



CHEM 548: Advanced Electronic Structure

Project #3 Report

Course Instructor

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1 Abstract

This report presents a discussion on the band structure of Polyaromatic Hydrocarbons, Polyacetylene, and Single Wall Carbon Nanotubes using the Extended Huckel model. It also discusses using the Su-Schrieffer-Heeger model to calculate the effect of bond length changes to σ and π energies for Benzene.

2 Questions

1. Huckel for molecules: Write a general Hückel MO program applicable to the π electronic structures of polycyclic aromatic hydrocarbon (PAH) molecules. Use “jacobi.f” subprogram available in the instructor’s directory (see below) for diagonalization of symmetric matrices. Interpret the photoelectron spectra of PAH’s [Boschi, Clar, and Schmidt, J. Chem. Phys. 60, 4406 (1974)] with this program.
2. Huckel 1D band structure: Write a general one-dimensional Hückel band structure program and apply it to π bands of polyacetylene and single-wall carbon nanotubes (SWNT). Plot energy bands. Use “hhbs.f” available in the instructor’s directory for diagonalization of complex, Hermitian matrices.
3. Hückel 2D band structure: Write a general two-dimensional Hückel band calculation program and apply it to π bands of graphene. Plot energy bands. The pioneering studies on graphene led to Nobel Prize in Physics in 2010 (Geim and Novoselov).
4. SSH and Jahn-Teller theorem: Modify the Hückel program for PAH’s in Subproject 1 to include the effect of bond length variations on both σ and π energies according to the Su-Schrieffer-Heeger model. Apply this program to benzene and benzene cation and plot their energies (the sum of σ and π energies) as a function of symmetry breaking geometry changes. Discuss the result in relation to the Jahn-Teller theorem.
5. SSH and Peierls theorem: Modify the Hückel program for one-dimensional solids in Subproject 2 to include the effect of bond length variations on the energy bands and total energy according to the SSH model. Apply this to polyacetylene and plot the energy with respect to the bond length alternation. Discuss the result in relation to the Peierls theorem.

3 Huckel Molecular Orbital Theory

Huckel Molecular Orbital theory is an approximation used to calculate molecular orbitals for π electrons in molecules with delocalised π electrons. It operates in π electron basis, and diagonalises the hamiltonian formed by interactions of neighbouring π orbitals.

The basics of creating molecular orbitals are representing them as a Linear Combination of Atomic Orbitals. In the case of Huckel Molecular Orbital Theory (or HMO theory), the atomic orbitals are the p_z orbitals on carbon atoms with conjugated π bonds.

For any molecule with n interacting carbons, that is, n interacting atomic orbitals χ_i , a molecular orbital can be represented by:

$$\psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + \cdots + c_n\chi_n \quad (1)$$

The coefficients of the atomic orbitals act as weights and pertain to how much "mixing" is happening for that atomic orbital.

Some salient features of the LCAO-MO mixing are[1]:

- (a) Mixing or quantum mechanical interaction of n atomic p orbitals (the χ 's) gives $n\pi$ molecular orbitals, some of higher energy (antibonding), some of lower energy (bonding), and sometimes some of the same energy (nonbonding) compared to the atomic orbitals mixed.
- (b) Orbitals in general and molecular orbitals specifically can accommodate at most two electrons per orbital. The lowest energy orbitals are preferentially populated.
- (c) The π energy of the system is the sum of the energies of all the π electrons. The energy of an electron is that of the orbital it occupies.
- (d) Each molecular orbital has its own LCAO form of the type

$$\psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + \cdots + c_n\chi_n,$$

where the c 's indicate the extent to which each atomic orbital is weighted in the MO.

- (e) The π -electron density contributed by an electron to a given atom is given by the square of the coefficient of that atom in the MO containing the electron.
- (f) The total π -electron density at a given atom is the sum of the π -electron density contributions, as outlined in (e), due to all electrons.
- (g) Since the sum of the squares of the coefficients in any particular MO gives the total electron density for one electron in that MO and since this total must be one electron, the sum of squares of coefficients of a MO should equal unity. Such an orbital is said to be normalized.

Given this ansatz molecular orbital, we can find the coefficients of the atomic orbitals by solving the secular equation:

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (2)$$

where \mathbf{H} is the Hamiltonian matrix, \mathbf{S} is the overlap matrix, E is the energy of the molecular orbital, and \mathbf{c} is the vector of coefficients.

The matrix elements of the Hamiltonian and overlap matrices are given by:

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int_{\mathbb{R}^3} \phi_i^* \phi_j dV \quad (3)$$

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \int_{\mathbb{R}^3} \phi_i^* \hat{H} \phi_j dV \quad (4)$$

where ϕ_i and ϕ_j are the atomic orbitals, and \hat{H} is the Hamiltonian operator.

Since we want the energy to be minimum with respect to the coefficients, we can use the Rayleigh-Ritz variational principle. We obtain a set of n simultaneous equations for the coefficients c_i and the energy E by differentiating the secular equation with respect to c_i and setting the result equal to zero. This gives us a set of n equations in n unknowns, which can be solved to obtain the coefficients and the energy.

$$\sum_{j=1}^n c_j (H_{ij} - E S_{ij}) = 0 \quad (i = 1, \dots, n) \quad (5)$$

When $i \neq j$, S_{ij} and H_{ij} are called the overlap and resonance (or exchange) integrals, respectively, while H_{ii} is called the Coulomb integral.

The huckel approximation modifies the hamiltonian and overlap matrices in the following way:

$$H_{ij} = \begin{cases} \alpha, & i = j; \\ \beta, & i, j \text{ adjacent}; \\ 0, & \text{otherwise.} \end{cases} \quad (**) \quad (6)$$

and the overlap matrix becomes the identity matrix as overlap between orbitals is considered to be zero.

For example, the matrix for ethylene, which has two carbon atoms, can be represented as:

$$\mathbf{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \quad (7)$$

Diagonalisation of this matrix gives us 2 eigenvalues:

$$E_1 = \alpha + \beta \quad (8)$$

$$E_2 = \alpha - \beta \quad (9)$$

These represent the energies of the bonding and antibonding orbitals, respectively. The coefficients of the atomic orbitals in the molecular orbitals can be obtained by substituting these eigenvalues back into the secular equation.

One thing of note here is that beta is a negative quantity, which means that the antibonding orbital has a higher energy than the bonding orbital. This is consistent with the fact that antibonding orbitals are less stable than bonding orbitals. Since 2 electrons are present in ethylene, they both occupy the bonding orbital, which leads to a total energy of:

$$E = 2 \cdot E_1 + 0 \cdot E_2 = 2(\alpha + \beta) + 0(\alpha - \beta) = 2\alpha + 2\beta \quad (10)$$

Similarly, for benzene, which has 6 carbon atoms, the hamiltonian matrix can be represented as:

$$\mathbf{H} = \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{bmatrix} \quad (11)$$

Diagonalisation of this matrix gives us 4 distinct eigenvalues:

$$E_1 = \alpha + 2\beta \quad (12)$$

$$E_2 = \alpha + \beta \quad (13)$$

$$E_3 = \alpha - \beta \quad (14)$$

$$E_4 = \alpha - 2\beta \quad (15)$$

E_2 and E_3 are doubly degenerate, which is due to the symmetry of the benzene molecule. The electrons occupy the 3 lowest energy orbitals, leading to a total energy of:

$$E = 6\alpha + 8\beta \quad (16)$$

If we calculate the energy of 3 ethylene molecules, we get:

$$E = 3(2\alpha + 2\beta) = 6\alpha + 6\beta \quad (17)$$

Since beta is negative, the energy of benzene is lower than that of 3 ethylene molecules by a factor of 2β . This is called resonance energy, and it is a measure of the stability of the molecule due to the delocalisation of electrons.

Using this approach we can confirm the aromatic and antiaromatic nature of molecules. For example, cyclobutadiene has 4 pi electrons and is antiaromatic, which can be shown through the huckel method.

The huckel method was implemented in python for benzene, naphthalene, anthracene, and pyrene. The values of alpha and beta were used as: $\alpha = 0, \beta = -1$ and $\alpha = 5.937, \beta = -2.944$.

In this approach α sets the zero energy and β determines the spread of the energies and is only required to be negative. The second set of alpha and beta values were calculated using the molecular orbital energies of benzene given in the project assignment. The results of the calculation are shown in Tables 1 and 2.

Table 1: π Orbital Energies: Benzene and Naphthalene

Molecule	$\alpha = 0, \beta = -1$	$\alpha = 5.937, \beta = -2.944$
Benzene	-2.0000	0.0490
	-1.0000	2.9930
	-1.0000	2.9930
	+1.0000	8.8810
	+1.0000	8.8810
	+2.0000	11.8250
Naphthalene	-2.3028	-0.8424
	-1.6180	1.1735
	-1.3028	2.1016
	-1.0000	2.9930
	-0.6180	4.1175
	+0.6180	7.7565
	+1.0000	8.8810
	+1.3028	9.7724
	+1.6180	10.7005
	+2.3028	12.7164

Table 2: π Orbital Energies: Anthracene and Pyrene

Molecule	$\alpha = 0, \beta = -1$	$\alpha = 5.937, \beta = -2.944$
Anthracene	-2.4142	-1.1704
	-2.0000	0.0490
	-1.4142	1.7736
	-1.4142	1.7736
	-1.0000	2.9930
	-0.4142	4.7176
	+0.4142	7.1564
	+1.0000	8.8810
	+1.0000	8.8810
	+1.4142	10.1004
	+1.4142	10.1004
	+2.0000	11.8250
	+2.4142	13.0444
Pyrene	-2.5321	-1.5175
	-2.0000	0.0490
	-1.8019	0.6321
	-1.3473	1.9706
	-1.2470	2.2660
	-1.0000	2.9930
	-0.8794	3.3481
	-0.4450	4.6268
	+0.4450	7.2472
	+0.8794	8.5260
	+1.0000	8.8810
	+1.2470	9.6081
	+1.3473	9.9034
	+1.8019	11.2420
	+2.0000	11.8250
	+2.5321	13.3915

4 Huckel 1D Band Structure

4.1 Structure and Unit Cell Definition

Trans-polyacetylene consists of a 1D periodic chain of carbon atoms with alternating single and double bonds. Due to this bond-length alternation, the smallest unit cell contains two carbon atoms, which we label as $L = 0$ and $L = 1$:

- Each unit cell is indexed by an integer n .
- Within each cell, atom $L = 0$ precedes the single bond; atom $L = 1$ precedes the double bond.

We denote localized atomic orbitals by $|n, L\rangle$ with $L \in \{0, 1\}$ and $n \in \mathbb{Z}$. The hopping integrals are:

$$\beta_1 = -0.9 \quad (\text{intra-cell hopping}), \quad \beta_2 = -1.1 \quad (\text{inter-cell hopping})$$

4.2 Real-Space Hamiltonian

The second-quantized tight-binding Hamiltonian is:

$$\hat{H} = \sum_n \left(\beta_1 c_{n,0}^\dagger c_{n,1} + \beta_2 c_{n+1,0}^\dagger c_{n,1} + \text{h.c.} \right)$$

4.3 Bloch's Theorem and Wavefunctions

By Bloch's theorem, the eigenstates can be written as:

$$|\psi_k\rangle = \sum_n e^{ikna} [\phi_0(k) |n, 0\rangle + \phi_1(k) |n, 1\rangle]$$

Applying $\hat{H} |\psi_k\rangle$ yields a 2×2 matrix eigenvalue problem in the basis $\{|L = 0\rangle, |L = 1\rangle\}$.

4.4 k-Dependent Hückel Hamiltonian

The effective Bloch Hamiltonian becomes:

$$H(k) = \begin{pmatrix} 0 & \beta_1 + \beta_2 e^{-ika} \\ \beta_1 + \beta_2 e^{ika} & 0 \end{pmatrix}$$

Substituting $\beta_1 = -0.9$, $\beta_2 = -1.1$, we obtain:

$$H(k) = \begin{pmatrix} 0 & -0.9 - 1.1e^{-ika} \\ -0.9 - 1.1e^{ika} & 0 \end{pmatrix}$$

4.5 Eigenvalues: Band Dispersion

The energy bands are given by the eigenvalues of $H(k)$:

$$\begin{aligned} E(k) &= \pm |\beta_1 + \beta_2 e^{ika}| \\ &= \pm \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(ka)} \\ &= \pm \sqrt{0.81 + 1.21 + 2 \cdot (0.9)(1.1) \cos(ka)} \\ &= \pm \sqrt{2.02 + 1.98 \cos(ka)} \end{aligned}$$

4.6 Band Gap

At the Brillouin zone edge $k = \pi/a$:

$$E\left(\frac{\pi}{a}\right) = \pm \sqrt{2.02 - 1.98} = \pm \sqrt{0.04} = \pm 0.2 \text{ eV} \Rightarrow \Delta E_{\text{gap}} = 0.4 \text{ eV} \quad (18)$$

This band gap is consistent with the graph shown in Figure 1.

4.7 Trans-polyacetylene

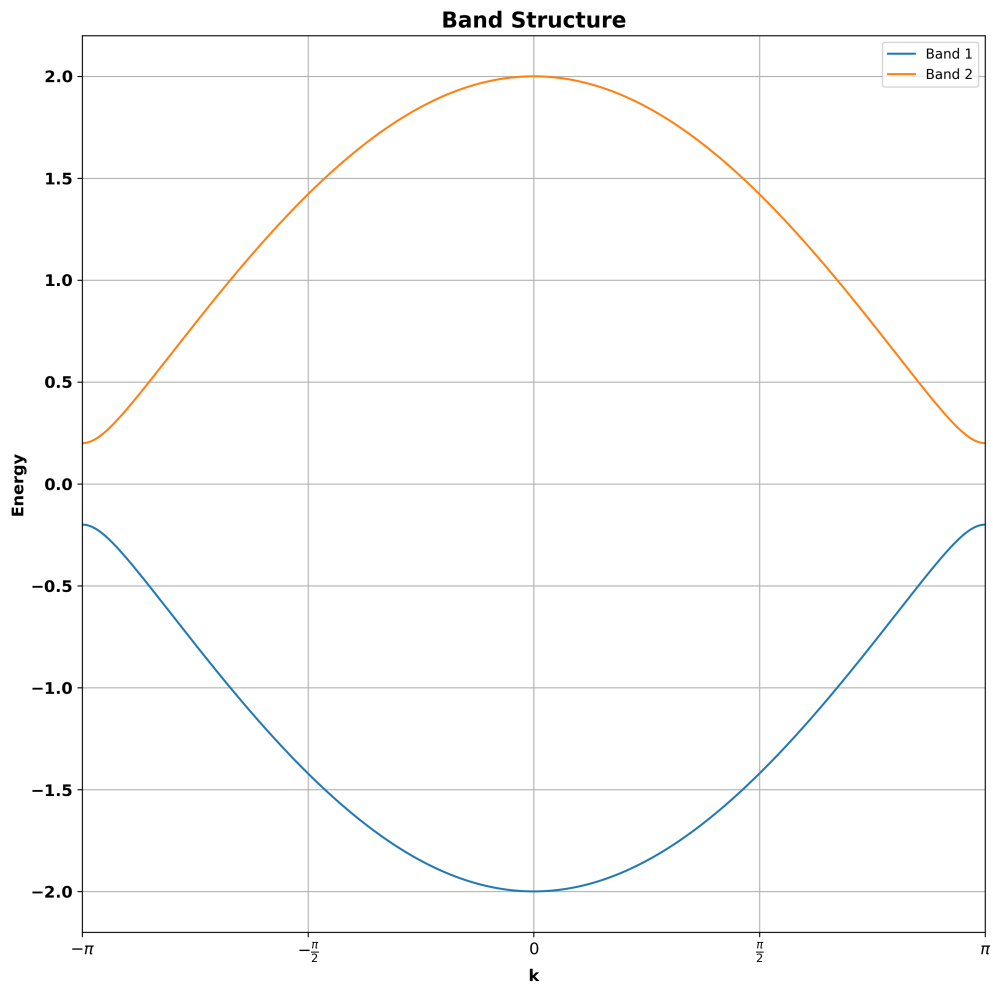


Figure 1: Trans-polyacetylene with alternating short and long bonds.

For the case where the bonds are equidistant, the band gap is zero, and the system becomes metallic.

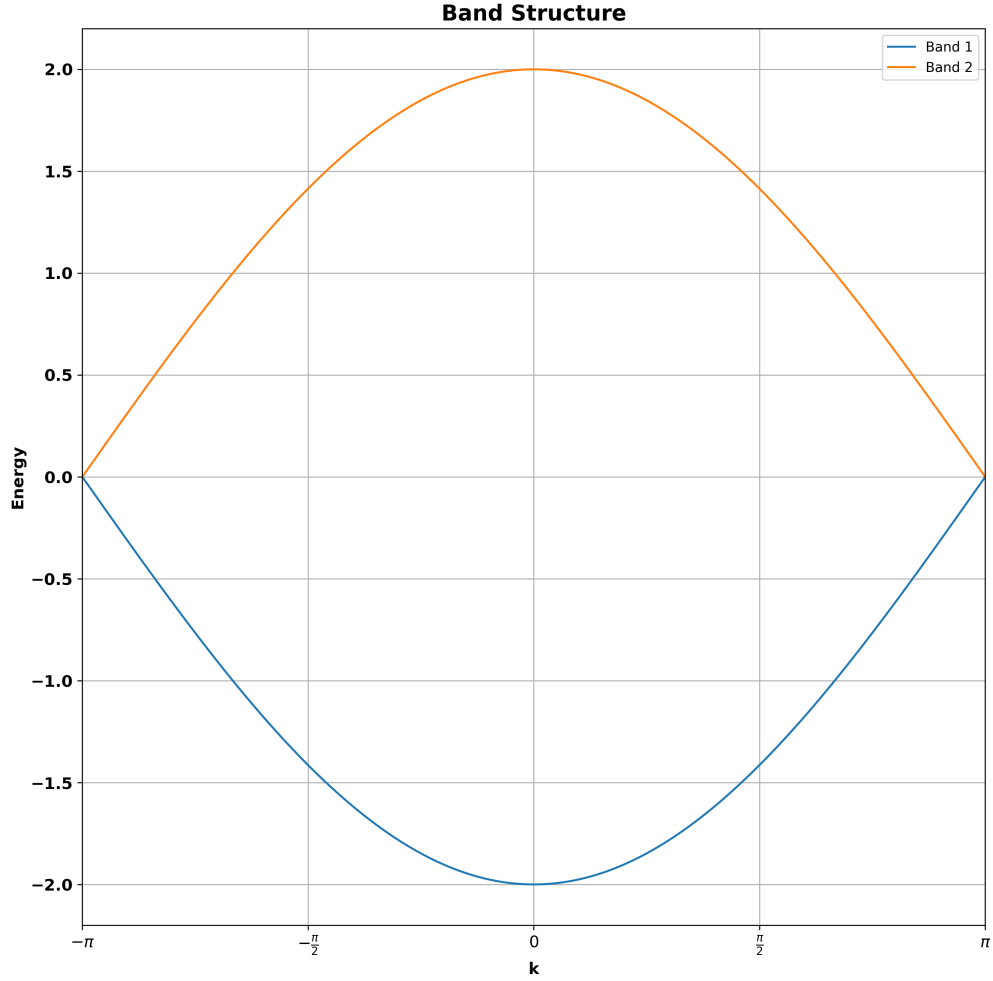
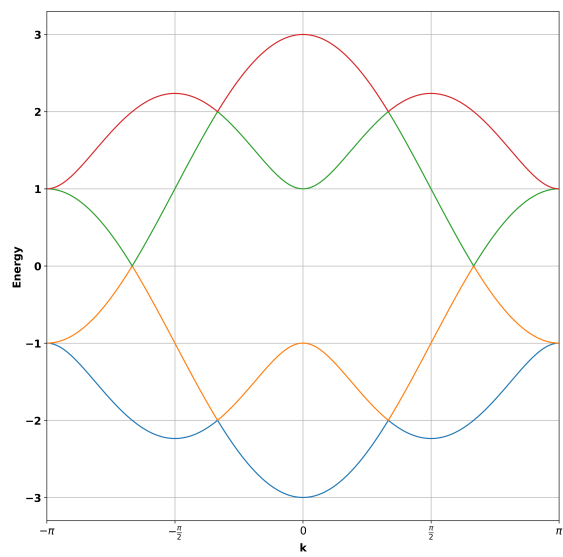


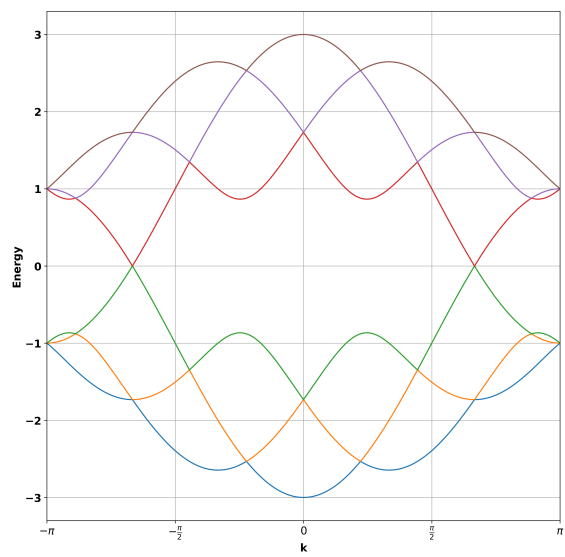
Figure 2: Trans-polyacetylene with metallic nature and equidistant bonds.

4.8 Single Wall Nanotube

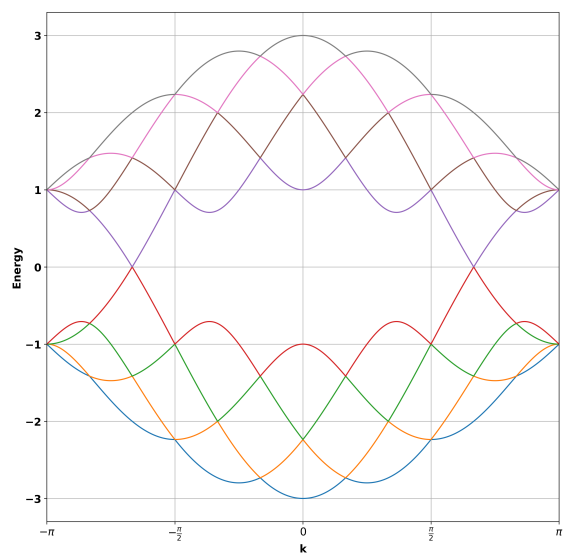
Similar concept can be applied to get the band structure of single wall carbon nanotubes. The program was implemented in python and the band structure was calculated for single wall carbon nanotubes with 4, 6, 8, and 10 carbons.



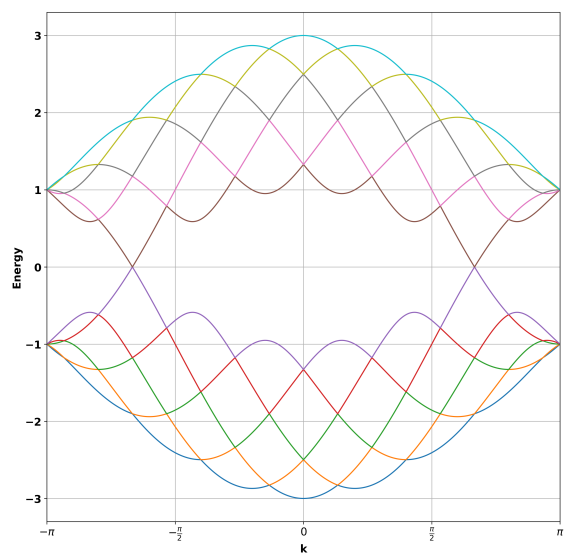
(a)



(b)



(c)



(d)

Figure 3: Circumference of SWNT with a) 4 carbons b) 6 carbons c) 8 carbons d) 10 carbons.

5 Huckel 2D Band Structure

The 2D band structure of graphene can be calculated by considering the graphene sheet as a 2D periodic lattice of carbon atoms. The unit cell contains two carbon atoms, but we have 2 K grids here. The image displays the pointwise degeneracy of the valence and conduction bands.

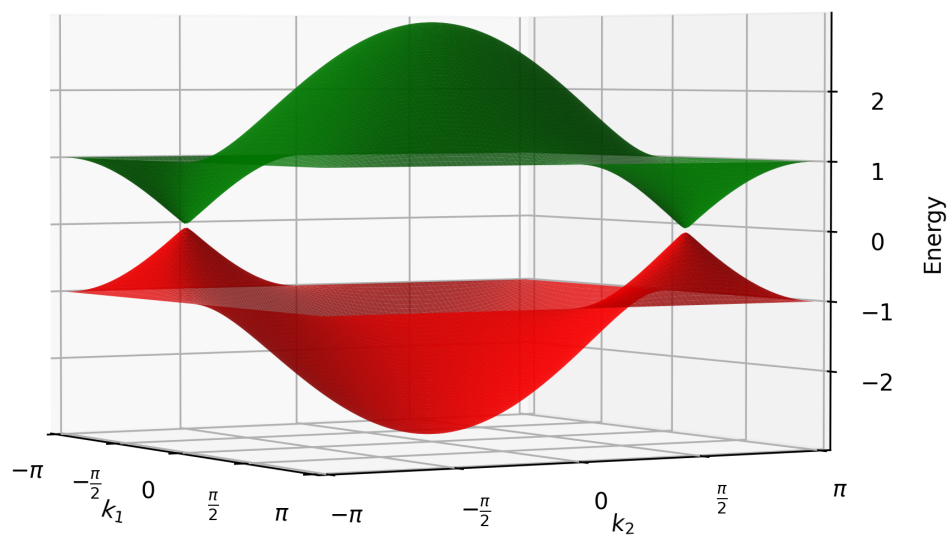


Figure 4: Graphene Energy Bands

6 Su-Schrieffer-Heeger Model and Jahn-Teller Theorem

The Su-Schrieffer-Heeger (SSH) model is a one-dimensional model that describes the electronic properties of polyacetylene and other conjugated polymers. It accounts for the effect of bond length alternation on the electronic structure.

The pi energies of benzene and benzene cation were calculated using the SSH model.

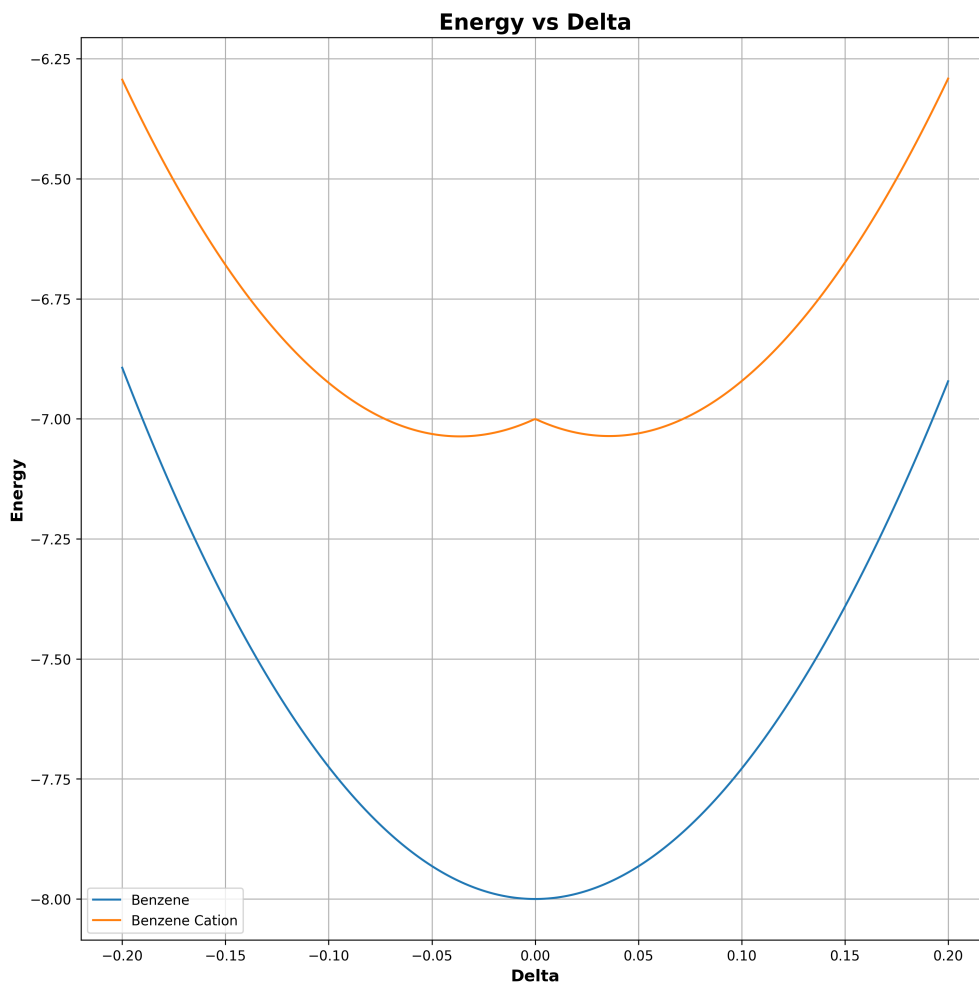


Figure 5: Energies of benzene and benzene cation as a function of symmetry breaking geometry distortions.

7 Su-Schrieffer-Heeger Model and Peierls theorem

The π and $\pi + \sigma$ energies of polyacetylene were calculated using the SSH model. The total energy and π electron energy were plotted as a function of bond length alternation.

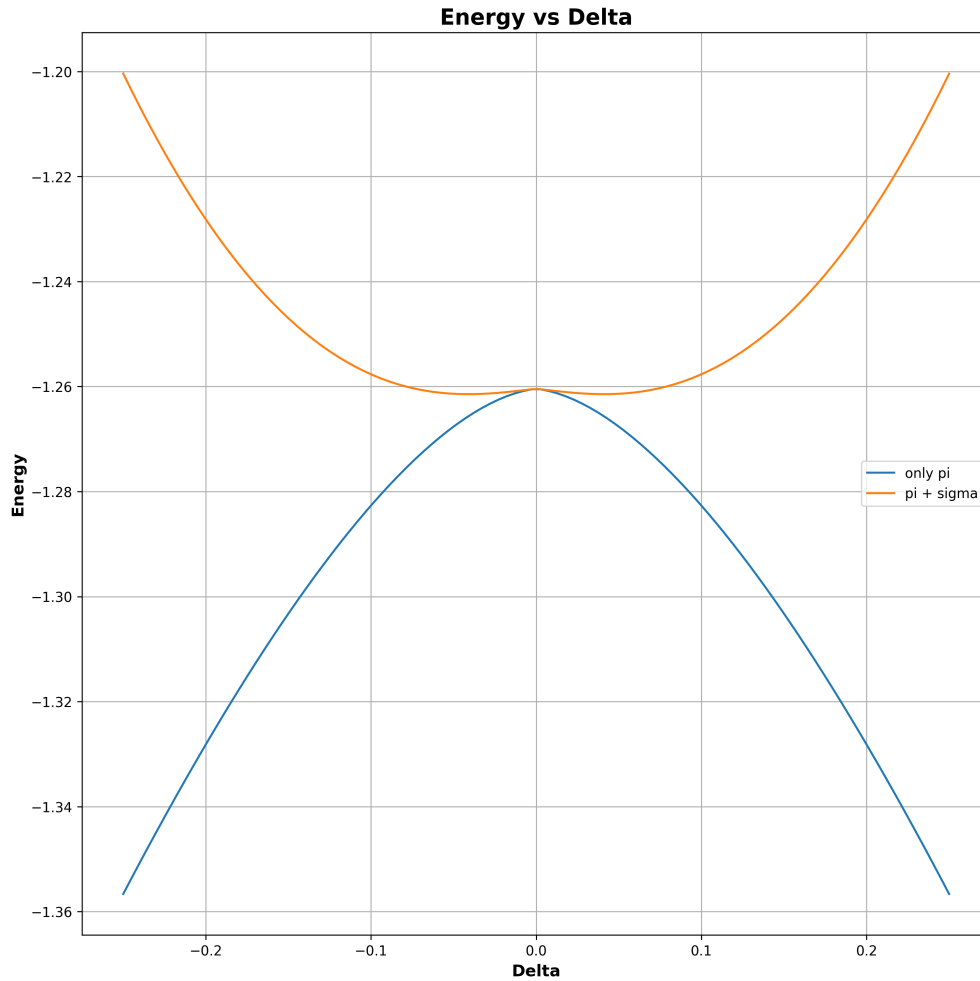


Figure 6: Total energy (green) and π electron energy (red) of polyacetylene as a function of bond length alternation

References

- [1] H. Zimmerman, Quantum mechanics for organic chemists, Elsevier, 2012.