



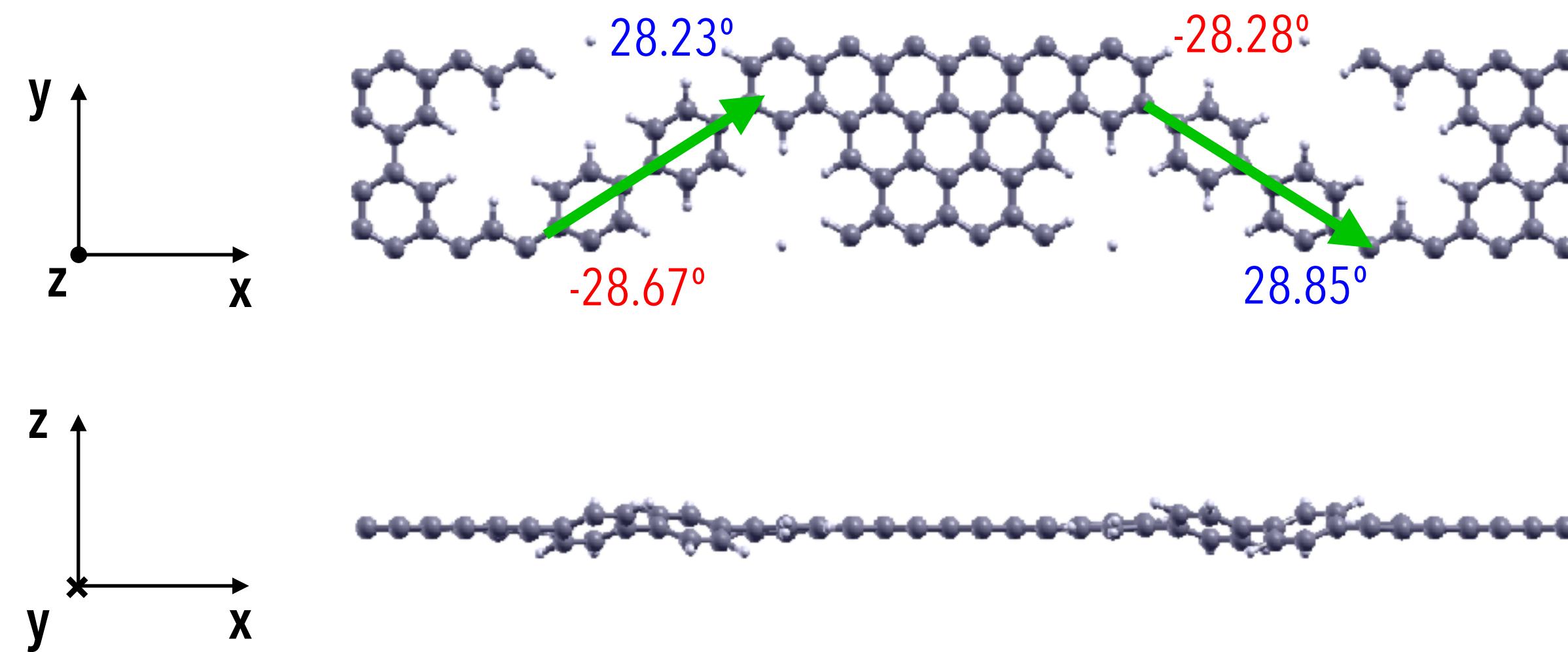
# Phenylation NPG

## Para-Para connections

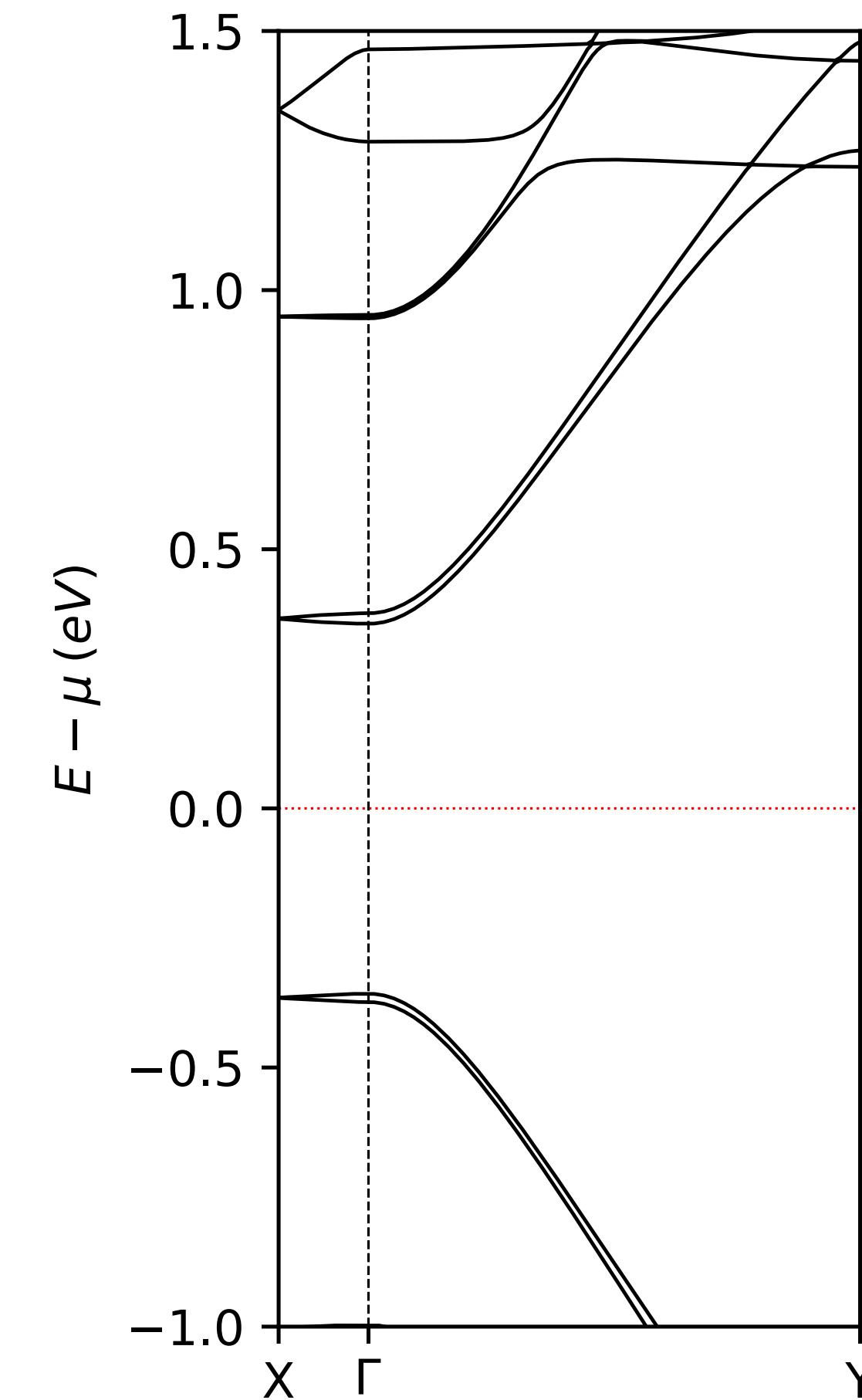
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# Relaxed and unconstrained structure

The only constrain is that the unit cell must be orthogonal. Apart from that the coordinates are relaxed without contrains and variable cell was used.



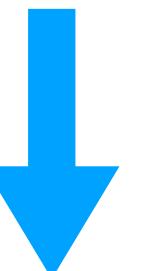
- Angles are with respect to the green axes.
- Only close to the bridges the ribbons show slight deformation in z-direction. Bond lenghts change significantly in that region too.
- The longitudinal valence and conduction band splitting evidence some crosstalk between adjacent ribbons.
- In the following slides different cases are analysed in order to isolate the effect of phenyl tilting from other variables such as vertical displacement.



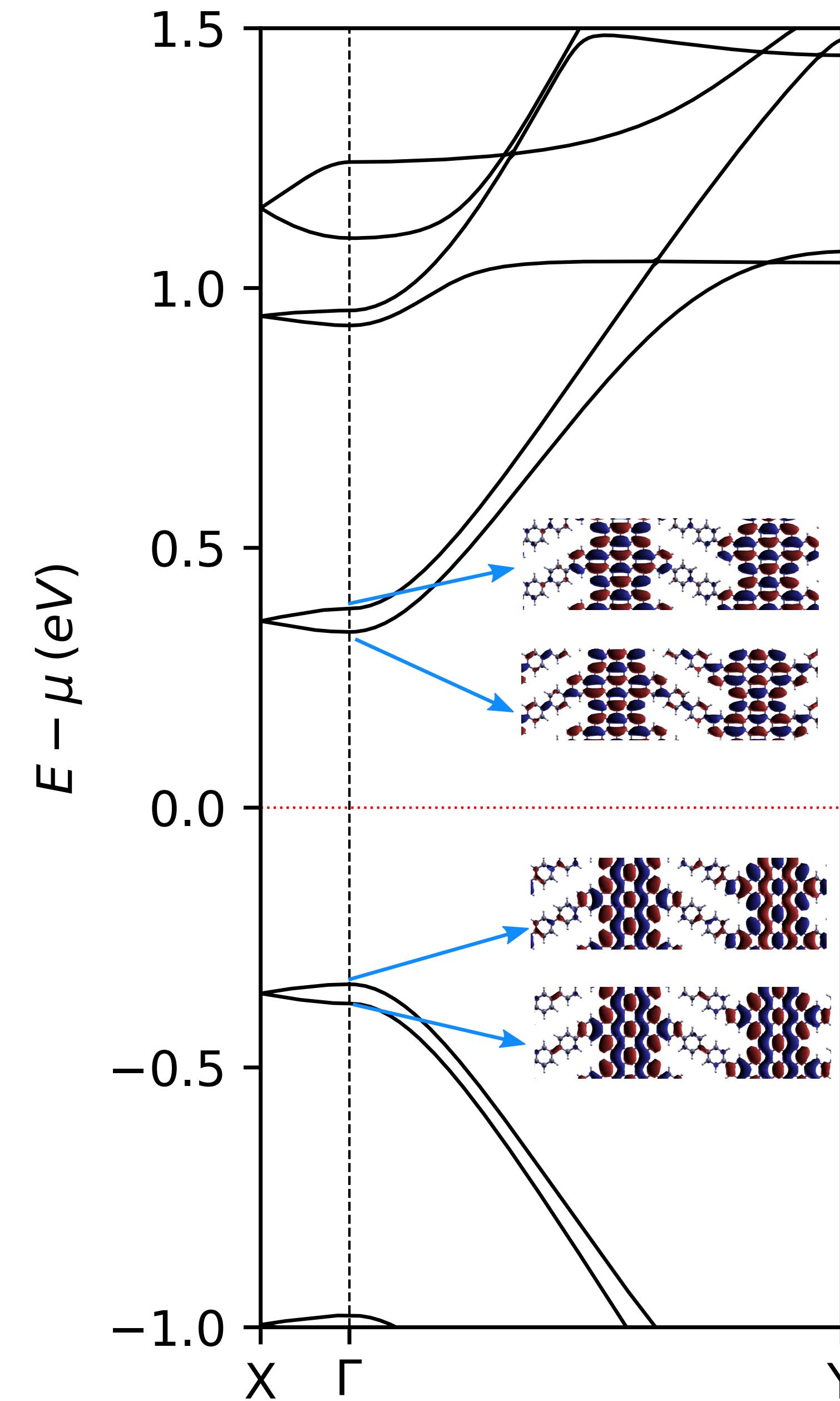
# Planar-relaxed structure

The atomic structure is forced to remain planar and the cell orthogonal. This way we neglect the effect of vertical deformation.

- The longitudinal valence and conduction bands are splitted by a  $\Delta k$ .
- The bands are degenerated in the X point of the Brillouin zone, showing that the two ribbons in the unit cell are equivalent.
- The wave functions (WF) at the  $\Gamma$  point are combinations of the longitudinal wave functions of individual ribbons.

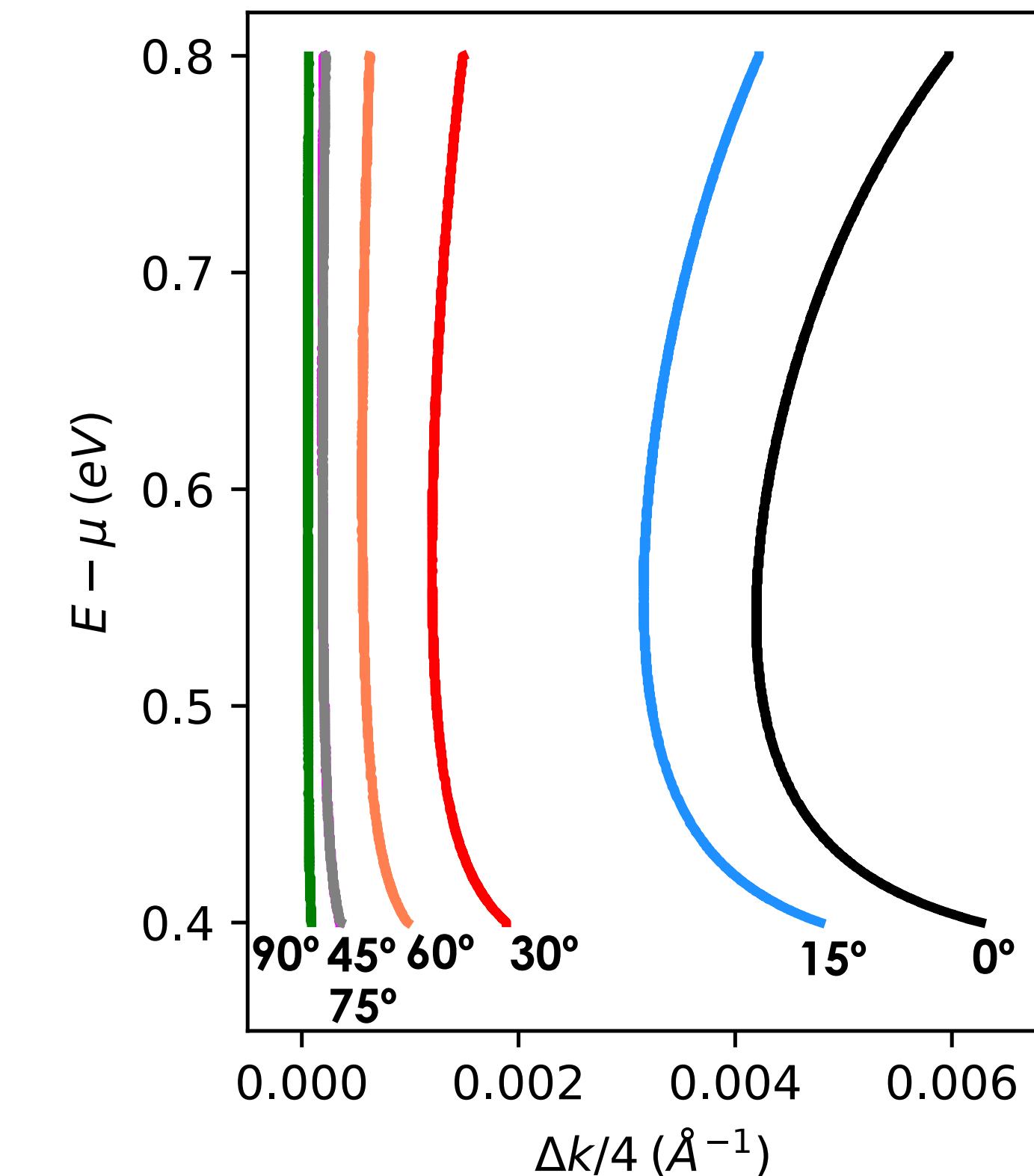
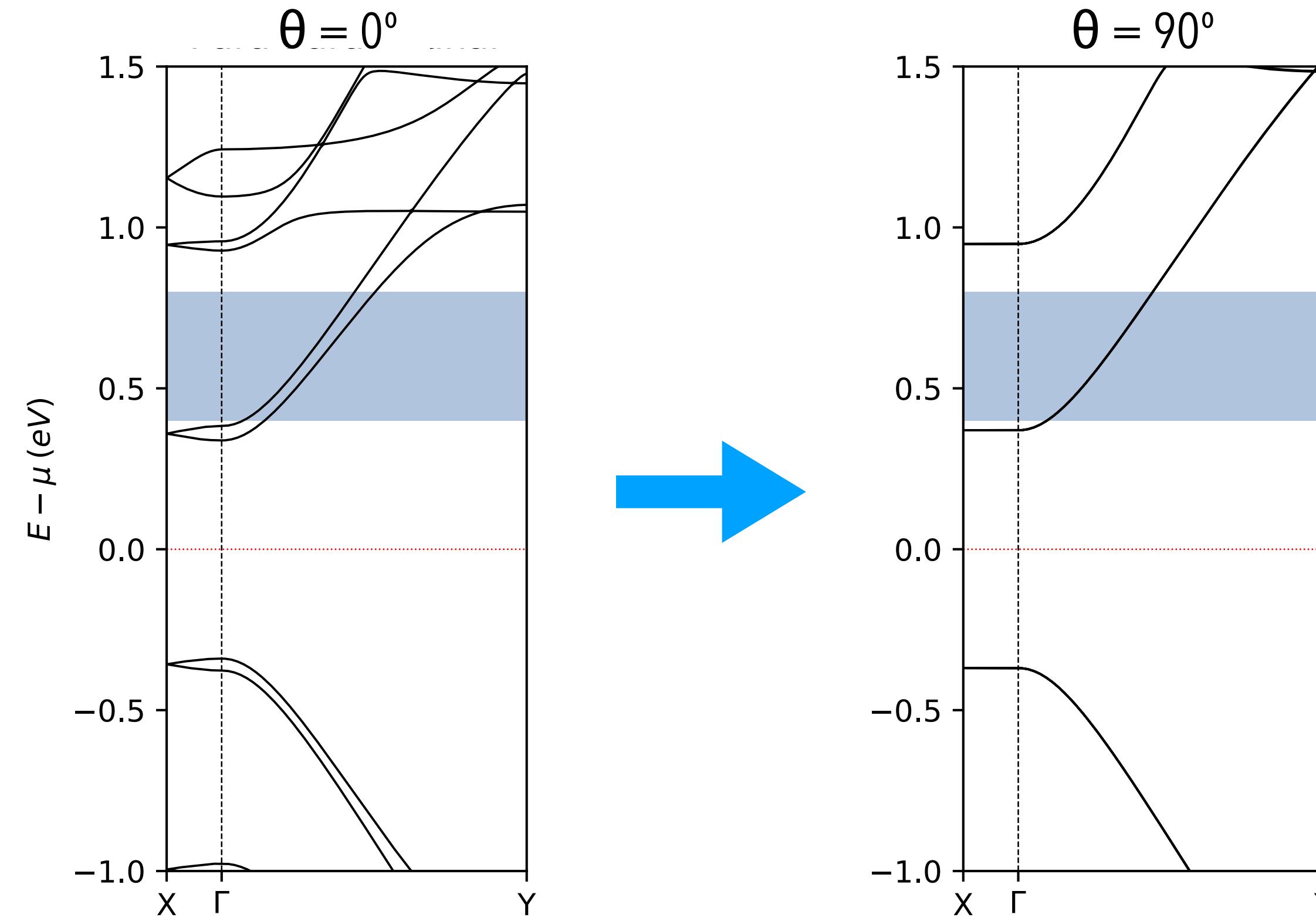


- The last three points confirm that the ribbons are coupled and  $\Delta k$  is a good quantity to measure the crosstalk.



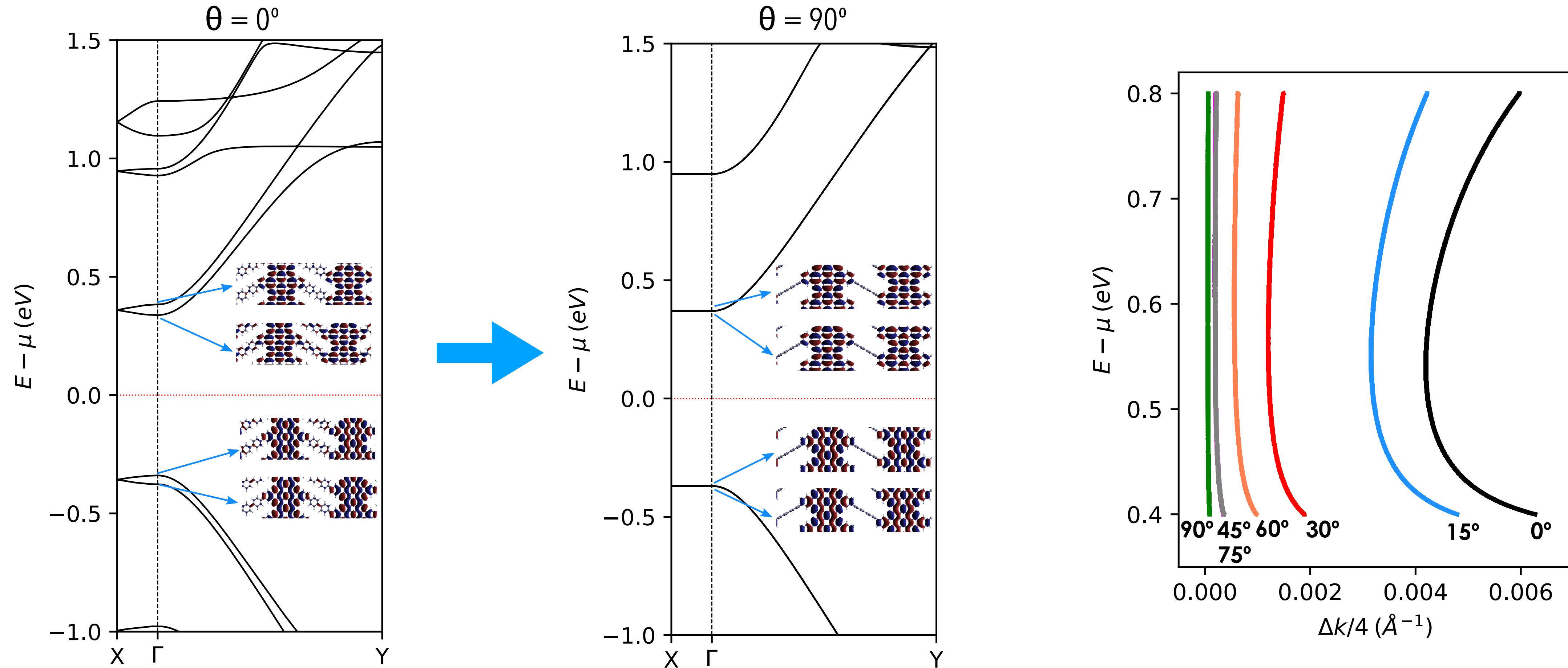
# Phenyl rotation: both phenyls in each bridge

Starting from the previous structure (planar-relaxed) we rotate all phenyls in the bridges in the same way as in the relaxed and unconstrained structure (slide 2). We explore  $\Delta k$  for different angles of the phenyls, going from  $0^\circ$  (planar-relaxed case) to  $90^\circ$ .



In general terms, the higher the rotation angle of the phenyls the lower  $\Delta k$ .

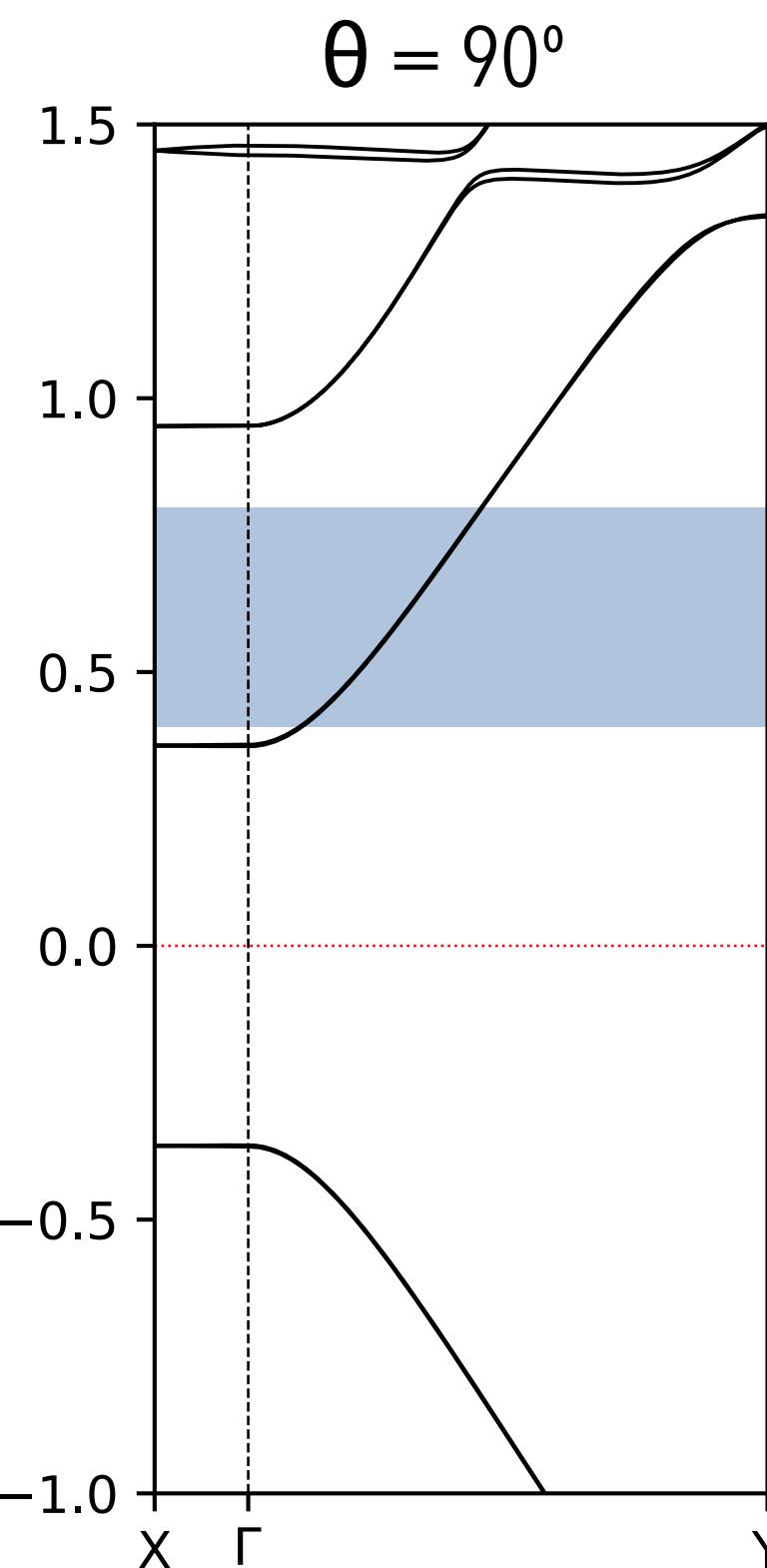
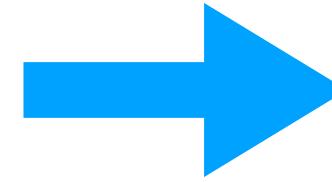
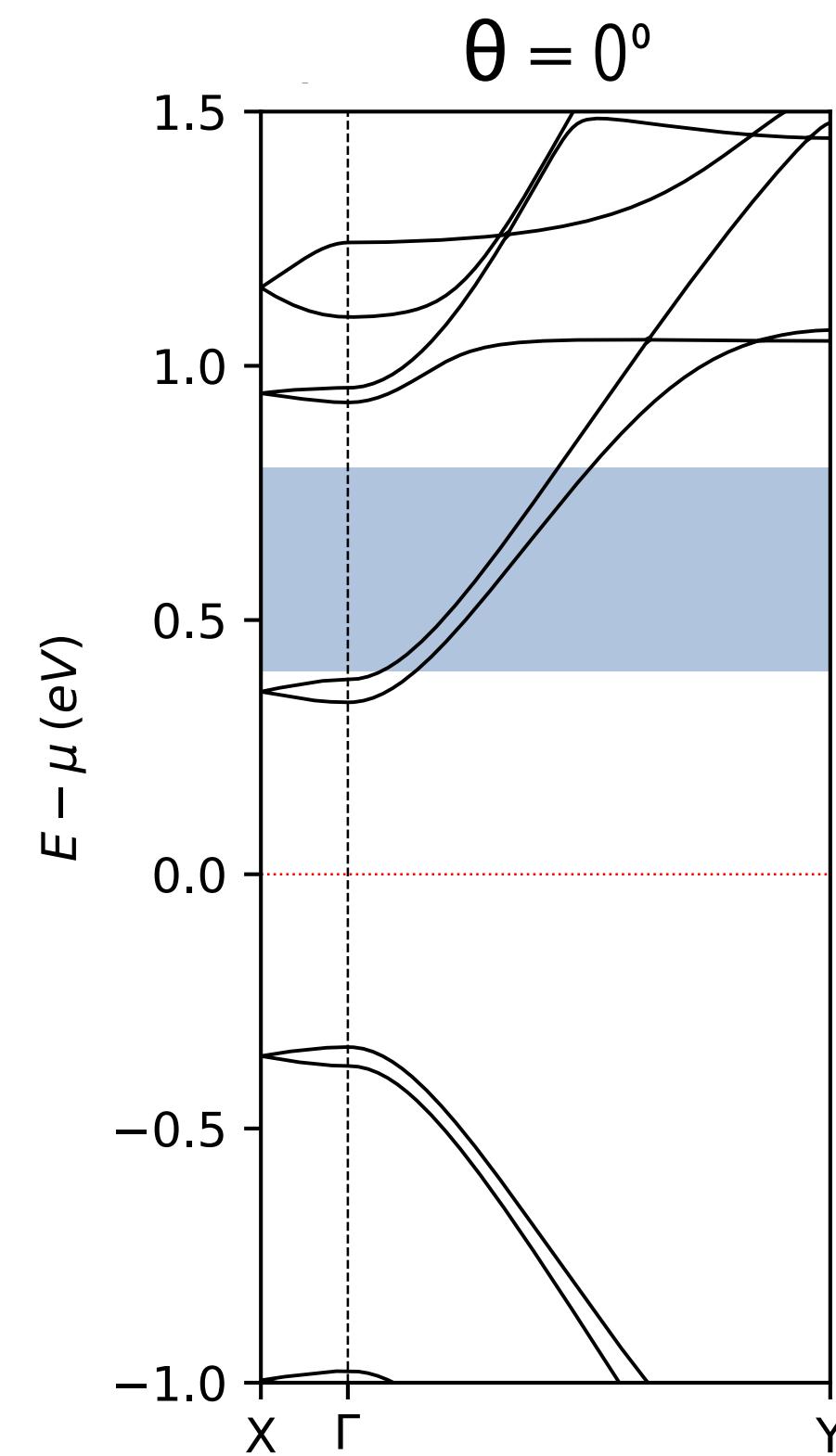
# Phenyl rotation: both phenyls in each bridge



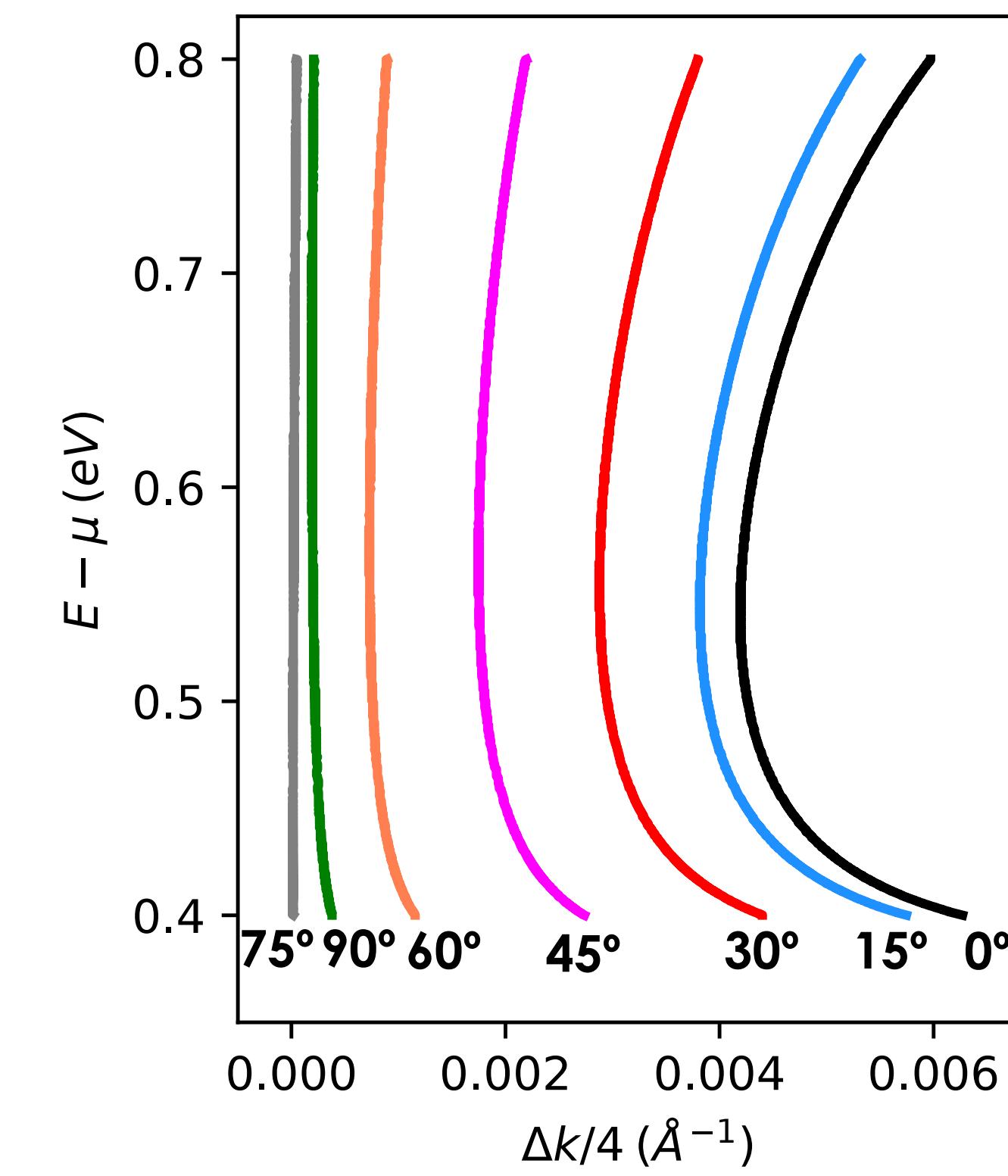
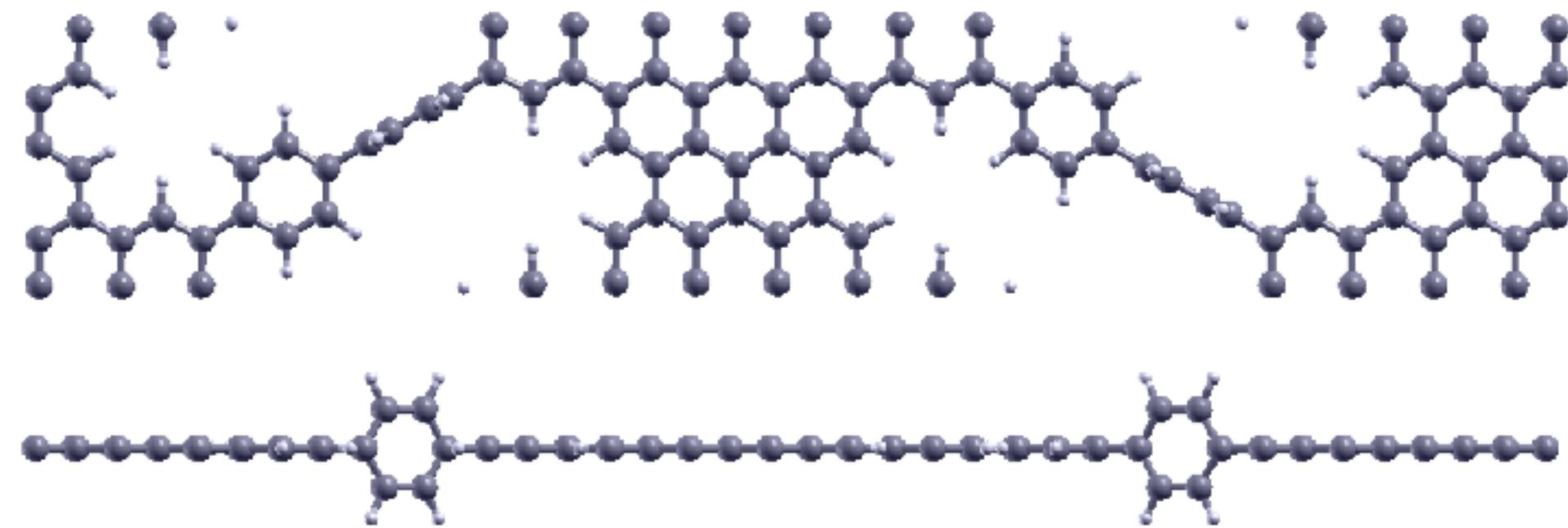
In this case, even if the crosstalk is negligible for  $\theta = 90^\circ$  the WF are still a combination of the longitudinal eigenstates of each ribbon. Although there is no term in the Hamiltonian mixing states of adjacent ribbons, the fact that the ribbons are equivalent (same on-site energy) for this kind of rotation enables a solution of that form.

# Phenyl rotation: single phenyl in each bridge

*Equivalent ribbons*

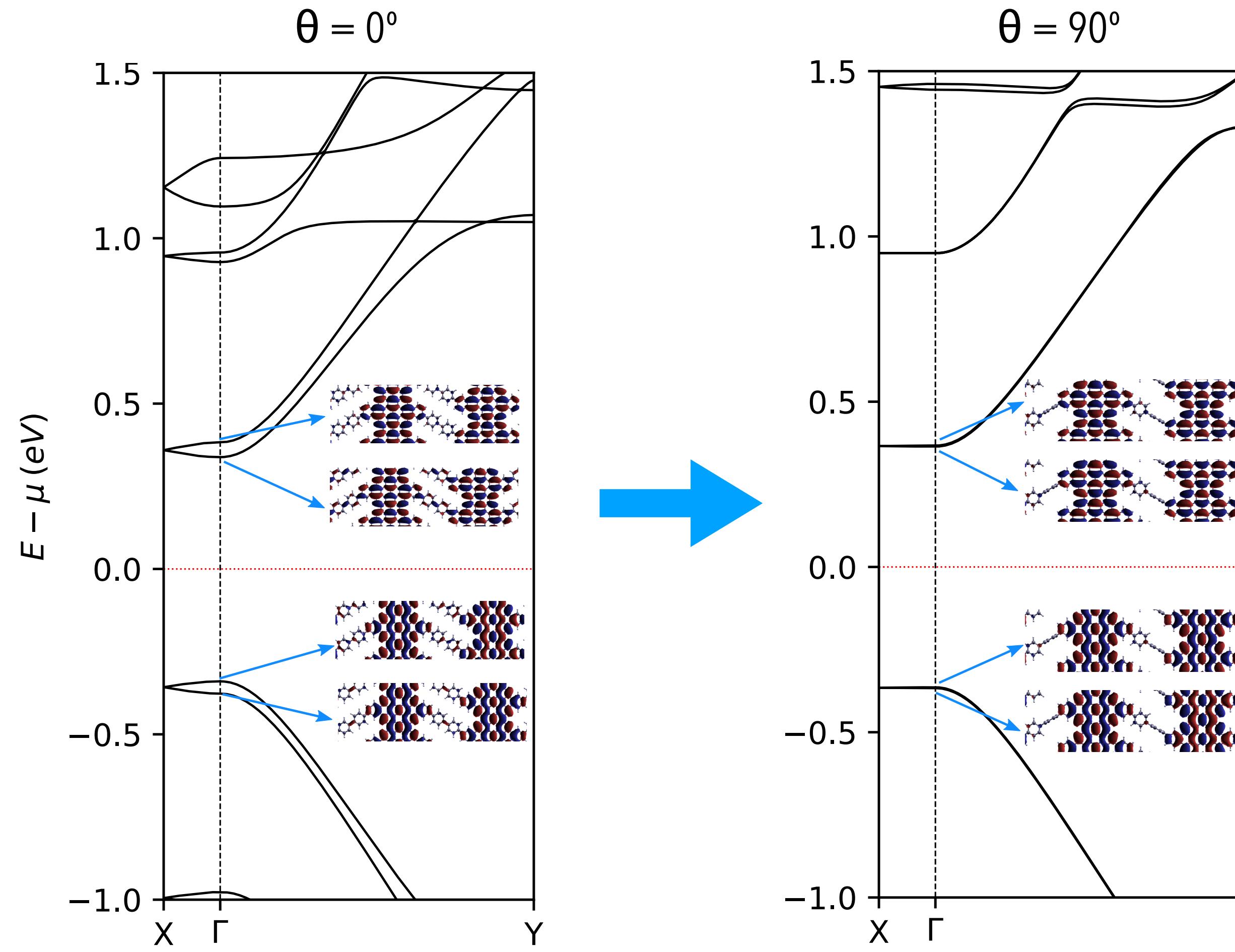


Atomic structure in the  $\theta = 90^\circ$  case

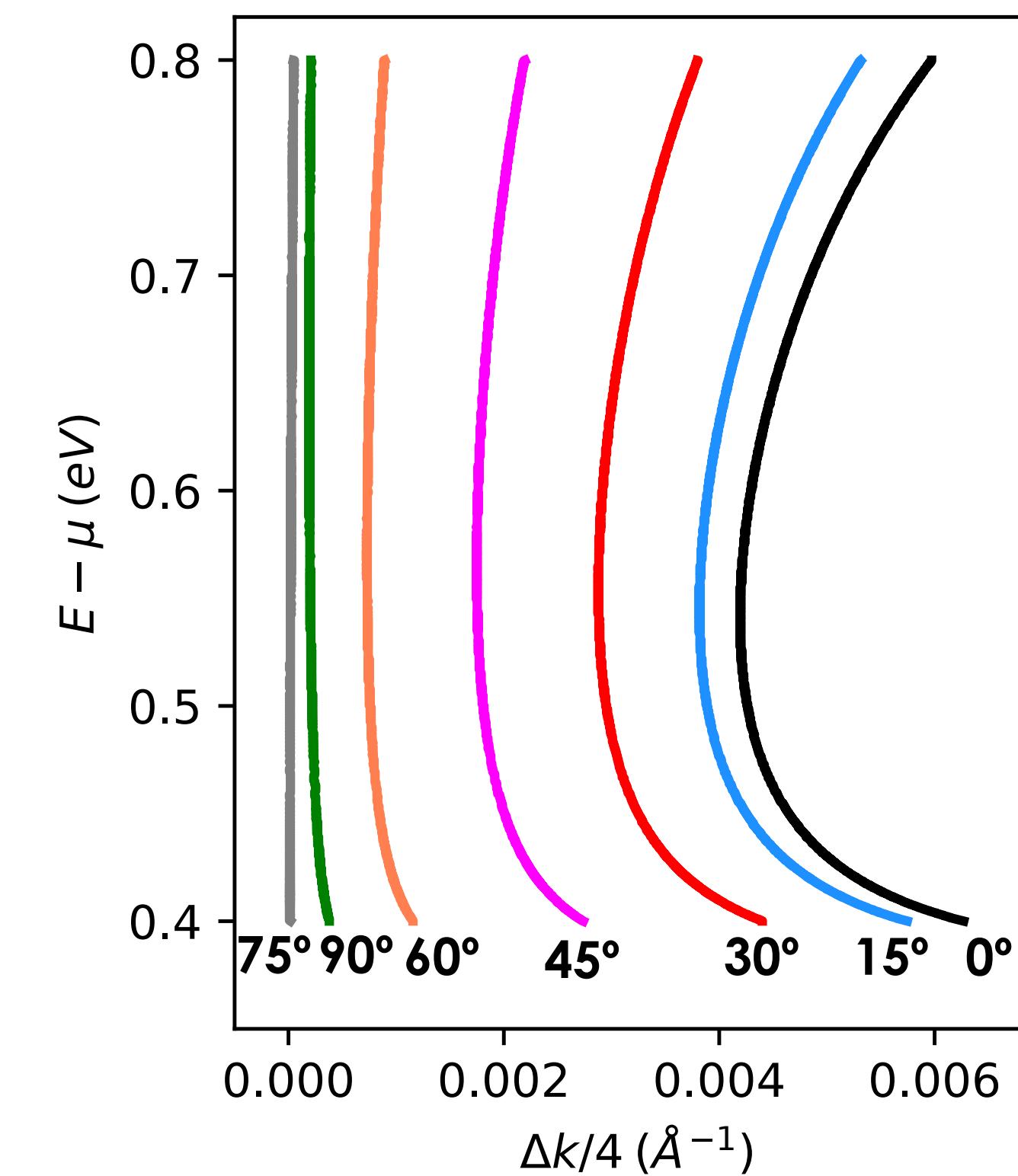


# Phenyl rotation: single phenyl in each bridge

*Equivalent ribbons*



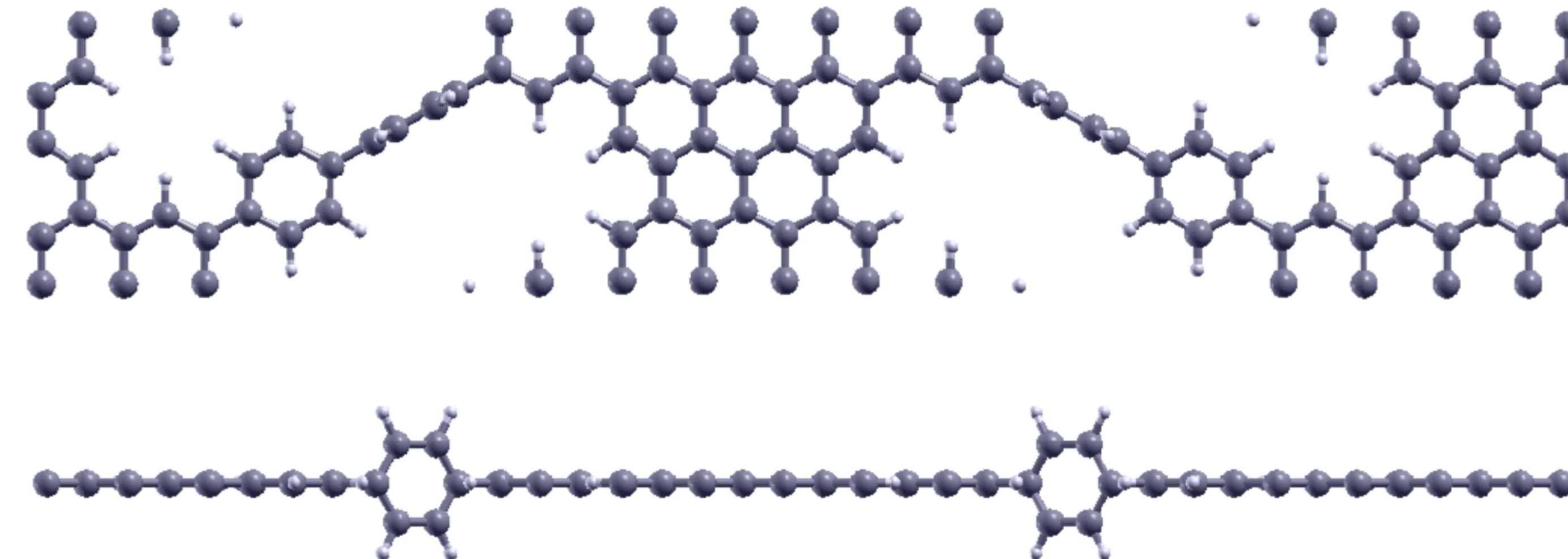
The ribbons are once again equivalent and the WF are a combination of the eigenstates of both ribbons.



# Phenyl rotation: single phenyl in each bridge

## *Non-equivalent ribbons*

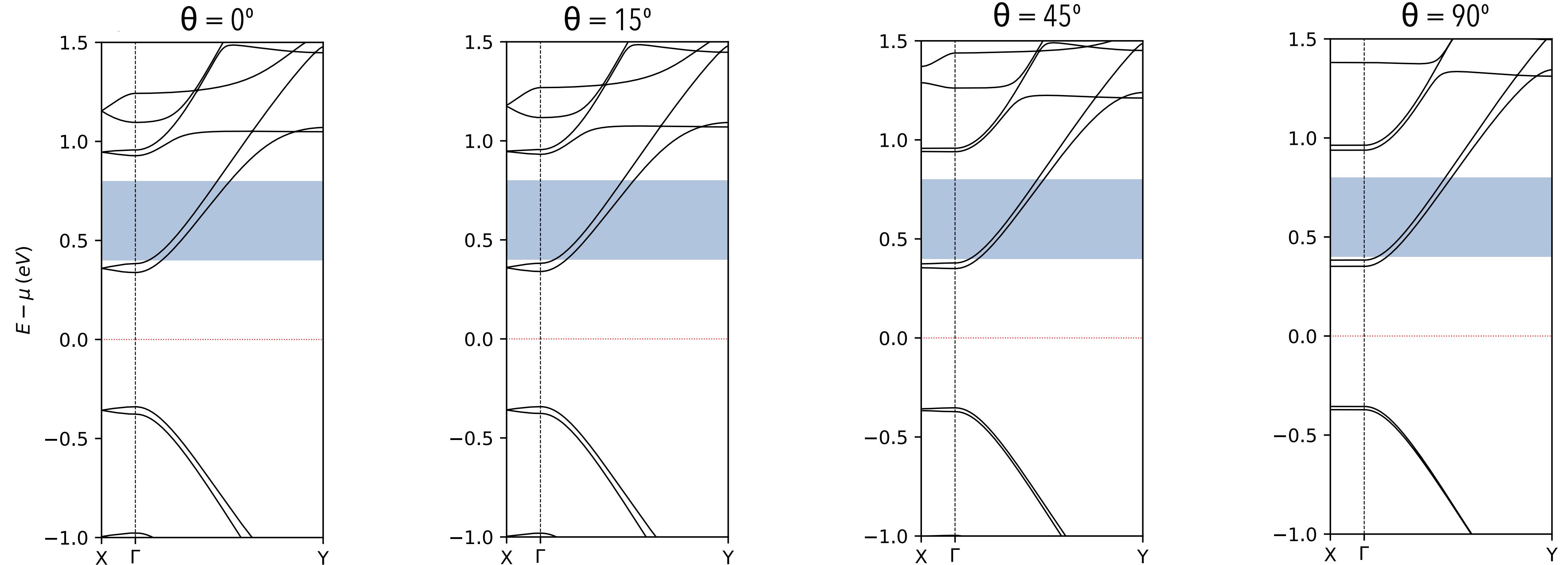
This is an example of a structure where the ribbons are not equivalent and thus  $\Delta k$  is not a good quantity to measure the coupling between adjacent ribbons. Only the phenyls close to one of the ribbons were rotated, taking different angles from  $0^\circ$  to  $90^\circ$



Atomic structure in the  $\Theta=90^\circ$  case

# Phenyl rotation: single phenyl in each bridge

*Non-equivalent ribbons*

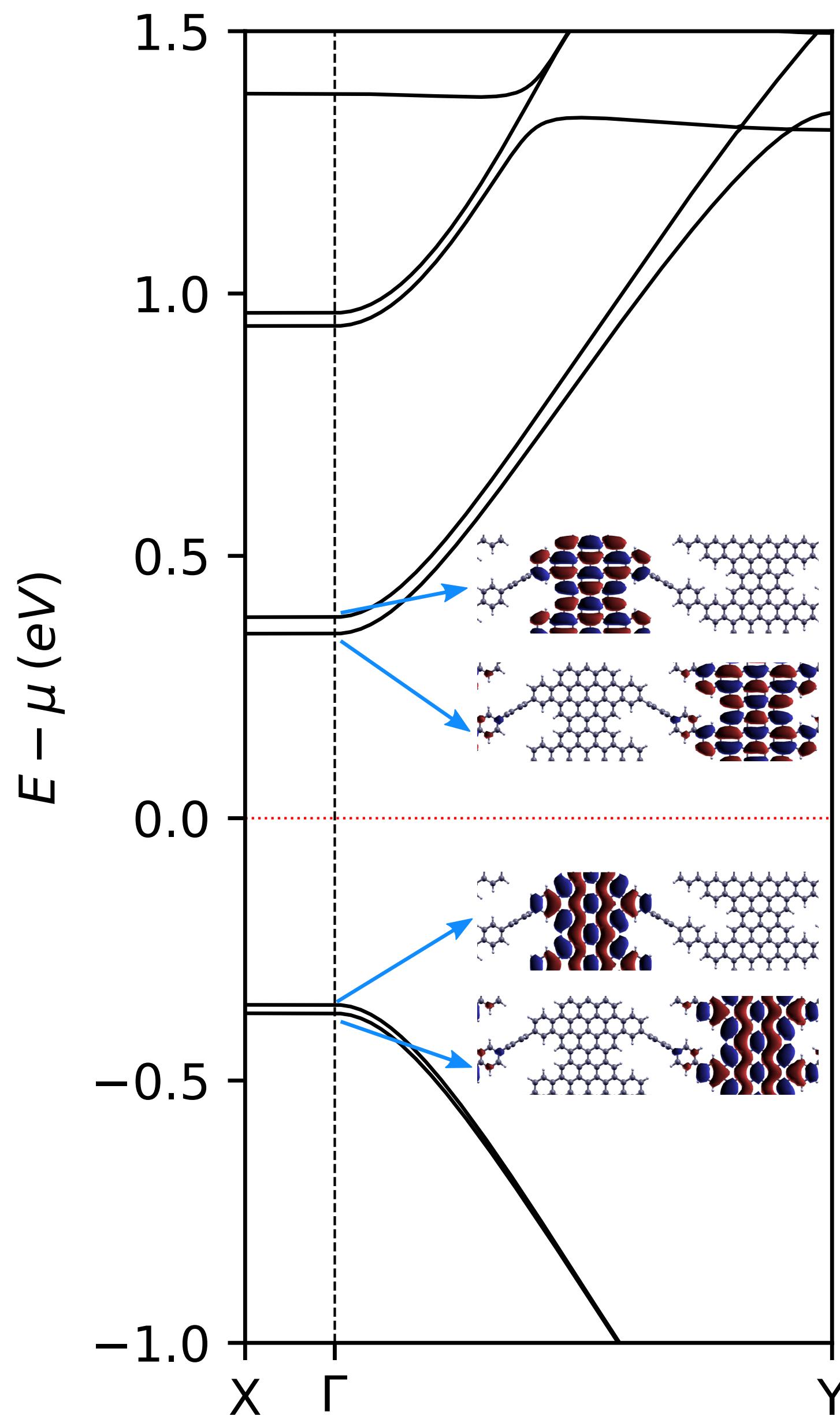


Apart from breaking the coupling, the rotation of the phenyl angles induces a difference in the on-site energies of the ribbons, what ends up breaking the degeneracy at the  $X$  point.

# Phenyl rotation: single phenyl in each bridge

## *Non-equivalent ribbons*

- As the phenyls are rotated the interaction between adjacent ribbons is killed.
- The on-site energies also change:
  - ♦ The ribbon whose phenyls are rotated is more confined. Therefore, its band-gap is bigger.
  - ♦ In addition, the rotation of the phenyls seems to destabilize the states of such ribbon. Then, its bands are shifted up in energy (look the band structure on the right).
- Thus here the observed  $\Delta k$  is not appropriate to draw conclusions about the coupling between ribbons.



# Where is the relaxed and unconstrained structure?

Coming back to the structure relaxed without constraints (slide2), does it follow the rules deduced from the present analysis?

The plot below shows the  $\Delta k$  corresponding to such structure (light green), together with those of the configurations shown in slide 4, where all phenyls were rotated.

