UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingeniería

Extension of Bloch Expansion to Helix-Like Molecules: An Analytical Tight Binding Model of DNA

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$$2 \times 2 = 0 + 1 + 0 + 1 + 2,$$

and

$$\vec{\epsilon}^i \vec{\epsilon}^j = \partial_i \partial_j \nabla^{-2} \delta^3(\boldsymbol{x} - \boldsymbol{y})$$

Angelo: Your friendship has been a beacon of support and understanding in my personal endeavours. Your presence and insights have enriched my experiences and provided much-needed perspective. Thank you so much for all you have done for me.

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Resumen

Esta tesis presenta un estudio exhaustivo de un modelo de unión fuerte aplicado a moléculas helicoidales, específicamente aquellas que se asemejan al ADN. Aborda la modelización de la estructura de doble hélice del ADN y sus bases, empleando principios de mecánica cuántica y física del estado sólido. La investigación tiene como objetivo explorar las bandas de electrones asociadas con los orbitales π de las bases del ADN, centrándose en los efectos de polarización de spin y los niveles de energía cercanos al nivel de Fermi. La tesis integra enfoques de mecánica clásica y cuántica, enfatizando la traducción y rotación de las bases dentro de la estructura helicoidal. El objetivo final es comprender el comportamiento del electrón en sistemas similares al ADN, contribuyendo así al campo más amplio de la electrónica molecular.

Abstract

The thesis presents a comprehensive study of a tight-binding model applied to helical molecules, specifically those resembling DNA. It addresses the modeling of DNA's double helix structure and bases, employing quantum mechanics and solid-state physics principles. The research aims to explore the electron bands associated with the π-orbitals of DNA bases, focusing on spin polarization effects and energy levels near the Fermi level. The thesis integrates classical and quantum mechanics approaches, emphasizing the translation and rotation of bases within the helical structure. The ultimate objective is to understand the electron behavior in DNA-like systems, contributing to the broader field of molecular electronics.

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Chapter 1

Introduction

This thesis develops a mathematical framework for a tight-binding model applied to chiral-like molecules, with a focus on a basic DNA-like system. It begins by examining the structure of a DNA molecule, which consists of two strands forming a helical shape. The thesis delves into the modeling of DNA bases and their atomic orbitals, aiming to understand the electronic properties of DNA through this model.

1.1 Problem Statement

A DNA molecule comprises two linked strands that wind around each other. It's similar to a ladder twisted in a helix-like shape. Each strand has a backbone made of alternating sugar and phosphate groups. Attached to each sugar, there is one of 4 bases: adenine (A), guanine(G), cytosine (C) and thymine (T). DNA bases are planar organic molecules bonded by sp^2hybridization, where the atoms have their p_z orbital perpendicular to the planar molecule [1]. These p_z orbitals represent the π-band; I will model the rest of these bases with hydrogen-like atoms, where the p_x and p_y orbitals represent the σ-bands. There are other parameters to consider, particularly a tilt of the organic molecule to the x, y plane; I will call this tilt θ. Also, the helix has a radius $a$and pitch b. The arc length between bases will be denoted by $\Delta\phi$. The detailed model will be as follows.

1.1.1 DNA Model

Consider, if you will, a double-stranded DNA type infinite helix along the z axis. Along these helices, there are evenly spaced hydrogen-like atoms with the p_x orbital parallel to the normal vector of the helix. The p_y orbital is almost parallel to the tangent vector, the specific orientation of the p_y and p_z orbitals is obtained as follows. Focus on the normal vector, call it $\boldsymbol{e}_{x_i}$ put $\boldsymbol{e}_{z_i'}$ parallel to the z axis and $\boldsymbol{e}_{y_i'} = \boldsymbol{e}_{z_i'} \times \boldsymbol{e}_{x_i}$ now rotate along $\boldsymbol{e}_{x_i}$ an angle θ, the new positions of $\boldsymbol{e}_{y_i'}$ and $\boldsymbol{e}_{z_i'}$ are parallel to the p_y and p_z orbitals respectably.

For one of the two helices, the atoms are located at

$$\boldsymbol{R}_i = a\cos\phi_i \boldsymbol{e}_x + a\sin\phi_i \boldsymbol{e}_y + \frac{b}{2\pi}\phi_i \boldsymbol{e}_z \tag{1.1}$$

where $\phi_n = n\Delta\phi$ the atoms of the other helix can be obtained by rotating $\boldsymbol{R}_i$ an angle π along the z axis. Now, focus on how to model each of the basis. For simplicity, we will assume that all bases are the same. Let ε_σ denote the energy of the σ-band and ε_π the one of the π-band. The Hamiltonian of one of this basis at the center of the coordinate system is.

$$\hat{h}_H = \begin{array}{c|ccc|} & |p_x\rangle & |p_y\rangle & |p_z\rangle \\ \langle p_x| & \varepsilon_\sigma & 0 & 0 \\ \langle p_y| & 0 & \varepsilon_\sigma & 0 \\ \langle p_z| & 0 & 0 & \varepsilon_\pi \end{array} \tag{1.2}$$

As mentioned before, I am interested in the spin polarization effect so I will put the spin-orbit correction from the fine structure. This Hamiltonian can be obtained by considering the effective magnetic field felt by the e^- since it is moving along a electric field. This Hamiltonian has the form

$$\hat{h}_{so} = \frac{\xi}{\hbar}\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{L}} \tag{1.3}$$

Where $\hat{\boldsymbol{\sigma}}$ denote the usual Pauli matrices, $\hat{\boldsymbol{L}}$ is the orbital angular momentum of the hydrogen atom, and ξ is a constant with units of energy.

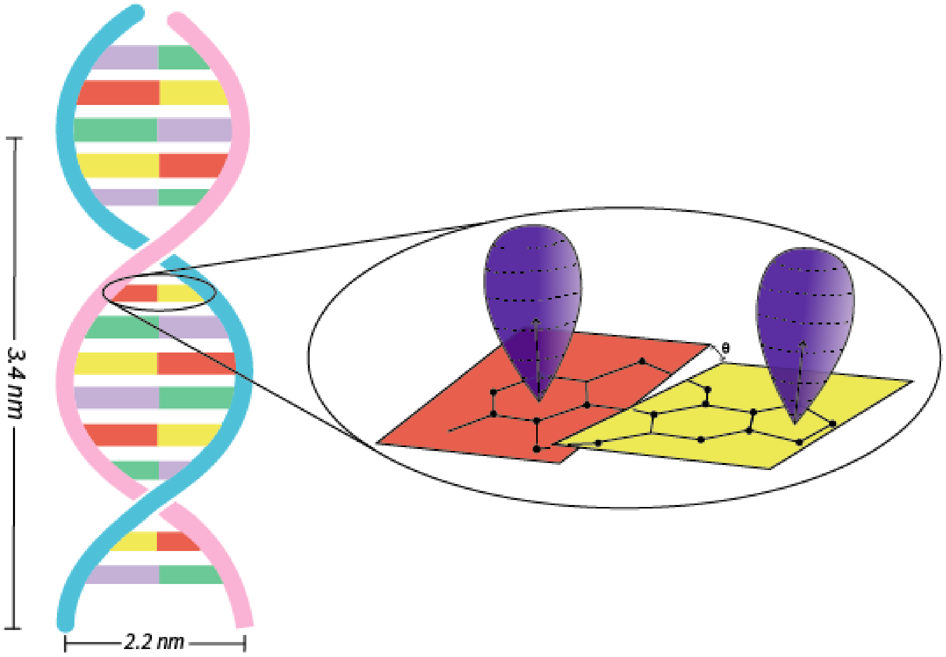

Figure 1.1: DNA double helix-like structure. Each helix is represented by one colour: light blue and pink. Bases (A), (C), (G), (T) have different colours as well. 2 p-orbitals are also represented with the tilt.

1.2 Objectives

I will be using all this information to obtain the electron bands associated with p_z orbitals. The main objective is to obtain energies of the electron in terms of the z component of the wave vector and the z component of the spin. Also, expand near the Fermi level with full and half full.

1.3 Approach to the Problem and Organization

The thesis adopts a structured approach to model DNA-like molecules using a tight-binding framework. It starts with classical and quantum mechanical analyses of a particle constrained to a helix, crucial for understanding helical structures like DNA. This is followed by adapting solid-state physics concepts to the helical context, particularly focusing on lattice vectors and Bloch's theorem. The core of the thesis involves developing a Hamiltonian model for the molecule in real and reciprocal space, examining electron bands, spin polarization effects, and the influence of spin orbit coupling. The organization is sequential, building from basic concepts to complex models, integrating both theoretical constructs and mathematical formalisms.

Chapter 2

Electron in a Helix

To begin the analisis of helix like molecules I will require some basic quantum information of an electron or any quantum particle moving along a said helix. With this in mind, I will first obtain all posible information for a classical particle confined to a helix. Then, I will use the canonical quantization procedure discussed in chapter 4 of Shankar [2] to obtain a quantum hamiltonian for a spin 0 particle. This will be our first step to analize a spin $\frac{1}{2}$ particle.

2.1 Classical Particle Along a Helix

2.1.1 Lagrangian Formalism

A free particle moving along a right-handed helix of radius a and pitch b at some arbitrary time t has a position.

$$x(t) = a\cos q(t) \qquad y(t) = a\sin q(t) \qquad z(t) = \frac{b}{2\pi}q(t) \tag{2.1}$$

With $q(t)$ being the independent or generalized coordinate. Something to note: I will drop the time dependencies from now on, remember they exist. Also, this trajectory came from imposing

$$x^2 + y^2 = a^2 \qquad z = \frac{b}{2\pi}\arctan\left(\frac{y}{x}\right) \tag{2.2}$$

These are holonomic constraints; hence, the Lagrangian of the system is only the kinetic energy and the Lagrange multipliers. I can remove the multipliers by putting the velocities in terms of q and $\dot{q}$. The velocities are

$$\dot{x} = -a\dot{q}\sin q \qquad \dot{y} = a\dot{q}\cos q \qquad \dot{z} = \frac{b}{2\pi}\dot{q} \tag{2.3}$$

The Lagrangian is

$$\begin{aligned} L(q,\dot{q}) &= \frac{1}{2}m\big(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\big) \\ &= \frac{1}{2}m\left(a^2 + \frac{b^2}{4\pi^2}\right)\dot{q}^2 \end{aligned} \tag{2.4}$$

Finally, for this section, at least, we need the conjugate momentum p.

$$\begin{aligned} p &= \frac{\partial L}{\partial \dot{q}} \\ p &= m\left(a^2 + \frac{b^2}{4\pi^2}\right)\dot{q} \\ \dot{q} &= \frac{1}{m}\left(a^2 + \frac{b^2}{4\pi^2}\right)^{-1} p \end{aligned} \tag{2.5}$$

2.1.2 Hamiltonian Formalism and Poisson Brackets

First, the Legendre Transformation to obtain the Hamiltonian; for this, I will be using the information from (2.4) and (2.5)

$$\begin{aligned} H(q,p) &= p\dot{q} - L(q,\dot{q}) \\ H(q,p) &= \frac{1}{2m}\left(a^2 + \frac{b^2}{4\pi^2}\right)^{-1} p^2 \end{aligned} \tag{2.6}$$

Recall the definition of the Poisson Brackets, let $\omega(q,p)$ and $\lambda(q,p)$ be 2 functions defined in the phase space the quantity $\{\omega,\lambda\}_{PB}$ is called the Poisson brackets between ω and λ, and is defined as

$$\{\omega,\lambda\}_{PB} = \frac{\partial \omega}{\partial q}\frac{\partial \lambda}{\partial p} - \frac{\partial \omega}{\partial p}\frac{\partial \lambda}{\partial q} \tag{2.7}$$

From this, it is a bit obvious that

$$\{q,p\}_{PB} = 1 \tag{2.8}$$

2.1.3 Other Quantities of Interest

To finish the classical procedure, I put some quantities of interest as functions of q and p. In particular, I will need both the z component of momentum and angular momentum. For completeness I will give the whole vectors $\boldsymbol{L}$ and $\boldsymbol{p}$, note that we already have $\boldsymbol{x}$ from (2.1)

$$\boldsymbol{p}(\varphi, p_\varphi) = m\frac{d\boldsymbol{x}}{d\varphi}\frac{d\varphi}{dt}$$

$$\boldsymbol{L}(\varphi, p_\varphi) = \boldsymbol{x}(\varphi, p_\varphi) \times \boldsymbol{p}(\varphi, p_\varphi)$$

After a straightforward calculation, the results are outlined below.

$$\begin{aligned} p_x &= \frac{-a}{a^2 + \frac{b^2}{4\pi^2}} \sin(q)p \\ p_y &= \frac{a}{a^2 + \frac{b^2}{4\pi^2}} \cos(q)p \\ p_z &= \frac{bp}{2\pi\left(a^2 + \frac{b^2}{4\pi^2}\right)} \end{aligned} \tag{2.9}$$

Also, something interesting, we can write $\boldsymbol{p}$ in terms of $\boldsymbol{x}$ and p

$$\boldsymbol{p} = \frac{1}{a^2 + \frac{b^2}{4\pi^2}}\left(-py,\ px,\ \frac{bp}{2\pi}\right)$$

Finally, the angular momentum

$$\begin{aligned} L_x &= \frac{-ab}{2\pi\left(a^2 + \frac{b}{4\pi^2}\right)}(q\cos q - \sin q)p \\ L_y &= \frac{-ab}{2\pi\left(a^2 + \frac{b}{4\pi^2}\right)}(\cos q + q\sin q)p \\ L_z &= \frac{a^2}{\left(a^2 + \frac{b^2}{4\pi^2}\right)}p \end{aligned} \tag{2.10}$$

From equations (2.6), (2.9) and (2.10) its clear that

$$\{p_z, H\}_{PB} = 0$$

$$\{L_z, H\}_{PB} = 0$$

Meaning that both p_z and L_z are constants of motion. I have completed the classical analysis for a particle moving along a helix. Time to go into the quantum realm.

2.2 Quantum Hamiltonian for Spin 0 Particle

Now, I need to promote q and p to operators, but most importantly, I need to find the Hilbert space $\mathbb{H}$ These operators act in Hilbert space $\mathbb{H}$. It should not be a surprise that $\mathbb{H}$ will be the set of bounded complex functions in a certain interval; Furthermore, the procedure will give some surprising and useful results.

2.2.1 Some Useful Definitions and a Very Important Assumption

Definition 1. Let $f : R \to R$ be a analytical function and $\hat{\omega}$ an operator acting on $\mathbb{H}$. Assume that $f(\omega) = a_0 + a_1\omega + a_2\omega^2 + \cdots$ then $f(\hat{\omega})$ is an operator acting on $\mathbb{H}$ defined by

$$f(\omega) = a_0\hat{\mathbb{1}} + a_1\hat{\omega} + a_2\hat{\omega}^2 + \cdots \tag{2.11}$$

Definition 2. Let $\omega : \mathbb{P} \longrightarrow \mathbb{R}$ mapping $(q, p) \to \omega(q, p)$ where $\omega(q, p)$ denotes a physical quantity, also ω is analytical at $(0, 0)$. The operator $\hat{\omega}$ is defined with the following recipe. First, expand ω in its Taylor series centred at $(0, 0)$. Second, whenever there is a product pq, write it as $\frac{1}{2}(pq + qp)$. Finally, change all $p \to \hat{p}$ $q \to \hat{q}$.

We can use these definitions to get the linear and angular momentum as operators. Obtaining the Hilbert space $\mathbb{H}$ requires to solve the Schrodinger equation with the appropriate boundary conditions. An excellent idea would be to confine the particle to the helix, meaning that after N turns, the wave function is 0. This will cause headaches in the long run. With the benefit of hindsight, we will choose another condition.

Definition 3. The very important assumption

The wave function will have periodic boundary conditions with period $\Delta\phi$ i.e.

$$\psi(q) = \psi(q + \Delta\phi) \tag{2.12}$$

I will justify this later. Let us continue with the quantization.

2.2.2 Quantizatization Procedure

Now, I will promote our canonical variables to operators with the appropriate commutation relation $p \to \hat{p}$ and $q \to \hat{q}$. The commutation can be obtained from (2.8).

$$\begin{aligned} [\hat{q}, \hat{p}] &= i\hbar\{q, p\}_{PB} \\ [\hat{q}, \hat{p}] &= i\hbar\hat{\mathbb{1}} \end{aligned} \tag{2.13}$$

The representation of the $\hat{p}$ and $\hat{q}$ will be similar to the position representation, where $\hat{q}$ multiplies and $\hat{p}$ differentiates. Let $\psi : \mathbb{R} \to \mathbb{C}$, map q to a probability density amplitude $\psi(q)$ the operators $\hat{q}$ and $\hat{p}$ acting on ψ are defined as follows.

$$\begin{aligned}\left(\hat{q}\psi\right)(q') &= q'\psi(q') \\ \left(\hat{p}\psi\right)(q') &= -i\hbar\frac{\mathrm{d}\psi}{\mathrm{d}q}\bigg|_{q'}\end{aligned} \tag{2.14}$$

Which, of course, are consistent with (2.13), in case the function on which $\hat{q}$ and $\hat{p}$ operate are multivariable, the only change in equation (2.14) is $\frac{\mathrm{d}}{\mathrm{d}q} \to \frac{\partial}{\partial q}$. The final piece of the the puzzle is obtained from the Schrodinger equation.

$$\begin{gathered}\left(\hat{H}\Psi\right)(q,t) = i\hbar\dot{\Psi}(q,t) \\ \frac{-\hbar^2}{2m}\left(a^2 + \frac{b^2}{4\pi^2}\right)^{-1}\frac{\partial^2\Psi}{\partial q^2} = i\hbar\frac{\partial\Psi}{\partial t}\end{gathered} \tag{2.15}$$

Equation (2.15) is the same equation of a free particle in one dimenssion with mass $m^* = m\left(a^2 + \frac{b^2}{4\pi^2}\right)$. The boundary conditions are obtained from (2.12). Take $\Psi(q,t) = e^{-i\omega t}\psi(q)$, then

$$\psi_n(q) = \frac{1}{\sqrt{\Omega}}e^{il_n q} \qquad\qquad l_n = \frac{2\pi}{\Delta\phi}n \tag{2.16}$$

Finally, from equation (2.10) and (2.9): $\left[\hat{L}_z, \hat{H}\right] = 0$, $\left[\hat{p}_z, \hat{H}\right] = 0$ and $\left[\hat{L}_z, \hat{p}_z\right] = 0$ meaning there exists a complete set of eigenvectors for them. Equation (2.16) was chosen with that condition in mind. The eigenvalues are outlined below.

$$\begin{aligned}(\hat{p}_z\psi)(q) &= \frac{\hbar b l_n}{2\pi\left(a^2+\frac{b^2}{4\pi^2}\right)}\psi(q)\\ \left(\hat{L}_z\psi\right)(q) &= \frac{\hbar a^2 l_n}{\left(a^2+\frac{b^2}{4\pi^2}\right)}\psi(q)\\ \left(\hat{H}\psi\right)(q) &= \frac{\hbar^2 a^2 (l_n)^2}{2m\left(a^2+\frac{b^2}{4\pi^2}\right)}\psi(q)\end{aligned} \tag{2.17}$$

We now convert the "very important assumption" into something a bit more useful: treating $\hat{p}$ as the generator of translations along the helix, we can rewrite the very important assumption as

$$(e^{-i\hat{p}\Delta\phi}\psi)(q) = \psi(q+\Delta\phi) = \psi(q) \qquad \hbar = 1 \tag{2.18}$$

We can also write it in terms of $\hat{p}_z$ and $\hat{L}_z$, the generators of translation and rotations along the z-axis.

$$\begin{aligned}\hat{p}\Delta\phi &= \frac{a^2}{a^2+\frac{b^2}{4\pi^2}}\hat{p}\Delta\phi + \frac{\frac{b}{2\pi}}{a^2+\frac{b^2}{4\pi^2}}\hat{p}\frac{b}{2\pi}\Delta\phi\\ \hat{p}\Delta\phi &= \hat{L}_z\Delta\phi + \hat{p}_z\frac{b}{2\pi}\Delta\phi\end{aligned}$$

Definition 4. Let $f : \mathbb{R} \longrightarrow \mathbb{R}$ be any function defined along the helix. Let q be a point in the helix the value $f(q+\Delta\phi)$ can be obtained by the application of the operator $\hat{T}$ to f evaluated at q. Where

$$\hat{T} = \exp\left(-i\hat{p}_z \frac{b\Delta\phi}{2\pi\hbar}\right) \exp\left(-i\hat{L}_z \frac{\Delta\phi}{\hbar}\right) \tag{2.19}$$

The very important assumption has now evolved to

$$\hat{T}\psi = \psi \tag{2.20}$$

2.3 Spin $\frac{1}{2}$ Particle

As we all know, considering only $\hat{\boldsymbol{L}}$ with the electron is incomplete, it also has an intrinsic angular momentum: spin. How do we add the spin to our result? What I am going to do is to evolve the very important assumption once more. Version 3 of the assumption is to change $\hat{L}_z$ in (2.19) to $\hat{J}_z$ where

$$\hat{J}_z = \hat{L}_z + \hat{S}_z \tag{2.21}$$

The translation operator can now be written as

$$\hat{T}_{new} = e^{-i\Delta\phi\hat{p}}\hat{R}_z(\Delta\phi) \qquad \hat{R}_z(\Delta\phi) = e^{-i\hat{S}_z\Delta\phi} \tag{2.22}$$

$$\hat{T}_{new} = \hat{T}_{old}\hat{R}_z(\Delta\phi) \tag{2.23}$$

$$\tag{2.24}$$

Definition 1. I am going to use some abuse of notation here: let $\hat{T}$ be defined as in (2.19). define a function with the same letter that maps a integer n to a translation i.e.

$$\hat{T}(n) = \left(\hat{T}\right)^n \hat{R}_z(n\Delta\phi) \tag{2.25}$$

Sorry, dear reader, for the notation, remember $\hat{T}$ with no argument is $\hat{T} = \hat{T}(1)$. Finally, the two notations are equivalent. $\hat{T}(n) = \hat{T}_n$ Additionally, it is not hard to show that

$$\hat{T}(-n) = \hat{T}^{-1}(n) = \hat{T}^{\dagger}(n)$$

The new translator operator acts over a new Hilbert space.

Definition 2. Let $\sigma =\uparrow, \downarrow$ with $\hat{S}_z \left|\uparrow\right\rangle = \frac{\hbar}{2} \left|\uparrow\right\rangle$ and $\hat{S}_z \left|\downarrow\right\rangle = -\frac{\hbar}{2} \left|\downarrow\right\rangle$ define our new Hilbert Space $\mathbb{V}$ as the direct product of $\mathbb{H}$ with $\{\left|\uparrow\right\rangle, \left|\downarrow\right\rangle\}$ i.e.

$$\mathbb{V} = \mathbb{H} \otimes \{\left|\uparrow\right\rangle, \left|\downarrow\right\rangle\} \tag{2.26}$$

Let $\psi, \varphi \in \mathbb{H}$. The following notations are equivalent

$$\psi \left|\uparrow\right\rangle + \varphi \left|\downarrow\right\rangle = \begin{pmatrix} \psi \\ \varphi \end{pmatrix} \tag{2.27}$$

The elements of $\mathbb{V}$ are called spinors The spinor that obeys the ”very important assumption” is

$$\left|l_n\right\rangle = \psi_n \, \hat{R}_z(n\Delta\phi) \left|\sigma\right\rangle \tag{2.28}$$

Chapter 3

From Crystals to Helices. What can we apply from solid-state physics?

Crystals, as systems, have a gigantic advantage over many others in the periodicity of the unit cell. Any physical quantity that depends on the position say the electron density ρ, have the propriety

$$\rho(\boldsymbol{x}) = \rho(\boldsymbol{x} + \boldsymbol{R})$$

Where $\boldsymbol{R}$ is any of the so-called lattice vectors. All the necessary calculations can be done in 1 unit cell instead of the whole crystal. Unfortunately, the DNA-Molecule is twisted, so treating it as a one-dimensional crystal will make the unit cell contain ten bases per helix; with two helices, there are 20 bases, and for three orbitals per base, we have 60 matrix elements in the Hamiltonian, if we add the spin degree of freedom, we now have 120. So, the fantastic advantage of periodicity has flown out the window.

That said, this doesn't mean we can't use the idea of crystals in helices. Most quantum results of solid-state physics have an analogous result in helices. In this chapter, I will generalize these results to any helix. These conclusions may even work for any material in a manifold-like shape, but I will stay with helices for now.

3.1 The New Lattice Vectors

How to move inside the molecule?

Recall in Chapter 1 that the arc length between sites is the same. Also, each site is rotated about the other by the same amount, meaning the molecule has some periodicity.

3.1.1 The Translation Operator

Let $|\boldsymbol{x}\rangle$ be a position eigenket and $\boldsymbol{R}$ denote any site in the helix. An operator that maps $|\boldsymbol{R}\rangle$ to $|\boldsymbol{R'}\rangle$ was defined in the "very important assumption" (2.25). But how do we know this is the correct generalization? Well, we see what made the original lattice vectors so important.

For any lattice with lattice vectors $\boldsymbol{R}_i$, all the information is contained in the Hamiltonian $\hat{H}$. If the lattice is truly infinite, moving the lattice by a vector $\boldsymbol{R}_j$ leaves the lattice the same. i.e

$$[e^{-i\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{R}}}, \hat{H}] = 0 \tag{3.1}$$

Our translation operator $\hat{T}(n)$ rotates an angle $\Delta\phi$ along the z-axis and moves the helix upwards by a distance $\frac{b}{2\pi}\Delta\phi$ as shown in (2.19). This means that whatever the Hamiltonian is, it must be that

$$\left[\hat{T}_n, \hat{H}\right] = 0 \tag{3.2}$$

The operator $\hat{T}_n$ defines the periodicity in the system.

With this, it is time to justify our ”very important assumptions”.

Proof. Since $\hat{T}_n$ commutes with $\hat{H}$, then they share a set of eigenvectors. Also, $\hat{T}_n$ is a unitary operator, meaning the eigenvalues of $\hat{T}_n$ are of the form $e^{i\alpha}$ where $\alpha \in \mathbb{R}$. Finally, the probability amplitude is determined up to a constant phase; I choose the eigenvectors so that the eigenvalue of $\hat{T}_1$ is 1. □

3.1.2 What Becomes of the Reciprocal Lattice Vectors

To define the reciprocal lattice, we consider the equation (2.16). If we change $q \to q + n\Delta\phi$ we obtain the same result. Now consider the wave function at one of the sites, meaning $q = m\Delta\phi$ then we can change $l_n \to l_n + l_k$ and again obtain the same wave function i.e.

$$\psi_n(q) = \psi_n(q + \Delta\phi) \tag{3.3}$$

$$\psi_n(\Delta\phi) = \psi_{n+1}(\Delta\phi) \tag{3.4}$$

This allows us to define the Brillouin Zone for the conjugate momentum l as the interval centered at 0 with a length equal to the smallest value of $|l_n|$.

Definition 1. For a right-handed helix with sites separated by an angle $\Delta\phi$, the first Brillouin Zone is the interval

$$\left[-\frac{\pi}{\Delta\phi}, \frac{\pi}{\Delta\phi}\right] \tag{3.5}$$

3.2 What becomes of Bloch's Theorem?

At this point, dear reader, this section should be quite clear. Bloch's Theorem is a inmediate consecuece of (3.2). What can we add to our solution (2.28) such that is an eigenket of $\hat{T}(n)$?

$$\Psi_l(q) = \frac{1}{\sqrt{\Omega}} e^{iql} u_l(q) \tag{3.6}$$

$$u_l(q) = u_l(q + \Delta\phi) \tag{3.7}$$

$$l \in \left[-\frac{\pi}{\Delta\phi}, \frac{\pi}{\Delta\phi} \right] \tag{3.8}$$

For the tight binding method, e now write the Bloch Expansion for the helix, let $|\psi\rangle$ be a spinor eigenket of a site of the helix. Then,he Bloch Expansion is given by

$$|\Psi_l\rangle = \sum_n e^{il\phi_n} \hat{R}_z(-n\Delta\phi) \hat{T}(n) |\psi\rangle \tag{3.9}$$

Chapter 4

Hamiltonian of the Molecule in Real Space

4.1 Sites Hamiltonian

As the Tight Binding model suggests, the Hamiltonian is hydrogen-like for each site, with the energies denoted in (1.2). First, I will work with the spin-orbit Hamiltonian for the hydrogen atom. Then, I will use translations and rotations on the Hamiltonian to displace it to the correct position and with the correct orientation.

4.1.1 Spin Orbit Hamiltonian In p Orbitals Basis

Definition 1. Let, $|1\rangle$, $|0\rangle$, $|-1\rangle$ denote the eigenkets of $\hat{L}_z$ in the hydrogen-like atom with $l = 1$ and $m = 1, 0, -1$ respectively. The p orbitals are defined as:

$$\begin{aligned}
|p_x\rangle &= \frac{-1}{\sqrt{2}}(|1\rangle - |-1\rangle), \\
|p_y\rangle &= \frac{i}{\sqrt{2}}(|1\rangle + |-1\rangle), \qquad (4.1) \\
|p_z\rangle &= |0\rangle .
\end{aligned}$$

Using the typical tricks of angular momentum (see, for example, chapter 3.5 of [3]) I can evaluate the product $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ by using the following properties: Let $\hat{\boldsymbol{J}}$ denote either $\hat{\boldsymbol{L}}$ or $\hat{\boldsymbol{S}}$ define

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y.$$

For $\hat{\boldsymbol{L}}$ it is true that:

$$\begin{aligned}
&\hat{L}_+ |1\rangle = 0, && \hat{L}_+ |0\rangle = \hbar\sqrt{2}\,|1\rangle , && \hat{L}_+ |-1\rangle = \hbar\sqrt{2}\,|0\rangle , \\
&\hat{L}_- |1\rangle = \hbar\sqrt{2}\,|0\rangle , && \hat{L}_- |0\rangle = \hbar\sqrt{2}\,|-1\rangle , && \hat{L}_- |-1\rangle = 0,
\end{aligned}$$

for $|\uparrow\downarrow\rangle$ we have:

$$\hat{S}_+ |\uparrow\rangle = 0, \qquad \hat{S}_+ |\downarrow\rangle = \hbar |\uparrow\rangle ,$$
$$\hat{S}_- |\uparrow\rangle = \hbar |\downarrow\rangle , \qquad \hat{S}_- |\downarrow\rangle = 0.$$

Now, I can expand the product $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ as

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \frac{1}{2}\Big(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\Big) + \hat{L}_z\hat{S}_z$$

I list some matrix elements below

$$\langle p_x\sigma| \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} |p_y\sigma'\rangle = -i\hbar \langle\sigma| \hat{S}_z |\sigma'\rangle ,$$
$$\langle p_y\sigma| \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} |p_z\sigma'\rangle = -i\hbar \langle\sigma| \hat{S}_x |\sigma'\rangle ,$$
$$\langle p_z\sigma| \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} |p_x\sigma'\rangle = -i\hbar \langle\sigma| \hat{S}_y |\sigma'\rangle .$$

Clearly

$$\langle p_i\sigma| \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} |p_j\sigma'\rangle = -i\frac{\hbar^2}{2}\epsilon^{ijk} \langle\sigma| \hat{\sigma}_k |\sigma'\rangle \tag{4.2}$$

Thus, I can write $\hat{h}_{so}$ as

$$\hat{h}_{so} = \begin{array}{c} \\ \langle p_x| \\ \langle p_y| \\ \langle p_z| \end{array} \begin{array}{c} \begin{array}{ccc} |p_x\rangle & |p_y\rangle & |p_z\rangle \end{array} \\ \begin{bmatrix} 0 & -i\hat{\sigma}_z\xi_p & i\hat{\sigma}_y\xi_p \\ i\hat{\sigma}_z\xi_p & 0 & -i\hat{\sigma}_x\xi_p \\ -i\hat{\sigma}_y\xi_p & i\hat{\sigma}_x\xi_p & 0 \end{bmatrix} \end{array}. \tag{4.3}$$

The complete Hamiltonian is the sum of the last two equations. Let us call it $\hat{h}$

$$\hat{h} = \hat{h}_H + \hat{h}_{so}. \tag{4.4}$$

4.1.2 Putting the Hamiltonians in the Molecule

The solution of the hydrogen atom in terms of the spherical harmonics has the (x, y, z)-orbital along the (x, y, z)-axis. Meanwhile, for the model, we need them translated and rotated. Let's start with some definitions.

Definition 2. Let $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$. Define $\hat{U}(\theta)$, $\hat{U}_m$, $\hat{h}(\theta)$, and $|p_{\mu_0}\rangle$ as

$$\begin{aligned} \hat{U}_x(\theta) &= e^{-i\hat{p}_x a} e^{-i\hat{J}_x\theta}, \\ \hat{U}_m &= e^{-i\hat{p}m\Delta\phi} = e^{-i\left(\hat{p}_z\frac{b}{2\pi} + \hat{L}_z\right)m\Delta\phi}, \\ \hat{h}_0(\theta) &= \hat{U}_x(\theta)\hat{h}\hat{U}_x(-\theta), \\ |p_{\mu_0}\rangle &= \hat{U}_x(\theta)e^{i\hat{S}_x\theta}\,|p_\mu\rangle\,. \end{aligned}$$

The operator $\hat{U}_x(\theta)$ translates and rotates along the x-axis, which tilts and moves any object to the border of a cylinder with radius a. The Helix's complete Hamiltonian (without hopping) can be obtained by summing over the Hamiltonians for each site.

$$\hat{H}_{so} = \sum_{n=-\infty}^{\infty} \hat{T}_n \hat{h}_0(\theta_n) \hat{T}_n^{\dagger} \tag{4.5}$$

With $\hat{T}_n$ as defined in (2.25).

4.2 Hopping Hamiltonian

Let μ, ν stand for x, y, z, and m, n for integers. Greek letters will denote orbitals and Latin letters will denote sites in the helix. The Slater-Koster overlaps only depend on the position of the orbitals and they don't affect their spin. Hence, I define the hopping Hamiltonian as

$$\hat{H} = \sum_{\mu,\nu} \sum_{m,n} |p_{\mu_n}\rangle \, t_{\mu\nu}^{mn} \, \langle p_{\nu_m}| \otimes \hat{\mathbb{1}}_s \tag{4.6}$$

Where $|p_{\mu_m}\rangle = \hat{U}_m |p_\mu\rangle$ is the μ orbital with the correct orientation for the site m. The hopping energies $t_{\mu\nu}^{mn}$ depend on the orientation between orbitals. Therefore, I need to define a unit vector associated with each orbital. Since the p_μ orbital is in the μ direction, I can get the unit vectors by first rotating along the z axis and then rotating on the new x axis.

Definition 1. Define, just for this section, $R_\mu(\theta)$ as the rotation matrix of angle θ along the μ axis. The first rotation is along the z-axis an angle ϕ_m

$$R_{z_m} = \begin{pmatrix} \cos\phi_m & -\sin\phi_m & 0 \\ \sin\phi_m & \cos\phi_m & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The second rotation is the tilt, which is obtained by rotating along the new x axis which we will call x' for the moment.

$$R_{x'}(\theta) = R_{z_m} R_x(\theta) (R_{z_m})^{-1}$$

The new orientation of the p orbitals can be calculated with a rotation matrix $\mathbb{A}_m$

$$\begin{aligned} \mathbb{A}_m &= R_{x'}(\theta) R_{z_m} = R_{z_m} R_x \\ \mathbb{A}_m &= \begin{pmatrix} \cos\phi_m & -\sin\phi_m\cos\theta & \sin\phi_m\sin\theta \\ \sin\phi_m & \cos\phi_m\cos\theta & -\cos\phi_m\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \end{aligned} \tag{4.7}$$

With this matrix, we can obtain the normal vector parallel to the p_μ orbital on the mth site by

$$\boldsymbol{n}(p_{\mu_m}) = \mathbb{A}_m \boldsymbol{e}_\mu$$

$$\begin{aligned} \boldsymbol{n}\left(p_{x_m}\right) &= (\cos\phi_m, \sin\phi_m, 0) \\ \boldsymbol{n}\left(p_{y_m}\right) &= (-\sin\phi_m\cos\theta, \cos\phi_m\cos\theta, \sin\theta) \\ \boldsymbol{n}\left(p_{z_m}\right) &= (\sin\phi_m\sin\theta, -\cos\phi_m\sin\theta, \cos\theta) \end{aligned} \tag{4.8}$$

4.2.1 Slater-Koster two Center Aproximation

The hopping energies $t^{mn}_{\mu\nu}$ can be obtained by integrating the respective spherical harmonics. Thankfully, [4] have already done it and obtained a result that only depends on the orientation of the orbitals and the interatomic distance. The hopping energy for two parallel orbitals is called $(pp\pi)$, whereas if the orbitals are facing each other then is called ($pp\sigma$). For an arbitrary rotation, there is a linear combination of ($pp\sigma$) and ($pp\pi$) [5]. Since I am only working with p orbitals, I will call them V_π and V_σ. The final approximation is

$$V_{\sigma,\pi} = \kappa_{\sigma,\pi}\frac{\hbar}{mR_{mn}^2} \tag{4.9}$$

Where κ depends on the particular atom and $\boldsymbol{R}_{nm} = \boldsymbol{R}_n - \boldsymbol{R}_m$. Some illustrations of the σ and π hopping are shown in figures 4.1, 4.2 and 4.3

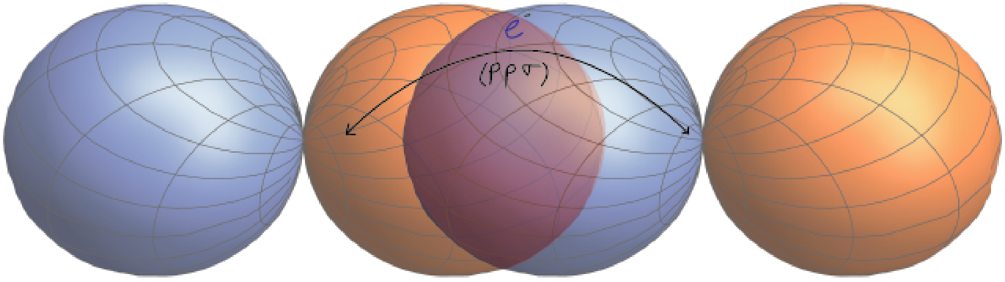

Figure 4.1: Two p-orbitals connected by a σ bond

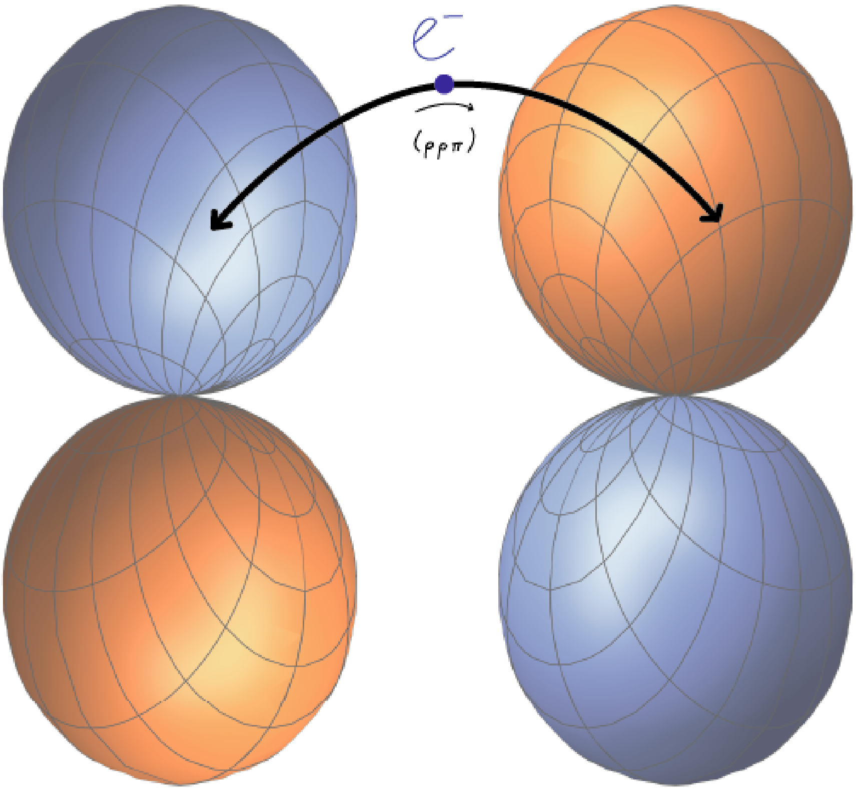

Figure 4.2: Two p-orbitals connected by a π bond

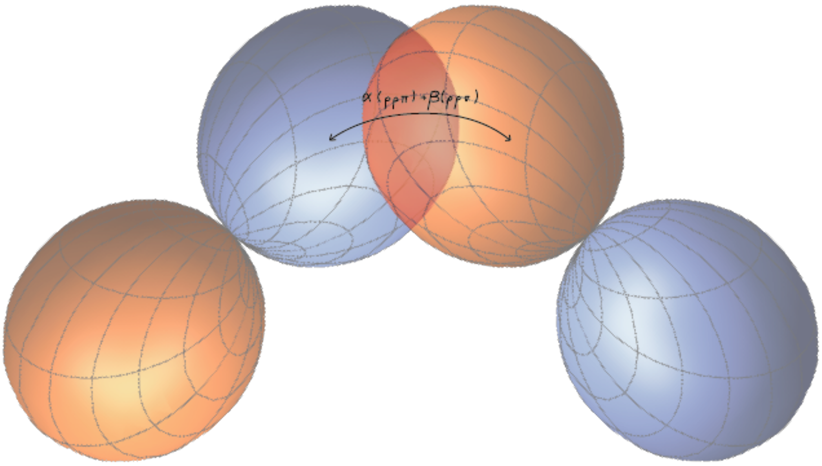

Figure 4.3: Two p-orbitals connected by a combination of π and σ bonds

The hopping energies are given by

$$t_{\mu\nu}^{mn} = \boldsymbol{n}\left(p_{\mu_m}\right) \cdot \boldsymbol{n}\left(p_{\nu_n}\right) V_{pp}^{\pi} + \frac{\boldsymbol{n}\left(p_{\mu_m}\right) \cdot \boldsymbol{R}_{nm} \;\; \boldsymbol{n}\left(p_{\nu_n}\right) \cdot \boldsymbol{R}_{nm}}{\boldsymbol{R}_{nm} \cdot \boldsymbol{R}_{nm}} \left(V_{pp}^{\sigma} - V_{pp}^{\pi}\right) \tag{4.10}$$

I now work with this expression to obtain a more useful result. I can write the dot product as $\boldsymbol{a} \cdot \boldsymbol{b} = \boldsymbol{a}^T \boldsymbol{b}$. Putting this information in the previous expression and changing $\boldsymbol{n}(p_{\mu_m}) = \mathbb{A}_m \boldsymbol{e}_\mu$ I can remove the unit bases.

$$\begin{aligned} t^{ij} &= \mathbb{A}_i^T \left(V_\pi + \boldsymbol{R}_{ji} \boldsymbol{R}_{ji}^T \frac{V_\sigma - V_\pi}{\left|\boldsymbol{R}_{ij}\right|^2} \right) \mathbb{A}_j \\ t_{\mu\nu}^{ij} &= \boldsymbol{e}_\mu^T t^{ij} \boldsymbol{e}_\nu \end{aligned} \tag{4.11}$$

For a Helix, the term inside the parenthesis only depends on the radius, pitch and angle between bases. Note that I can write $\boldsymbol{R}_{ji}$ as

$$\begin{aligned}\boldsymbol{R}_{ji} &= \begin{pmatrix} -2a\sin\frac{\phi_j-\phi_i}{2}\sin\frac{\phi_j+\phi_i}{2} \\ 2a\sin\frac{\phi_j-\phi_i}{2}\cos\frac{\phi_j+\phi_i}{2} \\ \frac{b}{2\pi}(\phi_j-\phi_i) \end{pmatrix} \\ &= R_z\left(\frac{\phi_j+\phi_i}{2}\right)\begin{pmatrix} 0 \\ 2a\sin\frac{\phi_j-\phi_i}{2} \\ \frac{b}{2\pi}(\phi_j-\phi_i) \end{pmatrix}\end{aligned}$$

Take

$$\boldsymbol{r}_{j-i} = \frac{1}{\sqrt{4a^2\sin^2(\phi_j-\phi_i)+\frac{b^2}{4\pi^2}(\phi_j-\phi_i)^2}}\begin{pmatrix} 0 \\ 2a\sin\frac{\phi_j-\phi_i}{2} \\ \frac{b}{2\pi}(\phi_j-\phi_i) \end{pmatrix}$$

The expression for t^{ij} is now

$$\begin{aligned} t^{ij} &= R_x(-\theta_i)\Big(R_z(\phi_j-\phi_i)V_\pi \\ &+ R_z\left(\frac{\phi_j-\phi_i}{2}\right)\boldsymbol{r}_{(j-i)}\boldsymbol{r}^T_{(j-i)}R_z\left(\frac{\phi_i-\phi_j}{2}\right)(V_\sigma-V_\pi)\Big)R_x(\theta_j)\end{aligned} \tag{4.12}$$

The tilt angle θ is different for each base. A list of all possible angles can be found in [6]. The tilt angle is half of the propeller twist, meaning that θ_i is in the order of 6.3^o or 0.1 radians. Since I am simply approximating, I will take $\theta = 0$.

For the Bloch Expansion, it will be useful to separate the t^{ij} matrix in its symmetric and anti-symmetric components i.e. $(t^{ij})_{(m,n)}$ and $(t^{ij})_{[m,n]}$. We only consider the first neighbours so $i = 1; j = 2$.

$$t_s^{12} = \frac{t^{ij} + \left(t^{ij}\right)^T}{2} = \begin{pmatrix} t_{xx} & t_{(xy)} & t_{zx} \\ t_{(xy)} & t_{yy} & t_{yz} \\ t_{zx} & t_{yz} & t_{zz} \end{pmatrix} \tag{4.13}$$

$$t_A^{12} = \frac{t^{ij} - \left(t^{ij}\right)^T}{2} = \begin{pmatrix} 0 & -t_{[xy]} & 0 \\ t_{[xy]} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.14}$$

Where

$$\begin{aligned}
t_{xx} &= \frac{16\pi a^2 \sin^4\left(\frac{\Delta\phi}{2}\right)((pp\sigma) - (pp\pi))}{16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2} + (pp\pi)\cos(\Delta\phi), \\
t_{(xy)} &= \frac{8\pi a^2 \sin^2\left(\frac{\Delta\phi}{2}\right)\sin(\Delta\phi)((pp\sigma) - (pp\pi))}{16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2}, \\
t_{zx} &= \frac{2ab\Delta\phi(\cos(\Delta\phi) - 1)((pp\pi) - (pp\sigma))}{16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2}, \\
t_{yy} &= \frac{4\pi a^2 \sin^2(\Delta\phi)((pp\sigma) - (pp\pi))}{16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2} + (pp\pi)\cos(\Delta\phi), \\
t_{yz} &= \frac{2ab\Delta\phi\sin(\Delta\phi)((pp\sigma) - (pp\pi))}{16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2}, \\
t_{zz} &= \frac{b^2\Delta\phi^2((pp\sigma) - (pp\pi))}{\pi\left(16\pi a^2 \sin^2(\Delta\phi) + b^2\Delta\phi^2\right)} + (pp\pi), \\
t_{[xy]} &= (pp\pi)\sin(\Delta\phi).
\end{aligned} \tag{4.15}$$

With this information, I can plot the energy contribution as a function of the angle ϕ. Figure 4.4 represents the values of the energy as a function of distance. It's not hard to see that considering only first neighbours is not enough, in particular we can see that the biggest contribution of t_{zx} is in the forth neighbour. Either way, the purpose of this and the following chapter is to show the use fullness of the method, hence I will only take into account first neighbours.

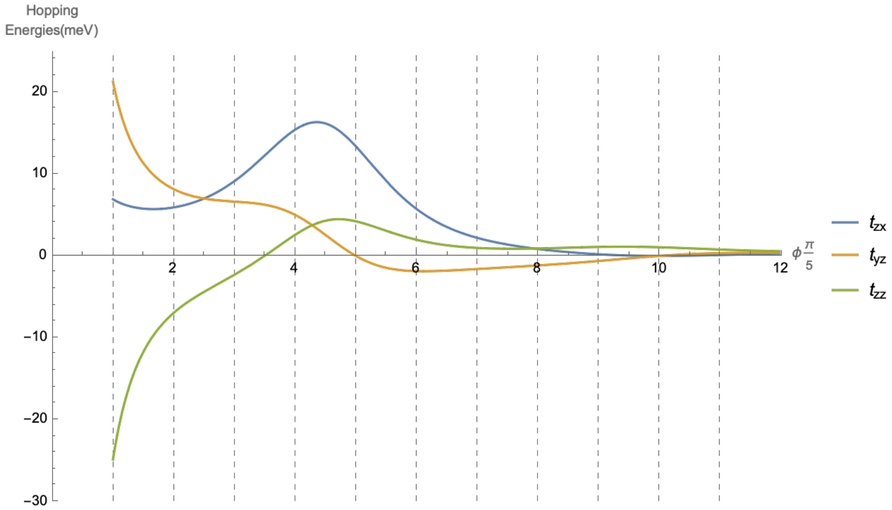

Figure 4.4: Hopping energies involving z-orbitals each dashed line represent a neighbour. We present $\Delta\phi \in \left[\frac{\pi}{5}, \frac{11\pi}{5}\right]$ i.e. the first 11 neighbours

Chapter 5

Hamiltonian In Reciprocal Space

5.1 Electron Bands For a Particle With No Spin

Definition 1. Let $|p_{\mu_i}\rangle$ denote the μ orbital at site i and l be the quantum number associated with the operator

$$\hat{L}_z + \hat{p}_z \frac{b}{2\pi}$$

Define the ket

$$|l, \mu\rangle = \frac{1}{N} \sum_i e^{il\phi_i} |p_{\mu_i}\rangle \tag{5.1}$$

where N is the number of sites and l is in the first Brillouin Zone.

Note that this definition is very similar to the usual Bloch expansion in crystals.

Also, it is consistent with (3.9) only with the spin part removed. It's not hard to show that $|l, \mu\rangle$ is an eigenket of $\hat{T}(n)$ for any integer n. Finally, for this crude model I will assume that $\langle p_{\mu_j} | p_{\mu_i} \rangle = \delta_i^j$. With this, I now calculate the matrix elements of the site Hamiltonian and the hopping Hamiltonian in this base

$$\begin{aligned}
\langle l'\mu | \hat{H}_1 | l\nu \rangle &= \frac{1}{N} \sum_{i,j} e^{-il'\phi_i} e^{il\phi_j} \langle p_{\mu_i} | \hat{H}_1 | p_{\nu_j} \rangle \\
\hat{H}_1 | p_{\nu_j} \rangle &= \varepsilon_\nu | p_{\nu_j} \rangle \\
\langle l'\mu | \hat{H}_1 | l\nu \rangle &= \frac{1}{N} \sum_{i,j} e^{-il'\phi_i} e^{il\phi_j} \varepsilon_\nu \delta_i^j \delta_\mu^\nu \\
\langle l'\mu | \hat{H}_1 | l\nu \rangle &= \frac{1}{N} \sum_{i} e^{-i(l'-l)\phi_i} \varepsilon_\nu \delta_\mu^\nu \\
\langle l'\mu | \hat{H}_1 | l\nu \rangle &= \delta_l^{l'} \delta_\mu^\nu \varepsilon_\nu
\end{aligned}$$

For a fixed l I can write

$$\hat{H}_1(l) = \begin{array}{c} \\ \langle lx| \\ \langle ly| \\ \langle lz| \end{array} \begin{array}{c} \begin{array}{ccc} |lx\rangle & |ly\rangle & |lz\rangle \end{array} \\ \begin{bmatrix} \varepsilon_\sigma & 0 & 0 \\ 0 & \varepsilon_\sigma & 0 \\ 0 & 0 & \varepsilon_\pi \end{bmatrix} \end{array} \tag{5.2}$$

Now for the hopping Hamiltonian.

$$\begin{aligned}
\langle l'\mu|\,\hat{H}_2\,|l\nu\rangle &= \frac{1}{N}\sum_{i,j} e^{-il'\phi_i}e^{il\phi_j}\,\langle p_{\mu_i}|\,\hat{H}_2\,|p_{\nu_j}\rangle \\
\hat{H}_2\,|p_{\nu_j}\rangle &= \sum_{\mu=x,y,z}\left[t^{j-1,j}_{\mu\nu}\,|p_{\mu_{j-1}}\rangle + t^{j+1,j}_{\mu\nu}\,|p_{\mu_{j+1}}\rangle\right] \\
\langle l'\mu|\,\hat{H}_2\,|l\nu\rangle &= \frac{1}{N}\sum_{i,j} e^{-il'\phi_i}e^{il\phi_j}\left[t^{12}_{\mu\nu}\delta^i_{j-1} + t^{21}_{\mu\nu}\delta^i_{j+1}\right] \\
\langle l'\mu|\,\hat{H}_2\,|l\nu\rangle &= \frac{1}{N}\sum_{i} e^{-i(l'-l)\phi_i}\left[e^{il'\Delta\phi}t^{12}_{\mu\nu} + e^{-il'\Delta\phi}t^{21}_{\mu\nu}\right] \\
\langle l'\mu|\,\hat{H}_2\,|l\nu\rangle &= \delta^{l'}_{l}\Big(\cos{(l\Delta\phi)}(t_{SIM})_{\mu\nu} + i\sin(l\Delta\phi)(t_{ASIM})_{\mu\nu}\Big)
\end{aligned}$$

Once again, for a fixed l I can write the Hamiltonian as a 3 × 3 matrix

$$\hat{H}_2(l) = \begin{pmatrix} t_{xx} & t_{(xy)} & t_{zx} \\ t_{(xy)} & t_{yy} & t_{yz} \\ t_{zx} & t_{yz} & t_{zz} \end{pmatrix}\cos(l\Delta\phi) + \begin{pmatrix} 0 & it_{[xy]} & 0 \\ -it_{[xy]} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\sin(l\Delta\phi) \tag{5.3}$$

The values for V_π and V_σ can be find in [7]. The pitch, radius and angle between bases are in [6]. Substituting in (4.15)

$$\begin{aligned}
&t_{xx} = -30meV, \qquad t_{(xy)} = 10meV, \qquad t_{zx} = 5meV, \\
&t_{yy} = 5meV, \qquad t_{yz} = 20meV, \\
&t_{zz} = -20meV, \\
&t_{[xy]} = -20meV.
\end{aligned}$$

Since I am only considering first neighbours, take $\Delta\phi = \frac{\pi}{5}$.

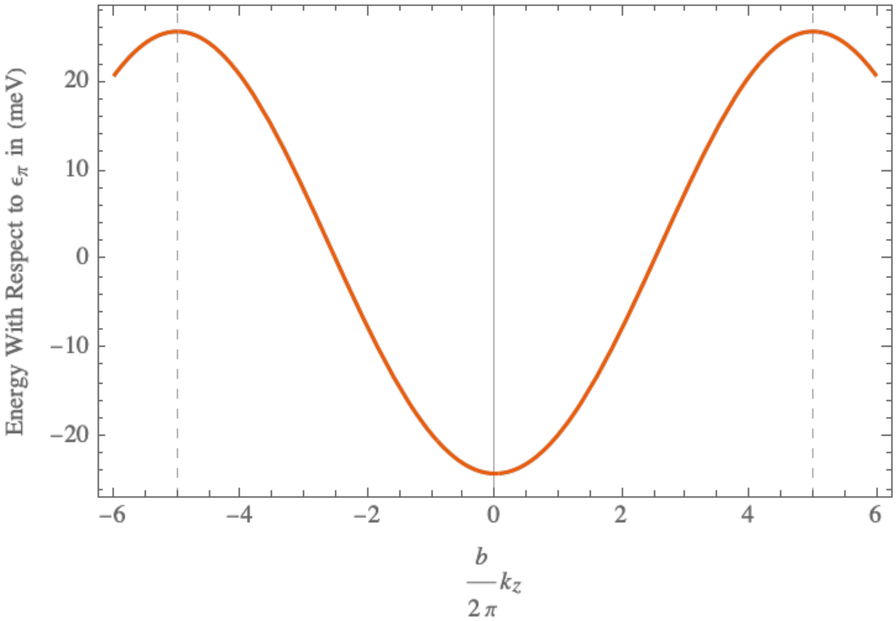

Figure 5.1: Electron band associated to the z-orbital in the First Brillouin Zone, defined over the quantum number l. The dashed lines represent the border of the zone. The energy is measured with respect to ε_π

5.2 Electron Bands for a particle with spin

Definition 1. Take all the information from equation (5.1). Define the ket

$$|l,\sigma,\mu\rangle = \frac{1}{\sqrt{N}}\sum_i e^{il\phi_i}\,|p_{\mu_i}\rangle\,\hat{R}_z(\phi_i)\,|\sigma\rangle \tag{5.4}$$

The process for expressing the Hamiltonians on the basis (5.4) is analogous to that of the previous section. The main difference is in the arguments of the sine and cosine in equation (5.2): for spin ↑ we change $l \to l+\frac{1}{2}$ and for spin ↓, $l \to l-\frac{1}{2}$. The only Hamiltonian I am missing is $\hat{H}_{so}$, which can be calculated from:

$$\langle l',\sigma';\mu|\,\hat{H}_{so}\,|l,\sigma;\nu\rangle = \frac{1}{N}\sum_{i,j} e^{-i(l'\phi_i - l\phi_j)}\,\langle\sigma'|\,\hat{R}_z(-\phi_i)\,\langle p_{\mu_i}|\,\hat{H}_{so}\,|p_{\nu_j}\rangle\,\hat{R}_z(\phi_j)\,|\sigma\rangle$$

Recall that, by my assumption, the p-orbitals of different sites are taken to be orthogonal to each other. Also, using the fact that $\hat{H}_{so}$ is a sum over the spin-orbit Hamiltonian of each atom, it is not hard to show that

$$\langle p_{\mu_i}|\,\hat{H}_{so}\,|p_{\nu_j}\rangle = -i\delta_{ij}\epsilon_{\mu\nu\gamma}\xi\hat{R}_z(\phi_i)\hat{\sigma}_\gamma\hat{R}_z(-\phi_i)$$

From this, it follows that:

$$\begin{aligned}\langle l',\sigma';\mu|\,\hat{H}_{so}\,|l,\sigma;\nu\rangle &= -i\xi\epsilon_{\mu\nu\gamma}\frac{1}{N}\sum_i e^{-i(l'-l)\phi_i}\,\langle\sigma'|\,\hat{\sigma}_\gamma\,|\sigma\rangle \\ &= \delta_{l,l'}(-i\xi\ \epsilon_{\mu\nu\gamma})\,\langle\sigma'|\,\hat{\sigma}_\gamma\,|\sigma\rangle\end{aligned}$$

The complete Hamiltonian for a fixed l is a 6×6 matrix. We use the same notation from equation (4.3) to write it as a 3×3 matrix:

$$
\begin{aligned}
\hat{H}(l) = {} & \begin{pmatrix} \varepsilon_\sigma & 0 & 0 \\ 0 & \varepsilon_\sigma & 0 \\ 0 & 0 & \varepsilon_\pi \end{pmatrix} \otimes \mathbb{1}_s \\
& + \begin{pmatrix} t_{xx} & t_{(xy)} & t_{zx} \\ t_{(xy)} & t_{yy} & t_{yz} \\ t_{zx} & t_{yz} & t_{zz} \end{pmatrix} \otimes \begin{pmatrix} \cos[(l+\frac{1}{2})\Delta\phi] & 0 \\ 0 & \cos[(l-\frac{1}{2})\Delta\phi] \end{pmatrix} \\
& + \begin{pmatrix} 0 & it_{[xy]} & 0 \\ -it_{[xy]} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} \sin[(l+\frac{1}{2})\Delta\phi] & 0 \\ 0 & \sin[(l-\frac{1}{2})\Delta\phi] \end{pmatrix} \\
& + \begin{pmatrix} 0 & -i\hat{\sigma}_z\xi & i\hat{\sigma}_y\xi \\ i\hat{\sigma}_z\xi & 0 & -i\hat{\sigma}_x\xi \\ -i\hat{\sigma}_y\xi & i\hat{\sigma}_x\xi & 0 \end{pmatrix}
\end{aligned}
\tag{5.5}
$$

Something important to note about equation (5.5) is that the first 3 terms are already diagonal on the spin space, so I need not consider the fourth term for polarization to occur. This is a direct consequence of the symmetry from equation (3.2), in which the rotation in $\hat{T}_n$ uses the total angular momentum $\hat{\vec{J}}$. I can also examine what happens when $\xi \to 0$. It appears that the spin-orbit term goes to 0 but spin polarization does not. The mathematical reason for this is that $\hat{T}_n$ contains a rotation along the z-axis, and when the spin-orbit Hamiltonian is taken into account, both the spin and orbital angular momenta must be rotated. Without a term in the hamiltonian that affects spin the generator of rotations is not $\hat{\boldsymbol{J}}$, but $\hat{\boldsymbol{L}}$.

5.3 Diagonalization

Equation (5.5) is a 6×6 matrix with degenerate states. I will treat the degeneracy using hte SW transformation. A really nice derivation of the method can be found in [8]. The first order correction in the $\{|z\uparrow\rangle, |z\downarrow\rangle\}$ is:

$$\hat{H}_1 = \begin{pmatrix} t_{zz}\cos\left(\Delta\phi\left(l+\frac{1}{2}\right)\right) & 0 \\ 0 & t_{zz}\cos\left(\Delta\phi\left(l-\frac{1}{2}\right)\right) \end{pmatrix} \tag{5.6}$$

Using only this correction the new bands are in figure 5.2. As we can see the bands are separated from the centre a distance ±1/2 this correspond to the shift obtained by considering the total angular momentum $\hat{\boldsymbol{J}}$. The second correction to the Hamiltonian is:

$$\hat{H}_2 = \begin{pmatrix} \frac{\left(t_{yz}^2+t_{zx}^2\right)\cos^2\left(\Delta\phi\left(l+\frac{1}{2}\right)\right)+2\xi^2}{\epsilon\pi-\epsilon\sigma} & \frac{2i\xi\sin\left(\frac{\Delta\phi}{2}\right)\left(t_{yz}+it_{zx}\right)\sin(\Delta\phi l)}{\epsilon\pi-\epsilon\sigma} \\ -\frac{2i\xi\sin\left(\frac{\Delta\phi}{2}\right)\left(t_{yz}-it_{zx}\right)\sin(\Delta\phi l)}{\epsilon\pi-\epsilon\sigma} & \frac{\left(t_{yz}^2+t_{zx}^2\right)\cos^2\left(\Delta\phi\left(l-\frac{1}{2}\right)\right)+2\xi^2}{\epsilon\pi-\epsilon\sigma} \end{pmatrix} \tag{5.7}$$

This correction has interaction between spin states, the interaction (non diagonal elements) are proportional to xi meaning they are small. Obtaining the allowed energies of this Hamiltonian we get figure 5.3.

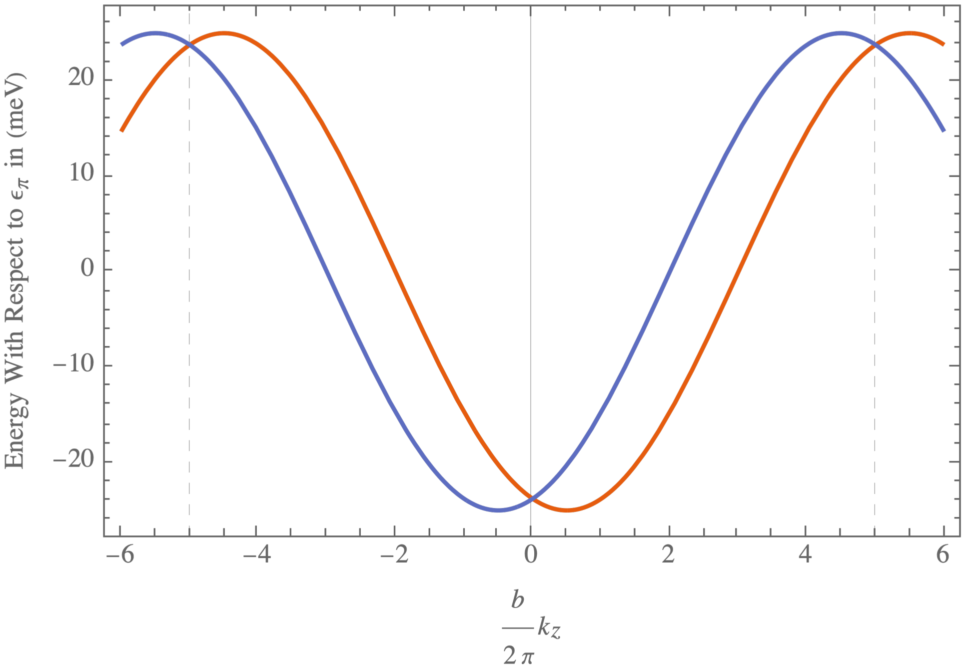

Figure 5.2: Electron bands with spin included and corrections up to first order. Again, the energy is measured with respect to ε_π, and the dashed lines denote the zone boundary

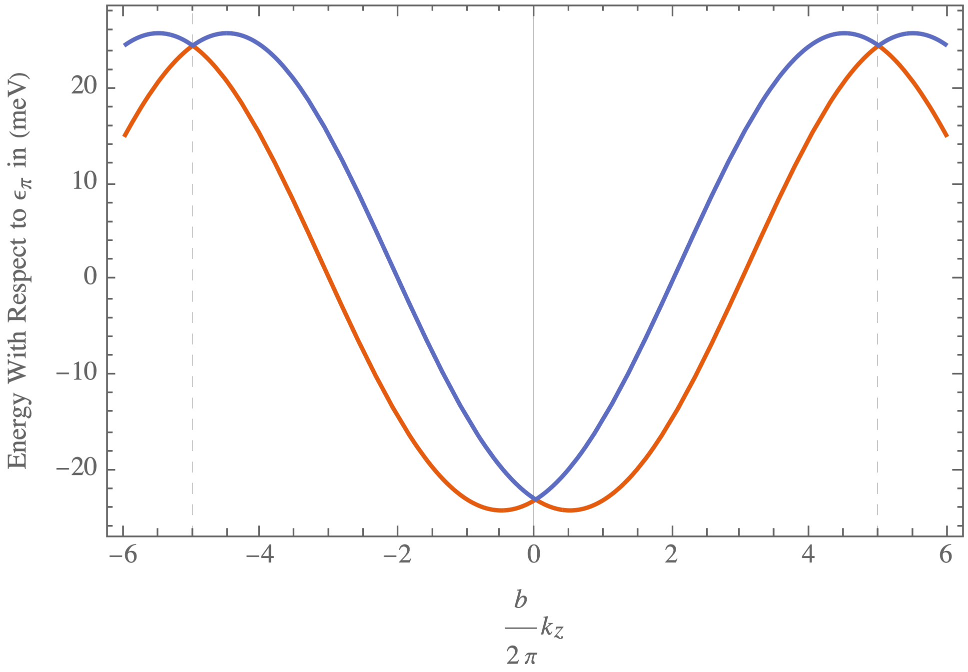

Figure 5.3: Electron bands with spin included and corrections up to second order. Again, the energy is measured with respect to ε_π, and the dashed lines denote the zone boundary

5.4 Conclusion

The thesis concludes by demonstrating the successful application of the tight-binding model to helical molecules, specifically a DNA-like system. It highlights the complexity and uniqueness of electronic behaviors in these structures, significantly influenced by their helical nature. The research contributes to understanding molecular electronics and the properties of DNA, with implications for future studies in both physics and biology. The study's innovative approach of integrating solid-state physics concepts with molecular structures provides a new perspective on studying complex biological molecules.

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