Tight-Binding calculations with PythTB code

https://www.physics.rutgers.edu/pythtb/index.html

I. Gerber 21/01/25

Making tight-binding models is easy, why should I use PythTB?

- It works in real space only
- It computes band structure and eigenvectors easily
- One can create 1D, slab, bulk, or other finite boundary conditions easily
- It corresponds to a first pedagogical step for handling more complex approaches such as DFT in PBC

Tight-binding degrees of freedom in PythTB

Atoms located at $\vec{r}_\alpha$ positions in unit cell

Each atom has orbitals labelled by $j = 1,...,n$

To model a physical system, we need to decide which atoms/orbitals are relevant!

$$\phi_{\vec{T},\alpha i}(\vec{r}) = \varphi_{\alpha i}(\vec{r} - \vec{T} - \vec{r}_\alpha)$$

Unit cell

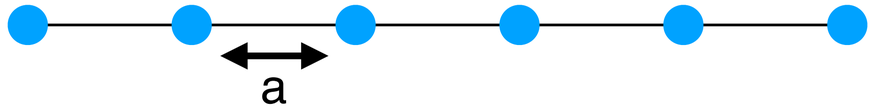
Atom

Orbital

Orthogonality : $\langle \phi_{\vec{T}',\alpha i} | \chi_{\vec{T},\beta j} \rangle = \delta_{\vec{T}\vec{T}'}\delta_{\alpha\beta}\delta_{ij}$

Hamiltonian consists of hopping terms mainly: $H_{\alpha i,\beta j}(\vec{T}) = \langle \phi_{\vec{T}',\alpha i} | \hat{H} | \chi_{\vec{T},\beta j} \rangle = \langle \phi_{\vec{0},\alpha i} | \hat{H} | \chi_{\vec{T},\beta j} \rangle$

1D chain of H atoms



1 orbital/site ⇒ trivial subscripts: $\vec{r}_\alpha = \vec{r}_1 = \vec{0} \quad i = 1$

$$H(\vec{T} = \pm a) = -t$$
$$H(\vec{T} \neq \pm a) = 0$$

Nearest neighbor hopping only

Lattice vectors:
(we only have one)

Orbitals in units of lattice vecs
(we only have one)

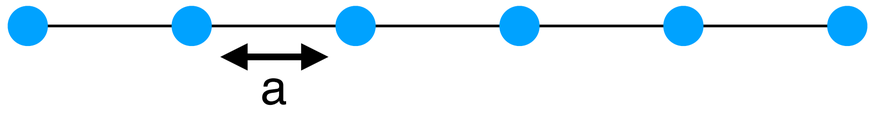
Define model: (dim k space, dim realspace, lattice vecs, orbital vecs)

Hopping term: (amplitude, $i\alpha, j\beta, \overrightarrow{T}$)

```
# specify model
# lattice vectors
lat=[[1.0]]
# positions of orbitals
orb=[[0.0]]

# define the model
my_model=tb_model(1,1,lat,orb)
# assign hopping terms
my_model.set_hop(-1., 0, 0, [1])
```

1D chain of H atoms



k path to plot in units of
reciprocal lattice vectors (-$\vec{\pi}$ to $\vec{\pi}$)

Labels of k-points on path

Repeat this line for more bands, up to evals[n]

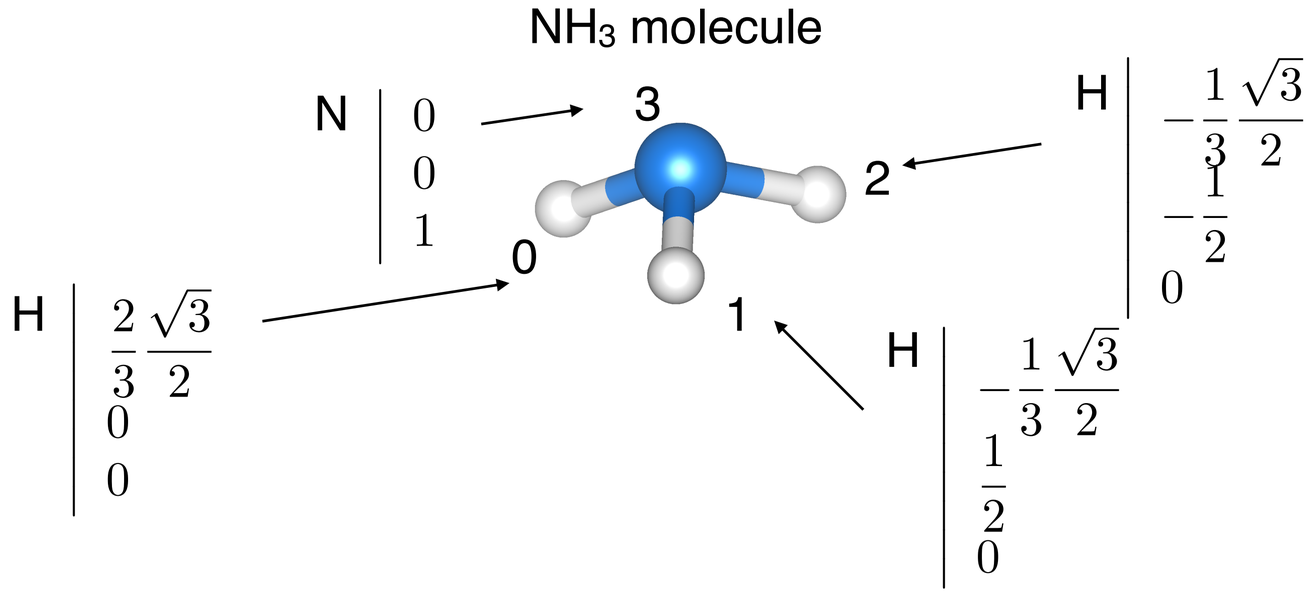
Where to put ticks (from path and numsteps)

```
# define a path in k-space
(k_vec,k_dist,k_node)=my_model.k_path('fullc',100)
k_label=[r"-$\pi$",r"$0$", r"$\pi$"]

# solve model
evals=my_model.solve_all(k_vec)

# plot band structure
fig, ax = plt.subplots()
ax.plot(k_dist,evals[0])
ax.set_title("1D chain band structure")
ax.set_xlabel("Path in k-space")
ax.set_ylabel("Band energy")
ax.set_xticks(k_node)
ax.set_xticklabels(k_label)
ax.set_xlim(k_node[0],k_node[-1])
for n in range(len(k_node)):
  ax.axvline(x=k_node[n], linewidth=0.5, color='k')
fig.tight_layout()
fig.savefig("1D-linchain.png")
```

Examples without PBC: 0D systems



— change on-site energies so that N and H don't have the same energy

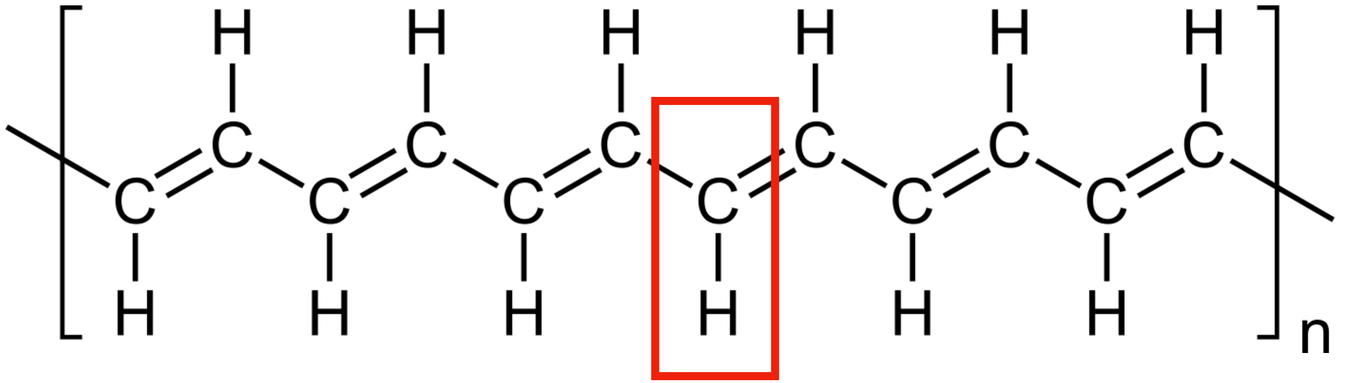
— Try first with a single hopping for H-H and N-H

— Compare with the correct description of the MO diagram

— How to solve this issue ?

Examples with PBC: 1D systems

Polyacetylene



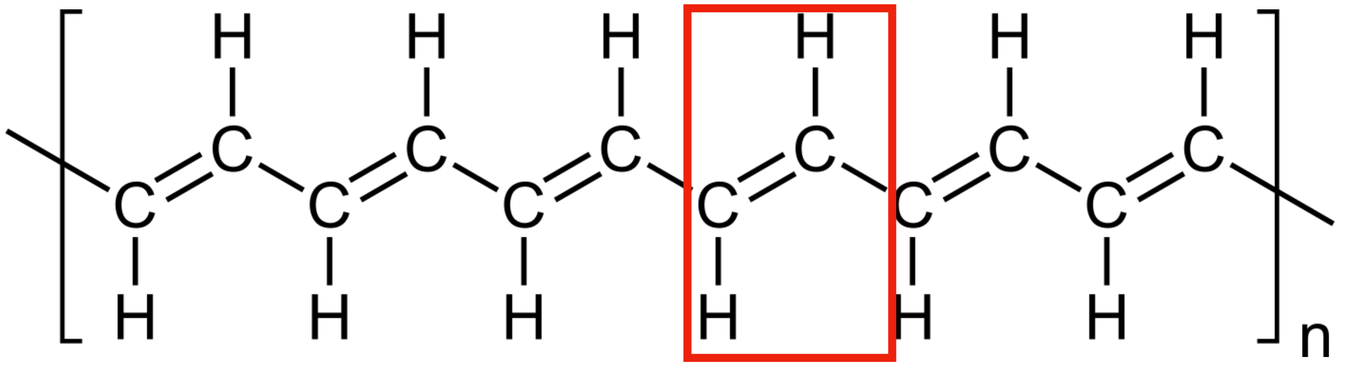
• Carbon atoms are all sp^2 hybridized (one *2s* orbital together with the $2p_x$ and the $2p_y$ orbitals generate three sp^2 orbitals)
• Two sp^2 orbitals form σ-bonds with the sp^2 orbitals of the neigboring carbon atoms and one remaining sp_2 orbital forms a σ-bond with the *1s* orbital of the hydrogen atom
• The bonding orbital associated with each σ-bond is occupied by two electrons (spin-up and spin-down)
• There is one electron per carbon atom left in the $2p_z$ orbital
• The $2p_z$ orbital stick out of the plane of the chain and form π-bonds with neigboring $2p_z$ orbitals

Average band model: Neglect the bond alternation

Define the metallic/semi-conductor behavior of the system

Examples with PBC: 1D systems

Polyacetylene



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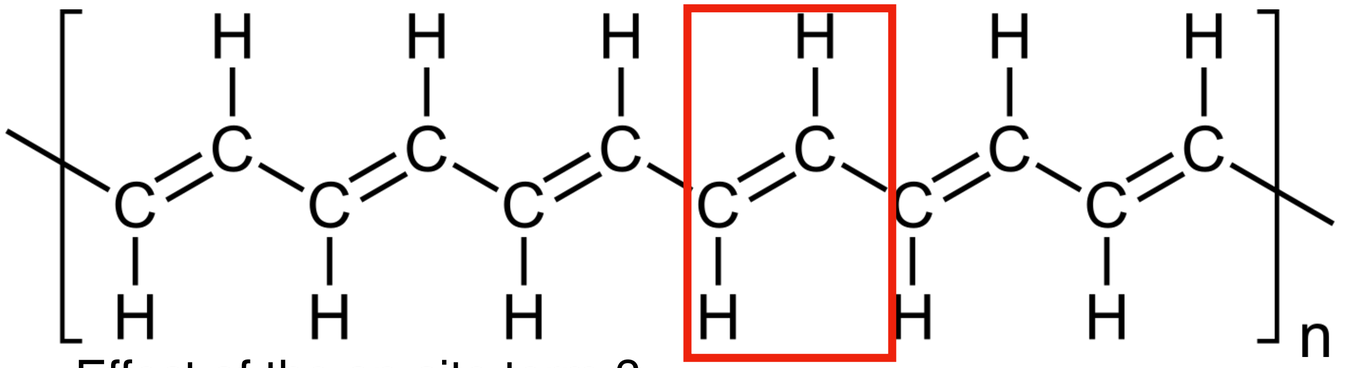
Alternating band model

Define the metallic/semi-conductor behavior of the system

Examples with PBC: 1D systems

Polyacetylene



Effect of the on-site term ?

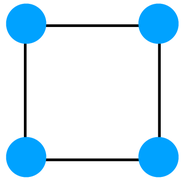
Effect of differentiating the hopping value ? Change of signs ?

To push further: be more precise with the geometry ?

Alternating band model

Examples with PBC: 2D systems

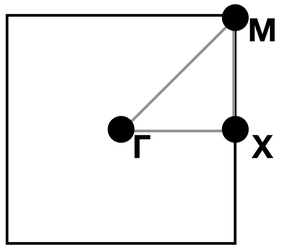
Square lattice



$$\begin{cases} H(\vec{T}) = -t & \text{if } \overrightarrow{T} = \pm a\overrightarrow{e_x}, \pm a\overrightarrow{e_y} \\ 0 & \text{else} \end{cases}$$

How to plot the 2D band structure ?

Identification high-symmetry path in BZ

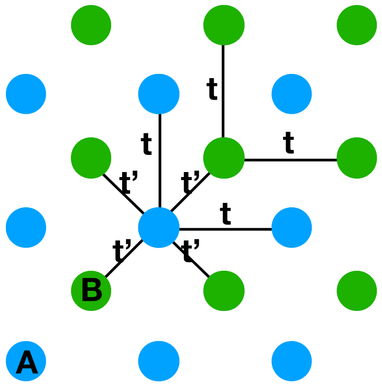


$$\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$$

Play again with on-site term and hopping values

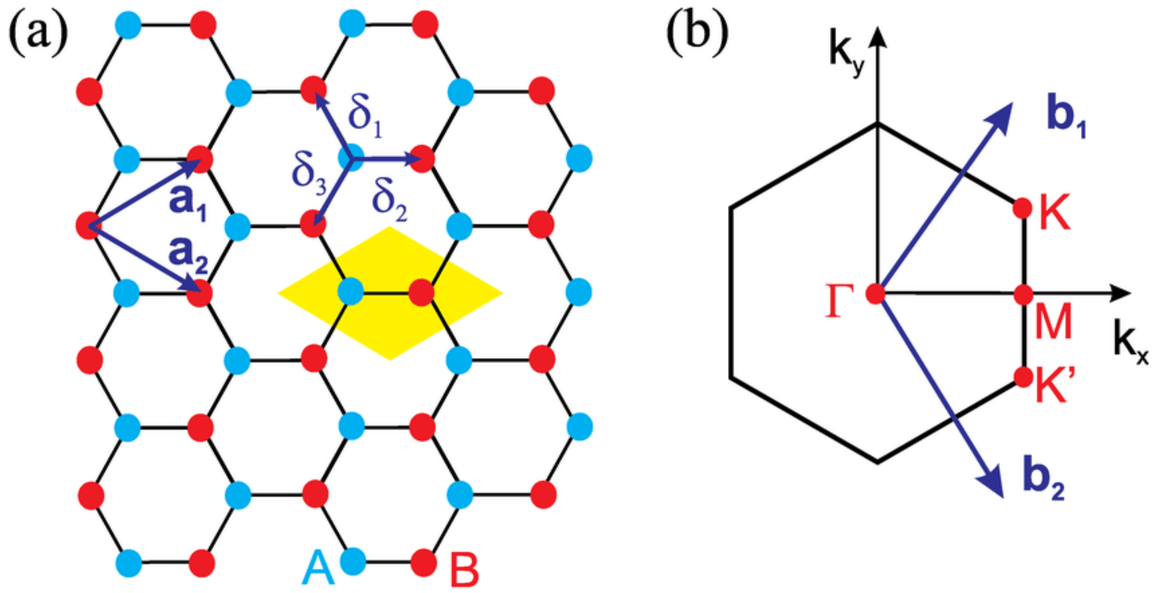
Examples with PBC: 2D systems

Interpenetrating square lattices



Examples with PBC: 2D systems

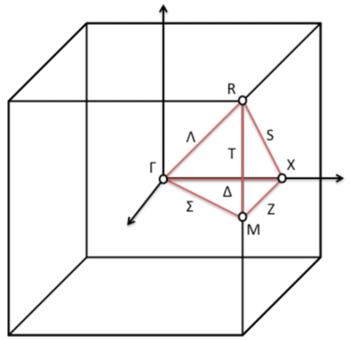
Graphene band structure



Examples with PBC: 3D systems

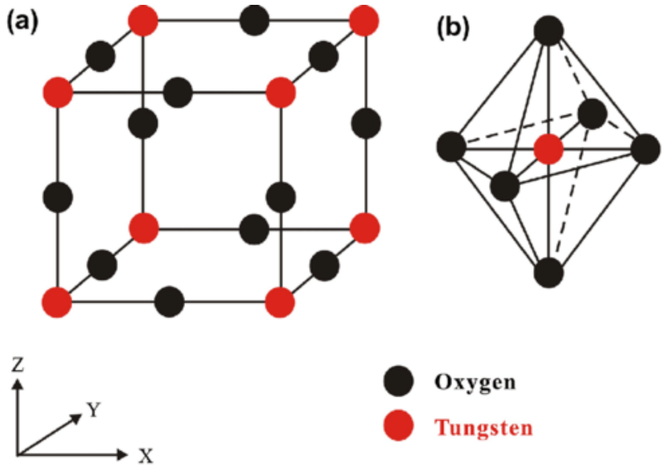
Simple cubic

BZ

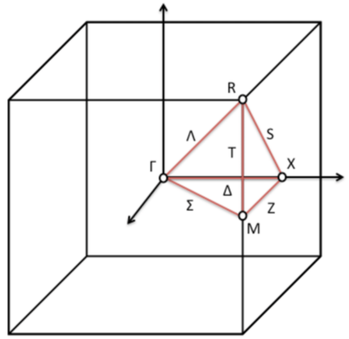


Examples with PBC: 3D systems

WO_3



BZ



cell constant a	3.7845 Å
first neighbor distance d	1.9 Å
on-site oxygen s	−29.14 eV
on-site oxygen p	−14.13 eV
on-site tungsten d	−10.96 eV
$V_{sd\sigma}$	−3.6976 eV
$V_{pd\sigma}$	−3.4519 eV
$V_{pd\pi}$	+1.5914 eV