Quantum Transport in Nanoporous Graphene

Bachelor defense

Christoffer Vendelbo Sørensen (s163965)

June 25, 2019

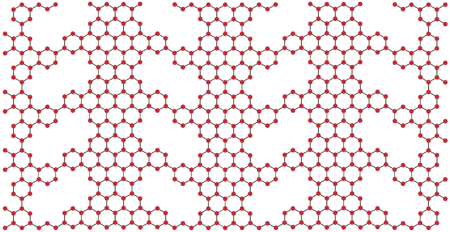
Outline

Project aim

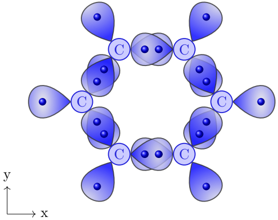
"Development of tight-binding routines in Python in order to understand electron transport in novel nanoporous graphene devices (NPGs)"

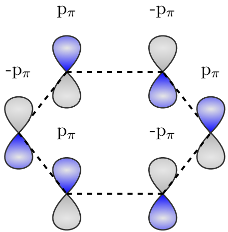
Nanoporous graphene

- Planar graphene sheets
- Periodically removed atoms
- Ribbons and bridges
- Ballistic electron movement
- Potential for controlling currents on nanoscale



- How are the electric orbitals structured?
- σ- and π-systems
- 1 p_z-electron per site
- "Tightly bound" hops between sites





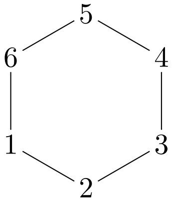
TB approximation

- What is Tight Binding?
- Electrons tightly bound to sites
- Hops with potential
- Average electron energy on site
- The Hamiltonian is a hop matrix

$$V_{pp\pi} = \langle \phi_\pi(m) | \hat{\mathbf{H}} | \phi_\pi(n) \rangle$$
$$\epsilon_0 = \langle \phi_\pi(i) | \hat{\mathbf{H}} | \phi_\pi(i) \rangle$$

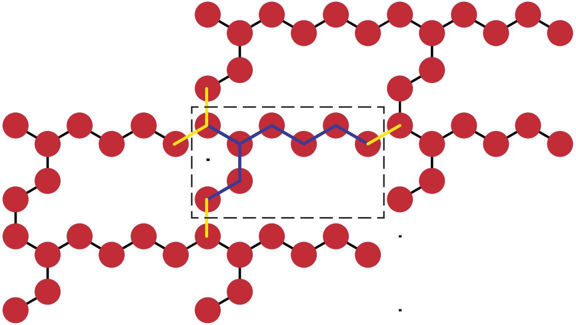
Hamiltonian for benzene

$$\mathbf{H} = V_{pp\pi} \begin{array}{cc} & \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} & \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \end{array}$$



Creating the first Hamiltonian

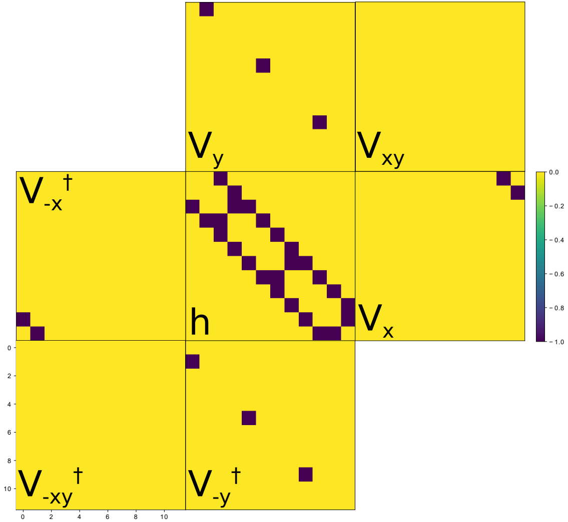
- How do obtain the Hamiltonian
- Atom coordinates
- Interatomic distances
- Find nearest neighbours
- Fill out Hamiltonian
- Subtract diagonal



```python
h = np.zeros((xyz.shape[0], xyz.shape[0]))  # Empty matrix
for i in range(xyz.shape[0]):  # Take an atomic coordinate
    for j in range(xyz.shape[0]):  # Take another atomic coordinate
        h[i, j] = LA.norm(np.subtract(xyz[i], xyz[j]))  # Measure distances
h = np.where(h < 1.6, Vppi, 0)  # Replace distances under 1.6 angstrom with Vppi
h = np.subtract(h, Vppi * np.identity(xyz.shape[0]))  # Remove the diagonal
```

Hopping matrices

- What is hopping matrices and how do we get them?
- Shift by lattice vector
- Resulting matrices: $\mathbf{h_0}, \mathbf{V}, \mathbf{V}^\dagger$



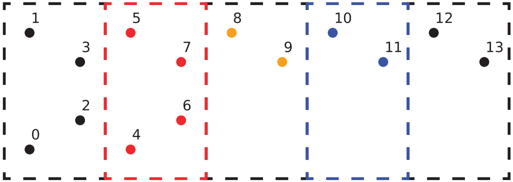
Full Hamiltonian and first band plots

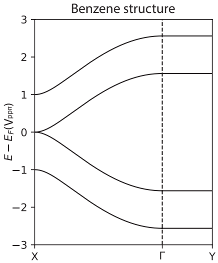
$$\mathbf{H}(k_x, k_y)\boldsymbol{\phi}_k = \boldsymbol{\epsilon}_n(k_x, k_y)\boldsymbol{\phi}_k$$

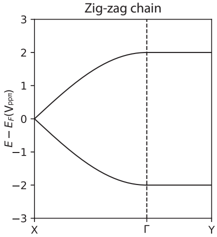
$$\begin{aligned}\mathbf{H}(k_x, k_y) = \mathbf{h}_0 + (&\mathbf{V}_x e^{-ik_x} + \mathbf{V}_x^\dagger e^{ik_x} + \mathbf{V}_y e^{-ik_y} + \mathbf{V}_y^\dagger e^{ik_y} \\ &+ \mathbf{V}_{xy} e^{-ik_x} e^{-ik_y} + \mathbf{V}_{xy}^\dagger e^{ik_x} e^{ik_y})\end{aligned}$$

```
        Ham = Ham + (V1 * np.exp(-1.0j * x)  # Onsite hops and hops in x
                    + np.transpose(V1) * np.exp(1.0j * x)  # Hops in -x
                    + V2 * np.exp(-1.0j * y)  # Hops in y
                    + np.transpose(V2) * np.exp(1.0j * y)  # Hops in -y
                    + V3 * np.exp(-1.0j * x) * np.exp(-1.0j * y)  # Hops in both x and y
                    + np.transpose(V3) * np.exp(1.0j * x) * np.exp(1.0j * y)) # Hops in both -x and -y
        e = LA.eigh(Ham)[0]  # Eigen energies from the Hamiltonian
        v = LA.eigh(Ham)[1]  # Eigen vectors from the Hamiltonian
```

Full Hamiltonian and first band plots







$$\begin{aligned}
\text{X:}\quad \mathbf{H}_X &= \mathbf{h}_0 + (\mathbf{V}_x e^{ik_x} + \mathbf{V}_x^\dagger e^{-ik_x} + \mathbf{V}_y + \mathbf{V}_y^\dagger \\
&\qquad + \mathbf{V}_{xy} e^{ik_x} + \mathbf{V}_{xy}^\dagger e^{-ik_x}) \\
\text{Y:}\quad \mathbf{H}_Y &= \mathbf{h}_0 + (\mathbf{V}_x + \mathbf{V}_x^\dagger + \mathbf{V}_y e^{-ik_y} + \mathbf{V}_y^\dagger e^{ik_y} \\
&\qquad + \mathbf{V}_{xy} e^{-ik_y} + \mathbf{V}_{xy}^\dagger e^{ik_y})
\end{aligned}$$

Green's matrix

- What is it?
- Solution to the Schrödinger Equation
- Propagator
- Why do we need it?
- How do we obtain it?

$$[(E + i\eta)\mathbf{1} - \mathbf{H}]\mathbf{G}(E) = \mathbf{1}$$

$$\downarrow$$

$$\mathbf{G}(E) = \mathbf{1}([(E + i\eta)\mathbf{1} - \mathbf{H}])^{-1}$$

Recursion

- Solution to the system requires recursion
- Semi-infinite chain

$$\begin{pmatrix} z\mathbf{1}-\mathbf{H}_c & -\mathbf{V}^\dagger \\ -\mathbf{V} & (z-\varepsilon')\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{G}_{0c} \\ \mathbf{G}_{c0} & \mathbf{G}_{00} \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

$$\mathbf{G}_{00}(z) = \left[(z-\varepsilon') - \mathbf{V}(z\mathbf{1}-\mathbf{H}_c)\mathbf{V}^\dagger\right]^{-1}$$
$$= (z-\varepsilon'-\Sigma(z))^{-1}$$

where

$$z = E + i\eta$$

$$a_0 = \mathbf{V}^\dagger, \quad b_0 = \mathbf{V}$$
$$e_{s0} = \mathbf{h}_s, \quad e_0 = \mathbf{h}$$

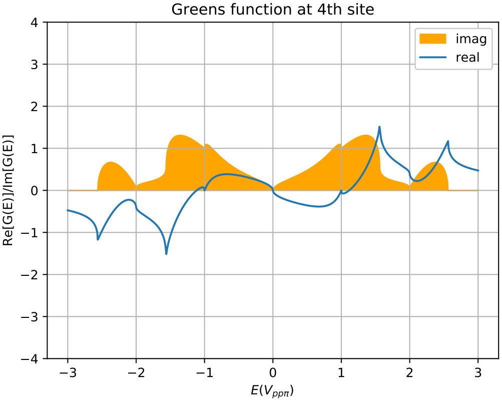
in loop:

$$a_1 = a_0 \times g_0 \times a_0$$
$$b_1 = b_0 \times g_0 \times b_0$$
$$e_1 = e_0 + a_0 \times g_0 \times b_0 + b_0 \times g_0 \times a_0$$
$$e_{1s} = e_{0s} + a_0 \times g_0 \times b_0$$
$$g_1 = (z - e_1)^{-1}$$
$$\mathbf{\Sigma}_R = e_s - h$$
$$\mathbf{\Sigma}_L = e - h - \mathbf{\Sigma}_R$$
$$\mathbf{G00} = (z - e_s)^{-1}$$

Recursion

```python
        while np.max(np.abs(a0)) > 1e-6:  # Loop with hop matrix as threshold
            ag = a0 @ g0  # Product defined here and used multiple times
            a1 = ag @ a0  # New hop matrix (transposed)
            bg = b0 @ g0  # Product defined here and used multiple times
            b1 = bg @ b0  # New hop matrix
            e1 = e0 + ag @ b0 + bg @ a0  # New onsite for "other cells"
            es1 = es0 + ag @ b0  # New onsite
            g1 = LA.inv(z - e1)  # New Green's function
            a0 = a1  # Overwrite old variable
            b0 = b1  # Overwrite old variable
            e0 = e1  # Overwrite old variable
            es0 = es1  # Overwrite old variable
            g0 = g1  # Overwrite old variable
            q = q + 1  # Counter (for diagnostic purposes)
        e, es = e0, es0  # Define the onsite Hamiltonians
        SelfER = es - h  # Self-energy from the right
        SelfEL = e - h - SelfER  # Self-energy from the left
        G00 = LA.inv(z - es)  # Green's functions
```

LDOS

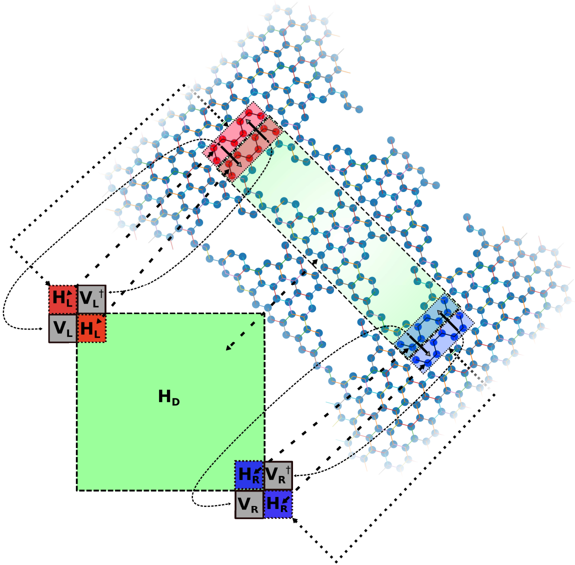



```
G00 = np.zeros((En.shape[0]), dtype=complex)  # Empty data matrix for Green's functions
for i in range(En.shape[0]):  # Loop iterating over energies
    G, SelfER, SelfEL = RecursionRoutine(En[i], h, V, eta)  # Invoking the RecursionRoutine
    G = np.diag(G)  # The Green's functions for each site is in the diagonal of the G matrix
    G00[i] = G[4]  # Chosen Green's function (here the 4th site)
```

Transmission

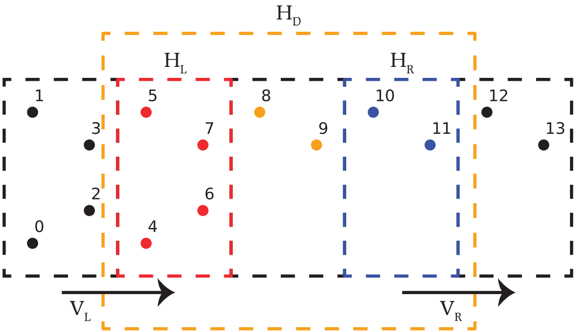
Transmission is the probability of an electron being transported through a specific region for a specific range of energies.

Translating from system to matrices



The left and right self-energy

- Device Hamiltonian
- Left *and* right self-energy
- Device Green's matrix




```python
for i in En:   # Iteration over each energy
    gl, scrap, SEL = RecursionRoutine(i, HL, VL, eta=eta)   # From the left
    gr, SER, scrap = RecursionRoutine(i, HR, VR, eta=eta)   # From the right
```

Getting Transmission

- Considering corrections from both contact regions

$$\mathbf{G}_D = \left[\mathbf{1}(E + i\eta) - \mathbf{H}_D - \mathbf{\Sigma}_L(E) - \mathbf{\Sigma}_R(E)\right]^{-1}$$

- How to account for states going in/out?

$$\mathbf{\Gamma}_{L,R} = i\left(\mathbf{\Sigma}_{L,R} - \mathbf{\Sigma}^{\dagger}_{L,R}\right)$$

```
GD["GD{:d}".format(q)] = scp.linalg.inv(  # Device Green's functions are saved
    scp.identity(HD.shape[0]) * (i + eta) - HD - SEL - SER)  # in a dictionary.
GammaL["GammaL{:d}".format(q)] = 1j * (SEL - SEL.conj().transpose())  # Rate matrices are
GammaR["GammaR{:d}".format(q)] = 1j * (SER - SER.conj().transpose())  # likewise saved.
```

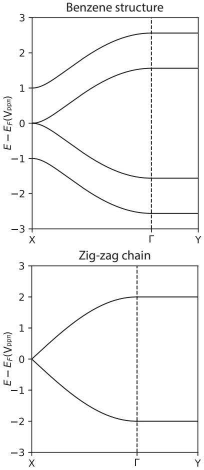
Getting Transmission

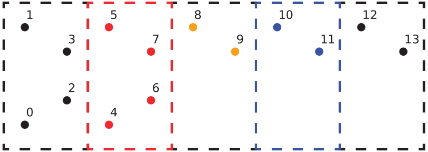
- States propagating through device
- Entering/Exiting by rate Γ

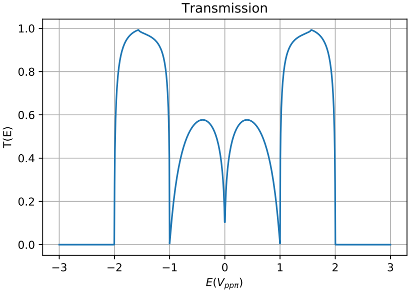
$$T(E) = \mathrm{Tr}\left[\boldsymbol{\Gamma}_R \mathbf{G}_D \boldsymbol{\Gamma}_L \mathbf{G}_D^\dagger\right](E)$$

```python
    for i in range(En.shape[0]):  # Iteration for every energy point.
        T[i] = np.trace((GammaR["GammaR{:d}".format(i)] @ GD["GD{:d}".format(
            i)] @ GammaL["GammaL{:d}".format(i)] @ GD["GD{:d}".format(i)].conj(
        ).transpose()).todense())  # Calculate transmission (equation V.9).
```

Getting Transmission



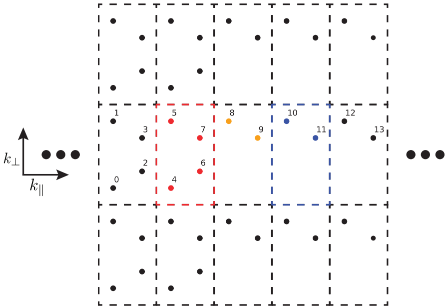




Transmission in 2D

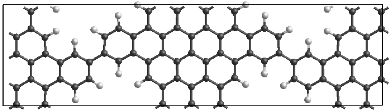
- Periodic boundary conditions
- Shift of cells in transverse direction
- Bloch phase added

$$\mathbf{H} = \mathbf{h} + \mathbf{V}\mathrm{e}^{ik_\perp} + \mathbf{V}^\dagger \mathrm{e}^{i(-k_\perp)}$$

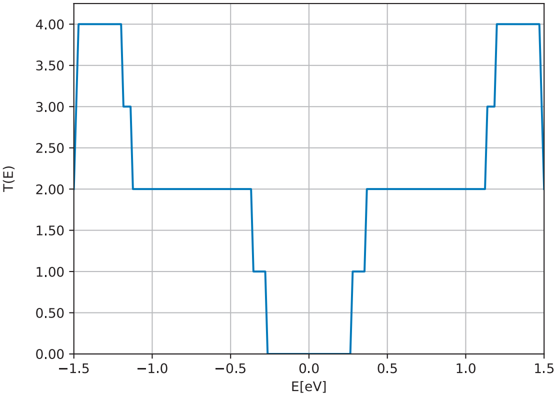


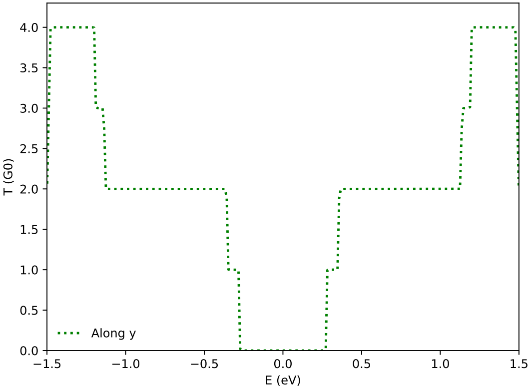

```
h, p = Onsite(xyz=xyz, Vppi=-1, f=1)  # Calculate onsite hops
V = Hop(xyz=xyz, xyz1=xyz + np.array([0, UY, 0]), Vppi=-1)  # Calculate hops
print('Number of hopping elements: {}'.format(np.sum(np.abs(V))))  # Number of hops
Ham = h + V * np.exp(1j * i) + np.transpose(V) * np.exp(-1j * i)  # Hamiltonian for ith kp
```

Code validity

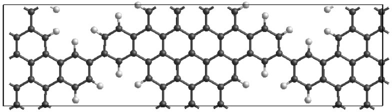


$$k = \frac{\pi}{2}$$

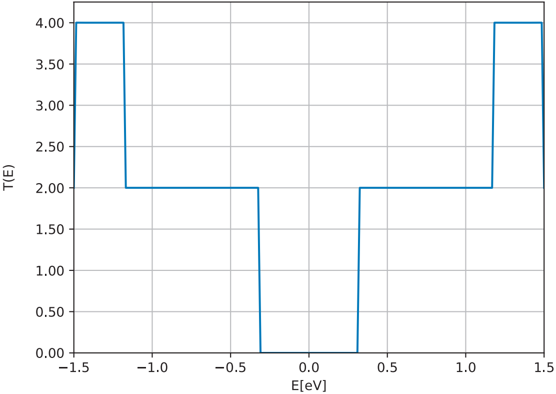


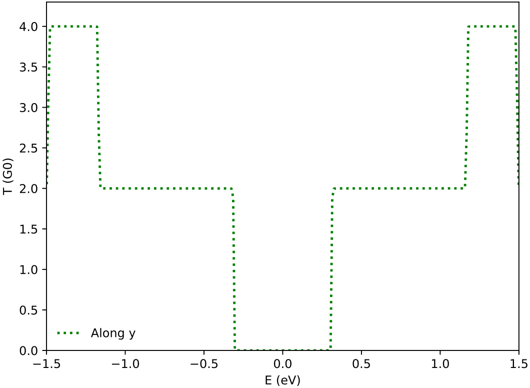


Code validity

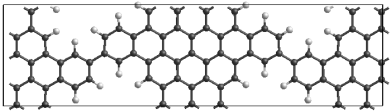


$$k = \pi$$

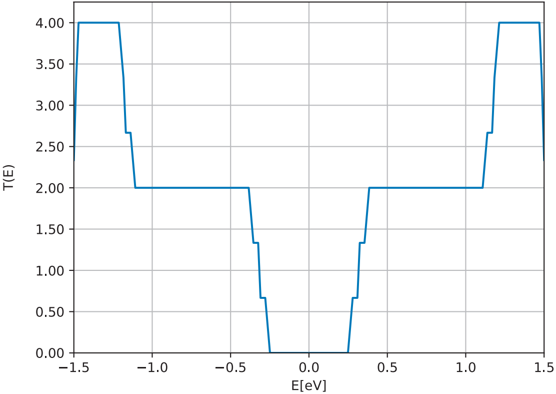


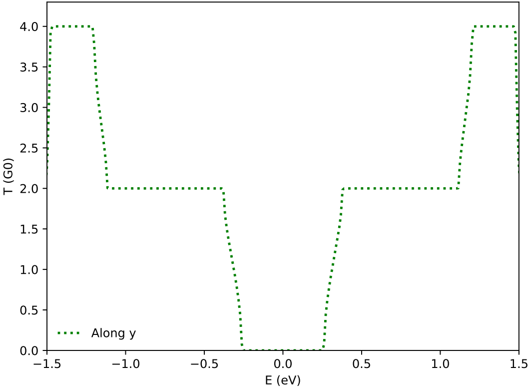


Code validity

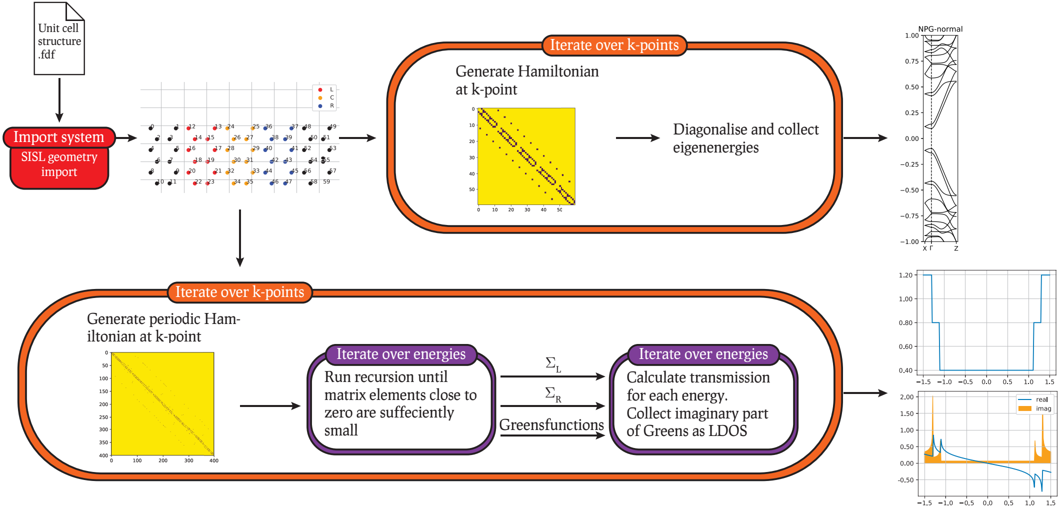


$$k = \mathrm{AVG}\left(0, \frac{\pi}{2}, \pi\right)$$

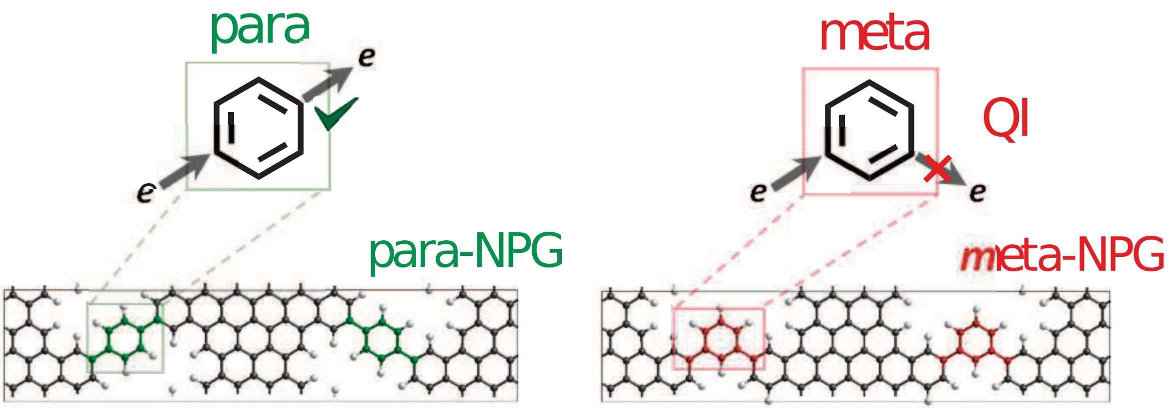




Summary of code structure

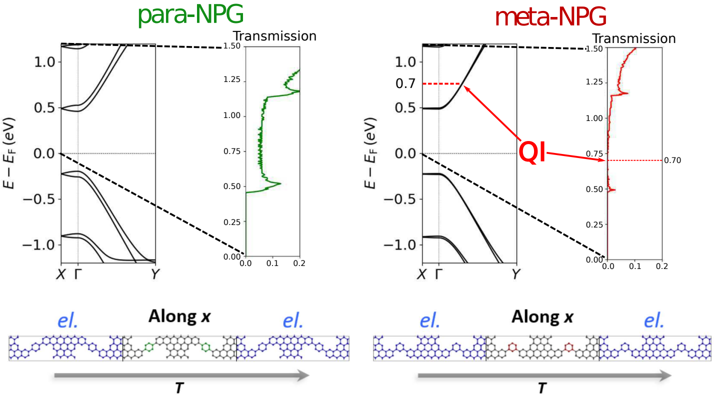


Para and meta bridges

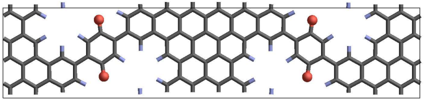


Para and meta bridges

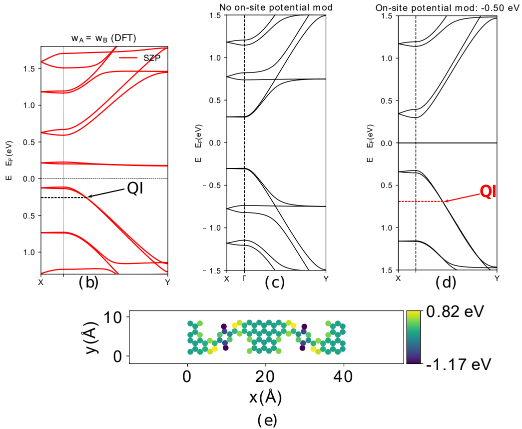
- Path length difference
- Quantum interference
- Transmission
- coupling/decoupling of GNR

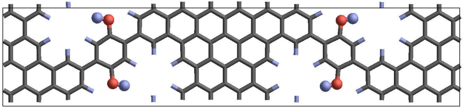


Para-O_4-NPG

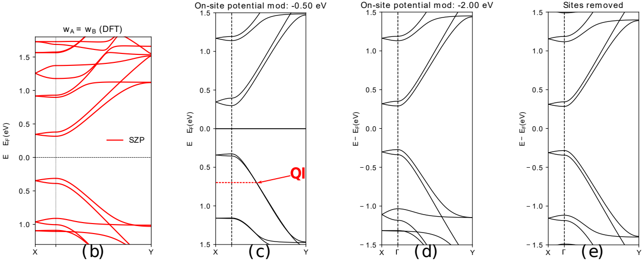


- Functionalisation with oxygen
- Quantum inteference at valence band
- Reproducing DFT result
- Decoupling of GNR

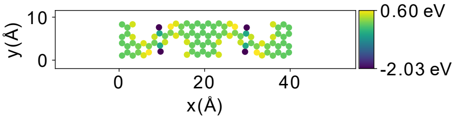



(a)

- Hydrogenation of oxygen
- Band splitting of DFT
- GNR coupling and resemblance with Para-NPG
- Reproducing DFT results



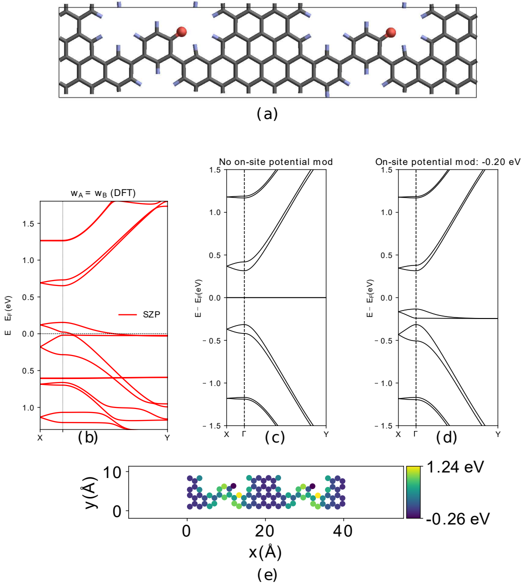
(b) (c) (d) (e)



(f)

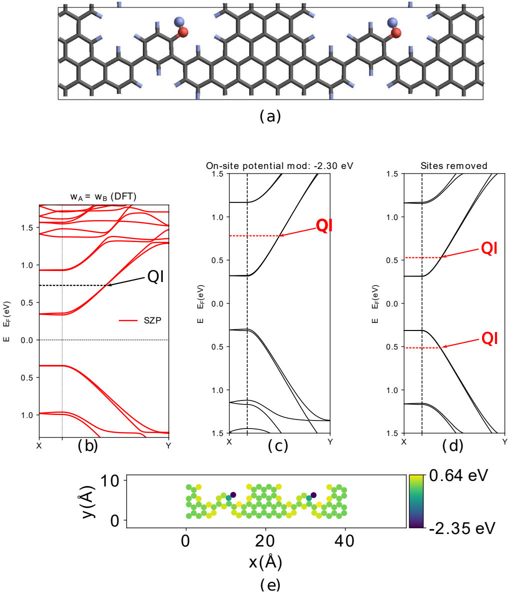
Meta-O_2-NPG

- Split in the valence for DFT
- Similarity in valence/conduction difference for meta/para
- Trying different potentials



Meta-$(OH)_2$-NPG

- Hydrogenation lowering potential of oxygen
- Decoulping of oxygen = decouplig of GNR
- Resemblance with pristine Meta-NPG
- In agreement with DFT



Conclusion

"A tight-binding routine has successfully been developed in Python. This makes it easier to, qualitatively, understand electron transport in nanoporous graphene devices (NPG)" ✓

Questions

Christoffer Vendelbo Sørensen (s163965)

June 25, 2019