaction, and we do not allow them. We should focus then on the SOC interaction that preserves spin in the d orbitals. There are only two of them, as seen in 5.3. The first involves the orbitals d_{xy} and $d_{x^2-y^2}$, while the second does it with the d_{xz} and d_{yz}. We discard the first one because both orbitals do not interact with the p_z because of the electric field. So, the path that preserves spin for the first-neighbor atoms of the same helix should have the following form:

$$\left|p_z^{A_0}\sigma\right\rangle \xrightarrow{\vec{E}} \left|d_{xz}^{A_0}\sigma\right\rangle \xrightarrow{SOC} \left|d_{yz}^{A_0}\sigma\right\rangle \xrightarrow{E_{d_{yz},p_z}} \left|p_z^{A_1}\sigma\right\rangle \tag{5.22}$$

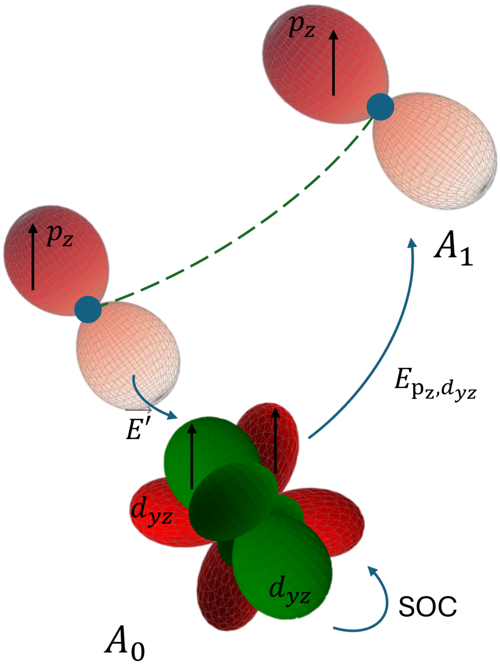
We plot some of those processes in figure 5.3, where we exaggerated the curvature of the helix to visualize the orientation of p_z orbitals in the binormal direction and the p_y orbital in the tangential direction of the helix.



(a) Spin-flip process without electric field with p_y orbital



(b) Spin-flip process with electric field with d_{z^2} and d_{yz} orbital



(c) Spin-conserving process with electric field with d_{xz} and d_{yz} orbitals

Figure 5.3: Interactions of first-neighbors atoms in the same helix

Chapter 6

Conclusions

In this work, we presented a new approach for understanding spin-active processes in a double helix system, which can be useful to explain spin transport in helicoidal molecules such as DNA. We chose a proper line group to represent a double-helix molecule. This could be done with more complexity, assuming that the different bases are a collection of different atoms and not just single atoms. This would lead to a multi-orbital system, and we would be able to understand better some of the symmetries of the system.

However, with this simplification, we derived a Hamiltonian for spin-active processes using symmetry considerations. This was demonstrated to be a good approach to finding spin-orbit Hamiltonians because we were able to obtain them without knowing the precise form of the Hamiltonian. It was sufficient to define just some matrix elements and then apply the symmetry operations to find the other elements as functions of the previously defined ones.

The Hamiltonian in reciprocal space should also be further analyzed. Something that should be noted is that the base is $(|A_{k,m}\downarrow\rangle, |A_{k,m-1}\uparrow\rangle, |B_{k,m}\downarrow\rangle, |B_{k,m-1}\uparrow\rangle)$. This dependence on m and $m-1$ differs from the Varela model [9] and may cause a parity break in the energy as a function of k. Future investigations should analyze the eigenenergies of the Hamiltonian to find the role of the results obtained merely by symmetry considerations.

Finally, we analyzed the nature of the interactions. It was shown that just by finding the possible paths involving spin, we arrive at processes of spin-flipping for atoms in the same plane and both spin-flipping and spin-conserving for first-neighbor atoms in the same helix. These are the same results predicted by symmetry considerations.

The Rashba effect showed a surprising relevance to these processes and was responsible for most of them. However, we only considered it an electric field breaking the space-inversion symmetry. Some works in the field [21, 20] explain with further analysis the role of the Rashba effect and how to understand it. Something that should also be analyzed in more detail is the orientation of the orbitals. We placed them in the directions given by the Frenet frame of the helix to be invariant to the point subgroup of the line group describing the system. Future investigations should explain if this choice of orientations of the orbitals is appropriate and how it will change if we choose another one. Finally, we must include the obtained Hamiltonian in certain models of spin polarization in helices, such as those explaining the CISS effect.

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