

Bachelor Thesis

Theoretical Study of the CISS Effect in Helicenes

Using the Tight-Binding Model



Submitted by

Farhan Alibrahim

Supervisor: Prof. Dr. Andrea Donarini

Department of Physics
University of Regensburg

August 2026

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1 Introduction

The way electrons move and their spin in molecules that're not the same when turned upside down is known as Chirality-Induced Spin Selectivity or CISS for short. People have been studying this a lot in years. It is an effect that happens when electrons are moving through these molecules and it depends on the spin of the electrons. This means that some electrons can move through the molecule easily than others. This was first seen in things like DNA. Then it was also seen in other types of molecules. When people did experiments they found out that the way the molecule is shaped has a lot to do with this effect. If the molecule is not shaped in a way then this effect does not happen. This is weird because a lot of these molecules are made up of light atoms and you would not expect this to happen. Although many experimental results exist, the exact physical origin of CISS is still not fully understood. Different theoretical models have been proposed to explain this effect. These include phenomenological models in which electrons move or scatter in a helical potential, tight-binding models with intrinsic and Rashba-type spin-orbit coupling and first-principles approaches based on spin-dependent density functional theory. More advanced approaches also use Green-function or density-matrix methods to include the influence of electrodes, open transport channels, and many-body effects.[1, 5, 6]

This thesis studies the CISS effect in helicene with the tight-binding model of Geyer et al. Helicene is a interesting system because it is made only of carbon and hydrogen, has no chiral centre, and obtains its chirality directly from its non-planar helical structure. The main question is how this geometry converts the weak atomic spin-orbit coupling of carbon into effective spin-dependent hopping and under which transport conditions this can produce a finite spin polarization.[1, 2]

The calculation is built in several steps. The microscopic Hamiltonian contains the carbon orbitals s, p_x, p_y, p_z , their on-site energies, atomic spin-orbit coupling, electric-field terms and Slater-Koster hopping. Ethene and benzene are first used as planar reference systems. Ethene checks the bonding and antibonding π -states, while benzene tests a larger delocalized π -system and its symmetry-related degeneracies. In addition, they show that the intrinsic spin-orbit effect of carbon is weak and that the states remain at least twofold degenerate at zero magnetic field. The calculations also confirm that, in planar molecules, the p_z -orbitals are largely separated from the in-plane s, p_x , and p_y -orbitals. Benzene therefore provides a useful planar reference for the later comparison with non-planar helicene. The benzene calculation also provides a simple example of the projection to an effective p_z -Hamiltonian.

The same Loewdin-like projection is then applied to helicene. The full orbital model is reduced to an effective Hamiltonian with one p_z -orbital per carbon site. The eliminated orbitals remain indirectly through geometry-dependent kinetic and spin-dependent hopping parameters. The full and effective helicene spectra are compared as a numerical check. Finally, the effective Hamiltonian is connected to electrodes and the spin-resolved transmission is calculated with Green functions. The results show that the physical carbon parameters give only a small polarization, while an external electric field and local leakage channels increase the signal. This provides a microscopic route from the helical molecular structure to CISS, but it also shows the limitations of the single-particle model.

2 Theory

2.1 Microscopic tight-binding Hamiltonian

In this section, we introduce the tight-binding model used in this work. In this model, the electrons are described by atomic orbitals. They can stay on one atom, but they can also hop from one atom to another. For carbon atoms, we use the valence orbitals

$$s, \quad p_x, \quad p_y, \quad p_z. \quad (2.1)$$

Spin is included, so every orbital has a spin-up and a spin-down state.[1, 2]

The full tight-binding Hamiltonian is written as

$$\hat{H} = \sum_{i,\mu,\nu} \hat{a}_{\mu,i}^\dagger \hat{h}_{\mu\nu}^{(i)} \hat{a}_{\nu,i} + \sum_{i,j} \sum_{\mu,\nu} \hat{a}_{\mu,i}^\dagger \hat{H}_{\mu\nu}^{(ij)} \hat{a}_{\nu,j}. \quad (2.2)$$

Here, $\hat{a}_{\mu,i}^\dagger$ creates an electron in orbital μ on atom i . The operator $\hat{a}_{\mu,i}$ destroys such an electron. The indices μ and ν run over s, p_x, p_y, p_z . The first term in Eq. (2.2) describes the on-site part. The second term describes the hopping between different atoms.[1]

2.2 On-site Hamiltonian

The on-site part contains all terms which act on one atom only. It includes the orbital energies, the atomic spin-orbit coupling and the coupling to an external electric field. For one carbon atom at site i , we write

$$\hat{h}^{(i)} = \hat{h}_{\text{atomic}}^{(i)} + \hat{H}_{\text{SOC}}^{(i)} + \hat{H}_{\text{field}}^{(i)}. \quad (2.3)$$

The orbital basis is

$$(s, p_x, p_y, p_z). \quad (2.4)$$

In this basis, the on-site Hamiltonian has the form

$$\hat{h}^{(i)} = \begin{pmatrix} \epsilon_s & E_x & E_y & E_z \\ E_x & \epsilon_{p\sigma} & -i\xi_p\hat{\sigma}_z & i\xi_p\hat{\sigma}_y \\ E_y & i\xi_p\hat{\sigma}_z & \epsilon_{p\sigma} & -i\xi_p\hat{\sigma}_x \\ E_z & -i\xi_p\hat{\sigma}_y & i\xi_p\hat{\sigma}_x & \epsilon_{p\pi} \end{pmatrix}. \quad (2.5)$$

Each entry in Eq. (2.5) is a 2×2 matrix in spin space. The matrices $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ are Pauli matrices. The parameters $\epsilon_s, \epsilon_{p\sigma}, \epsilon_{p\pi}, \xi_p$, and E_x, E_y, E_z have units of energy. In the numerical calculations, all energies are given in eV.[1, 2]

2.2.1 Electric field part

For an electron in an external electric field, the field contribution is

$$\hat{H}_{\text{field}} = -e \mathbf{E} \cdot \hat{\mathbf{r}}. \quad (2.6)$$

Here, $\mathbf{E} = (E_x, E_y, E_z)$ is the external electric field and $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$ is the position operator. Written out, this gives

$$\hat{H}_{\text{field}} = -e (E_x \hat{x} + E_y \hat{y} + E_z \hat{z}). \quad (2.7)$$

The electric field can couple the s -orbital to the p -orbitals. As an example, we look at the matrix element between s and p_x ,

$$\langle s | \hat{H}_{\text{field}} | p_x \rangle = -e \langle s | E_x \hat{x} + E_y \hat{y} + E_z \hat{z} | p_x \rangle. \quad (2.8)$$

By symmetry, only the x -term remains. Therefore

$$\langle s | \hat{H}_{\text{field}} | p_x \rangle = -e E_x \langle s | \hat{x} | p_x \rangle. \quad (2.9)$$

In the tight-binding Hamiltonian, this matrix element is written as the energy parameter E_x . In the same way, the field gives the matrix elements E_y and E_z . These are the entries E_x, E_y, E_z in Eq. (2.5). If no external electric field is included, we use

$$E_x = E_y = E_z = 0. \quad (2.10)$$

This notation makes the on-site matrix easy to use in the numerical calculation.[1, 2]

2.2.2 Atomic spin-orbit coupling

The atomic spin-orbit coupling acts only inside the p -orbital subspace. In the convention used here, it is written as

$$\hat{H}_{\text{SOC}} = \xi_p \left(\hat{L}_x \hat{\sigma}_x + \hat{L}_y \hat{\sigma}_y + \hat{L}_z \hat{\sigma}_z \right). \quad (2.11)$$

The matrices $\hat{L}_x, \hat{L}_y, \hat{L}_z$ act on the orbital part. The Pauli matrices act on the spin part. The parameter ξ_p is the atomic spin-orbit coupling strength.[1, 2]

In the real orbital basis (p_x, p_y, p_z) , the orbital angular momentum matrices are

$$\hat{L}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \hat{L}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad \hat{L}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.12)$$

These matrices give the spin-orbit entries in Eq. (2.5). For example, the matrix element between p_z and p_y including spin is

$$\langle p_z | \hat{H}_{\text{SOC}} | p_y \rangle = \xi_p \langle p_z | \hat{L}_x | p_y \rangle \hat{\sigma}_x \quad (2.13)$$

$$= i \xi_p \hat{\sigma}_x. \quad (2.14)$$

The Hermitian conjugate element is

$$\langle p_y | \hat{H}_{\text{SOC}} | p_z \rangle = -i \xi_p \hat{\sigma}_x. \quad (2.15)$$

The sign is important because the full on-site matrix must be Hermitian.

The other non-zero spin-orbit matrix elements are

$$\langle p_x | \hat{H}_{\text{SOC}} | p_y \rangle = -i \xi_p \hat{\sigma}_z, \quad \langle p_y | \hat{H}_{\text{SOC}} | p_x \rangle = i \xi_p \hat{\sigma}_z, \quad (2.16)$$

and

$$\langle p_x | \hat{H}_{\text{SOC}} | p_z \rangle = i \xi_p \hat{\sigma}_y, \quad \langle p_z | \hat{H}_{\text{SOC}} | p_x \rangle = -i \xi_p \hat{\sigma}_y. \quad (2.17)$$

Together these terms form the p_x, p_y, p_z -block of Eq. (2.5) The s -orbital has orbital angular momentum $l = 0$. Therefore it does not couple directly through atomic spin-orbit coupling.[2]

2.2.3 Zeeman term

For some numerical checks, we also include a small magnetic field in z -direction. In this work B_z denotes the Zeeman energy. With this convention, the Zeeman term is

$$\hat{H}_Z = B_z \hat{\sigma}_z. \quad (2.18)$$

This term shifts spin-up and spin-down states in opposite directions. It does not mix the two spin directions. The splitting between the two spin states is

$$\Delta E_Z = 2B_z. \quad (2.19)$$

2.3 Hopping between atoms

The hopping matrix element between orbital μ on atom i and orbital ν on atom j is

$$H_{\mu\nu}^{(ij)} = \langle \phi_\mu^{(i)} | \hat{H} | \phi_\nu^{(j)} \rangle. \quad (2.20)$$

This matrix element depends on the direction of the bond and on the orientation of the two orbitals. We calculate it with the Slater–Koster method.[2, 3]

The bond vector from atom i to atom j is

$$\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i. \quad (2.21)$$

The corresponding unit vector is

$$\hat{\mathbf{R}}_{ij} = \frac{\mathbf{R}_{ij}}{|\mathbf{R}_{ij}|}. \quad (2.22)$$

For a p -orbital, $\mathbf{n}(\mu, i)$ gives the direction of the orbital at atom i . This direction can be split into a part parallel to the bond and a part perpendicular to the bond,

$$\mathbf{n}^{\parallel}(\mu, ij) = [\mathbf{n}(\mu, i) \cdot \hat{\mathbf{R}}_{ij}] \hat{\mathbf{R}}_{ij}, \quad (2.23)$$

$$\mathbf{n}^{\perp}(\mu, ij) = \mathbf{n}(\mu, i) - \mathbf{n}^{\parallel}(\mu, ij). \quad (2.24)$$

For an s -orbital, there is no fixed orbital direction. In this case we use

$$\mathbf{n}^{\parallel}(s, ij) = \hat{\mathbf{R}}_{ij}, \quad \mathbf{n}^{\perp}(s, ij) = 0. \quad (2.25)$$

The Slater–Koster hopping formula is

$$\begin{aligned} H_{\mu\nu}^{(ij)} &= \mathbf{n}^{\parallel}(\mu, ij) \cdot \mathbf{n}^{\parallel}(\nu, ji) V_{\mu\nu\sigma} \\ &\quad + \mathbf{n}^{\perp}(\mu, ij) \cdot \mathbf{n}^{\perp}(\nu, ji) V_{\mu\nu\pi}. \end{aligned} \quad (2.26)$$

The parameter $V_{\mu\nu\sigma}$ describes a σ -type overlap. The parameter $V_{\mu\nu\pi}$ describes a π -type overlap. This formula is used for the hopping blocks of ethene, benzene and helicene.[2, 3]

If the bond direction is written as

$$\hat{\mathbf{R}}_{ij} = (x, y, z), \quad (2.27)$$

we obtain the standard hopping elements

$$H_{ss}^{(ij)} = V_{ss\sigma}, \quad (2.28)$$

$$H_{sp_x}^{(ij)} = xV_{sp\sigma}, \quad H_{sp_y}^{(ij)} = yV_{sp\sigma}, \quad H_{sp_z}^{(ij)} = zV_{sp\sigma}, \quad (2.29)$$

and

$$H_{p_x s}^{(ij)} = -xV_{sp\sigma}, \quad H_{p_y s}^{(ij)} = -yV_{sp\sigma}, \quad H_{p_z s}^{(ij)} = -zV_{sp\sigma}. \quad (2.30)$$

The minus sign appears because p -orbitals have odd parity.

For the p - p terms, the general expression is

$$H_{p_\alpha p_\beta}^{(ij)} = d_\alpha d_\beta V_{pp\sigma} + (\delta_{\alpha\beta} - d_\alpha d_\beta) V_{pp\pi}, \quad (2.31)$$

where $(d_\alpha, d_\beta) = (x, y)$. For example,

$$H_{p_x p_x}^{(ij)} = x^2 V_{pp\sigma} + (1 - x^2) V_{pp\pi}, \quad (2.32)$$

$$H_{p_y p_y}^{(ij)} = y^2 V_{pp\sigma} + (1 - y^2) V_{pp\pi}, \quad (2.33)$$

and

$$H_{p_x p_y}^{(ij)} = xy (V_{pp\sigma} - V_{pp\pi}). \quad (2.34)$$

These formulas are used later for the explicit ethene and benzene Hamiltonian blocks.

For planar molecules, the p_z -orbitals are perpendicular to the molecular plane. If two carbon atoms are connected by a bond inside this plane, the direct $p_z - p_z$ hopping is

$$H_{p_z p_z}^{(ij)} = V_{pp\pi}. \quad (2.35)$$

This gives the usual π -system of ethene and benzene.[2, 3]

2.4 Microscopic parameters

The numerical calculations use the same microscopic parameters that are used in the paper of Geyer et al. They are collected in Table 1.

Table 1: Microscopic tight-binding parameters used throughout this work.

Parameter	Value
ϵ_s	-18.0 eV
ϵ_H	-13.6 eV
$\epsilon_{p\sigma}$	-18.0 eV
$\epsilon_{p\pi}$	-10.5 eV
$V_{ss\sigma}$	-7.92 eV
$V_{sp\sigma}$	8.08 eV
$V_{pp\sigma}$	7.09 eV
$V_{pp\pi}$	-3.44 eV
ξ_p	0.006 eV

2.5 Physical meaning

The hopping terms from the Slater–Koster method do not mix spin by themselves. The spin dependence enters through the on-site spin-orbit coupling. For planar molecules such

as ethene and benzene, the effective spin-orbit effects in the p_z -system are very small. The reason is that the p_z -orbitals are almost separated from the σ -system.

For helicene, the situation is different. Helicene is not planar, and the local orbital directions change along the molecule. Because of this geometry, the hopping elements change from bond to bond. After projection to the p_z -subspace this can produce effective spin-dependent hopping terms. These terms are important for the later discussion of spin-selective transport.[1, 4]

When $\xi_p=0$, this means that atomic spin-orbit coupling is switched off. Also, $B_z = 0$ means that no Zeeman splitting is included.

3 Full Tight-Binding Hamiltonians: From Ethene to Benzene

3.1 Ethene

We now apply the tight-binding model from Sec. 2 to ethene. Ethene is a good first test system because it is small, planar and still contains the basic carbon π -bond. In the full Hamiltonian, all carbon valence orbitals s, p_x, p_y, p_z are included, together with the hydrogen s -orbitals. The hopping terms are calculated with the Slater–Koster formula from Eq. (2.26) and the on-site spin-orbit coupling is taken from Eq. (2.5).[1, 2, 3]

3.1.1 Structure of ethene

Ethene, C_2H_4 consists of two carbon atoms and four hydrogen atoms. Each carbon atom contributes the orbitals s, p_x, p_y, p_z while each hydrogen atom contributes one s -orbital. The molecule is planar and the carbon atoms have an approximately sp^2 -like bonding environment. In the tight-binding calculation however we do not build the hybrid orbitals by hand. Instead, the full orbital basis is kept and the mixing between orbitals comes from the hopping matrix elements.

3.1.2 Choice of basis

For the carbon atoms we use the basis

$$\{s, p_x, p_y, p_z\} \otimes \{\uparrow, \downarrow\}. \quad (3.1)$$

For the hydrogen atoms we use

$$\{s\} \otimes \{\uparrow, \downarrow\}. \quad (3.2)$$

Thus the full basis contains both spin directions and all valence orbitals which are used in the model.

3.1.3 Hamiltonian structure

With this ordering, the Hamiltonian can be written in block form as

$$H = \begin{pmatrix} H_{C1} & H_{C1C2} & H_{C1H} \\ H_{C1C2}^\dagger & H_{C2} & H_{C2H} \\ H_{C1H}^\dagger & H_{C2H}^\dagger & H_H \end{pmatrix}. \quad (3.3)$$

The blocks H_{C1} and H_{C2} contain the on-site terms of the two carbon atoms. The block H_{C1C2} contains the carbon-carbon hopping and therefore includes both σ - and π -type contributions. The blocks H_{C1H} and H_{C2H} describe the carbon-hydrogen hopping. Since hydrogen has only an s -orbital in this model these bonds are of σ -type. The block H_H contains the hydrogen on-site energies.

3.2 Computed Hamiltonian blocks for ethene

Using the parameters from the tight-binding model in Table 1 the numerical blocks take the following form. The carbon on-site block is

$$H_{C1} = \begin{pmatrix} -18 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -18 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -18 & 0 & -0.006i & 0 & 0 & 0.006 \\ 0 & 0 & 0 & -18 & 0 & 0.006i & -0.006 & 0 \\ 0 & 0 & 0.006i & 0 & -18 & 0 & 0 & -0.006i \\ 0 & 0 & 0 & -0.006i & 0 & -18 & -0.006i & 0 \\ 0 & 0 & 0 & -0.006 & 0 & 0.006i & -10.5 & 0 \\ 0 & 0 & 0.006 & 0 & 0.006i & 0 & 0 & -10.5 \end{pmatrix} \text{ [eV]}.$$

The hopping block between the two carbon atoms is

$$H_{C1C2} = \begin{pmatrix} -7.92 & 0 & 8.08 & 0 & 0 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & 8.08 & 0 & 0 & 0 & 0 \\ -8.08 & 0 & 7.09 & 0 & 0 & 0 & 0 & 0 \\ 0 & -8.08 & 0 & 7.09 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3.44 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -3.44 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \text{ [eV]}.$$

The values -3.44 eV belong to the direct $p_z - p_z$ hopping and therefore to the π -part of the molecule.

For the coupling between an s -orbital and a p -orbital we use

$$H_{sp} = V_{sp\sigma}(x, y, z),$$

where $V_{sp\sigma} = 8.08$ eV and (x, y, z) are the direction cosines of the bond. As an example, we consider the bond between $C1$ and $H1$. The positions are

$$C1 = (-0.67, 0, 0), \quad H1 = (-1.3107, 0.8818, 0).$$

The bond vector is

$$\vec{R} = H1 - C1 = (-0.6407, 0.8818, 0)$$

and its length is

$$|\vec{R}| \approx 1.089 \text{ \AA}.$$

The normalized bond direction is therefore

$$(x, y, z) = \left(\frac{-0.6407}{1.089}, \frac{0.8818}{1.089}, 0 \right) \approx (-0.588, 0.809, 0).$$

This gives

$$H_{s,p_x} = V_{sp\sigma}x = 8.08(-0.588) \approx -4.75 \text{ eV},$$

and

$$H_{s,p_y} = V_{sp\sigma}y = 8.08(0.809) \approx 6.54 \text{ eV}.$$

With the same construction for the two hydrogens connected to $C1$ we obtain

$$H_{C1H_{1,2}} = \begin{pmatrix} -7.92 & 0 & -7.92 & 0 & 0 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & -7.92 & 0 & 0 & 0 & 0 \\ 4.75 & 0 & 4.75 & 0 & 0 & 0 & 0 & 0 \\ 0 & 4.75 & 0 & 4.75 & 0 & 0 & 0 & 0 \\ -6.54 & 0 & 6.54 & 0 & 0 & 0 & 0 & 0 \\ 0 & -6.54 & 0 & 6.54 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} [\text{eV}].$$

For the two hydrogens connected to $C2$ the corresponding block is

$$H_{C2H_{3,4}} = \begin{pmatrix} 0 & 0 & 0 & 0 & -7.92 & 0 & -7.92 & 0 \\ 0 & 0 & 0 & 0 & 0 & -7.92 & 0 & -7.92 \\ 0 & 0 & 0 & 0 & -4.75 & 0 & -4.75 & 0 \\ 0 & 0 & 0 & 0 & 0 & -4.75 & 0 & -4.75 \\ 0 & 0 & 0 & 0 & -6.54 & 0 & 6.54 & 0 \\ 0 & 0 & 0 & 0 & 0 & -6.54 & 0 & 6.54 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} [\text{eV}].$$

The hydrogen on-site block is diagonal

$$H_H = \begin{pmatrix} -13.6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -13.6 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -13.6 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -13.6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -13.6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -13.6 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -13.6 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -13.6 \end{pmatrix} [\text{eV}].$$

3.2.1 Eigenvalues and eigenstates of ethene

The eigenvalues give the energy levels of the full ethene Hamiltonian. The eigenvectors show which atomic orbitals contribute most strongly to each state.

$$E_1 = E_2 = -34.6278 \text{ eV}$$

$$\psi_1 = \begin{cases} C1 s \uparrow : -0.5802 \\ C2 s \uparrow : -0.5802 \\ C2 p_x \uparrow : 0.3534 \\ C1 p_x \uparrow : -0.3534 \end{cases} \quad \psi_2 = \begin{cases} C2 s \downarrow : 0.5802 + 0.0003i \\ C1 s \downarrow : 0.5802 + 0.0003i \\ C1 p_x \downarrow : 0.3534 + 0.0002i \\ C2 p_x \downarrow : -0.3534 - 0.0002i \end{cases}$$

$$E_3 = E_4 = -29.1080 \text{ eV}$$

$$\psi_3 = \begin{cases} C2 s \uparrow : -0.4152 \\ C1 s \uparrow : 0.4152 \\ C2 p_x \uparrow : -0.3512 \\ C1 p_x \uparrow : -0.3512 \\ H4 s \uparrow : -0.3196 - 0.0004i \\ H3 s \uparrow : -0.3196 + 0.0004i \\ H1 s \uparrow : 0.3196 + 0.0004i \\ H2 s \uparrow : 0.3196 - 0.0004i \end{cases} \quad \psi_4 = \begin{cases} C1 s \downarrow : -0.4152 - 0.0024i \\ C2 s \downarrow : 0.4152 + 0.0024i \\ C1 p_x \downarrow : 0.3512 + 0.0021i \\ C2 p_x \downarrow : 0.3512 + 0.0021i \\ H1 s \downarrow : -0.3196 - 0.0015i \\ H2 s \downarrow : -0.3196 - 0.0023i \\ H4 s \downarrow : 0.3196 + 0.0015i \\ H3 s \downarrow : 0.3196 + 0.0023i \end{cases}$$

$$E_5 = E_6 = -27.5654 \text{ eV}$$

$$\psi_5 = \begin{cases} C1 p_y \uparrow : 0.4317i \\ C2 p_y \uparrow : 0.4317i \\ C1 p_y \downarrow : -0.4009 + 0.0229i \\ C2 p_y \downarrow : -0.4009 + 0.0229i \\ H2 s \uparrow : -0.0004 - 0.2021i \\ H4 s \uparrow : 0.0004 - 0.2021i \\ H3 s \uparrow : 0.0004 + 0.2021i \\ H1 s \uparrow : -0.0004 + 0.2021i \end{cases} \quad \psi_6 = \begin{cases} C1 p_y \downarrow : -0.4310 + 0.0246i \\ C2 p_y \downarrow : -0.4310 + 0.0246i \\ C1 p_y \uparrow : -0.4015i \\ C2 p_y \uparrow : -0.4015i \\ H1 s \downarrow : -0.2018 + 0.0119i \\ H3 s \downarrow : -0.2018 + 0.0111i \\ H2 s \downarrow : 0.2018 - 0.0111i \\ H4 s \downarrow : 0.2018 - 0.0119i \end{cases}$$

$$E_7 = E_8 = -27.4308 \text{ eV}$$

$$\psi_7 = \begin{cases} C1 p_x \uparrow : 0.5402 \\ C2 p_x \uparrow : -0.5402 \\ H1 s \uparrow : -0.2936 - 0.0002i \\ H3 s \uparrow : -0.2936 + 0.0002i \\ H2 s \uparrow : -0.2936 + 0.0002i \\ H4 s \uparrow : -0.2936 - 0.0002i \end{cases} \quad \psi_8 = \begin{cases} C2 p_x \downarrow : 0.5402 - 0.0001i \\ C1 p_x \downarrow : -0.5402 + 0.0001i \\ H4 s \downarrow : 0.2936 - 0.0003i \\ H2 s \downarrow : 0.2936 + 0.0002i \\ H3 s \downarrow : 0.2936 + 0.0002i \\ H1 s \downarrow : 0.2936 - 0.0003i \end{cases}$$

$$E_9 = E_{10} = -23.3414 \text{ eV}$$

$$\psi_9 = \begin{cases} C2 p_y \downarrow : 0.4555 + 0.1387i \\ C1 p_y \downarrow : -0.4555 - 0.1387i \\ H3 s \downarrow : 0.3057 + 0.0933i \\ H4 s \downarrow : -0.3059 - 0.0929i \\ H2 s \downarrow : 0.3057 + 0.0933i \\ H1 s \downarrow : -0.3059 - 0.0929i \end{cases} \quad \psi_{10} = \begin{cases} C2 p_y \uparrow : 0.4762i \\ C1 p_y \uparrow : -0.4762i \\ H4 s \uparrow : 0.0002 - 0.3197i \\ H3 s \uparrow : 0.0002 + 0.3197i \\ H1 s \uparrow : 0.0002 - 0.3197i \\ H2 s \uparrow : 0.0002 + 0.3197i \end{cases}$$

$$E_{11} = E_{12} = -13.9400 \text{ eV}$$

$$\psi_{11} = \begin{cases} C2 p_z \downarrow : 0.7071 \\ C1 p_z \downarrow : 0.7071 \end{cases} \quad \psi_{12} = \begin{cases} C2 p_z \uparrow : -0.7069 + 0.0166i \\ C1 p_z \uparrow : -0.7069 + 0.0166i \end{cases}$$

$$E_{13} = E_{14} = -7.4746 \text{ eV}$$

$$\psi_{13} = \begin{cases} H2 s \uparrow : 0.0004 - 0.3929i \\ H1 s \uparrow : 0.0004 + 0.3929i \\ H3 s \uparrow : -0.0004 + 0.3929i \\ H4 s \uparrow : -0.0004 - 0.3929i \\ C1 p_y \uparrow : -0.3680i \\ C2 p_y \uparrow : -0.3680i \end{cases} \quad \psi_{14} = \begin{cases} H2 s \downarrow : 0.2064 - 0.3343i \\ H1 s \downarrow : -0.2070 + 0.3340i \\ H3 s \downarrow : -0.2064 + 0.3343i \\ H4 s \downarrow : 0.2070 - 0.3340i \\ C1 p_y \downarrow : 0.1936 - 0.3130i \\ C2 p_y \downarrow : 0.1936 - 0.3130i \end{cases}$$

$$E_{15} = E_{16} = -7.0600 \text{ eV}$$

$$\psi_{15} = \begin{cases} C2 p_z \downarrow : -0.7070 \\ C1 p_z \downarrow : 0.7070 \end{cases} \quad \psi_{16} = \begin{cases} C1 p_z \uparrow : -0.7003 - 0.0972i \\ C2 p_z \uparrow : 0.7003 + 0.0972i \end{cases}$$

$$E_{17} = E_{18} = -5.4816 \text{ eV}$$

$$\psi_{17} = \begin{cases} C2 p_x \uparrow : 0.5829 \\ C1 p_x \uparrow : 0.5829 \\ H3 s \uparrow : -0.2788 - 0.0005i \\ H4 s \uparrow : -0.2788 + 0.0005i \\ H1 s \uparrow : 0.2788 - 0.0005i \\ H2 s \uparrow : 0.2788 + 0.0005i \end{cases} \quad \psi_{18} = \begin{cases} C1 p_x \downarrow : -0.5829 + 0.0039i \\ C2 p_x \downarrow : -0.5829 + 0.0039i \\ H1 s \downarrow : -0.2788 + 0.0014i \\ H3 s \downarrow : 0.2788 - 0.0024i \\ H4 s \downarrow : 0.2788 - 0.0014i \\ H2 s \downarrow : -0.2788 + 0.0024i \end{cases}$$

$$E_{19} = E_{20} = -4.8186 \text{ eV}$$

$$\psi_{19} = \begin{cases} C2 p_y \uparrow : -0.4842i \\ C1 p_y \uparrow : 0.4842i \\ H4 s \uparrow : -0.0003 - 0.3606i \\ H2 s \uparrow : -0.0003 + 0.3606i \\ H3 s \uparrow : -0.0003 + 0.3606i \\ H1 s \uparrow : -0.0003 - 0.3606i \end{cases} \quad \psi_{20} = \begin{cases} C2 p_y \downarrow : 0.0065 + 0.4841i \\ C1 p_y \downarrow : -0.0065 - 0.4841i \\ H4 s \downarrow : 0.0045 + 0.3606i \\ H2 s \downarrow : -0.0052 - 0.3606i \\ H3 s \downarrow : -0.0052 - 0.3606i \\ H1 s \downarrow : 0.0045 + 0.3606i \end{cases}$$

$$E_{21} = E_{22} = -2.5514 \text{ eV}$$

$$\psi_{21} = \begin{cases} H2 s \uparrow : -0.3736 - 0.0002i \\ H1 s \uparrow : -0.3736 + 0.0002i \\ H3 s \uparrow : -0.3736 - 0.0002i \\ H4 s \uparrow : -0.3736 + 0.0002i \\ C1 s \uparrow : 0.3512 \\ C2 s \uparrow : 0.3512 \\ C1 p_x \uparrow : -0.2834 \\ C2 p_x \uparrow : 0.2834 \end{cases} \quad \psi_{22} = \begin{cases} H2 s \downarrow : 0.3736 - 0.0008i \\ H1 s \downarrow : 0.3736 - 0.0003i \\ H3 s \downarrow : 0.3736 - 0.0008i \\ H4 s \downarrow : 0.3736 - 0.0003i \\ C1 s \downarrow : -0.3512 + 0.0005i \\ C2 s \downarrow : -0.3512 + 0.0005i \\ C2 p_x \downarrow : -0.2834 + 0.0004i \\ C1 p_x \downarrow : 0.2834 - 0.0004i \end{cases}$$

$$E_{23} = E_{24} = -0.0004 \text{ eV}$$

$$\psi_{23} = \begin{cases} C2 s \downarrow : -0.5688 - 0.0018i \\ C1 s \downarrow : 0.5688 + 0.0018i \\ H3 s \downarrow : 0.2646 + 0.0009i \\ H4 s \downarrow : 0.2646 + 0.0008i \\ H2 s \downarrow : -0.2646 - 0.0009i \\ H1 s \downarrow : -0.2646 - 0.0008i \end{cases} \quad \psi_{24} = \begin{cases} C1 s \uparrow : -0.5688 \\ C2 s \uparrow : 0.5688 \\ H1 s \uparrow : 0.2646 + 0.0000i \\ H2 s \uparrow : 0.2646 - 0.0000i \\ H3 s \uparrow : -0.2646 + 0.0000i \\ H4 s \uparrow : -0.2646 - 0.0000i \end{cases}$$

3.3 From ethene to benzene

The same full tight-binding model can also be set-up for benzene, C_6H_6 . Benzene is still planar, but it is larger than ethene and forms a closed carbon ring. All carbon and hydrogen atoms lie in the plane $z = 0$. The six carbon p_z -orbitals form the delocalized π -system of benzene. Because of the ring structure, benzene has more π -states than ethene and also shows additional degeneracies.[1, 2]

3.3.1 Carbon block structure

$$H_C = \begin{pmatrix} H_{C1} & H_{C1C2} & \cdots & H_{C1C6} \\ H_{C2C1} & H_{C2} & \cdots & H_{C2C6} \\ \vdots & \vdots & \ddots & \vdots \\ H_{C6C1} & H_{C6C2} & \cdots & H_{C6} \end{pmatrix}.$$

The diagonal blocks have the same on-site structure as in ethene. The off-diagonal blocks contain the nearest-neighbour carbon-carbon hopping terms. To show how one of these blocks is built, we first look at the bond between $C1$ and $C2$. The atomic positions are

$$\mathbf{R}_1 = (0.00000, 1.40272, 0.00000), \quad \mathbf{R}_2 = (-1.21479, 0.70136, 0.00000).$$

The bond vector is

$$\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1 = (-1.21479, -0.70136, 0),$$

Its length is

$$R = \sqrt{(-1.21479)^2 + (-0.70136)^2} \approx 1.4027 \text{ \AA}.$$

The direction cosines of the bond are therefore

$$x = \frac{-1.21479}{1.4027} \approx -0.866, \quad y = \frac{-0.70136}{1.4027} \approx -0.500, \quad z = 0.$$

We use the Slater–Koster parameters

$$V_{ss} = -7.92 \text{ eV}, \quad V_{sp\sigma} = 8.08 \text{ eV}, \quad V_{pp\sigma} = 7.09 \text{ eV}, \quad V_{pp\pi} = -3.44 \text{ eV}.$$

The $s - s$ coupling is simply

$$H_{ss} = V_{ss} = -7.92 \text{ eV}.$$

For the $s - p$ couplings we obtain

$$H_{sp_x} = xV_{sp\sigma} = (-0.866)(8.08) \approx -6.99 \text{ eV},$$

$$H_{sp_y} = yV_{sp\sigma} = (-0.500)(8.08) \approx -4.04 \text{ eV},$$

$$H_{sp_z} = 0 \text{ eV}.$$

For the $p - p$ interactions, the diagonal terms follow the Slater–Koster rules.

$$H_{p_x p_x} = x^2 V_{pp\sigma} + (1 - x^2) V_{pp\pi} = 0.75 \cdot 7.09 + 0.25 \cdot (-3.44) \approx 4.46 \text{ eV},$$

$$H_{p_y p_y} = y^2 V_{pp\sigma} + (1 - y^2) V_{pp\pi} = 0.25 \cdot 7.09 + 0.75 \cdot (-3.44) \approx -0.81 \text{ eV},$$

$$H_{p_z p_z} = V_{pp\pi} = -3.44 \text{ eV}.$$

The mixed p–p coupling is given by

$$H_{p_x p_y} = xy(V_{pp\sigma} - V_{pp\pi}) = (0.866)(0.500)(7.09 + 3.44) \approx 4.56 \text{ eV}.$$

All couplings involving p_z with p_x or p_y vanish due to symmetry.

$$H_{p_x p_z} = H_{p_y p_z} = 0 \text{ eV}.$$

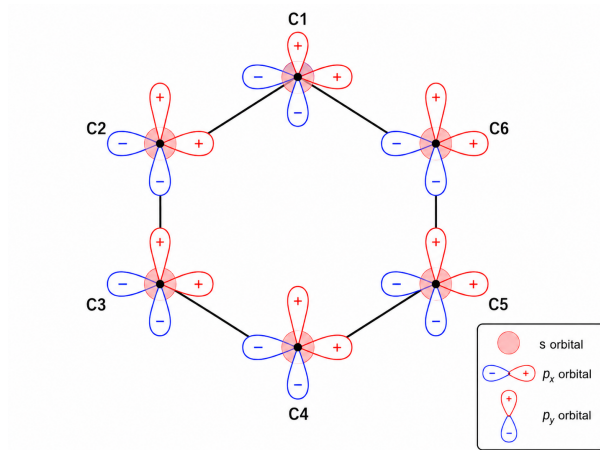


Figure 1: Schematic orbital phase diagram for benzene in the molecular plane. The red and blue lobes mark opposite signs of the orbital wave function. The picture helps to visualize why the planar geometry separates the p_z orbitals from the in-plane s, p_x, p_y orbitals in the hopping block.

The orbital orientation in Figure 1 was used to calculate the Hamiltonian.

$$H_{C_1C_2} = \begin{pmatrix} -7.92 & 0 & -6.99 & 0 & -4.04 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & -6.99 & 0 & -4.04 & 0 & 0 \\ 6.99 & 0 & 4.46 & 0 & 4.56 & 0 & 0 & 0 \\ 0 & 6.99 & 0 & 4.46 & 0 & 4.56 & 0 & 0 \\ 4.04 & 0 & 4.56 & 0 & -0.81 & 0 & 0 & 0 \\ 0 & 4.04 & 0 & 4.56 & 0 & -0.81 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \text{ [eV]}.$$

For the next bond, between C_2 and C_3 , the coordinates are

$$\mathbf{R}_{C_2} = (-1.21479, 0.70136, 0), \quad \mathbf{R}_{C_3} = (-1.21479, -0.70136, 0).$$

This bond is aligned with the negative y -direction, so the direction cosines are

$$x = 0, \quad y = -1, \quad z = 0.$$

The $s - p$ couplings are

$$H_{sp_x} = xV_{sp\sigma} = 0 \text{ eV}$$

$$H_{sp_y} = yV_{sp\sigma} = -8.08 \text{ eV}$$

$$H_{sp_z} = zV_{sp\sigma} = 0 \text{ eV}$$

Since this bond is along the y -direction, the p_y -orbital gives the σ -type overlap. The p_x - and p_z -orbitals are perpendicular to the bond and therefore give π -type overlaps.

$$H_{p_y p_y} = V_{pp\sigma} = 7.09 \text{ eV}$$

$$H_{p_x p_x} = V_{pp\pi} = -3.44 \text{ eV}$$

$$H_{p_z p_z} = V_{pp\pi} = -3.44 \text{ eV}$$

$$H_{C_2C_3} = \begin{pmatrix} -7.92 & 0 & 0 & 0 & -8.08 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & 0 & 0 & -8.08 & 0 & 0 \\ 0 & 0 & -3.44 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3.44 & 0 & 0 & 0 & 0 \\ 8.08 & 0 & 0 & 0 & 7.09 & 0 & 0 & 0 \\ 0 & 8.08 & 0 & 0 & 0 & 7.09 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \text{ [eV]}$$

$$H_{C_3C_4} = \begin{pmatrix} -7.92 & 0 & 6.99 & 0 & -4.04 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & 6.99 & 0 & -4.04 & 0 & 0 \\ -6.99 & 0 & 4.46 & 0 & -4.56 & 0 & 0 & 0 \\ 0 & -6.99 & 0 & 4.46 & 0 & -4.56 & 0 & 0 \\ 4.04 & 0 & -4.56 & 0 & -0.81 & 0 & 0 & 0 \\ 0 & 4.04 & 0 & -4.56 & 0 & -0.81 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \text{ [eV]}$$

$$\begin{aligned}
H_{C_4C_5} &= \begin{pmatrix} -7.92 & 0 & 6.99 & 0 & 4.04 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & 6.99 & 0 & 4.04 & 0 & 0 \\ -6.99 & 0 & 4.46 & 0 & 4.56 & 0 & 0 & 0 \\ 0 & -6.99 & 0 & 4.46 & 0 & 4.56 & 0 & 0 \\ -4.04 & 0 & 4.56 & 0 & -0.81 & 0 & 0 & 0 \\ 0 & -4.04 & 0 & 4.56 & 0 & -0.81 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \quad [\text{eV}] \\
H_{C_5C_6} &= \begin{pmatrix} -7.92 & 0 & 0 & 0 & 8.08 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & 0 & 0 & 8.08 & 0 & 0 \\ 0 & 0 & -3.44 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3.44 & 0 & 0 & 0 & 0 \\ -8.08 & 0 & 0 & 0 & 7.09 & 0 & 0 & 0 \\ 0 & -8.08 & 0 & 0 & 0 & 7.09 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \quad [\text{eV}]. \\
H_{C_6C_1} &= \begin{pmatrix} -7.92 & 0 & -6.99 & 0 & 4.04 & 0 & 0 & 0 \\ 0 & -7.92 & 0 & -6.99 & 0 & 4.04 & 0 & 0 \\ 6.99 & 0 & 4.46 & 0 & -4.56 & 0 & 0 & 0 \\ 0 & 6.99 & 0 & 4.46 & 0 & -4.56 & 0 & 0 \\ -4.04 & 0 & -4.56 & 0 & -0.81 & 0 & 0 & 0 \\ 0 & -4.04 & 0 & -4.56 & 0 & -0.81 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3.44 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.44 \end{pmatrix} \quad [\text{eV}] \\
H_{C_1H_1} &= \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ 0 & 0 \\ 0 & 0 \\ -8.08 & 0 \\ 0 & -8.08 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \quad [\text{eV}] & H_{C_4H_4} &= \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ 0 & 0 \\ 0 & 0 \\ 8.08 & 0 \\ 0 & 8.08 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \quad [\text{eV}] \\
H_{C_3H_3} &= \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ 6.99 & 0 \\ 0 & 6.99 \\ 4.04 & 0 \\ 0 & 4.04 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \quad [\text{eV}] & H_{C_2H_2} &= \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ 6.99 & 0 \\ 0 & 6.99 \\ -4.04 & 0 \\ 0 & -4.04 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \quad [\text{eV}]
\end{aligned}$$

$$H_{C_5H_5} = \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ -6.99 & 0 \\ 0 & -6.99 \\ 4.04 & 0 \\ 0 & 4.04 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \text{ [eV]} \quad H_{C_6H_6} = \begin{pmatrix} -7.92 & 0 \\ 0 & -7.92 \\ -6.99 & 0 \\ 0 & -6.99 \\ -4.04 & 0 \\ 0 & -4.04 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \text{ [eV]}$$

3.3.2 Eigenvalues and Eigenstates of benzene

After the full benzene Hamiltonian has been assembled, it is diagonalized in the same way as for ethene. The states that are most important for the later effective model are the six carbon p_z -derived orbital levels forming the delocalized π -system. Their eigenvalues occur at approximately -17.38 eV , -13.94 eV , -7.06 eV , and -3.62 eV . The two middle energies each contain two orbital levels while the lowest and highest π -energies contain one orbital level. Every state also has its time-reversed partner so all levels remain at least twofold degenerate for $B_z = 0$.

The dominant components of these π -states are listed first. They contain only carbon p_z -orbitals.

$$E_{25} = E_{26} = -17.38 \text{ eV}$$

$$\psi_{25} = \begin{cases} C5 p_z \uparrow : 0.1914 - 0.3297i \\ C6 p_z \uparrow : 0.1914 - 0.3297i \\ C3 p_z \uparrow : 0.1914 - 0.3297i \\ C2 p_z \uparrow : 0.1914 - 0.3297i \\ C4 p_z \uparrow : 0.1914 - 0.3297i \\ C1 p_z \uparrow : 0.1914 - 0.3297i \end{cases} \quad \psi_{26} = \begin{cases} C2 p_z \downarrow : -0.3812i \\ C6 p_z \downarrow : -0.3812i \\ C3 p_z \downarrow : -0.3812i \\ C5 p_z \downarrow : -0.3812i \\ C1 p_z \downarrow : -0.3812i \\ C4 p_z \downarrow : -0.3812i \end{cases}$$

$$E_{27} = E_{28} = -13.94 \text{ eV}$$

$$\psi_{27} = \begin{cases} C2 p_z \downarrow : -0.3536 + 0.2041i \\ C5 p_z \downarrow : 0.3536 - 0.2041i \\ C6 p_z \downarrow : 0.3536 + 0.2041i \\ C3 p_z \downarrow : -0.3536 - 0.2041i \\ C1 p_z \downarrow : -0.0000 + 0.4082i \\ C4 p_z \downarrow : 0.0000 - 0.4082i \end{cases} \quad \psi_{28} = \begin{cases} C2 p_z \uparrow : -0.1920 - 0.3603i \\ C5 p_z \uparrow : 0.1920 + 0.3603i \\ C3 p_z \uparrow : -0.4080 - 0.0139i \\ C6 p_z \uparrow : 0.4080 + 0.0139i \\ C4 p_z \uparrow : -0.2161 + 0.3464i \\ C1 p_z \uparrow : 0.2161 - 0.3464i \end{cases}$$

$$E_{29} = E_{30} = -13.94 \text{ eV}$$

$$\psi_{29} = \begin{cases} C1 p_z \uparrow : -0.3477 + 0.2140i \\ C4 p_z \uparrow : 0.3477 - 0.2140i \\ C6 p_z \uparrow : 0.0115 + 0.4081i \\ C3 p_z \uparrow : -0.0115 - 0.4081i \\ C5 p_z \uparrow : 0.3591 + 0.1941i \\ C2 p_z \uparrow : -0.3591 - 0.1941i \end{cases} \quad \psi_{30} = \begin{cases} C4 p_z \downarrow : 0.0000 - 0.4083i \\ C1 p_z \downarrow : -0.0000 + 0.4083i \\ C3 p_z \downarrow : 0.3536 - 0.2041i \\ C6 p_z \downarrow : -0.3536 + 0.2041i \\ C5 p_z \downarrow : -0.3536 - 0.2041i \\ C2 p_z \downarrow : 0.3536 + 0.2041i \end{cases}$$

$$E_{35} = E_{36} = -7.06 \text{ eV}$$

$$\psi_{35} = \begin{cases} C1 p_z \downarrow : -0.0000 + 0.4083i \\ C4 p_z \downarrow : -0.0000 + 0.4083i \\ C5 p_z \downarrow : 0.3535 - 0.2041i \\ C2 p_z \downarrow : 0.3535 - 0.2041i \\ C6 p_z \downarrow : -0.3535 - 0.2041i \\ C3 p_z \downarrow : -0.3535 - 0.2041i \end{cases} \quad \psi_{36} = \begin{cases} C1 p_z \uparrow : -0.3634 + 0.1860i \\ C4 p_z \uparrow : -0.3634 + 0.1860i \\ C6 p_z \uparrow : 0.3428 + 0.2217i \\ C3 p_z \uparrow : 0.3428 + 0.2217i \\ C5 p_z \uparrow : 0.0206 - 0.4077i \\ C2 p_z \uparrow : 0.0206 - 0.4077i \end{cases}$$

$$E_{37} = E_{38} = -7.06 \text{ eV}$$

$$\psi_{37} = \begin{cases} C3 p_z \downarrow : 0.3536 - 0.2041i \\ C6 p_z \downarrow : 0.3536 - 0.2041i \\ C5 p_z \downarrow : -0.3536 - 0.2041i \\ C2 p_z \downarrow : -0.3536 - 0.2041i \\ C4 p_z \downarrow : -0.0000 + 0.4082i \\ C1 p_z \downarrow : -0.0000 + 0.4082i \end{cases} \quad \psi_{38} = \begin{cases} C5 p_z \uparrow : -0.2418 - 0.3289i \\ C2 p_z \uparrow : -0.2418 - 0.3289i \\ C6 p_z \uparrow : -0.1639 + 0.3739i \\ C3 p_z \uparrow : -0.1639 + 0.3739i \\ C1 p_z \uparrow : 0.4058 - 0.0450i \\ C4 p_z \uparrow : 0.4058 - 0.0450i \end{cases}$$

$$E_{47} = E_{48} = -3.62 \text{ eV}$$

$$\psi_{47} = \begin{cases} C2 p_z \downarrow : 0.4082i \\ C3 p_z \downarrow : -0.4082i \\ C6 p_z \downarrow : 0.4082i \\ C5 p_z \downarrow : -0.4082i \\ C1 p_z \downarrow : -0.4082i \\ C4 p_z \downarrow : 0.4082i \end{cases} \quad \psi_{48} = \begin{cases} C2 p_z \uparrow : 0.2995 - 0.2774i \\ C3 p_z \uparrow : -0.2995 + 0.2774i \\ C6 p_z \uparrow : 0.2995 - 0.2774i \\ C5 p_z \uparrow : -0.2995 + 0.2774i \\ C4 p_z \uparrow : 0.2995 - 0.2774i \\ C1 p_z \uparrow : -0.2995 + 0.2774i \end{cases}$$

Remaining eigenstates. For completeness, all remaining eigenvalues and dominant eigenstate components are listed below.

3.3.3 Comparison between ethene and benzene

Ethene and benzene were calculated with the same tight-binding model. In both molecules the carbon orbitals s, p_x, p_y, p_z and the hydrogen s -orbitals are included. The hopping blocks are built from the Slater–Koster formula in Eq. (2.26) and spin-orbit coupling enters through the on-site matrix in Eq. (2.5). [1, 2, 3]

The main difference between the two systems is the size of the π -system. Ethene has only two carbon p_z -orbitals. They form one bonding π -state and one antibonding π^* -state. Benzene has six carbon p_z -orbitals arranged in a ring. This produces six π -states, and the ring symmetry leads to additional orbital degeneracies.

If

$$\xi_p = 0, \quad B_z = 0, \quad (3.4)$$

the Hamiltonian is spin independent. Every energy level is therefore at least twofold degenerate because of the two spin directions. In benzene, some π -levels are additionally degenerate because of the ring symmetry. This gives the characteristic degeneracy pattern of the benzene π -system.

If

$$\xi_p = 0.006 \text{ eV}, \quad B_z = 0, \quad (3.5)$$

spin-orbit coupling weakly mixes spin and orbital character. The effect is small because the atomic spin-orbit coupling of carbon is small. Time-reversal symmetry is still present so the states remain at least twofold degenerate.[1]

If

$$\xi_p = 0, \quad B_z \neq 0, \quad (3.6)$$

there is no spin mixing. The Zeeman term only shifts spin-up and spin-down states in opposite directions. With the convention used in Eq. (2.18), the splitting is

$$\Delta E \approx 2B_z. \quad (3.7)$$

If both $\xi_p \neq 0$ and $B_z \neq 0$, the two effects appear together. Spin-orbit coupling mixes spin and orbital character while the Zeeman term lifts the remaining spin degeneracy. [1]

3.4 Effective Hamiltonian

The full tight-binding Hamiltonian contains many orbitals. For the later discussion, we do not always need all of them explicitly. In benzene, the most important states for the π -system are the carbon p_z -orbitals. We therefore reduce the full Hamiltonian to an effective Hamiltonian which acts only in this p_z -subspace. The other orbitals are removed from the basis, but their influence is still kept. They enter through virtual hopping and spin-orbit processes. This is the idea behind the decimation procedure used in the Supplementary Information.[2]

The projection onto the p_z -subspace is written as

$$P|\mu, i, \sigma\rangle = \delta_{\mu z}|\mu, i, \sigma\rangle. \quad (3.8)$$

Here i labels the carbon atom, μ labels the orbital and σ labels the spin. It contains all orbitals which are not kept in the final π -subspace. For benzene, these are

$$\mathcal{B}_{P^\perp} = (s, x, y). \quad (3.9)$$

Thus, the decimation keeps the p_z -orbitals and eliminates the s, p_x, p_y -orbitals.[2]

The lowest-order expansion of the effective Hamiltonian obtained by decimation is

$$\hat{H}_{\text{eff}} \approx \epsilon_0 P + P \hat{H} P + P \hat{H} P^\perp \left(\epsilon_0 \mathbf{1}_{P^\perp} - P^\perp \hat{H} P^\perp \right)^{-1} P^\perp \hat{H} P. \quad (3.10)$$

The operator $P^\perp = \mathbf{1} - P$ is the complementary projector onto this subspace. The matrix $\mathbf{1}$ is the identity matrix acting inside the $P^\perp$ -subspace. [2]

For benzene, we choose

$$\epsilon_0 = \epsilon_{p\pi}. \quad (3.11)$$

With this choice, the decimation formula becomes

$$\hat{H}_{\text{eff}}^{\text{B}} \approx \epsilon_{p\pi} P + P \hat{H}_1 P + P \hat{H}_1 P^\perp \left(\epsilon_{p\pi} \mathbf{1}_{P^\perp} - P^\perp \hat{H}_0 P^\perp \right)^{-1} P^\perp \hat{H}_1 P. \quad (3.12)$$

This is the effective Hamiltonian used for the benzene π -system. The first term, $\epsilon_{p\pi} P$ gives the on-site energy of the carbon p_z -orbitals that remain in the effective model. The second term, $P \hat{H}_1 P$ describes the direct hopping between these p_z -orbitals. The last term describes virtual processes through the eliminated s , p_x , and p_y orbitals. Here, $\hat{H}_0$ contains the orbital energies, while $\hat{H}_1$ contains the hopping terms and the atomic spin-orbit coupling. It keeps the direct p_z -terms and adds corrections from the eliminated orbitals.[2]

In the eliminated basis $\mathcal{B}_{P^\perp} = (s, x, y)$, the denominator is diagonal. It is written as

$$D = \left(\epsilon_{p\pi} \mathbf{1}_{P^\perp} - P^\perp \hat{H}_0 P^\perp \right)^{-1} = \begin{pmatrix} \frac{1}{\epsilon_{p\pi} - \epsilon_s} & 0 & 0 \\ 0 & \frac{1}{\epsilon_{p\pi} - \epsilon_{p\sigma}} & 0 \\ 0 & 0 & \frac{1}{\epsilon_{p\pi} - \epsilon_{p\sigma}} \end{pmatrix}. \quad (3.13)$$

The entries are also diagonal in spin space. For this reason, the spin identity matrix is not written explicitly.[2]

The first term in Eq. (3.12) gives the on-site energy of the retained p_z -orbitals,

$$\epsilon_{p\pi} P = \epsilon_{p\pi} \sum_{i,\sigma} \hat{a}_{z,i,\sigma}^\dagger \hat{a}_{z,i,\sigma}. \quad (3.14)$$

This is the same p_z -energy which appears in the full on-site Hamiltonian.[2]

The second term gives the direct hopping between neighbouring p_z -orbitals,

$$P \hat{H}_1 P = \sum_{(i,j) \in N_{\text{B}}} \sum_{\sigma} H_{zz}^{(ij)} \hat{a}_{z,i,\sigma}^\dagger \hat{a}_{z,j,\sigma}. \quad (3.15)$$

Here N_{B} denotes the set of nearest-neighbour carbon bonds in benzene. Since benzene is planar, the p_z -orbitals are perpendicular to the molecular plane. The nearest-neighbour p_z - p_z hopping is therefore

$$H_{zz}^{(ij)} = V_{pp\pi}. \quad (3.16)$$

This is the usual π -hopping term from the Slater–Koster construction.[2, 3]

With this result, the direct part becomes

$$P \hat{H}_1 P = V_{pp\pi} \sum_{(i,j) \in N_{\text{B}}} \hat{a}_{z,i}^\dagger \hat{a}_{z,j}. \quad (3.17)$$

This is the normal nearest-neighbour π -Hamiltonian of benzene.[2, 3] For planar benzene, the nearest-neighbour hopping matrix does not couple the p_z -orbitals to the eliminated s , p_x , and p_y orbitals. Therefore,

$$H_{zs}^{(ij)} = H_{zx}^{(ij)} = H_{zy}^{(ij)} = 0.$$

For planar benzene without an external electric field, the direct virtual paths involving the s -orbital vanish. The leading intrinsic spin-orbit correction instead proceeds through the in-plane p_x - and p_y -orbitals

$$p_{z,i} \xrightarrow{\text{SOC}} p_{x/y,i} \xrightarrow{H^{(ij)}} p_{x/y,j} \xrightarrow{\text{SOC}} p_{z,j}. \quad (3.18)$$

This process contains two local spin-orbit interactions and one hopping process inside the eliminated σ -subspace. It is therefore second order in ξ_p . [2]

The leading intrinsic spin-orbit correction for a bond (i, j) is

$$T_{ij}^{\text{SOC}} = \frac{1}{(\epsilon_{p\pi} - \epsilon_{p\sigma})^2} \begin{pmatrix} h_{zx}^{(i)} & h_{zy}^{(i)} \end{pmatrix} \begin{pmatrix} H_{xx}^{(ij)} & H_{xy}^{(ij)} \\ H_{yx}^{(ij)} & H_{yy}^{(ij)} \end{pmatrix} \begin{pmatrix} h_{xz}^{(j)} \\ h_{yz}^{(j)} \end{pmatrix}. \quad (3.19)$$

The lower indices i and j are important here. They show that this correction belongs to the hopping from carbon atom j to carbon atom i . In other words, T_{ij}^{SOC} is a bond-dependent correction, not one global number. [2]

Inserting the spin-orbit matrix elements from the on-site Hamiltonian gives

$$T_{ij}^{\text{SOC}} = \frac{\xi_p^2}{(\epsilon_{p\pi} - \epsilon_{p\sigma})^2} \begin{pmatrix} -i\sigma_y & i\sigma_x \end{pmatrix} \begin{pmatrix} H_{xx}^{(ij)} & H_{xy}^{(ij)} \\ H_{yx}^{(ij)} & H_{yy}^{(ij)} \end{pmatrix} \begin{pmatrix} i\sigma_y \\ -i\sigma_x \end{pmatrix}. \quad (3.20)$$

This equation makes the role of the eliminated orbitals visible. Even though the final basis contains only p_z -orbitals, the spin-orbit effect survives because the electron can virtually move through p_x and p_y . [2]

The local second-order spin-orbit correction gives an on-site shift,

$$\delta\epsilon_{\text{SOC}} = \frac{h_{zx}^{(i)}h_{xz}^{(i)} + h_{zy}^{(i)}h_{yz}^{(i)}}{\epsilon_{p\pi} - \epsilon_{p\sigma}} = \frac{2\xi_p^2}{\epsilon_{p\pi} - \epsilon_{p\sigma}}. \quad (3.21)$$

This term is spin independent. In the numerical result below, ϵ_{eff} is read from the full effective matrix. It is therefore not only the local shift shown in Eq. (3.21). [2]

The effective benzene Hamiltonian can now be written as

$$\hat{H}_{\text{eff}}^{\text{B}} = (\epsilon_{p\pi} + \delta\epsilon_{\text{SOC}}) \sum_i \hat{a}_{z,i}^\dagger \hat{a}_{z,i} + \sum_{(i,j) \in N_{\text{B}}} \hat{a}_{z,i}^\dagger [V_{pp\pi} \mathbf{1}_2 + T_{ij}^{\text{SOC}}] \hat{a}_{z,j}. \quad (3.22)$$

Here

$$\hat{a}_{z,i} = \begin{pmatrix} \hat{a}_{z,i,\uparrow} \\ \hat{a}_{z,i,\downarrow} \end{pmatrix} \quad (3.23)$$

is a spinor. The matrix $\mathbf{1}_2$ is the identity matrix in spin space. [2]

The spin-orbit correction can be split into a spin-independent part and a spin-dependent part,

$$T_{ij}^{\text{SOC}} = \delta t_{ij} \mathbf{1}_2 + i\lambda_z^{\text{B}} \nu_{ij} \sigma_z. \quad (3.24)$$

Here δt_{ij} is the spin-independent correction to the hopping between atom i and atom j . The subscript z in λ_z^{B} means that the effective spin-orbit term is proportional to σ_z . For planar benzene, all nearest-neighbour bonds are equivalent, so the size of this effective spin-orbit coupling can be written as one common value. The factor $\nu_{ij} = \pm 1$ still depends on the bond direction and changes sign when the hopping direction is reversed.

With this decomposition, the compact form of the effective Hamiltonian is

$$\hat{H}_{\text{eff}}^{\text{B}} = \epsilon_{\text{eff}} \sum_i \hat{a}_{z,i}^\dagger \hat{a}_{z,i} + \sum_{(i,j) \in N_{\text{B}}} \hat{a}_{z,i}^\dagger [t_{\text{eff}} \mathbf{1}_2 + i\lambda_z^{\text{B}} \nu_{ij} \sigma_z] \hat{a}_{z,j}. \quad (3.25)$$

This Hamiltonian is used for the benzene energy spectrum. The index pair (i, j) is still needed in the hopping sum because it tells us which two carbon atoms are connected. The spin-orbit strength itself is written as λ_z^{B} , because in benzene its magnitude is the same on every nearest-neighbour bond.[2]

The effective parameters are

$$\epsilon_{\text{eff}} = \epsilon_{p\pi} + \delta\epsilon_{\text{SOC}} \quad (3.26)$$

and

$$t_{\text{eff}} = V_{pp\pi} + \delta t_{ij}. \quad (3.27)$$

The effective spin-orbit coupling is read from the σ_z -part of T_{ij}^{SOC} ,

$$\lambda_z^{\text{B}} = \frac{1}{2i\nu_{ij}} \text{Tr} [\sigma_z T_{ij}^{\text{SOC}}]. \quad (3.28)$$

This formula extracts the coefficient in front of $i\nu_{ij}\sigma_z$. The trace is taken over spin space. For benzene, this gives the same value λ_z^{B} for each nearest-neighbour bond, apart from the sign already included in ν_{ij} . [2]

The numerical values are obtained from the Python code. The code constructs the effective Hamiltonian from Eq. (3.12) and then reads off the effective parameters. Using the microscopic parameters in Table 1, the calculation gives

$$\epsilon_{\text{eff}} = -10.50 \text{ eV}, \quad (3.29)$$

$$t^{\text{B}} = -3.44 \text{ eV}, \quad (3.30)$$

and

$$\lambda_z^{\text{B}} = 3.99 \times 10^{-6} \text{ eV} = 0.00399 \text{ meV}. \quad (3.31)$$

The effective spin-orbit coupling is therefore much smaller than the normal π -hopping. This is expected for planar benzene.[2]

The energy levels obtained from Eq. (3.25) are

$$E = -17.38 \text{ eV}, \quad (3.32)$$

$$E = -13.94 \text{ eV}, \quad E = -13.94 \text{ eV}, \quad (3.33)$$

$$E = -7.06 \text{ eV}, \quad E = -7.06 \text{ eV}, \quad (3.34)$$

and

$$E = -3.62 \text{ eV}. \quad (3.35)$$

Each level is twofold degenerate. The small splitting of the middle levels comes from the small spin-orbit term in Eq. (3.31).[2]

The result is very close to the usual benzene π -Hamiltonian. This is physically reasonable because benzene is planar and the effective spin-orbit coupling is very weak. Still, $\hat{H}_{\text{eff}}^{\text{B}}$ is not the same as the full Hamiltonian. The full Hamiltonian also contains the s, p_x, p_y -orbitals.[2]

4 Effective Hamiltonian for Helicene

4.1 From benzene to helicene

The benzene calculation in Sec. 3.4 was used as a planar reference system. It showed how the full (s, p_x, p_y, p_z) -Hamiltonian can be reduced to a Hamiltonian which acts only on the carbon p_z -orbitals. The same projection idea is now applied to helicene. The important difference is the molecular shape. Benzene is planar, while helicene is non-planar and chiral. Because of this, the local orbital directions change from site to site, and the Slater–Koster hopping elements from Eq. (2.26) become geometry dependent.[1, 2]

In benzene, all p_z -orbitals are chosen parallel. This makes the first-order intrinsic spin-orbit paths vanish, so the remaining effective spin-orbit coupling is only a small second-order effect in ξ_p . In helicene, the carbon framework is twisted. The twist allows additional virtual paths through the eliminated p_x - and p_y -orbitals. After the projection, these paths appear as effective spin-dependent hopping terms in the final p_z -Hamiltonian.[1]

The main idea is therefore unchanged. Spin-orbit coupling is local in the full orbital model. After the decimation, the final model contains only p_z -orbitals. The removed orbitals are no longer part of the basis, but their effect remains inside the effective hopping parameters. In helicene these parameters carry information about the helical geometry.[1, 2]

4.2 Helicene geometry

Following Geyer et al., helicene is described by three coupled helical parts. We denote them by

$$I, \quad M, \quad A. \quad (4.1)$$

The set I describes the inner helix. The sets M and A describe the two outer helical parts. Hydrogen atoms are not included in this effective model, because the reduced Hamiltonian is built only from the carbon p_z -orbitals.[1]

The position of a carbon atom at site i is written as

$$\mathbf{R}_i = \left(R_i \cos \Phi_i, R_i \sin \Phi_i, \frac{b}{2\pi} \Phi_i \right). \quad (4.2)$$

Here R_i is the radius of the helix on which the atom lies. The angle Φ_i gives the angular position around the helical axis. The parameter b is the pitch of the helix. It measures how far the structure moves in the vertical direction after one full turn.[1]

The three radii used in the model are

$$r_0 = a_0, \quad r_1 = 2a_0, \quad r_2 = a_1 = \sqrt{7}a_0. \quad (4.3)$$

The inner sites lie on the radius r_0 . The other carbon sites lie on the outer radii r_1 and r_2 . In this way the molecule can be treated as a set of coupled helical chains.[1]

At each carbon site, a local orbital frame is used. The local directions are

$$\mathbf{n}(x, i) = (\cos \Phi_i, \sin \Phi_i, 0), \quad \mathbf{n}(y, i) = (-\sin \Phi_i, \cos \Phi_i, 0), \quad \mathbf{n}(z, i) = (0, 0, 1). \quad (4.4)$$

The vectors $\mathbf{n}(x, i)$, $\mathbf{n}(y, i)$, and $\mathbf{n}(z, i)$ give the local directions of the p_x -, p_y -, and p_z -orbitals. They are inserted into the Slater–Koster formula in Eq. (2.26). This is where the helical geometry enters the hopping matrix elements.[1, 3]

4.3 Projection onto the p_z -subspace

The projection is done in the same way as for benzene. The retained states are the carbon p_z -orbitals. The projector onto the retained subspace is

$$P|\mu, i, \sigma\rangle = \delta_{\mu z}|\mu, i, \sigma\rangle, \quad P^\perp = \hat{1} - P. \quad (4.5)$$

Here μ labels the orbital, i labels the carbon site, and σ labels the spin. The operator P keeps only the p_z -part, while $P^\perp$ contains the eliminated orbitals.[2]

With $\epsilon_0 = \epsilon_{p\pi}$, the decimation gives

$$\hat{H}_{\text{eff}}^H \approx \epsilon_{p\pi} P + P \hat{H}_1 P + P \hat{H}_1 P^\perp \left(\epsilon_{p\pi} \mathbf{1}_{P^\perp} - P^\perp \hat{H}_0 P^\perp \right)^{-1} P^\perp \hat{H}_1 P. \quad (4.6)$$

This is the same decimation formula as for benzene. The operator $\hat{H}_0$ contains the diagonal orbital energies. The operator $\hat{H}_1$ contains the hopping terms, the atomic spin-orbit coupling, and possible electric-field terms. The difference to benzene is not the formula itself, but the geometry inside the hopping elements.[1, 2]

4.4 Kinetic part

The kinetic part comes from $\hat{P} \hat{H}_1 \hat{P}$. It describes hopping between neighbouring retained p_z -orbitals. We write it as

$$\hat{H}_{\text{kin}} = \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} t^{\alpha} \hat{a}_i^{\dagger} \hat{a}_j. \quad (4.7)$$

Here $\hat{a}_i$ is the spinor annihilation operator for the retained p_z -orbital on site i . The set N_{α} contains all bonds of type α . The label α is used because helicene has different kinds of bonds, for example bonds along one helical part and bonds between different helical parts.[1]

For a bond along a helical chain, the hopping is not just the planar value $V_{pp\pi}$. The finite pitch b tilts neighbouring orbitals relative to each other. Therefore the hopping contains both a π -type and a σ -type contribution. To leading order one obtains

$$t^{\alpha} = V_{pp\pi} + f_{\text{geo}}^{\alpha} b^2 (V_{pp\sigma} - V_{pp\pi}). \quad (4.8)$$

The factor f_{geo}^{α} depends only on the geometry of the bond. It is different for different bond types α . In a planar system, the pitch is zero and this extra term disappears.[1]

For a simple helical chain with radius a and angular step ϕ , the geometry factor is

$$f_{\text{geo}}(a, \phi) = \frac{\phi^2}{8\pi^2 a^2 (1 - \cos \phi) + b^2 \phi^2}. \quad (4.9)$$

For the coupling between the two outer helical parts, the corresponding factor is

$$f_{\text{geo}}^{M,A} = \frac{\phi_1^2}{4\pi^2 (4a_0^2 - 4a_0 a_1 \cos \phi_1 + a_1^2) + b^2 \phi_1^2}. \quad (4.10)$$

These factors are obtained by inserting the helical coordinates from Eq. (4.2) into the Slater–Koster hopping expression. They show explicitly why the kinetic hopping depends on the shape of the molecule.[1, 3]

If the pitch is set to zero,

$$b \rightarrow 0, \quad (4.11)$$

the geometry correction in Eq. (4.8) vanishes and the hopping reduces to

$$t^\alpha \rightarrow V_{pp\pi}. \quad (4.12)$$

This is the planar limit. It gives the same physical situation as the usual π -hopping in benzene and is a useful check of the model.[1]

4.5 Intrinsic spin-orbit part

The intrinsic spin-orbit terms come from virtual paths through the eliminated p_x - and p_y -orbitals. In benzene, the planar geometry makes the first-order paths vanish. In helicene, these paths are allowed because the local orbital directions rotate along the molecule. This gives mixed hopping elements such as

$$H_{xz}^{(ij)}, \quad H_{yz}^{(ij)}, \quad H_{zx}^{(ij)}, \quad H_{zy}^{(ij)}. \quad (4.13)$$

These matrix elements connect p_z -orbitals to in-plane p_x - or p_y -orbitals. They are calculated from the Slater–Koster formula using the local orbital directions from Eq. (4.4).[1]

The first-order intrinsic spin-orbit contribution is

$$T_{ij}^{\text{SOC},(1)} = \sum_{\nu=x,y} \frac{h_{z\nu}^{(i)} H_{\nu z}^{(ij)} + H_{z\nu}^{(ij)} h_{\nu z}^{(j)}}{\epsilon_{p\pi} - \epsilon_{p\sigma}}. \quad (4.14)$$

This expression has a simple meaning. One path starts with a local spin-orbit step on atom i and then hops to atom j . The other path first hops and then uses local spin-orbit coupling on atom j . Both paths start and end in the retained p_z -subspace.[1, 2]

The second-order contribution has the same structure as in the benzene calculation,

$$T_{ij}^{\text{SOC},(2)} = \frac{1}{(\epsilon_{p\pi} - \epsilon_{p\sigma})^2} \begin{pmatrix} h_{zx}^{(i)} & h_{zy}^{(i)} \end{pmatrix} \begin{pmatrix} H_{xx}^{(ij)} & H_{xy}^{(ij)} \\ H_{yx}^{(ij)} & H_{yy}^{(ij)} \end{pmatrix} \begin{pmatrix} h_{xz}^{(j)} \\ h_{yz}^{(j)} \end{pmatrix}. \quad (4.15)$$

This term is of order ξ_p^2 . It produces the effective $\hat{\sigma}_z$ -type coupling when no external electric field is present.[1]

The total intrinsic spin-orbit operator is written as

$$\hat{H}_{\text{SOC}} = i \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} \sum_{k=x,y,z} \lambda_k^{\alpha} \nu_{ij} \hat{a}_i^{\dagger} \hat{\sigma}_k \hat{a}_j. \quad (4.16)$$

The notation is important here. The index $k = x, y, z$ tells which Pauli matrix appears in the spin-dependent hopping. The label α tells which type of bond is considered. Thus λ_k^{α} is the effective spin-orbit strength for spin direction k on bonds of type α . The factor $\nu_{ij} = \pm 1$ gives the sign of the hopping direction. It changes sign when the hopping direction is reversed and is needed together with the imaginary unit i to keep the Hamiltonian Hermitian.[1]

In this work we use

$$\nu_{ij} = \text{sgn}(j - i). \quad (4.17)$$

This is a compact way to assign opposite signs to opposite hopping directions. The exact sign convention is not the physical result by itself, it is the antisymmetric structure of the spin-orbit hopping which matters.

For zero external electric field, the leading nonzero spin-orbit couplings are

$$\lambda_y^{I,A,(M,A)} = \xi_p b g_{\text{geo},y}^{I,A,(M,A)} \frac{V_{pp\pi} - V_{pp\sigma}}{\epsilon_{p\pi} - \epsilon_{p\sigma}} + O(\xi_p^2), \quad (4.18)$$

and

$$\lambda_x^{(M,A)} = \xi_p b g_{\text{geo},x}^{(M,A)} \frac{V_{pp\pi} - V_{pp\sigma}}{\epsilon_{p\pi} - \epsilon_{p\sigma}} + O(\xi_p^2). \quad (4.19)$$

The factor b is the key point. It shows that these terms are directly caused by the helical pitch. If the molecule becomes planar, then $b = 0$, and the first-order terms vanish.[1]

For a simple helix, the geometry factor is

$$g_{\text{geo}}(a, \phi) = 4\pi a f_{\text{geo}}(a, \phi) \frac{1 - \cos \phi}{\phi}. \quad (4.20)$$

For the coupling between the two outer helical parts, the two relevant factors are

$$g_{\text{geo},y}^{M,A} = 2\pi(2a_0 + a_1) f_{\text{geo}}^{M,A} \frac{1 - \cos \phi_1}{\phi_1}, \quad g_{\text{geo},x}^{M,A} = 2\pi(2a_0 - a_1) f_{\text{geo}}^{M,A} \frac{\sin \phi_1}{\phi_1}. \quad (4.21)$$

These expressions show that the effective spin-orbit couplings are built from the same geometrical quantities that also enter the kinetic hopping. The spin dependence is therefore not added by hand. It appears when the local spin-orbit coupling is combined with the non-planar hopping geometry.[1]

The $\hat{\sigma}_z$ -type coupling behaves differently. Without an external electric field, it appears only at second order in ξ_p ,

$$\lambda_z^\alpha = O(\xi_p^2). \quad (4.22)$$

This is why the planar benzene case has only a very small intrinsic effective spin-orbit coupling.[1]

4.6 Rashba-like part from an external electric field

If an external electric field is included, the effective Hamiltonian also contains Rashba-like terms. These terms come from virtual paths that contain both the electric-field coupling between s - and p -orbitals and the local spin-orbit coupling. The corresponding operator is

$$\hat{H}_{\text{Rashba}} = i \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} \sum_{k=x,y,z} \rho_k^{\alpha} \nu_{ij} \hat{a}_i^{\dagger} \hat{\sigma}_k \hat{a}_j. \quad (4.23)$$

The coefficients ρ_k^{α} are effective Rashba-like couplings. They depend on the electric-field matrix elements and on the geometry of the bond. If no external electric field is used, the Rashba-like part is set to zero,

$$\hat{H}_{\text{Rashba}} = 0. \quad (4.24)$$

For this reason, the Rashba term is kept as an optional contribution in the compact helicene Hamiltonian.[1]

4.7 Final effective helicene Hamiltonian

The effective helicene Hamiltonian is the sum of the kinetic part, the intrinsic spin-orbit part, and the Rashba-like part,

$$\hat{H}_{\text{eff}}^{\text{H}} = \hat{H}_{\text{kin}} + \hat{H}_{\text{SOC}} + \hat{H}_{\text{Rashba}}. \quad (4.25)$$

This is the effective p_z -Hamiltonian for helicene. It has the same general structure as the benzene Hamiltonian in Eq. (3.25), but the hopping parameters now depend on the helical geometry. The spin-orbit part can also contain $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$ terms.[1]

Without an external electric field, the compact form becomes

$$\hat{H}_{\text{eff}}^{\text{H}} = \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} t^{\alpha} \hat{a}_i^{\dagger} \hat{a}_j + i \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} \sum_{k=x,y,z} \lambda_k^{\alpha} \nu_{ij} \hat{a}_i^{\dagger} \hat{\sigma}_k \hat{a}_j. \quad (4.26)$$

This is the form used when only intrinsic spin-orbit coupling is considered. The first term is the spin-independent hopping. The second term is the effective spin-dependent hopping generated by the combination of local spin-orbit coupling and the helical structure.[1]

The comparison with benzene gives a useful check. In benzene, the planar geometry removes the first-order spin-orbit terms. In helicene, the finite pitch b gives nonzero first-order terms proportional to $\hat{\sigma}_x$ and $\hat{\sigma}_y$, as shown in Eqs. (4.18) and (4.19). If the planar limit $b \rightarrow 0$ is taken, these first-order terms vanish again. The model then returns to the same physical situation as benzene.[1]

5 Full and Effective Helicene Hamiltonian

This section compares the full helicene Hamiltonian with the effective p_z -Hamiltonian. The comparison is used as a numerical check of the reduction. It does not test the complete CISS effect by itself. The main point is to see how the microscopic orbital model is connected to the smaller model used later for transport.

The full helicene model contains the carbon orbitals

$$s, \quad p_x, \quad p_y, \quad p_z. \quad (5.1)$$

Hydrogen atoms are not included in this coarse-grained model. There are 26 carbon sites and two spin states for every orbital. The dimension of the full Hamiltonian is therefore

$$26 \cdot 4 \cdot 2 = 208. \quad (5.2)$$

The effective model keeps one p_z -orbital with two spin states on every site. Its dimension is

$$26 \cdot 2 = 52. \quad (5.3)$$

This is the same reduction of the carbon valence basis that is used by Geyer et al.[1, 2]

The microscopic parameters are listed in Table 1. All results in this section use $\mathbf{B} = 0$, so time-reversal symmetry is preserved and every level forms a Kramers pair.[1, 2]

5.1 Hamiltonians used in the calculation

The full Hamiltonian is

$$\hat{H}_{\text{full}} = \sum_{i,\mu,\nu} \hat{a}_{\mu,i}^\dagger \hat{h}_{\mu\nu}^{(i)} \hat{a}_{\nu,i} + \sum_{(i,j)} \sum_{\mu,\nu} \hat{a}_{\mu,i}^\dagger \hat{H}_{\mu\nu}^{(ij)} \hat{a}_{\nu,j}. \quad (5.4)$$

The positions of the sites are taken from the geometry in the Supplementary Information. In particular, the angular position is

$$\Phi_i = \begin{cases} (i-20)\phi_0, & i \in I, \\ \left\lfloor \frac{i}{3} \right\rfloor \phi_2 + \left(i-1 - \left\lfloor \frac{i}{3} \right\rfloor \right) \phi_1, & i \in M \cup A. \end{cases} \quad (5.5)$$

The floor function in the second line is important. It fixes the positions of sites 3, 6, 9, ... on the outer part of the molecule. These positions enter directly into the bond vectors and therefore into the Slater–Koster hopping elements.[2]

For zero electric field, the Rashba-like part is absent. The compact form is

$$\hat{H}_{\text{eff}} = \epsilon_{p\pi} \sum_i \hat{a}_i^\dagger \hat{a}_i + \sum_{\alpha} \sum_{(i,j) \in N_{\alpha}} \hat{a}_i^\dagger [t_{\alpha} \mathbf{1}_2 + i\nu_{ij} (\lambda_x^{\alpha} \hat{\sigma}_x + \lambda_y^{\alpha} \hat{\sigma}_y + \lambda_z^{\alpha} \hat{\sigma}_z)] \hat{a}_j. \quad (5.6)$$

The label α identifies the bond classes I , A , (I, M) , and (M, A) . The set N_{α} contains the bonds of that class. The factor $\nu_{ij} = \text{sgn}(j-i)$ changes sign when the hopping direction is reversed. This antisymmetric sign, together with the imaginary unit i , keeps the spin-orbit hopping Hermitian. The parameters t_{α} are spin-independent hoppings, while λ_k^{α} are effective spin-dependent hoppings.[1, 2]

All values are given in eV.

Table 2: Effective helicene parameters for $\|\mathbf{E}\| = 0$, taken from Geyer et al.

Bond class	t_{α}	λ_x^{α}	λ_y^{α}	λ_z^{α}
I	-1.806	0	0.00305	-1.12×10^{-6}
A	-3.191	0	0.00048	-8.07×10^{-7}
(I, M)	-3.440	0	0	0
(M, A)	-3.247	0.00024	0	-7.23×10^{-7}

5.2 Ordered comparison for $\mathbf{E} = 0$ and $\mathbf{B} = 0$

The full Hamiltonian has 104 Kramers pairs, but the effective Hamiltonian has only 26. To construct a simple comparison, the code selects the 26 pairs with the largest total p_z -weight and orders them by energy. The effective levels are also ordered by energy. This gives an overview of both spectra, but it is not an exact state-by-state matching. Degenerate states can mix, and the order of two states can change when the other orbitals are removed.

	Level	E_{full}	p_z -weight	E_{eff}	$E_{\text{eff}} - E_{\text{full}}$
	1	-19.838685	0.705	-18.018478	1.820206
	2	-19.042827	0.668	-17.646208	1.396619
	3	-18.194408	0.705	-17.107661	1.086746

4	-17.235314	0.763	-16.463883	0.771431
5	-16.393286	0.656	-15.749476	0.643811
6	-16.043948	0.692	-14.982132	1.061815
7	-15.094232	0.527	-14.635001	0.459231
8	-14.646581	0.571	-13.773972	0.872608
9	-14.517346	0.744	-13.361563	1.155783
10	-13.449256	0.910	-13.145092	0.304163
11	-13.288565	0.778	-12.777355	0.511211
12	-12.859978	0.901	-12.495084	0.364894
13	-9.924270	0.744	-12.337331	-2.413060
14	-9.707861	0.721	-8.662669	1.045191
15	-8.740753	0.795	-8.504916	0.235837
16	-8.619494	0.677	-8.222645	0.396848
17	-7.510306	0.802	-7.854908	-0.344602
18	-7.388776	0.481	-7.638437	-0.249661
19	-6.829664	0.525	-7.226028	-0.396364
20	-6.409892	0.546	-6.364999	0.044893
21	-6.355872	0.655	-6.017868	0.338005
22	-5.056520	0.491	-5.250524	-0.194004
23	-4.189237	0.620	-4.536117	-0.346881
24	-3.464649	0.678	-3.892339	-0.427689
25	-2.963513	0.496	-3.353792	-0.390279
26	-2.281333	0.865	-2.981522	-0.700188

The selected full-model levels lie between

$$-19.838685 \text{ eV} \leq E_{\text{full}} \leq -2.281333 \text{ eV}, \quad 0.481 \leq w_{p_z} \leq 0.910. \quad (5.7)$$

The weights show that the states are not pure p_z -states. They also contain contributions from s , p_x , and p_y . This mixing is expected because helicene is not planar.

For the two ordered lists, the mean absolute energy difference is

$$\frac{1}{26} \sum_{n=1}^{26} |E_{\text{eff},n} - E_{\text{full},n}| = 0.691 \text{ eV}. \quad (5.8)$$

The signed differences range from -2.413 eV to 1.820 eV . These numbers only describe the two ordered spectra. They should not be read as errors of individually matched eigenstates. The deviations show that the low-order effective model is a reduced description, not an exact copy of the full spectrum over the complete energy range.

5.3 External electric field

Geyer et al. also give effective parameters for a physical electric field of 25 V/nm along the global z -direction. The physical field is not inserted directly as an energy. It gives the dipole matrix element

$$\xi_{sp} = 2qa_B \|\mathbf{E}\| \approx 2.65 \text{ eV} \quad \text{for} \quad \|\mathbf{E}\| = 25 \text{ V/nm}. \quad (5.9)$$

Here q is the elementary charge and a_B is the Bohr radius. The quantities E_x, E_y, E_z in the on-site matrix are energy matrix elements obtained from ξ_{sp} and the local field direction.[1]

Table 3: Effective helicene parameters for $\|\mathbf{E}\| = 25 \text{ V/nm}$ in the z -direction, taken from Geyer et al.

Bond class	t_α	λ_x^α	λ_y^α	λ_z^α
I	-0.817	-0.00363	0.00305	-1.12×10^{-6}
A	-2.202	-0.00443	0.00048	-8.08×10^{-7}
(I, M)	-2.451	0	-0.00456	0
(M, A)	-2.259	-0.00320	0.00313	-7.24×10^{-7}

The resulting effective spectrum is

Level	E_{eff}	Degeneracy
1	-15.587490	2
2	-15.385188	2
3	-15.071984	2
4	-14.672578	2
5	-14.211877	2
6	-13.705599	2
7	-13.521275	2
8	-12.431557	2
9	-12.265421	2
10	-12.069004	2
11	-12.042873	2
12	-11.833813	2
13	-11.794299	2
14	-9.205701	2
15	-9.166187	2
16	-8.957127	2
17	-8.930996	2
18	-8.734579	2
19	-8.568443	2
20	-7.478725	2
21	-7.294401	2
22	-6.788123	2
23	-6.327422	2
24	-5.928016	2
25	-5.614812	2
26	-5.412510	2

The electric field changes the spin-independent hopping parameters and adds Rashba-like spin-dependent terms. The spectrum therefore changes. Since the electric field does not break time-reversal symmetry, the Kramers degeneracy remains.

5.4 Physical interpretation and connection to CISS

The main physical result of the reduction can be summarized as

$$\text{helical geometry} + \text{atomic SOC} \implies \text{effective spin-dependent hopping.} \quad (5.10)$$

The terms proportional to λ_x^α , λ_y^α , and λ_z^α connect the motion of an electron to its spin. They are necessary for spin-selective transport, but they are not sufficient by themselves to guarantee a finite spin polarization.

The spin polarization is calculated from the spin-resolved transmissions,

$$P_z = \frac{T_{\uparrow} - T_{\downarrow}}{T_{\uparrow} + T_{\downarrow}}. \quad (5.11)$$

The value of P_z also depends on the transport setup. In the model of Geyer et al., a nonzero or strongly enhanced spin polarization requires additional open channels, such as several incoming and outgoing channels or local leakage channels that break unitarity.[1]

The energy comparison in this section is therefore only a consistency check. The full Hamiltonian contains the microscopic orbital structure. The effective Hamiltonian keeps the p_z -subspace and includes the removed orbitals through effective hopping parameters. The CISS-relevant result is the spin-dependent hopping structure of $\hat{H}_{\text{eff}}$. The transport calculation in the next section tests how this structure affects $T_{\uparrow}$, $T_{\downarrow}$, and P_z .

6 Transport and Spin Polarization

The effective Hamiltonian derived in the previous chapters contains spin-dependent hopping terms. These terms come from the helical shape of the molecule and from spin-orbit coupling. However, this is not yet a transport result. To obtain a CISS signal, the molecule must be connected to electrodes. We then calculate how well spin-up and spin-down electrons pass through the open system. The difference between these two transmissions gives the spin polarization. The transport method used here follows the Green-function approach of Geyer et al.[1]

6.1 From the closed molecule to an open system

The isolated molecule is described by the effective Hamiltonian

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{kin}} + \hat{H}_{\text{SOC}} + \hat{H}_{\text{Rashba}}. \quad (6.1)$$

In the transport calculation, the constant p_z on-site energy is subtracted. Therefore, the energy axis is measured relative to this on-site energy. This only shifts the energy origin and does not change the transmission.[1]

To describe transport, the molecule is connected to a left and a right electrode. Geyer et al. use two incoming and two outgoing real-space channels. The exact contact-site numbers are not listed in the paper. In the numerical check of this thesis, both helical parts are connected at both ends. The chosen contact sites are

$$L = \{1, 20\}, \quad R = \{19, 26\}. \quad (6.2)$$

Sites 1 and 19 belong to the outer part of the effective helicene structure. Sites 20 and 26 belong to the inner helix. This contact choice is therefore a concrete numerical realization of a two-channel setup. It is an assumption of this thesis and not an exact reproduction of an explicitly stated contact geometry in Geyer et al.

Each contact couples in the same way to spin-up and spin-down electrons. The coupling strength is chosen as

$$\tilde{\gamma} = 1 \text{ eV}. \quad (6.3)$$

This is the value used for the transport leads in Geyer et al.[1]

6.2 Self-energies and the retarded Green function

The electrodes are not added as large explicit Hamiltonians. Their effect is included through self-energy matrices. In the wide-band approximation, these self-energies are energy independent and have the form

$$\hat{\Sigma}_L^r = -\frac{i}{2}\hat{\Gamma}_L, \quad \hat{\Sigma}_R^r = -\frac{i}{2}\hat{\Gamma}_R. \quad (6.4)$$

The matrices $\hat{\Gamma}_L$ and $\hat{\Gamma}_R$ describe how strongly the molecule is coupled to the left and right electrodes. They are nonzero only at the contact sites. The imaginary part of the self-energy gives the finite lifetime of an electron inside the molecule. In simple words, an electron can enter the molecule from a lead and later leave it again. The molecular energy levels are therefore broadened instead of being perfectly sharp.[1]

The retarded Green function is

$$\hat{G}^r(E) = \left[(E + i\eta)\mathbf{1} - \hat{H}_{\text{eff}} - \hat{\Sigma}_L^r - \hat{\Sigma}_R^r - \hat{\Sigma}_{\text{leak}}^r(E) \right]^{-1}. \quad (6.5)$$

This matrix describes how an electron with energy E propagates through the open molecule. A matrix element of $\hat{G}^r$ gives the propagation amplitude between two molecular states. Large matrix elements normally appear close to molecular resonances, where transport through the molecule is easier. The small positive number η selects the retarded solution. This means that the Green function describes propagation forward in time and outgoing waves from the molecule. The advanced Green function is

$$\hat{G}^a(E) = \left(\hat{G}^r(E) \right)^\dagger. \quad (6.6)$$

The Green function is therefore the central object that connects the molecular Hamiltonian with the transmission through the electrodes.[1]

6.3 Local leakage channels

Geyer et al. also introduce local leakage channels. In this model, every molecular site is connected to an additional semi-infinite chain. An electron can leave the molecule through such a chain and does not return to the measured left-to-right current. The hopping inside a leakage chain is called t_0 , and the coupling between the molecule and the chain is called t_{leak} . The local retarded self-energy is written as

$$\Sigma_{\text{leak}}^r(E) = \frac{|t_{\text{leak}}|^2}{t_0} e^{iq}, \quad E = -2t_0 \cos q. \quad (6.7)$$

The retarded branch is chosen so that the imaginary part describes loss from the molecule. The parameters used in the paper and in the numerical check are

$$t_0 = 6 \text{ eV}, \quad t_{\text{leak}} = 0.6 \text{ eV}. \quad (6.8)$$

If leakage is switched off, then $\hat{\Sigma}_{\text{leak}}^r = 0$. If leakage is switched on, the same local self-energy is added to every molecular site. This is a simple model for absorption by the environment. It is not a fully self-consistent model of dephasing, because the lost current is not injected back into the molecule. The reduced two-terminal problem is therefore not unitary.[1]

6.4 Spin-resolved transmission

The incoming current is assumed to be unpolarized. This means that the left electrode injects spin-up and spin-down electrons with equal probability. The transmission into the outgoing spin state s is

$$T_s(E) = \text{Tr} \left[\hat{\Gamma}_L \hat{G}^a(E) \hat{\Gamma}_R \hat{\pi}_s \hat{G}^r(E) \right], \quad s = \uparrow, \downarrow. \quad (6.9)$$

The matrix $\hat{\pi}_\uparrow$ keeps only spin-up states, while $\hat{\pi}_\downarrow$ keeps only spin-down states. The trace sums over all molecular orbitals and all transport paths that contribute to the selected outgoing spin direction. Thus, $T_\uparrow$ is the total transmission into spin-up states and $T_\downarrow$ is the total transmission into spin-down states.[1]

The spin polarization along the z -direction is

$$P_z(E) = \frac{T_\uparrow(E) - T_\downarrow(E)}{T_\uparrow(E) + T_\downarrow(E)}. \quad (6.10)$$

If $P_z = 0$, both spin directions are transmitted equally. If $P_z > 0$, the transmitted current contains more spin-up electrons. If $P_z < 0$, spin-down transmission is larger. The value is normalized by the total transmission, so it lies between -1 and 1 whenever the denominator is nonzero. Reversing the handedness of the helix reverses the sign of the polarization at the same energy.[1]

The polarization can be separated into spin-conserving and spin-flip parts. For this purpose, the transmission from incoming spin s' to outgoing spin s is defined as

$$T_{ss'}(E) = \text{Tr} \left[\hat{\Gamma}_L \hat{\pi}_{s'} \hat{G}^a(E) \hat{\Gamma}_R \hat{\pi}_s \hat{G}^r(E) \right]. \quad (6.11)$$

The total transmission is

$$T = T_{\uparrow\uparrow} + T_{\downarrow\downarrow} + T_{\uparrow\downarrow} + T_{\downarrow\uparrow}. \quad (6.12)$$

The two contributions to the polarization are

$$P_{\text{nf}} = \frac{T_{\uparrow\uparrow} - T_{\downarrow\downarrow}}{T}, \quad P_{\text{f}} = \frac{T_{\uparrow\downarrow} - T_{\downarrow\uparrow}}{T}, \quad P_z = P_{\text{nf}} + P_{\text{f}}. \quad (6.13)$$

The term P_{nf} is the non-flip contribution. It compares the two processes in which the spin is conserved. The term P_{f} compares the two possible spin-flip processes. This separation shows whether the polarization mainly comes from different scattering of the two spin directions or from unequal spin-flip probabilities.[1]

6.5 Why the open-channel structure matters

Chirality and spin-orbit coupling are necessary, but they are not always sufficient for a finite polarization. In a coherent single-channel system with time-reversal symmetry, the spin-dependent hopping can be removed by a suitable unitary transformation. The two transmitted spin components then remain equivalent. A finite polarization becomes possible when several incoming and outgoing channels are present. Leakage gives another possibility because it breaks the unitarity of the reduced scattering problem.[1]

This point is important for CISS. The effective Hamiltonian creates spin-dependent motion inside the molecule. The contacts and the environment decide whether this spin dependence becomes visible in the transmitted current. Therefore, the contact geometry and the leakage model are physical parts of the transport calculation, not only technical details.[1, 6]

6.6 Numerical setup

The numerical calculation uses the effective 52×52 helicene Hamiltonian. The parameters for $|\mathbf{E}| = 0$ and $|\mathbf{E}| = 25 \text{ V/nm}$ are taken from the tables of Geyer et al. The energy is measured relative to the p_z on-site energy. The calculation uses the following settings[1]

Table 4: Settings used for the transport calculation in this thesis.

quantity	value
number of molecular sites	26
Hamiltonian dimension	52
left contact sites	1, 20
right contact sites	19, 26
lead coupling	$\tilde{\gamma} = 1 \text{ eV}$
energy interval	$[-4, 4] \text{ eV}$
number of energy points	1601
electric fields	0 and 25 V/nm
leakage parameters	$t_0 = 6 \text{ eV}$, $t_{\text{leak}} = 0.6 \text{ eV}$
magnetic field	$\mathbf{B} = 0$

The code uses the spin-dependent hopping matrix

$$t^\alpha \mathbf{1}_2 + i\nu_{ij} (\lambda_x^\alpha \hat{\sigma}_x + \lambda_y^\alpha \hat{\sigma}_y + \lambda_z^\alpha \hat{\sigma}_z). \quad (6.14)$$

The tabulated values of λ_z^α already contain their signs. Therefore, no additional minus sign is inserted. This point is important for a source-consistent implementation.[1]

6.7 Numerical results

Four cases are calculated. The electric field is either zero or 25 V/nm. For each field, the calculation is performed once without leakage and once with leakage. Table 5 lists the largest absolute polarization found on the chosen energy grid.

Table 5: Largest absolute spin polarization obtained in the numerical calculation. The energy is measured relative to the p_z on-site energy.

field	leakage	energy (eV)	P_z	polarization (%)
$ \mathbf{E} = 0$	no	1.995	-9.39×10^{-10}	-9.39×10^{-8}
$ \mathbf{E} = 0$	yes	2.005	1.68×10^{-7}	1.68×10^{-5}
$ \mathbf{E} = 25 \text{ V/nm}$	no	-1.320	-5.73×10^{-5}	-5.73×10^{-3}
$ \mathbf{E} = 25 \text{ V/nm}$	yes	1.345	3.52×10^{-4}	3.52×10^{-2}

Figure 2 shows the complete energy dependence of P_z . The upper panel shows the zero-field result. Without leakage, the curve stays extremely close to zero over the full energy range. Leakage increases the signal, but the polarization remains very small. This confirms that the intrinsic spin-orbit terms of carbon helicene are weak compared with the normal hopping terms.

The lower panel of Figure 2 shows the result for 25 V/nm. The electric field adds Rashba-like couplings and gives a clearly larger polarization. Leakage increases it further. The largest value in this calculation is $P_z = 3.52 \times 10^{-4}$, which corresponds to about 0.035%. The graph therefore confirms the qualitative order

$$|P_z|_{E=0, \text{closed}} < |P_z|_{E=0, \text{leak}} < |P_z|_{E=25, \text{closed}} < |P_z|_{E=25, \text{leak}}. \quad (6.15)$$

This order is a result of the present numerical implementation.

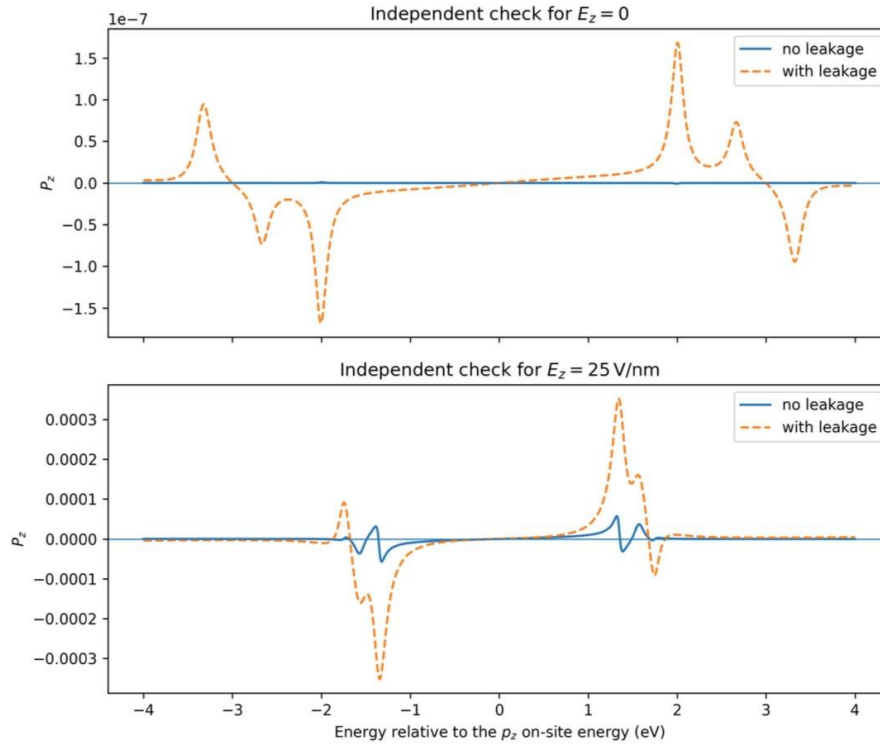


Figure 2: Calculated spin polarization for $|\mathbf{E}| = 0$ and $|\mathbf{E}| = 25$ V/nm, with and without leakage.

The spin-resolved transmissions for the case $|\mathbf{E}| = 25$ V/nm with leakage are shown in Figure 3. In the upper panel, $T_{\uparrow}$ and $T_{\downarrow}$ almost lie on top of each other. Their difference is very small compared with their absolute values. The lower panel shows that this small difference is still enough to produce a finite normalized polarization. The graph therefore explains why P_z can show visible peaks even when the two transmission curves appear nearly identical.

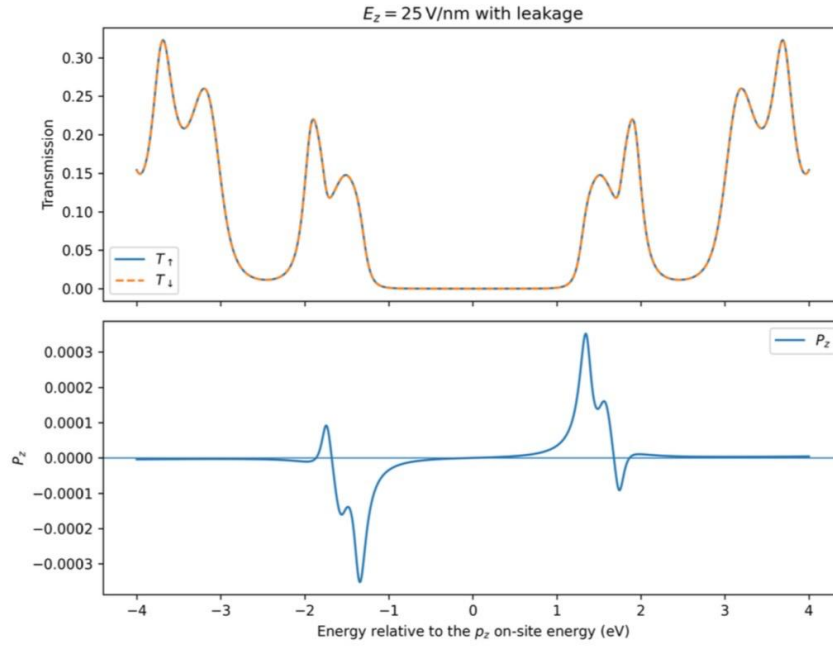


Figure 3: Spin-resolved transmission for $|\mathbf{E}| = 25 \text{ V/nm}$ with leakage. The upper panel shows $T_\uparrow$ and $T_\downarrow$. The lower panel shows the polarization calculated from their difference.

Figure 4 separates the polarization into the non-flip part P_{nf} and the spin-flip part P_{f} . In the zero-field case, the non-flip contribution is clearly larger. This means that the small polarization mainly comes from different spin-conserving scattering probabilities. In the large-field case, the spin-flip contribution becomes more important around the strongest polarization peaks. The Rashba-like terms therefore increase not only the total polarization, but also the role of spin-flip processes.

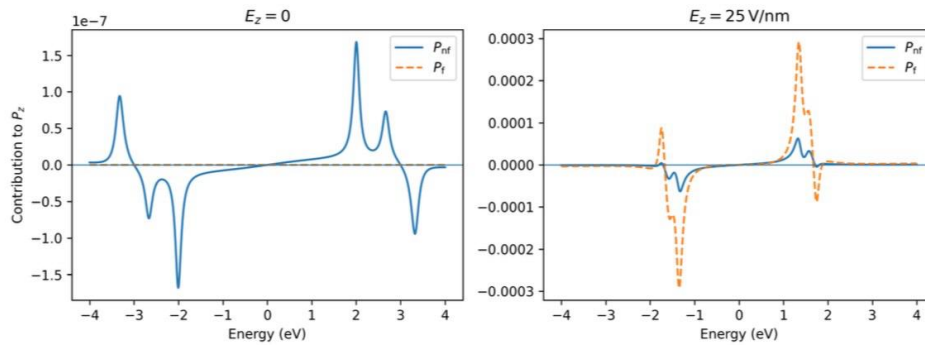


Figure 4: Decomposition of the leakage results into the non-flip contribution P_{nf} and the spin-flip contribution P_{f} .

The three figures support the same physical picture. The zero-field intrinsic effect is very small. An electric field gives stronger Rashba-like spin-orbit terms. Leakage breaks unitarity and further increases the difference between the two transmitted spin components. Even with both effects, the polarization remains below one tenth of one percent for the parameters and contacts used here.

6.8 Short comparison with Geyer et al.

The numerical results agree qualitatively with the results of Geyer et al. They also find a very small polarization for the physical parameters without leakage. An external Rashba field increases the polarization, and local leakage can increase it by several orders of magnitude. Their decomposition also shows that the zero-field signal is mainly spin conserving, while strong electric fields make spin-flip processes more important.[1]

Geyer et al. also show that much larger polarizations can be obtained by artificially increasing the ratio between spin-orbit coupling and normal hopping. Those modified parameters are not the physical carbon parameters. This comparison shows that the small ratio λ/t is one of the main reasons why the polarization remains small in the present calculation.[1]

6.9 Connection to the CISS effect

The transport calculation forms the final bridge to CISS. Atomic spin-orbit coupling first mixes the carbon orbitals. The helical geometry converts this local interaction into spin-dependent hopping in the effective p_z -Hamiltonian. The open transport setup then converts the spin-dependent hopping into different transmission probabilities,

$$T_{\uparrow}(E) \neq T_{\downarrow}(E). \quad (6.16)$$

A nonzero difference gives $P_z(E) \neq 0$. The complete chain is therefore

$$\begin{aligned} \text{helical geometry} + \text{spin-orbit coupling} &\longrightarrow \text{spin-dependent effective hopping,} \\ \text{spin-dependent hopping} + \text{open transport channels} &\longrightarrow T_{\uparrow} \neq T_{\downarrow}, \\ T_{\uparrow} \neq T_{\downarrow} &\longrightarrow P_z \neq 0. \end{aligned} \quad (6.17)$$

This is the basic mechanism of CISS in the model studied here.[1]

The calculation also shows an important limitation. The physical carbon spin-orbit couplings are much smaller than the normal hopping parameters. For this reason, the predicted polarization is small. Leakage and a strong electric field increase the signal, but the resulting value is still much smaller than the large spin polarizations reported in several experiments. Therefore, this simple single-particle model gives a clear microscopic route to spin selectivity, but it does not fully explain the size of the experimental CISS effect. Contact effects, coupling to the environment, electron-electron interactions, or other many-body processes may also be important in real molecular junctions.[1, 6] The important result is that the effective Hamiltonian produces a finite spin-dependent transmission under the correct open-system conditions. Figures 2–4 show how the electric field, leakage and spin-flip processes change this signal. Together, these results connect the microscopic tight-binding description of helicene with the CISS effect.

7 Conclusion

This thesis studied how the helical structure of helicene can produce spin-dependent electron transport. The starting point was a microscopic tight-binding Hamiltonian containing the carbon orbitals s, p_x, p_y, p_z , atomic spin-orbit coupling, electric-field terms and Slater-Koster hopping. Ethene and benzene were used as planar reference systems. Their spectra reproduce the expected π -states and show that the p_z -orbitals are largely separated from the in-plane orbitals in a planar molecule.

The full Hamiltonian was reduced to an effective p_z -Hamiltonian with a Loewdin-like projection. For planar benzene, the first-order spin-dependent terms vanish and the remaining intrinsic spin-orbit coupling is very small. In helicene, the non-planar geometry allows mixed hopping between p_z and the in-plane orbitals. Together with atomic spin-orbit coupling, these virtual processes generate geometry-dependent spin-dependent hopping. The first-order terms vanish again in the planar limit $b \rightarrow 0$, which connects the helicene result to the benzene reference.

The numerical comparison between the full 208×208 helicene Hamiltonian and the effective 52×52 model shows that the reduced model describes the general p_z -like energy range, but it is not an exact copy of the full spectrum. The selected full-model states have p_z -weights between 0.481 and 0.910, and the mean absolute difference between the two ordered energy lists is 0.691 eV. These values confirm that the eliminated orbitals still contribute to the full states and that the ordered rows should not be interpreted as exact state assignments.

The transport calculation gives the direct connection to CISS. With the chosen contacts and physical carbon parameters, the polarization is almost zero without an electric field and leakage. A field of 25 V/nm adds Rashba-like terms, and the leakage channels further increase the signal. The largest value obtained in this calculation is

$$P_z = 3.52 \times 10^{-4} = 0.035\%. \quad (7.1)$$

The decomposition into spin-conserving and spin-flip processes shows that the zero-field signal is mainly spin conserving, while spin-flip processes become more important for the strong electric-field case.

The main result is that the energy spectrum alone does not produce CISS. A finite spin polarization requires the combination of helical geometry, spin-orbit coupling, and an open transport setup. The model gives a clear microscopic mechanism for spin selectivity, but the predicted polarization remains much smaller than many experimental values. This indicates that contact effects, environmental coupling, electron-electron interactions, or other many-body processes may be needed for a more complete description of the CISS effect.

Remaining eigenstates:

$$E_1 = E_2 = -39.37 \text{ eV}$$

$$\psi_1 = \begin{cases} C4 s \downarrow : 0.3549 - 0.0002i \\ C1 s \downarrow : 0.3549 - 0.0002i \\ C5 s \downarrow : 0.3549 - 0.0002i \\ C6 s \downarrow : 0.3549 - 0.0002i \\ C3 s \downarrow : 0.3549 - 0.0002i \\ C2 s \downarrow : 0.3549 - 0.0002i \end{cases} \quad \psi_2 = \begin{cases} C4 s \uparrow : 0.3549 \\ C1 s \uparrow : 0.3549 \\ C3 s \uparrow : 0.3549 \\ C5 s \uparrow : 0.3549 \\ C6 s \uparrow : 0.3549 \\ C2 s \uparrow : 0.3549 \end{cases}$$

$$E_3 = E_4 = -35.59 \text{ eV}$$

$$\psi_3 = \begin{cases} C2 s \downarrow : -0.2991 - 0.1667i \\ C5 s \downarrow : 0.2991 + 0.1667i \\ C6 s \downarrow : 0.2950 - 0.1738i \\ C3 s \downarrow : -0.2950 + 0.1738i \\ C1 s \downarrow : -0.0041 - 0.3406i \\ C4 s \downarrow : 0.0041 + 0.3406i \end{cases} \quad \psi_4 = \begin{cases} C6 s \uparrow : -0.1703 + 0.2971i \\ C3 s \uparrow : 0.1703 - 0.2971i \\ C2 s \uparrow : -0.1703 - 0.2971i \\ C5 s \uparrow : 0.1703 + 0.2971i \\ C1 s \uparrow : -0.3406 \\ C4 s \uparrow : 0.3406 \end{cases}$$

$$E_5 = E_6 = -35.59 \text{ eV}$$

$$\psi_5 = \begin{cases} C1 s \downarrow : 0.1799 + 0.2922i \\ C4 s \downarrow : -0.1799 - 0.2922i \\ C6 s \downarrow : 0.3411 - 0.0086i \\ C3 s \downarrow : -0.3411 + 0.0086i \\ C2 s \downarrow : -0.1613 + 0.3007i \\ C5 s \downarrow : 0.1613 - 0.3007i \end{cases} \quad \psi_6 = \begin{cases} C4 s \uparrow : 0.3431 \\ C1 s \uparrow : -0.3431 \\ C2 s \uparrow : -0.1715 + 0.2950i \\ C5 s \uparrow : 0.1715 - 0.2950i \\ C6 s \uparrow : -0.1715 - 0.2950i \\ C3 s \uparrow : 0.1715 + 0.2950i \end{cases}$$

$$E_7 = E_8 = -32.31 \text{ eV}$$

$$\psi_7 = \begin{cases} C4 p_x \downarrow : 0.1019 + 0.2977i \\ C1 p_x \downarrow : -0.1019 - 0.2977i \\ C5 p_y \downarrow : -0.2640 - 0.0779i \\ C2 p_y \downarrow : 0.2640 + 0.0779i \\ C6 p_y \downarrow : 0.1608 - 0.2234i \\ C3 p_y \downarrow : -0.1608 + 0.2234i \\ C1 s \downarrow : 0.2127 - 0.0728i \\ C4 s \downarrow : 0.2127 - 0.0728i \\ C3 s \downarrow : -0.1689 - 0.1463i \\ C6 s \downarrow : -0.1689 - 0.1463i \\ C5 s \downarrow : -0.0438 + 0.2191i \\ C2 s \downarrow : -0.0438 + 0.2191i \end{cases} \quad \psi_8 = \begin{cases} C1 p_x \uparrow : 0.3147i \\ C4 p_x \uparrow : -0.3147i \\ C2 p_y \uparrow : 0.2245 - 0.1592i \\ C5 p_y \uparrow : -0.2245 + 0.1592i \\ C6 p_y \uparrow : 0.2245 + 0.1592i \\ C3 p_y \uparrow : -0.2245 - 0.1592i \\ C1 s \uparrow : 0.2248 \\ C4 s \uparrow : 0.2248 \\ C3 s \uparrow : -0.1124 + 0.1931i \\ C6 s \uparrow : -0.1124 + 0.1931i \\ C5 s \uparrow : -0.1124 - 0.1931i \\ C2 s \uparrow : -0.1124 - 0.1931i \end{cases}$$

$$E_9 = E_{10} = -32.30 \text{ eV}$$

$$\psi_9 = \begin{cases} C1 p_x \uparrow : -0.3173i \\ C4 p_x \uparrow : 0.3173i \\ C6 p_y \uparrow : 0.2229 - 0.1604i \\ C3 p_y \uparrow : -0.2229 + 0.1604i \\ C2 p_y \uparrow : 0.2229 + 0.1604i \\ C5 p_y \uparrow : -0.2229 - 0.1604i \\ C5 s \uparrow : -0.1115 + 0.1947i \\ C2 s \uparrow : -0.1115 + 0.1947i \\ C3 s \uparrow : -0.1115 - 0.1947i \\ C6 s \uparrow : -0.1115 - 0.1947i \\ C1 s \uparrow : 0.2230 \\ C4 s \uparrow : 0.2230 \end{cases} \quad \psi_{10} = \begin{cases} C4 p_x \downarrow : 0.0347 + 0.3154i \\ C1 p_x \downarrow : -0.0347 - 0.3154i \\ C6 p_y \downarrow : -0.2391 - 0.1351i \\ C3 p_y \downarrow : 0.2391 + 0.1351i \\ C5 p_y \downarrow : 0.2040 - 0.1839i \\ C2 p_y \downarrow : -0.2040 + 0.1839i \\ C2 s \downarrow : 0.1321 + 0.1813i \\ C5 s \downarrow : 0.1321 + 0.1813i \\ C3 s \downarrow : 0.0895 - 0.2057i \\ C6 s \downarrow : 0.0895 - 0.2057i \\ C4 s \downarrow : -0.2217 + 0.0244i \\ C1 s \downarrow : -0.2217 + 0.0244i \end{cases}$$

$$E_{11} = E_{12} = -30.35 \text{ eV}$$

$$\psi_{11} = \begin{cases} C4 p_x \uparrow : -0.3420i \\ C1 p_x \uparrow : -0.3420i \\ C5 p_y \uparrow : 0.0001 + 0.2962i \\ C3 p_y \uparrow : 0.0001 - 0.2962i \\ C6 p_y \uparrow : 0.0001 - 0.2962i \\ C2 p_y \uparrow : 0.0001 + 0.2962i \\ C4 p_x \downarrow : 0.2116 + 0.0703i \\ C1 p_x \downarrow : 0.2116 + 0.0703i \end{cases} \quad \psi_{12} = \begin{cases} C1 p_x \downarrow : -0.3245 - 0.1078i \\ C4 p_x \downarrow : -0.3245 - 0.1078i \\ C2 p_y \downarrow : 0.2810 + 0.0934i \\ C3 p_y \downarrow : -0.2811 - 0.0933i \\ C6 p_y \downarrow : -0.2811 - 0.0933i \\ C5 p_y \downarrow : 0.2810 + 0.0934i \\ C4 p_x \uparrow : -0.2230i \\ C1 p_x \uparrow : -0.2230i \end{cases}$$

$$E_{13} = E_{14} = -29.12 \text{ eV}$$

$$\psi_{13} = \begin{cases} C1 p_y \downarrow : 0.3068 + 0.0102i \\ C4 p_y \downarrow : -0.3068 - 0.0102i \\ C2 p_x \downarrow : -0.2657 - 0.0088i \\ C6 p_x \downarrow : 0.2657 + 0.0088i \\ C5 p_x \downarrow : 0.2657 + 0.0088i \\ C3 p_x \downarrow : -0.2657 - 0.0088i \\ H6 s \downarrow : 0.2305 + 0.0076i \\ H2 s \downarrow : 0.2305 + 0.0076i \\ H5 s \downarrow : 0.2305 + 0.0076i \\ H3 s \downarrow : 0.2305 + 0.0076i \\ H1 s \downarrow : 0.2305 + 0.0076i \\ H4 s \downarrow : 0.2305 + 0.0076i \end{cases} \quad \psi_{14} = \begin{cases} C1 p_y \uparrow : 0.3070 \\ C4 p_y \uparrow : -0.3070 \\ C6 p_x \uparrow : 0.2659 + 0.0000i \\ C5 p_x \uparrow : 0.2659 - 0.0000i \\ C3 p_x \uparrow : -0.2659 - 0.0000i \\ C2 p_x \uparrow : -0.2659 + 0.0000i \\ H5 s \uparrow : 0.2306 - 0.0000i \\ H6 s \uparrow : 0.2306 + 0.0000i \\ H2 s \uparrow : 0.2306 - 0.0000i \\ H3 s \uparrow : 0.2306 + 0.0000i \\ H1 s \uparrow : 0.2306 \\ H4 s \uparrow : 0.2306 \end{cases}$$

$$E_{15} = E_{16} = -27.38 \text{ eV}$$

$$\psi_{15} = \begin{cases} C4 p_y \downarrow : 0.3105 - 0.1253i \\ C1 p_y \downarrow : 0.3105 - 0.1253i \\ C5 p_x \downarrow : -0.0518 + 0.2905i \\ C2 p_x \downarrow : -0.0518 + 0.2905i \\ C3 p_x \downarrow : 0.2389 + 0.1732i \\ C6 p_x \downarrow : 0.2389 + 0.1732i \\ H5 s \downarrow : -0.0291 + 0.2217i \\ H2 s \downarrow : 0.0291 - 0.2217i \\ H3 s \downarrow : -0.1748 - 0.1395i \\ H6 s \downarrow : 0.1748 + 0.1395i \\ H4 s \downarrow : -0.2039 + 0.0822i \\ H1 s \downarrow : 0.2039 - 0.0822i \end{cases} \quad \psi_{16} = \begin{cases} C1 p_y \uparrow : -0.3348 \\ C4 p_y \uparrow : -0.3348 \\ C3 p_x \uparrow : -0.1567 + 0.2500i \\ C6 p_x \uparrow : -0.1567 + 0.2500i \\ C5 p_x \uparrow : 0.1567 + 0.2500i \\ C2 p_x \uparrow : 0.1567 + 0.2500i \\ H3 s \uparrow : 0.1099 - 0.1948i \\ H6 s \uparrow : -0.1099 + 0.1948i \\ H5 s \uparrow : 0.1099 + 0.1948i \\ H2 s \uparrow : -0.1099 - 0.1948i \\ H1 s \uparrow : -0.2198 \\ H4 s \uparrow : 0.2198 \end{cases}$$

$$E_{17} = E_{18} = -27.38 \text{ eV}$$

$$\psi_{17} = \begin{cases} C4 p_y \downarrow : -0.3335 + 0.0787i \\ C1 p_y \downarrow : -0.3335 + 0.0787i \\ C3 p_x \downarrow : -0.1000 + 0.2747i \\ C6 p_x \downarrow : -0.1000 + 0.2747i \\ C2 p_x \downarrow : 0.2122 + 0.2011i \\ C5 p_x \downarrow : 0.2122 + 0.2011i \\ H1 s \downarrow : -0.2188 + 0.0516i \\ H4 s \downarrow : 0.2188 - 0.0516i \\ H6 s \downarrow : -0.0657 + 0.2110i \\ H3 s \downarrow : 0.0657 - 0.2110i \\ H2 s \downarrow : -0.1531 - 0.1594i \\ H5 s \downarrow : 0.1531 + 0.1594i \end{cases} \quad \psi_{18} = \begin{cases} C1 p_y \uparrow : 0.3426 \\ C4 p_y \uparrow : 0.3426 \\ C5 p_x \uparrow : -0.1603 + 0.2444i \\ C2 p_x \uparrow : -0.1603 + 0.2444i \\ C3 p_x \uparrow : 0.1603 + 0.2444i \\ C6 p_x \uparrow : 0.1603 + 0.2444i \\ H1 s \uparrow : 0.2248 \\ H4 s \uparrow : -0.2248 \\ H5 s \uparrow : -0.1124 + 0.1903i \\ H2 s \uparrow : 0.1124 - 0.1903i \\ H3 s \uparrow : -0.1124 - 0.1903i \\ H6 s \uparrow : 0.1124 + 0.1903i \end{cases}$$

$$E_{19} = E_{20} = -25.27 \text{ eV}$$

$$\psi_{19} = \begin{cases} H4 s \uparrow : -0.2831 \\ H1 s \uparrow : 0.2831 \\ H2 s \uparrow : -0.2831 + 0.0000i \\ H6 s \uparrow : -0.2831 - 0.0000i \\ H3 s \uparrow : 0.2831 + 0.0000i \\ H5 s \uparrow : 0.2831 - 0.0000i \\ C4 p_y \uparrow : 0.2336 \\ C1 p_y \uparrow : 0.2336 \\ C2 p_x \uparrow : 0.2023 + 0.0001i \\ C6 p_x \uparrow : -0.2023 + 0.0001i \\ C3 p_x \uparrow : -0.2023 + 0.0001i \\ C5 p_x \uparrow : 0.2023 + 0.0001i \end{cases} \quad \psi_{20} = \begin{cases} H1 s \downarrow : 0.2830 - 0.0059i \\ H4 s \downarrow : -0.2830 + 0.0059i \\ H6 s \downarrow : -0.2830 + 0.0059i \\ H2 s \downarrow : -0.2830 + 0.0059i \\ H5 s \downarrow : 0.2830 - 0.0059i \\ H3 s \downarrow : 0.2830 - 0.0059i \\ C1 p_y \downarrow : 0.2336 - 0.0048i \\ C4 p_y \downarrow : 0.2336 - 0.0048i \\ C6 p_x \downarrow : -0.2023 + 0.0040i \\ C5 p_x \downarrow : 0.2023 - 0.0043i \\ C3 p_x \downarrow : -0.2023 + 0.0040i \\ C2 p_x \downarrow : 0.2023 - 0.0043i \end{cases}$$

$$E_{21} = E_{22} = -24.09 \text{ eV}$$

$$\psi_{21} = \begin{cases} C4 p_y \downarrow : -0.2174 - 0.0830i \\ C1 p_y \downarrow : 0.2174 + 0.0830i \\ H5 s \downarrow : -0.0347 - 0.2173i \\ H2 s \downarrow : -0.0347 - 0.2173i \\ H3 s \downarrow : -0.1707 + 0.1388i \\ H6 s \downarrow : -0.1707 + 0.1388i \\ H4 s \downarrow : 0.2054 + 0.0785i \\ H1 s \downarrow : 0.2054 + 0.0785i \\ C2 p_x \downarrow : -0.0468 + 0.2118i \\ C5 p_x \downarrow : 0.0468 - 0.2118i \\ C3 p_x \downarrow : 0.1064 - 0.1890i \\ C6 p_x \downarrow : -0.1064 + 0.1890i \end{cases} \quad \psi_{22} = \begin{cases} C4 p_y \uparrow : -0.2327 \\ C1 p_y \uparrow : 0.2327 \\ H6 s \uparrow : -0.1099 - 0.1906i \\ H3 s \uparrow : -0.1099 - 0.1906i \\ H2 s \uparrow : -0.1099 + 0.1906i \\ H5 s \uparrow : -0.1099 + 0.1906i \\ H4 s \uparrow : 0.2199 \\ H1 s \uparrow : 0.2199 \\ C6 p_x \uparrow : -0.0319 - 0.2145i \\ C3 p_x \uparrow : 0.0319 + 0.2145i \\ C5 p_x \uparrow : -0.0319 + 0.2145i \\ C2 p_x \uparrow : 0.0319 - 0.2145i \end{cases}$$

$$E_{23} = E_{24} = -24.08 \text{ eV}$$

$$\psi_{23} = \begin{cases} C4 p_y \uparrow : 0.2361 \\ C1 p_y \uparrow : -0.2361 \\ H4 s \uparrow : -0.2231 \\ H1 s \uparrow : -0.2231 \\ H2 s \uparrow : 0.1116 + 0.1930i \\ H5 s \uparrow : 0.1116 + 0.1930i \\ H6 s \uparrow : 0.1116 - 0.1930i \\ H3 s \uparrow : 0.1116 - 0.1930i \\ C2 p_x \uparrow : -0.0323 - 0.2172i \\ C5 p_x \uparrow : 0.0323 + 0.2172i \\ C6 p_x \uparrow : 0.0323 - 0.2172i \\ C3 p_x \uparrow : -0.0323 + 0.2172i \end{cases} \quad \psi_{24} = \begin{cases} C4 p_y \downarrow : 0.2361 + 0.0047i \\ C1 p_y \downarrow : -0.2361 - 0.0047i \\ H4 s \downarrow : -0.2231 - 0.0044i \\ H1 s \downarrow : -0.2231 - 0.0044i \\ H3 s \downarrow : 0.1077 + 0.1952i \\ H6 s \downarrow : 0.1077 + 0.1952i \\ H5 s \downarrow : 0.1153 - 0.1908i \\ H2 s \downarrow : 0.1153 - 0.1908i \\ C3 p_x \downarrow : -0.0280 - 0.2178i \\ C6 p_x \downarrow : 0.0280 + 0.2178i \\ C5 p_x \downarrow : 0.0366 - 0.2166i \\ C2 p_x \downarrow : -0.0366 + 0.2166i \end{cases}$$

$$E_{31} = E_{32} = -8.49 \text{ eV}$$

$$\psi_{31} = \begin{cases} C1 p_x \uparrow : 0.2670i \\ C4 p_x \uparrow : 0.2670i \\ C2 p_y \uparrow : 0.2471 + 0.0352i \\ C5 p_y \uparrow : 0.2471 + 0.0352i \\ C6 p_y \uparrow : 0.2471 - 0.0352i \\ C3 p_y \uparrow : 0.2471 - 0.0352i \\ H4 s \uparrow : 0.2446 \\ H1 s \uparrow : -0.2446 \\ H3 s \uparrow : 0.1223 + 0.2115i \\ H6 s \uparrow : -0.1223 - 0.2115i \\ H2 s \uparrow : -0.1223 + 0.2115i \\ H5 s \uparrow : 0.1223 - 0.2115i \\ C2 p_x \uparrow : 0.0353 + 0.2060i \\ C5 p_x \uparrow : 0.0353 + 0.2060i \\ C6 p_x \uparrow : -0.0353 + 0.2060i \\ C3 p_x \uparrow : -0.0353 + 0.2060i \end{cases} \quad \psi_{32} = \begin{cases} C4 p_x \downarrow : 0.1955 + 0.1819i \\ C1 p_x \downarrow : 0.1955 + 0.1819i \\ C6 p_y \downarrow : -0.1941 + 0.1569i \\ C3 p_y \downarrow : -0.1941 + 0.1569i \\ C5 p_y \downarrow : -0.1425 + 0.2049i \\ C2 p_y \downarrow : -0.1425 + 0.2049i \\ H1 s \downarrow : 0.1666 - 0.1790i \\ H4 s \downarrow : -0.1666 + 0.1790i \\ H5 s \downarrow : -0.2381 - 0.0545i \\ H2 s \downarrow : 0.2381 + 0.0545i \\ H6 s \downarrow : -0.0715 - 0.2336i \\ H3 s \downarrow : 0.0715 + 0.2336i \\ C6 p_x \downarrow : 0.1748 + 0.1145i \\ C3 p_x \downarrow : 0.1748 + 0.1145i \\ C5 p_x \downarrow : 0.1267 + 0.1662i \\ C2 p_x \downarrow : 0.1267 + 0.1662i \end{cases}$$

$$E_{33} = E_{34} = -8.48 \text{ eV}$$

$$\psi_{33} = \begin{cases} C1 p_x \uparrow : 0.2674i \\ C4 p_x \uparrow : 0.2674i \\ C3 p_y \uparrow : -0.2467 - 0.0352i \\ C6 p_y \uparrow : -0.2467 - 0.0352i \\ C2 p_y \uparrow : -0.2467 + 0.0352i \\ C5 p_y \uparrow : -0.2467 + 0.0352i \\ H2 s \uparrow : 0.1221 + 0.2118i \\ H5 s \uparrow : -0.1221 - 0.2118i \\ H3 s \uparrow : -0.1221 + 0.2118i \\ H6 s \uparrow : 0.1221 - 0.2118i \\ H1 s \uparrow : 0.2442 \\ H4 s \uparrow : -0.2442 \\ C6 p_x \uparrow : 0.0352 + 0.2064i \\ C3 p_x \uparrow : 0.0352 + 0.2064i \\ C2 p_x \uparrow : -0.0352 + 0.2064i \\ C5 p_x \uparrow : -0.0352 + 0.2064i \end{cases} \quad \psi_{34} = \begin{cases} C4 p_x \downarrow : -0.2289 + 0.1382i \\ C1 p_x \downarrow : -0.2289 + 0.1382i \\ C2 p_y \downarrow : 0.0974 + 0.2294i \\ C5 p_y \downarrow : 0.0974 + 0.2294i \\ C3 p_y \downarrow : 0.1577 + 0.1930i \\ C6 p_y \downarrow : 0.1577 + 0.1930i \\ H6 s \downarrow : 0.1182 - 0.2140i \\ H3 s \downarrow : -0.1182 + 0.2140i \\ H5 s \downarrow : 0.2444 - 0.0050i \\ H2 s \downarrow : -0.2444 + 0.0050i \\ H1 s \downarrow : -0.1262 - 0.2090i \\ H4 s \downarrow : 0.1262 + 0.2090i \\ C5 p_x \downarrow : -0.1585 + 0.1368i \\ C2 p_x \downarrow : -0.1585 + 0.1368i \\ C3 p_x \downarrow : -0.1949 + 0.0766i \\ C6 p_x \downarrow : -0.1949 + 0.0766i \end{cases}$$

$$E_{39} = E_{40} = -5.66 \text{ eV}$$

$$\psi_{39} = \begin{cases} H1 s \uparrow : -0.3241 \\ H4 s \uparrow : -0.3241 \\ H6 s \uparrow : -0.3241 + 0.0000i \\ H3 s \uparrow : -0.3241 + 0.0000i \\ H5 s \uparrow : -0.3241 - 0.0000i \\ H2 s \uparrow : -0.3241 - 0.0000i \end{cases} \quad \psi_{40} = \begin{cases} H4 s \downarrow : 0.2488 - 0.2077i \\ H1 s \downarrow : 0.2488 - 0.2077i \\ H2 s \downarrow : 0.2488 - 0.2076i \\ H5 s \downarrow : 0.2488 - 0.2076i \\ H3 s \downarrow : 0.2488 - 0.2076i \\ H6 s \downarrow : 0.2488 - 0.2076i \end{cases}$$

$$E_{41} = E_{42} = -5.64 \text{ eV}$$

$$\psi_{41} = \begin{cases} C4 p_x \uparrow : -0.3967i \\ C1 p_x \uparrow : 0.3967i \\ C5 p_y \uparrow : 0.0218 - 0.3436i \\ C2 p_y \uparrow : -0.0218 + 0.3436i \\ C6 p_y \uparrow : -0.0218 - 0.3436i \\ C3 p_y \uparrow : 0.0218 + 0.3436i \\ C3 p_x \uparrow : 0.0378 - 0.1983i \\ C6 p_x \uparrow : -0.0378 + 0.1983i \\ C5 p_x \uparrow : -0.0378 - 0.1983i \\ C2 p_x \uparrow : 0.0378 + 0.1983i \end{cases} \quad \psi_{42} = \begin{cases} C4 p_x \downarrow : 0.3909 - 0.0672i \\ C1 p_x \downarrow : -0.3909 + 0.0672i \\ C5 p_y \downarrow : 0.3349 - 0.0797i \\ C2 p_y \downarrow : -0.3349 + 0.0797i \\ C3 p_y \downarrow : -0.3423 + 0.0367i \\ C6 p_y \downarrow : 0.3423 - 0.0367i \\ C6 p_x \downarrow : -0.1890 + 0.0708i \\ C3 p_x \downarrow : 0.1890 - 0.0708i \\ C2 p_x \downarrow : -0.2018 - 0.0036i \\ C5 p_x \downarrow : 0.2018 + 0.0036i \end{cases}$$

$$E_{43} = E_{44} = -5.55 \text{ eV}$$

$$\psi_{43} = \begin{cases} C4 p_y \downarrow : 0.2949 - 0.0878i \\ C1 p_y \downarrow : -0.2949 + 0.0878i \\ C3 p_x \downarrow : -0.2217 - 0.1513i \\ C6 p_x \downarrow : 0.2217 + 0.1513i \\ C2 p_x \downarrow : -0.1029 + 0.2479i \\ C5 p_x \downarrow : 0.1029 - 0.2479i \\ H4 s \downarrow : 0.2404 - 0.0716i \\ H1 s \downarrow : 0.2404 - 0.0716i \\ H6 s \downarrow : -0.1817 - 0.1708i \\ H3 s \downarrow : -0.1817 - 0.1708i \\ H2 s \downarrow : -0.0587 + 0.2424i \\ H5 s \downarrow : -0.0587 + 0.2424i \end{cases} \quad \psi_{44} = \begin{cases} C1 p_y \uparrow : -0.3077 \\ C4 p_y \uparrow : 0.3077 \\ C2 p_x \uparrow : -0.1693 - 0.2083i \\ C5 p_x \uparrow : 0.1693 + 0.2083i \\ C6 p_x \uparrow : 0.1693 - 0.2083i \\ C3 p_x \uparrow : -0.1693 + 0.2083i \\ H4 s \uparrow : 0.2508 \\ H1 s \uparrow : 0.2508 \\ H2 s \uparrow : -0.1254 - 0.2155i \\ H5 s \uparrow : -0.1254 - 0.2155i \\ H6 s \uparrow : -0.1254 + 0.2155i \\ H3 s \uparrow : -0.1254 + 0.2155i \end{cases}$$

$$E_{45} = E_{46} = -5.54 \text{ eV}$$

$$\psi_{45} = \begin{cases} C4 p_y \downarrow : 0.1020 - 0.2876i \\ C1 p_y \downarrow : -0.1020 + 0.2876i \\ C5 p_x \downarrow : 0.2540 - 0.0882i \\ C2 p_x \downarrow : -0.2540 + 0.0882i \\ C3 p_x \downarrow : 0.1417 + 0.2284i \\ C6 p_x \downarrow : -0.1417 - 0.2284i \\ H5 s \downarrow : -0.2465 + 0.0447i \\ H2 s \downarrow : -0.2465 + 0.0447i \\ H3 s \downarrow : 0.1632 + 0.1900i \\ H6 s \downarrow : 0.1632 + 0.1900i \\ H4 s \downarrow : 0.0832 - 0.2346i \\ H1 s \downarrow : 0.0832 - 0.2346i \end{cases} \quad \psi_{46} = \begin{cases} C1 p_y \uparrow : 0.3052 \\ C4 p_y \uparrow : -0.3052 \\ C6 p_x \uparrow : -0.1680 - 0.2099i \\ C3 p_x \uparrow : 0.1680 + 0.2099i \\ C2 p_x \uparrow : 0.1680 - 0.2099i \\ C5 p_x \uparrow : -0.1680 + 0.2099i \\ H6 s \uparrow : 0.1245 + 0.2173i \\ H3 s \uparrow : 0.1245 + 0.2173i \\ H2 s \uparrow : 0.1245 - 0.2173i \\ H5 s \uparrow : 0.1245 - 0.2173i \\ H4 s \uparrow : -0.2490 \\ H1 s \uparrow : -0.2490 \end{cases}$$

$$E_{49} = E_{50} = -3.37 \text{ eV}$$

$$\psi_{49} = \begin{cases} C4 p_y \uparrow : -0.2868 \\ C1 p_y \uparrow : -0.2868 \\ H4 s \uparrow : -0.2817 \\ H1 s \uparrow : 0.2817 \\ H6 s \uparrow : -0.2817 - 0.0000i \\ H3 s \uparrow : 0.2817 + 0.0000i \\ H2 s \uparrow : -0.2817 + 0.0000i \\ H5 s \uparrow : 0.2817 - 0.0000i \\ C6 p_x \uparrow : 0.2483 - 0.0000i \\ C2 p_x \uparrow : -0.2483 - 0.0000i \\ C5 p_x \uparrow : -0.2483 - 0.0000i \\ C3 p_x \uparrow : 0.2483 - 0.0000i \end{cases} \quad \psi_{50} = \begin{cases} C1 p_y \downarrow : 0.2819 - 0.0526i \\ C4 p_y \downarrow : 0.2819 - 0.0526i \\ H1 s \downarrow : -0.2769 + 0.0517i \\ H4 s \downarrow : 0.2769 - 0.0517i \\ H6 s \downarrow : 0.2769 - 0.0517i \\ H5 s \downarrow : -0.2769 + 0.0517i \\ H3 s \downarrow : -0.2769 + 0.0517i \\ H2 s \downarrow : 0.2769 - 0.0517i \\ C2 p_x \downarrow : 0.2441 - 0.0456i \\ C3 p_x \downarrow : -0.2441 + 0.0455i \\ C6 p_x \downarrow : -0.2441 + 0.0455i \\ C5 p_x \downarrow : 0.2441 - 0.0456i \end{cases}$$

$$E_{51} = E_{52} = -2.24 \text{ eV}$$

$$\psi_{51} = \begin{cases} C4 p_x \uparrow : 0.2468i \\ C1 p_x \uparrow : 0.2468i \\ H5 s \uparrow : 0.1106 + 0.1926i \\ H2 s \uparrow : -0.1106 - 0.1926i \\ H3 s \uparrow : 0.1106 - 0.1926i \\ H6 s \uparrow : -0.1106 + 0.1926i \\ H1 s \uparrow : -0.2212 \\ H4 s \uparrow : 0.2212 \\ C3 p_y \uparrow : -0.1593 - 0.1499i \\ C6 p_y \uparrow : -0.1593 - 0.1499i \\ C5 p_y \uparrow : -0.1593 + 0.1499i \\ C2 p_y \uparrow : -0.1593 + 0.1499i \\ C5 s \uparrow : -0.1082 - 0.1885i \\ C2 s \uparrow : 0.1082 + 0.1885i \\ C3 s \uparrow : -0.1082 + 0.1885i \\ C6 s \uparrow : 0.1082 - 0.1885i \\ C1 s \uparrow : 0.2164 \\ C4 s \uparrow : -0.2164 \end{cases} \quad \psi_{52} = \begin{cases} C1 p_x \downarrow : 0.2154 - 0.1203i \\ C4 p_x \downarrow : 0.2154 - 0.1203i \\ H2 s \downarrow : -0.2221 - 0.0026i \\ H5 s \downarrow : 0.2221 + 0.0026i \\ H3 s \downarrow : -0.1142 + 0.1905i \\ H6 s \downarrow : 0.1142 - 0.1905i \\ H1 s \downarrow : -0.1078 - 0.1931i \\ H4 s \downarrow : 0.1078 + 0.1931i \\ C6 p_y \downarrow : -0.2086 - 0.0660i \\ C3 p_y \downarrow : -0.2086 - 0.0660i \\ C2 p_y \downarrow : 0.0532 - 0.2122i \\ C5 p_y \downarrow : 0.0532 - 0.2122i \\ C2 s \downarrow : 0.2173 + 0.0026i \\ C5 s \downarrow : -0.2173 - 0.0026i \\ C3 s \downarrow : 0.1118 - 0.1864i \\ C6 s \downarrow : -0.1118 + 0.1864i \\ C4 s \downarrow : -0.1055 - 0.1889i \\ C1 s \downarrow : 0.1055 + 0.1889i \end{cases}$$

$$E_{53} = E_{54} = -2.24 \text{ eV}$$

$$\psi_{53} = \begin{cases} C1 p_x \downarrow : -0.2438 + 0.0275i \\ C4 p_x \downarrow : -0.2438 + 0.0275i \\ H4 s \downarrow : 0.0250 + 0.2210i \\ H1 s \downarrow : -0.0250 - 0.2210i \\ H6 s \downarrow : -0.2028 - 0.0890i \\ H3 s \downarrow : 0.2028 + 0.0890i \\ H2 s \downarrow : 0.1778 - 0.1320i \\ H5 s \downarrow : -0.1778 + 0.1320i \\ C2 p_y \downarrow : -0.1661 - 0.1424i \\ C5 p_y \downarrow : -0.1661 - 0.1424i \\ C3 p_y \downarrow : 0.1302 - 0.1759i \\ C6 p_y \downarrow : 0.1302 - 0.1759i \\ C1 s \downarrow : 0.0244 + 0.2162i \\ C4 s \downarrow : -0.0244 - 0.2162i \\ C6 s \downarrow : 0.1984 + 0.0871i \\ C3 s \downarrow : -0.1984 - 0.0871i \\ C2 s \downarrow : -0.1740 + 0.1291i \\ C5 s \downarrow : 0.1740 - 0.1291i \end{cases} \quad \psi_{54} = \begin{cases} C4 p_x \uparrow : 0.2454i \\ C1 p_x \uparrow : 0.2454i \\ H1 s \uparrow : 0.2224 \\ H4 s \uparrow : -0.2224 \\ H3 s \uparrow : -0.1112 - 0.1915i \\ H6 s \uparrow : 0.1112 + 0.1915i \\ H5 s \uparrow : -0.1112 + 0.1915i \\ H2 s \uparrow : 0.1112 - 0.1915i \\ C2 p_y \uparrow : 0.1602 + 0.1491i \\ C5 p_y \uparrow : 0.1602 + 0.1491i \\ C3 p_y \uparrow : 0.1602 - 0.1491i \\ C6 p_y \uparrow : 0.1602 - 0.1491i \\ C1 s \uparrow : -0.2176 \\ C4 s \uparrow : 0.2176 \\ C3 s \uparrow : 0.1088 + 0.1874i \\ C6 s \uparrow : -0.1088 - 0.1874i \\ C2 s \uparrow : -0.1088 + 0.1874i \\ C5 s \uparrow : 0.1088 - 0.1874i \end{cases}$$

$$E_{55} = E_{56} = 0.43 \text{ eV}$$

$$\psi_{55} = \begin{cases} C1 s \downarrow : -0.3315 + 0.0394i \\ C4 s \downarrow : -0.3315 + 0.0394i \\ C6 s \downarrow : 0.1992 + 0.2621i \\ C3 s \downarrow : 0.1992 + 0.2621i \\ C5 s \downarrow : 0.1322 - 0.3015i \\ C2 s \downarrow : 0.1322 - 0.3015i \end{cases} \quad \psi_{56} = \begin{cases} C1 s \uparrow : 0.3338 \\ C4 s \uparrow : 0.3338 \\ C2 s \uparrow : -0.1669 - 0.2838i \\ C5 s \uparrow : -0.1669 - 0.2838i \\ C6 s \uparrow : -0.1669 + 0.2838i \\ C3 s \uparrow : -0.1669 + 0.2838i \end{cases}$$

$$E_{57} = E_{58} = 0.43 \text{ eV}$$

$$\psi_{57} = \begin{cases} C2 s \downarrow : -0.2715 + 0.1916i \\ C5 s \downarrow : -0.2715 + 0.1916i \\ C3 s \downarrow : 0.3039 + 0.1345i \\ C6 s \downarrow : 0.3039 + 0.1345i \\ C1 s \downarrow : -0.0324 - 0.3261i \\ C4 s \downarrow : -0.0324 - 0.3261i \end{cases} \quad \psi_{58} = \begin{cases} C6 s \uparrow : -0.1638 - 0.2891i \\ C3 s \uparrow : -0.1638 - 0.2891i \\ C2 s \uparrow : -0.1638 + 0.2891i \\ C5 s \uparrow : -0.1638 + 0.2891i \\ C1 s \uparrow : 0.3277 \\ C4 s \uparrow : 0.3277 \end{cases}$$

$$E_{59} = E_{60} = 3.58 \text{ eV}$$

$$\psi_{59} = \begin{cases} C4\ s\ \uparrow : -0.3601 \\ C1\ s\ \uparrow : 0.3601 \\ C3\ s\ \uparrow : 0.3601 \\ C5\ s\ \uparrow : 0.3601 \\ C2\ s\ \uparrow : -0.3601 \\ C6\ s\ \uparrow : -0.3601 \end{cases}$$

$$\psi_{60} = \begin{cases} C4\ s\ \downarrow : 0.3601 + 0.0006i \\ C1\ s\ \downarrow : -0.3601 - 0.0006i \\ C5\ s\ \downarrow : -0.3601 - 0.0006i \\ C3\ s\ \downarrow : -0.3601 - 0.0006i \\ C6\ s\ \downarrow : 0.3601 + 0.0006i \\ C2\ s\ \downarrow : 0.3601 + 0.0006i \end{cases}$$

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