

First principles to low energy

First principles

$$\hat{H} = -\frac{1}{2}\nabla_i^2 - \frac{1}{2m_\alpha}\nabla_\alpha^2 + \frac{1}{r_{ij}} + \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} - \frac{Z_\alpha}{r_{i\alpha}}$$

Interactions ~ 30 eV/electron

$$\hat{H}\Phi_i(R, X) = E_i\Phi_i(R, X)$$

Many-body coordinate

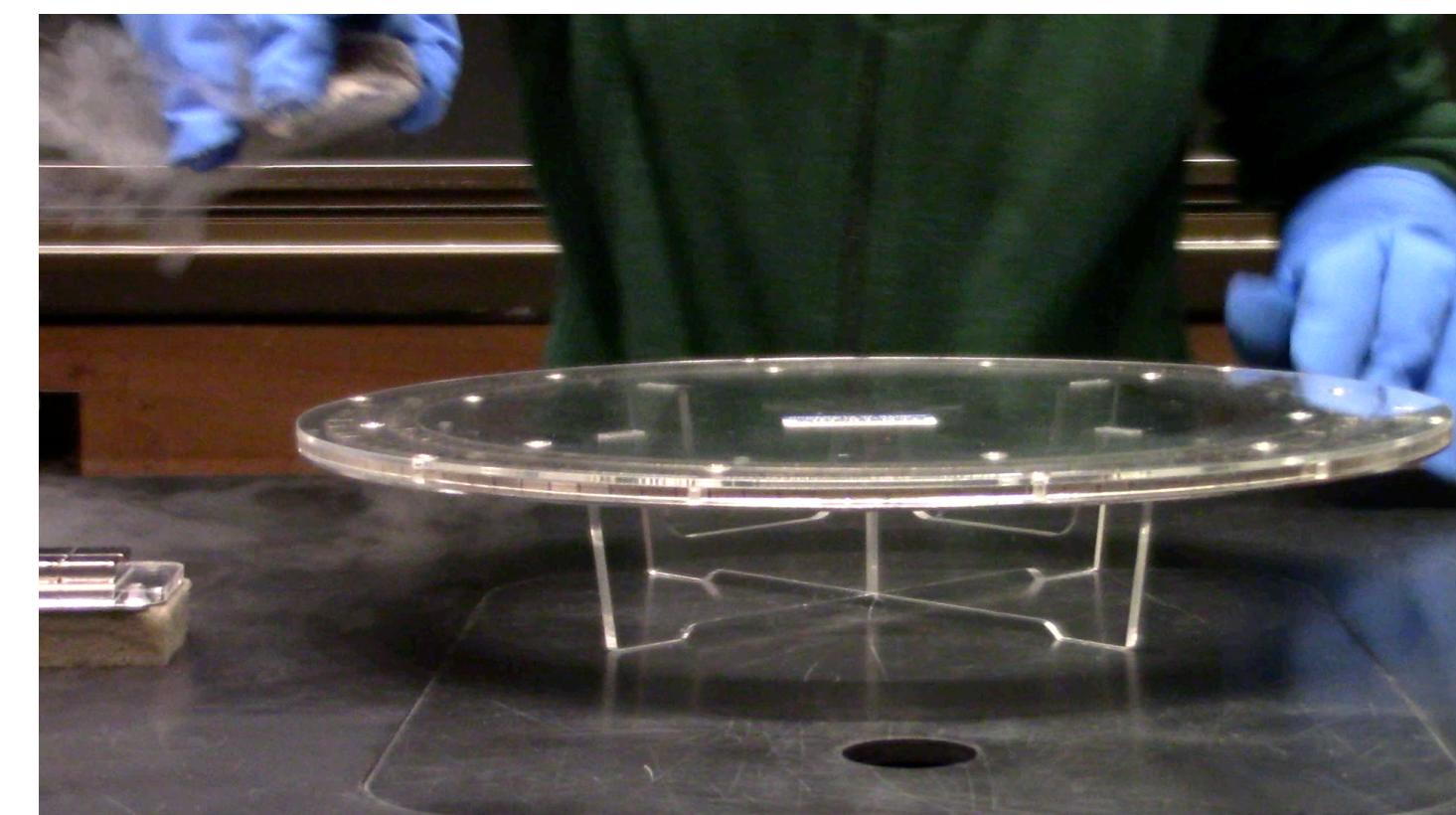
Low-energy (entire material)



Gaps: ~ 1 eV



Magnetism: ~ 0.01 eV



Superconductivity: ~ 0.001 eV

Why create models?

Simplification and communication

Best simple approximation to a complex system

Scaling up in system size/timescale

Create model on small system -> apply on big system

Higher accuracy on a challenging subspace

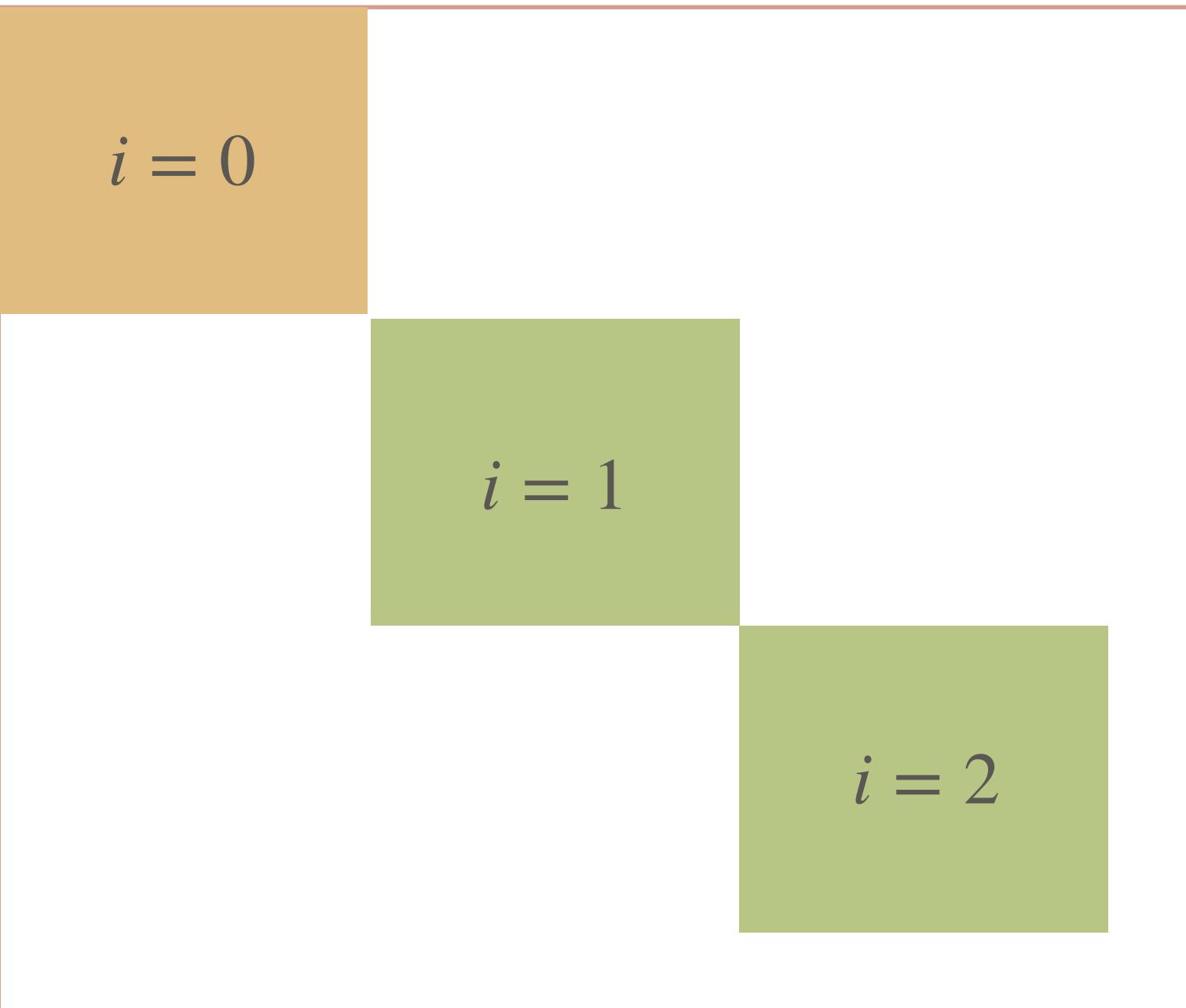
Remove “easy” physics and solve only the hard part.

Today

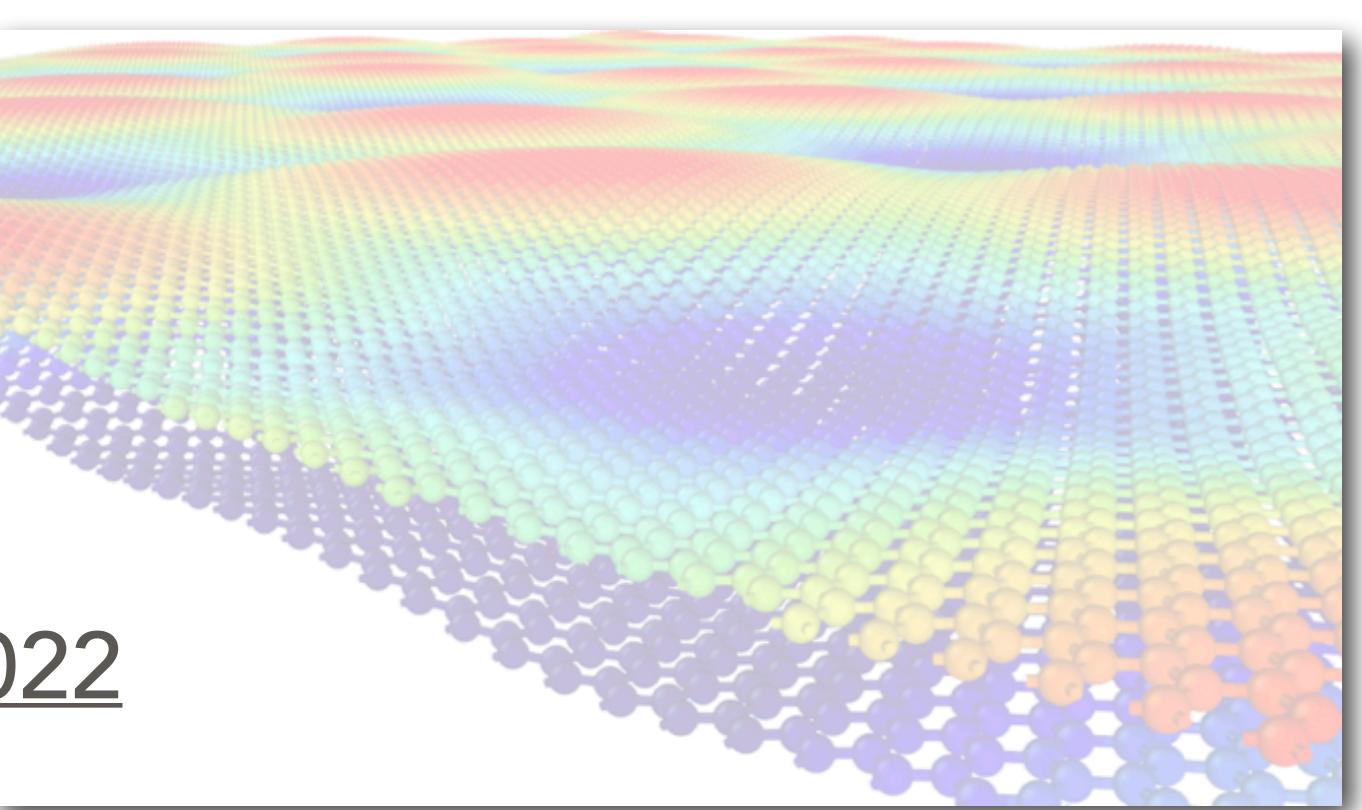
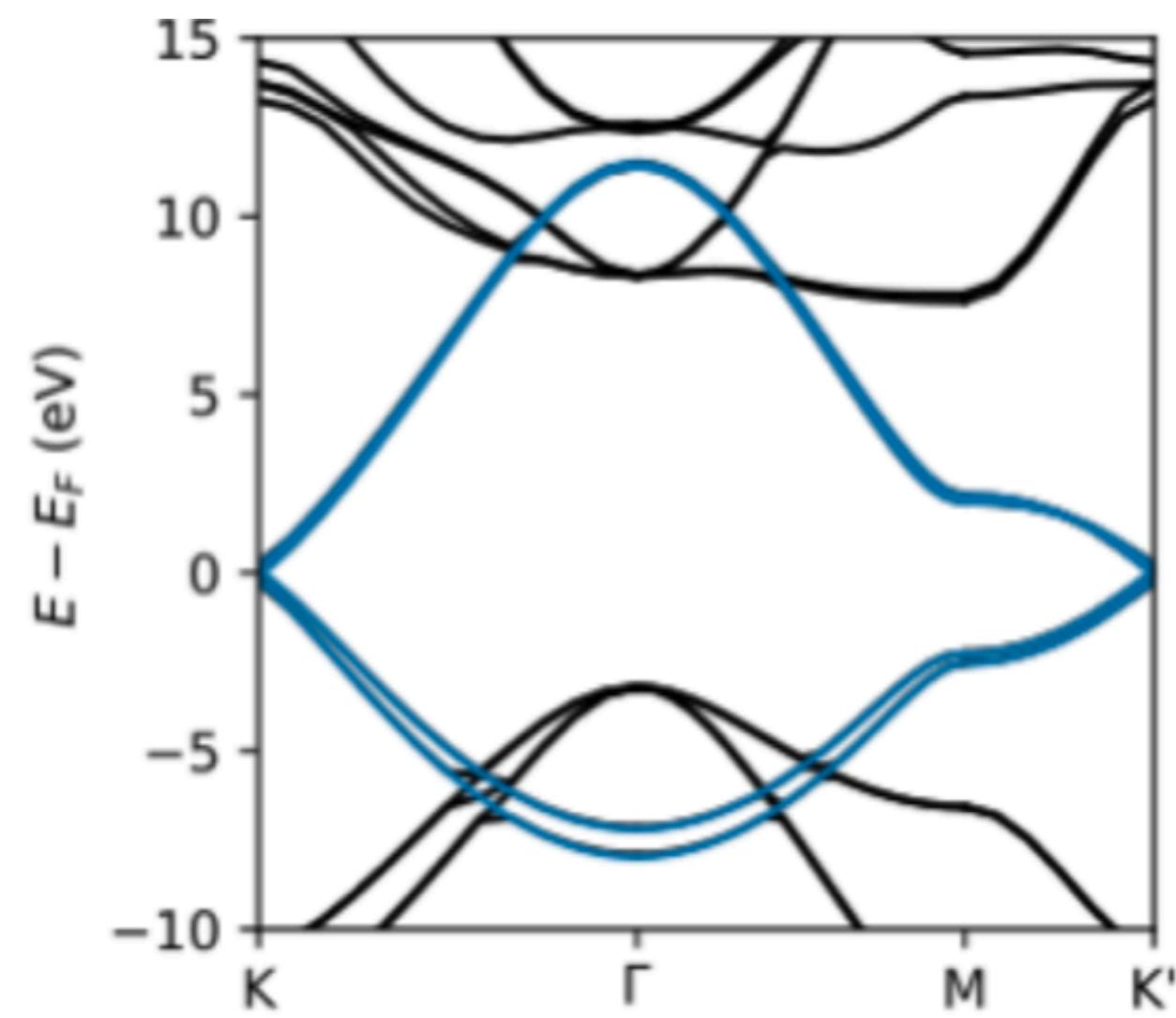
Basic idea of downfolding



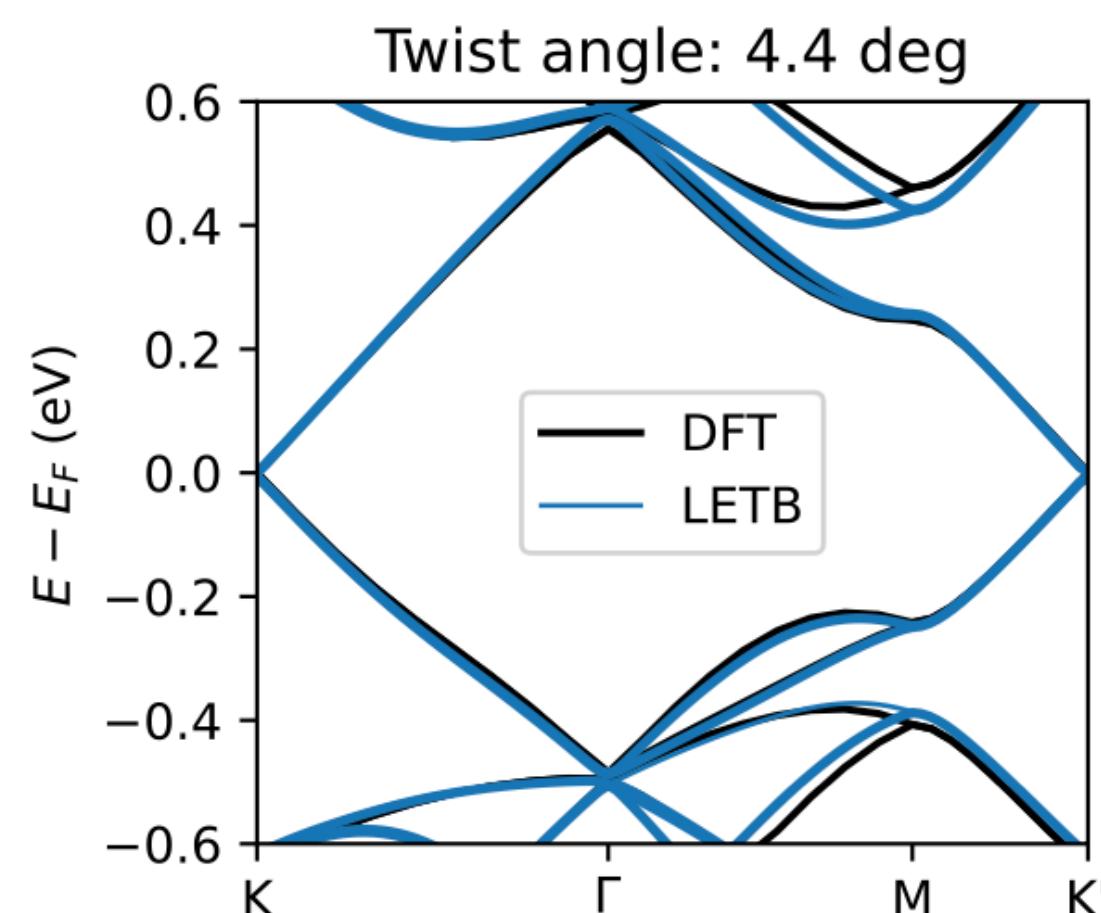
Downfolding to atomic potentials



Downfolding to tight-binding



github.com/lkwagner/Simons_downfolding_2022



Fundamental principle

H_{eff}

Accurate representation for energies less than E_N .

- 1) Find low-energy eigenstates
- 2) Write out H

BUT:

- a) Not transferable to other systems (even other k-points!)
- b) Hard to understand; e.g. driving force of transitions.

$$H_{eff} = \sum_i^N |\Phi_i\rangle E_i \langle\Phi_i|$$

Introduction to models and “downfolding”

First principles

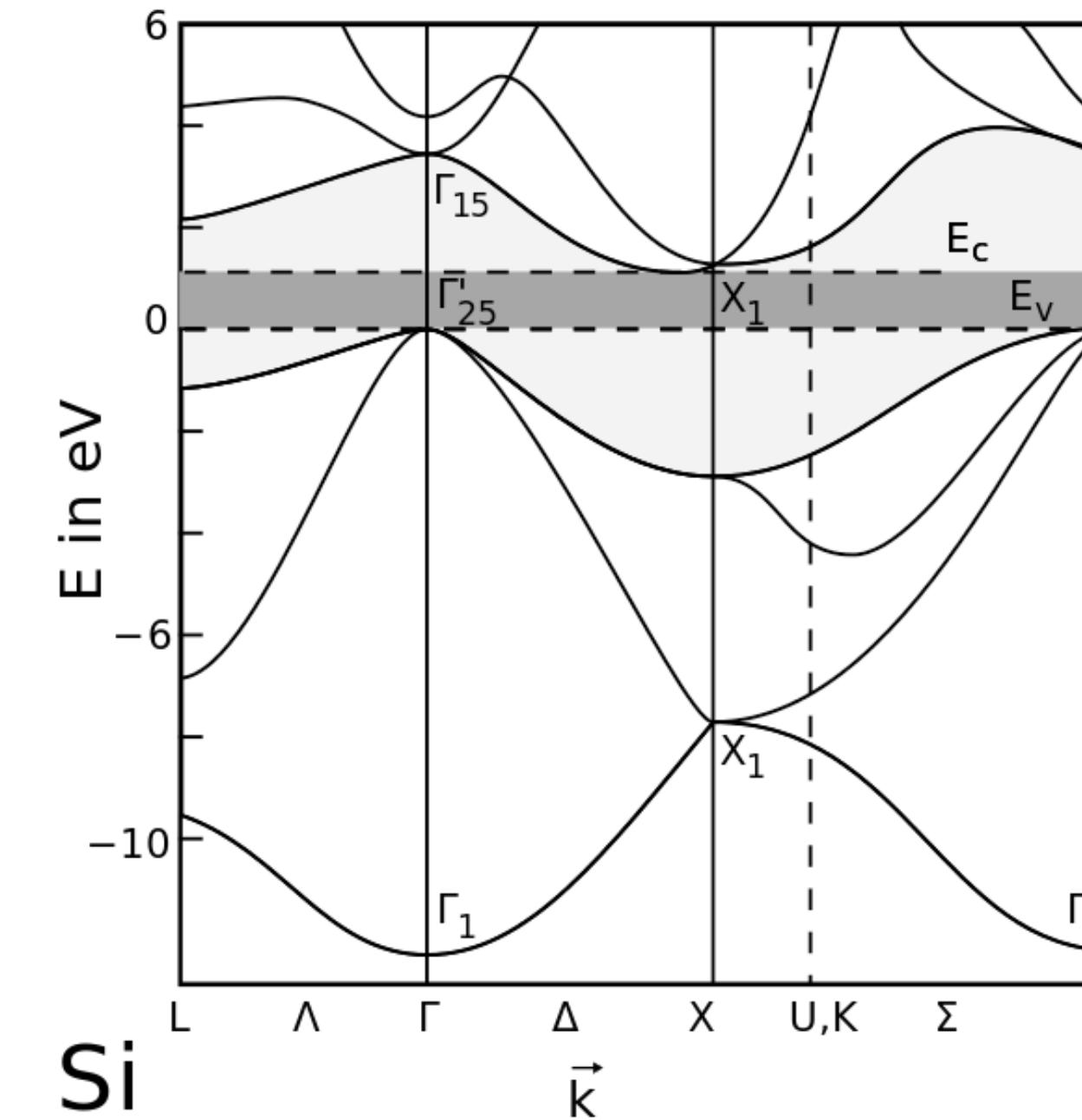
$$\hat{H}_e(X) = -\frac{1}{2}\nabla_i^2 + \frac{1}{r_{ij}} + \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} - \frac{Z_\alpha}{r_{i\alpha}}$$

Interactions ~ 30 eV/electron

$$\hat{H}_e(X)\Phi_i(R | X) = E_i\Phi_i(R | X)$$

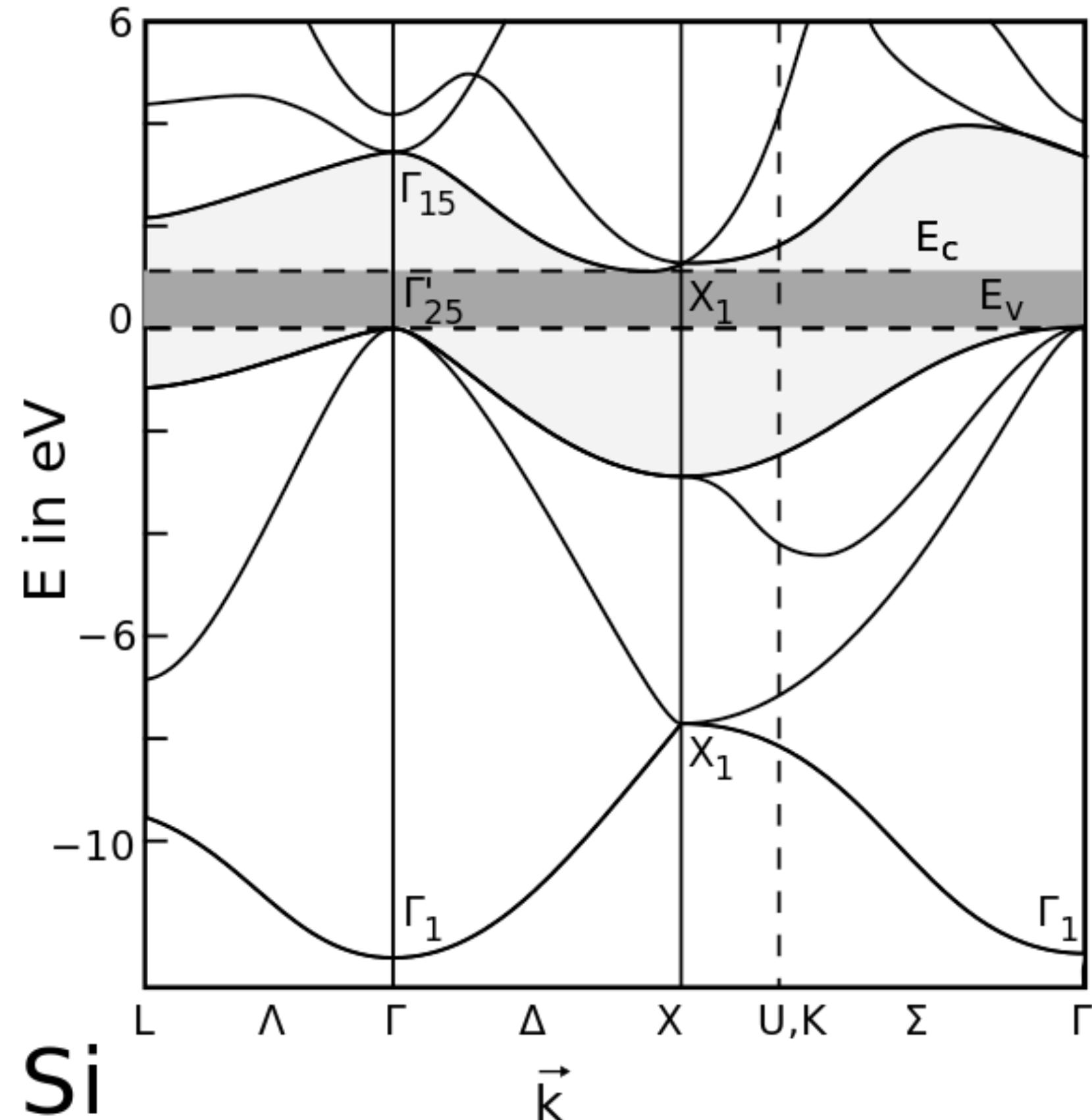
Many-body coordinate

Band structure



$$\hat{H}_{band} = \epsilon_{i,k} c_{i,k}^\dagger c_{i,k}$$

The importance of correlations



Gap in Hartree-Fock from first principles, ignoring correlations: ~ 6 eV

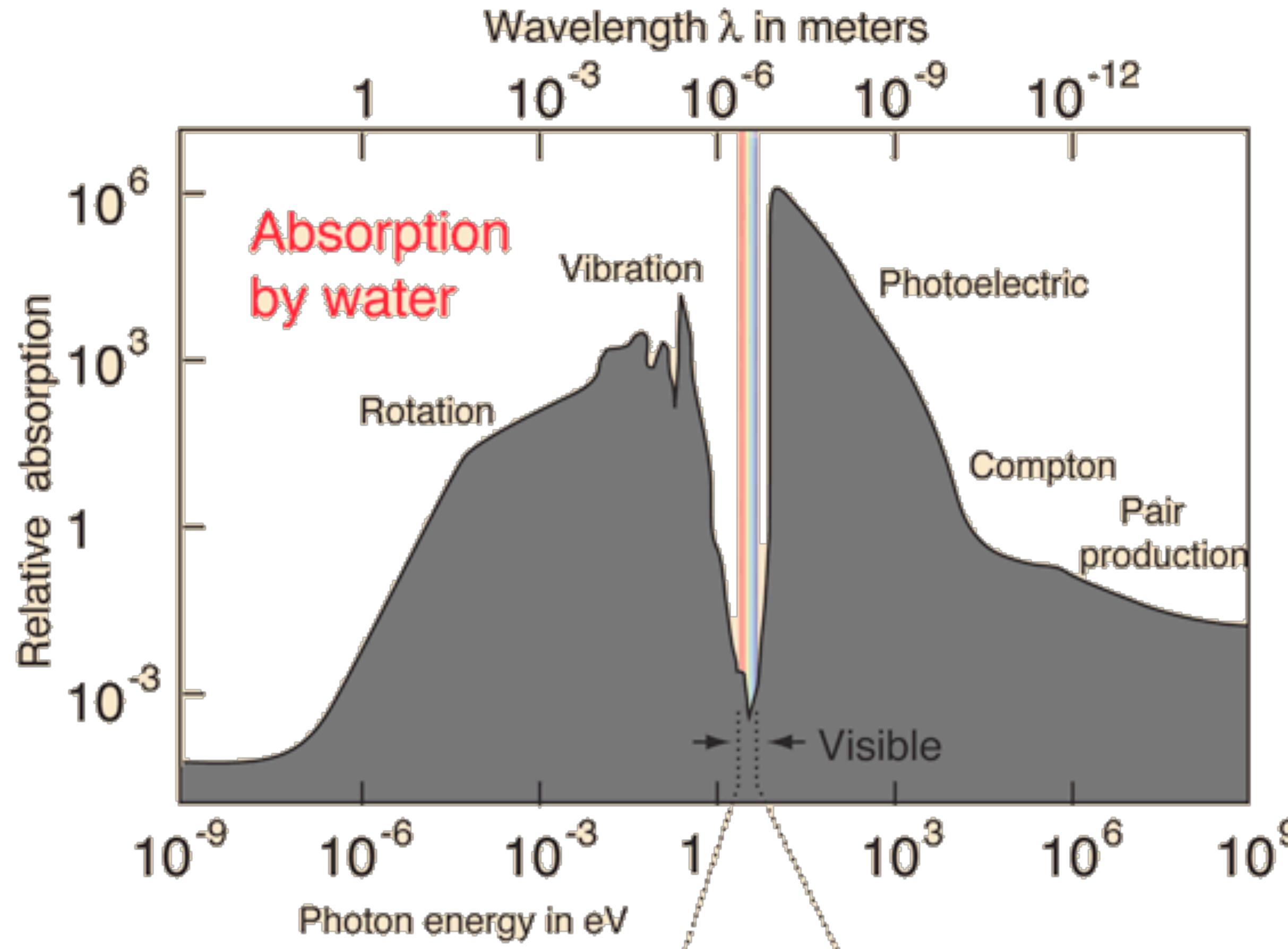
Gap in reality: ~ 1.1 eV

In first principles, silicon looks like a strongly interacting, strongly correlated material.

The effective low-energy model looks like a non-interacting, uncorrelated material.

Emergence!

The simplest downfolding: atomic potentials



At low energy, all excitations are rotation and vibration.

Described by atomic positions.

Note that this does not mean that the electrons "do nothing."

Assumption:

$$H_{eff} = -\frac{p_\alpha^2}{2m_\alpha} + V(X)$$

Born-Oppenheimer approximation

$$H = -\frac{p_\alpha^2}{2m_\alpha} + H_e$$

Define electronic eigenstates

$$H_e(X) |\Psi_i(X)\rangle = V_i(X) |\Psi_i(X)\rangle$$

Then the Born-Oppenheimer approximation says

$$H \Phi_{i,j}(X) \Psi_i(R, X) \simeq E_{i,j} \Phi_{i,j}(X) \Psi_i(R, X)$$

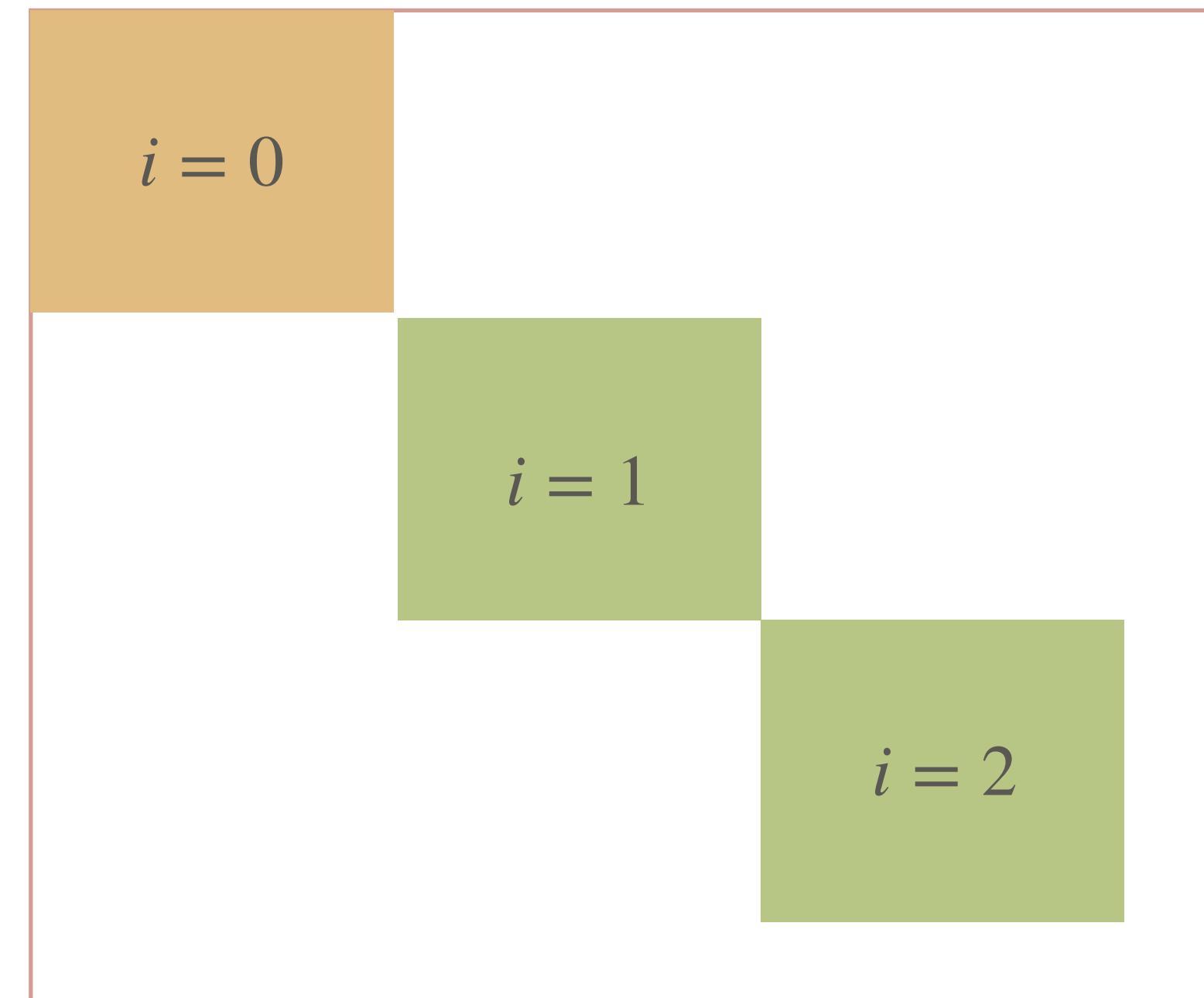
The low-energy space

$$H\Phi_{i,j}(X)\Psi_i(R, X) \simeq E_{i,j}\Phi_{i,j}(X)\Psi_i(R, X)$$

$$H_{eff} = -\frac{p_\alpha^2}{2m_\alpha} + E_0(X)$$

Atomic wave function

Electronic wave function
(quantum chemistry)



Plan to find this low-energy space: solve for the ground state as a function of X.

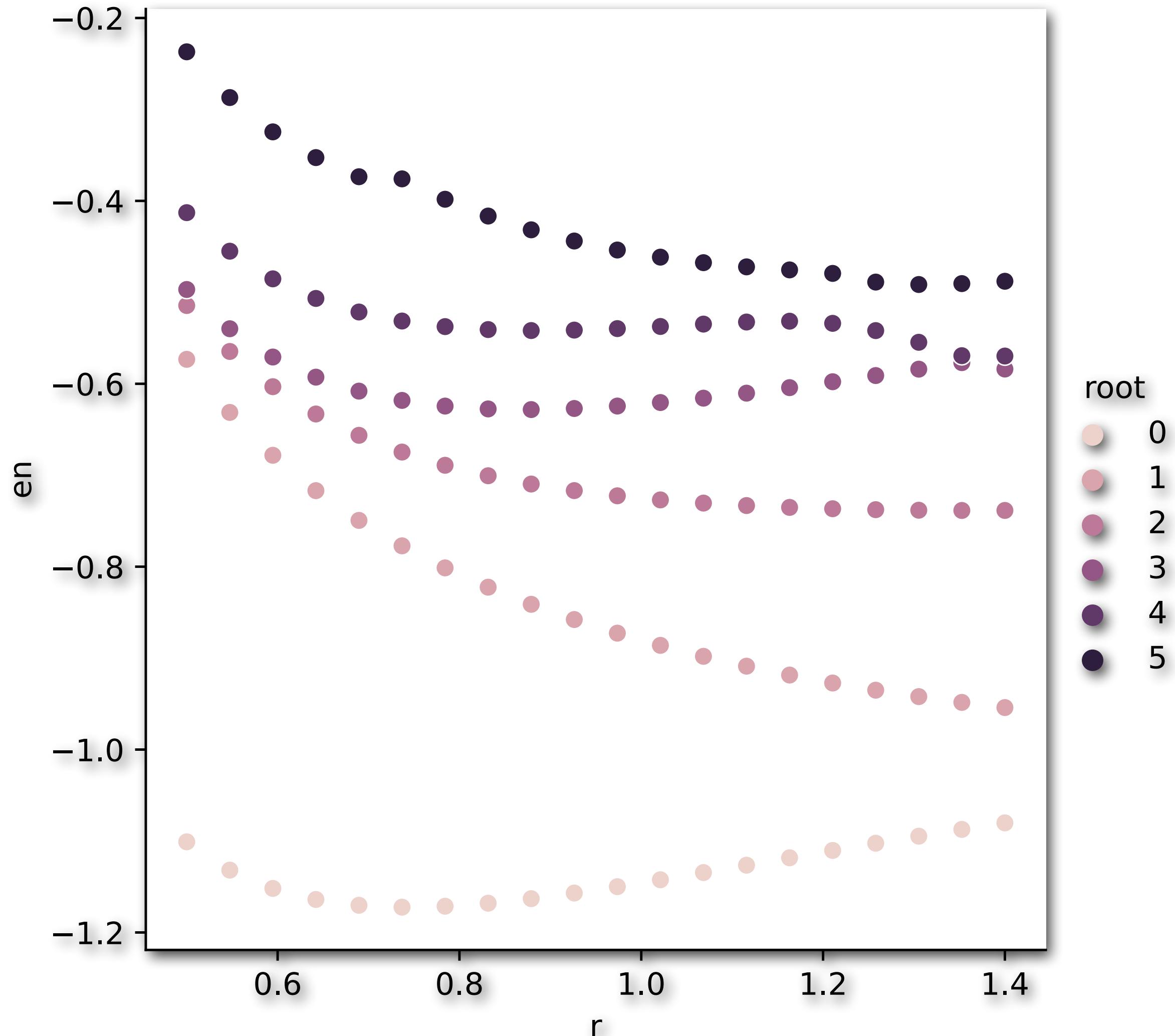
Example: PES for H₂

Next step: compression

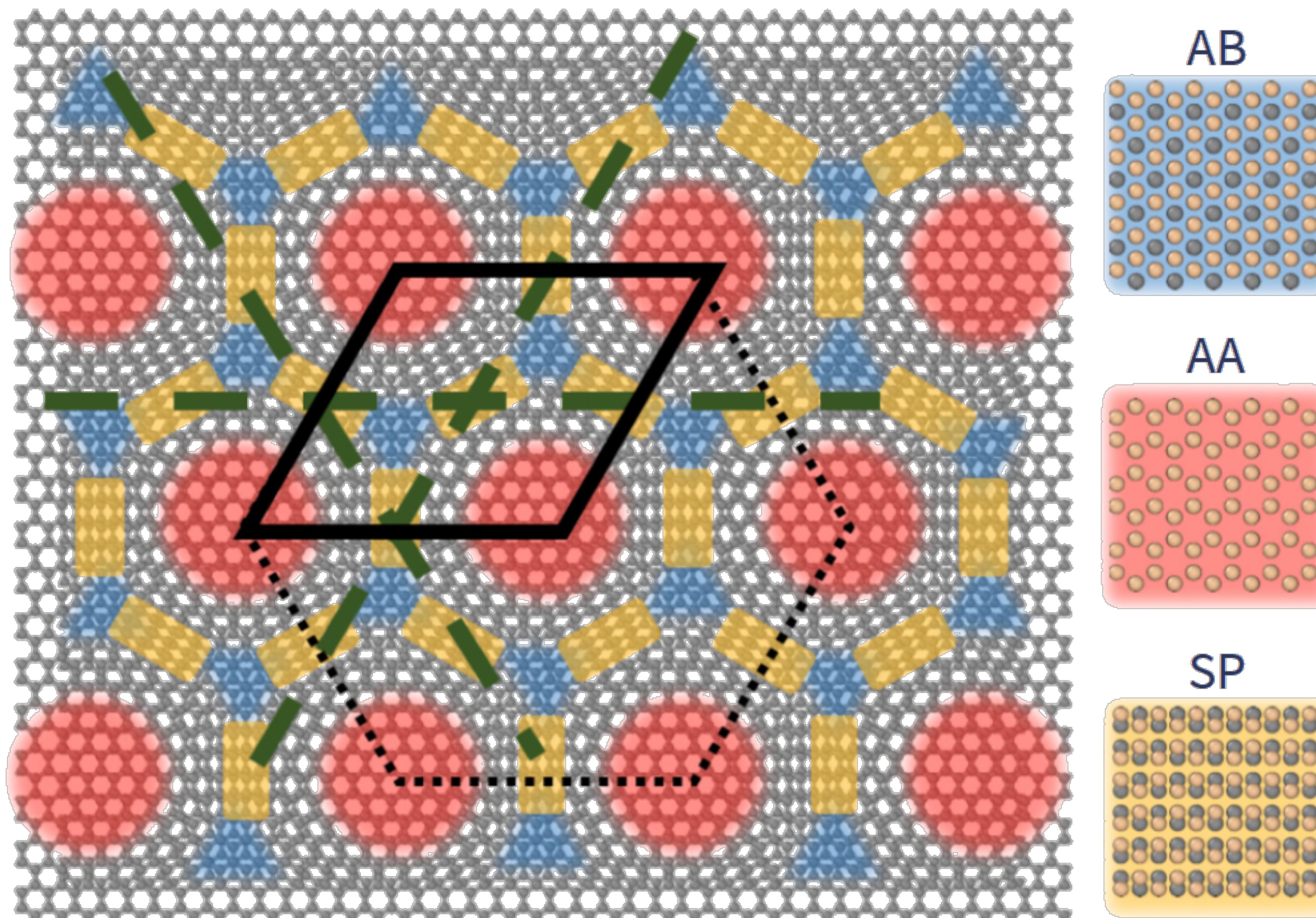
Data is useful but suppose we'd like to solve for the vibrational levels.

Easiest with a closed-form function for $V(X)$.

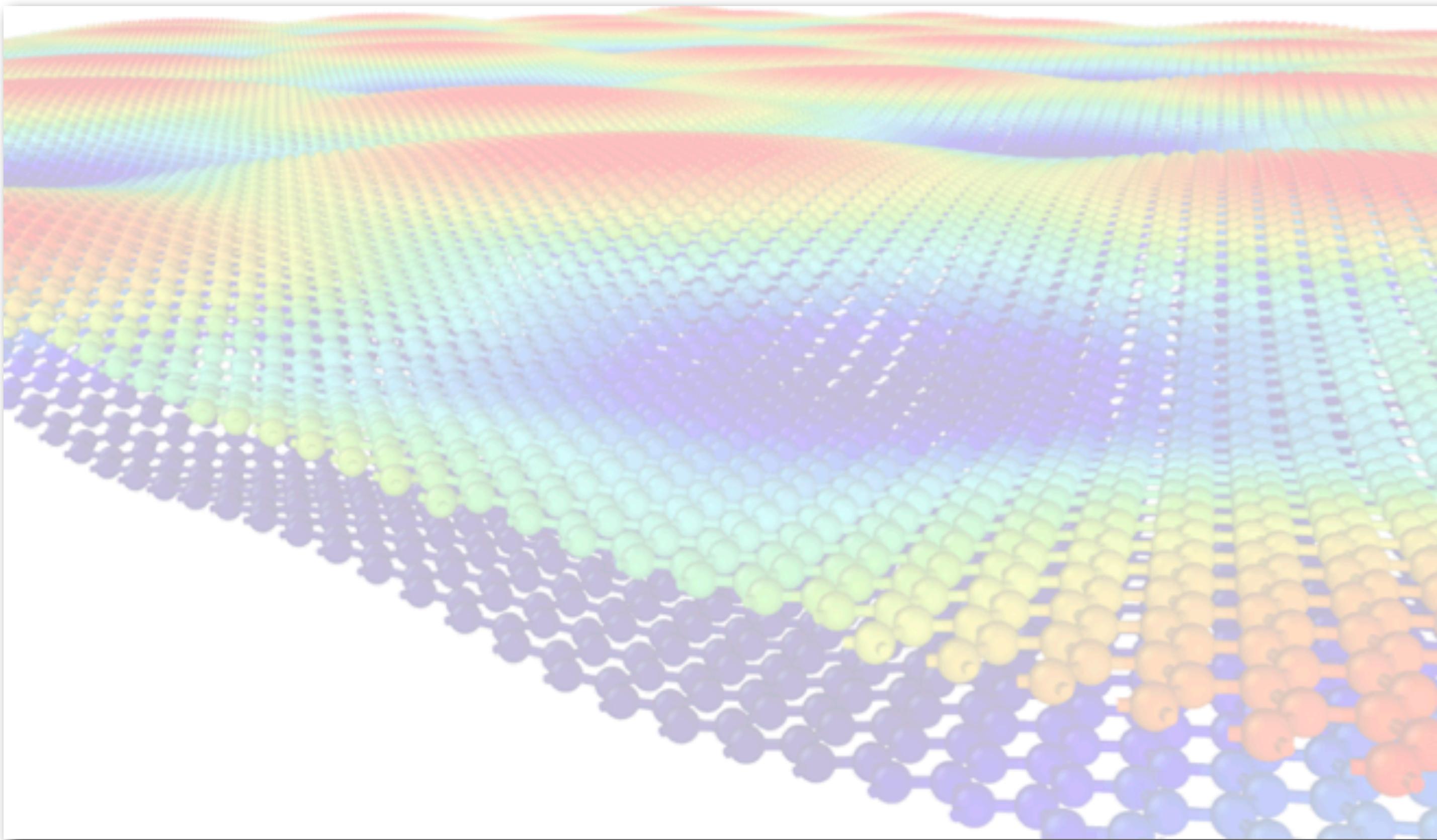
This is done by fitting!



Application: twisted bilayer graphene



Focus of today: Interlayer interaction in graphene bilayers

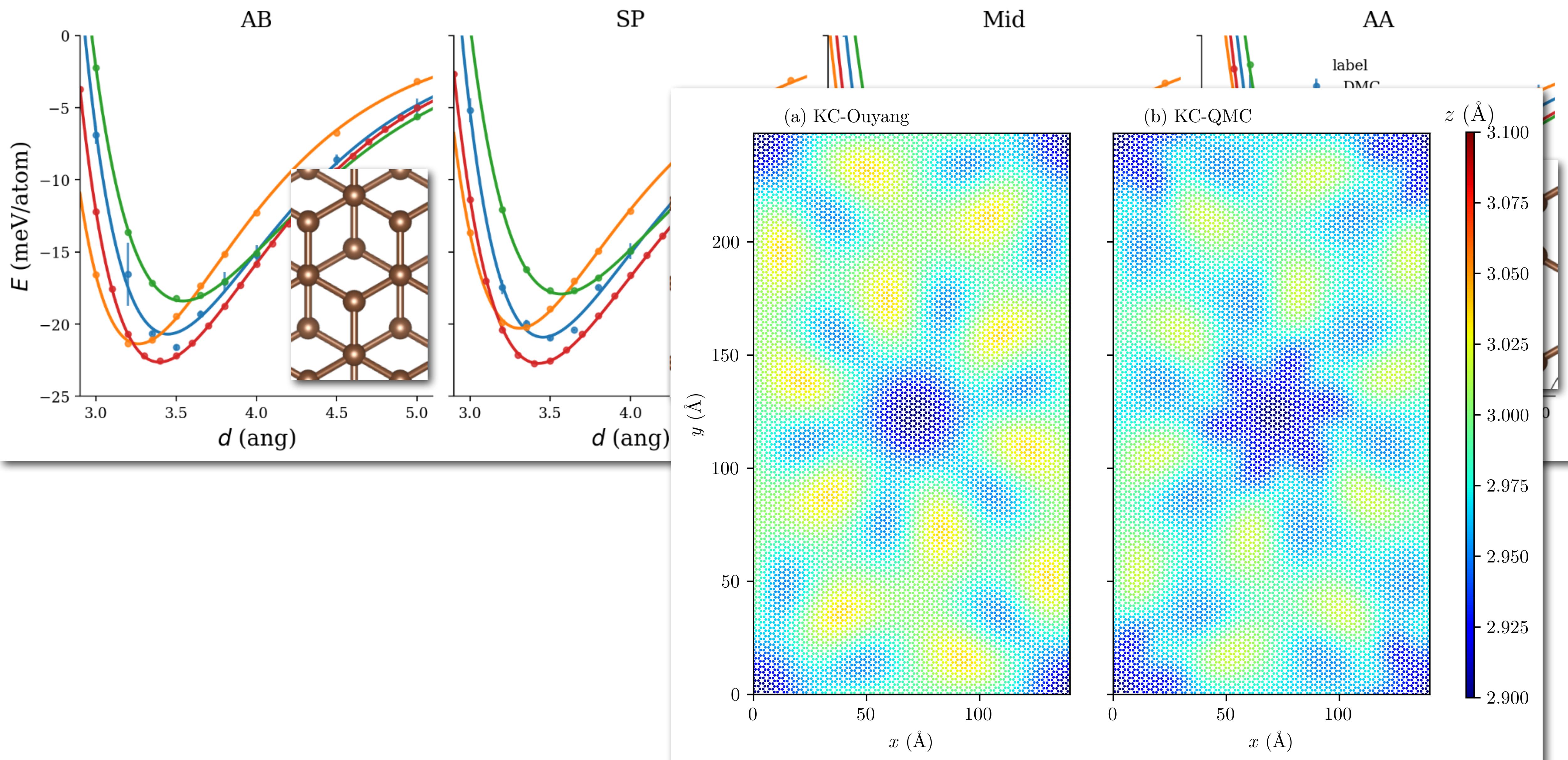


AA stacking: pushed apart

AB stacking: pulled closer

-> corrugations

Example: graphene interaction energy (Mick)



Summary for part 1

Separation into separate sectors via (Born-Oppenheimer)

1

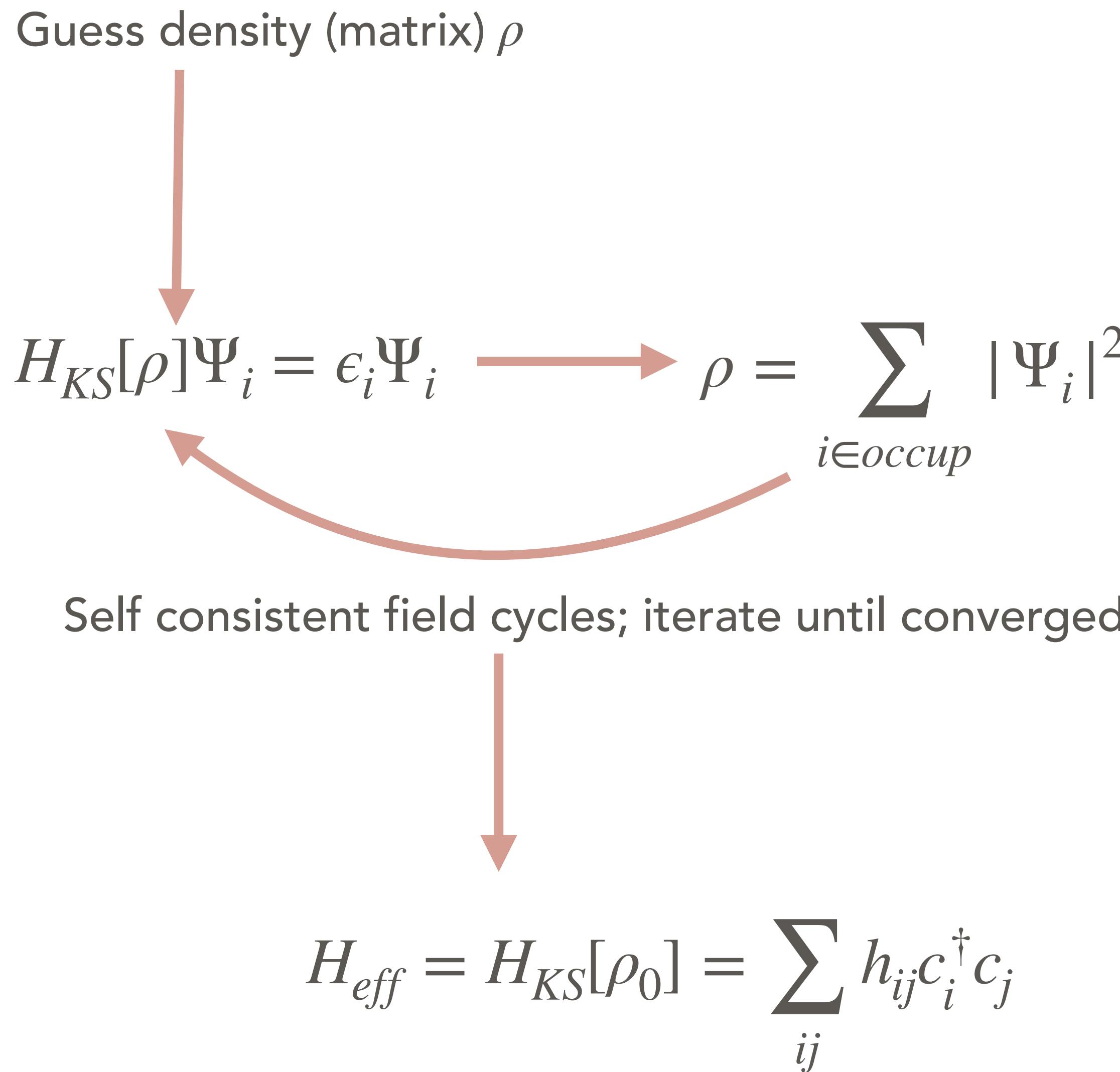
Find states within each sector (quantum chemistry in B-O approx)

2

Fit Hamiltonian within each sector (Fit to $V(x)$)

3

Mean-field band structure models



Downfolding electrons: band structure

Now consider fixed nuclei at X.

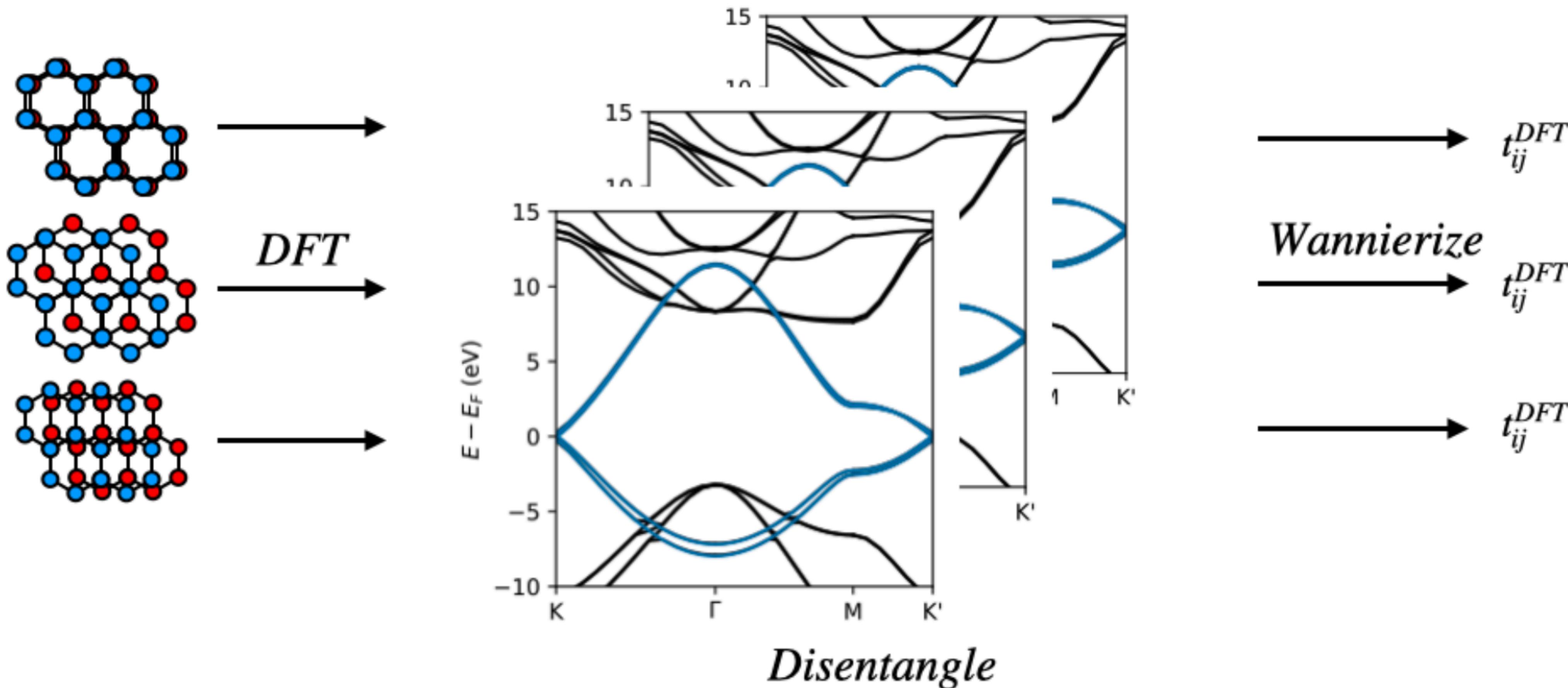
DFT “band structure” is the eigenenergies of H_{KS}

Since we’ve already diagonalized this Hamiltonian, we can choose any separation into sectors. Some will compress better than others.

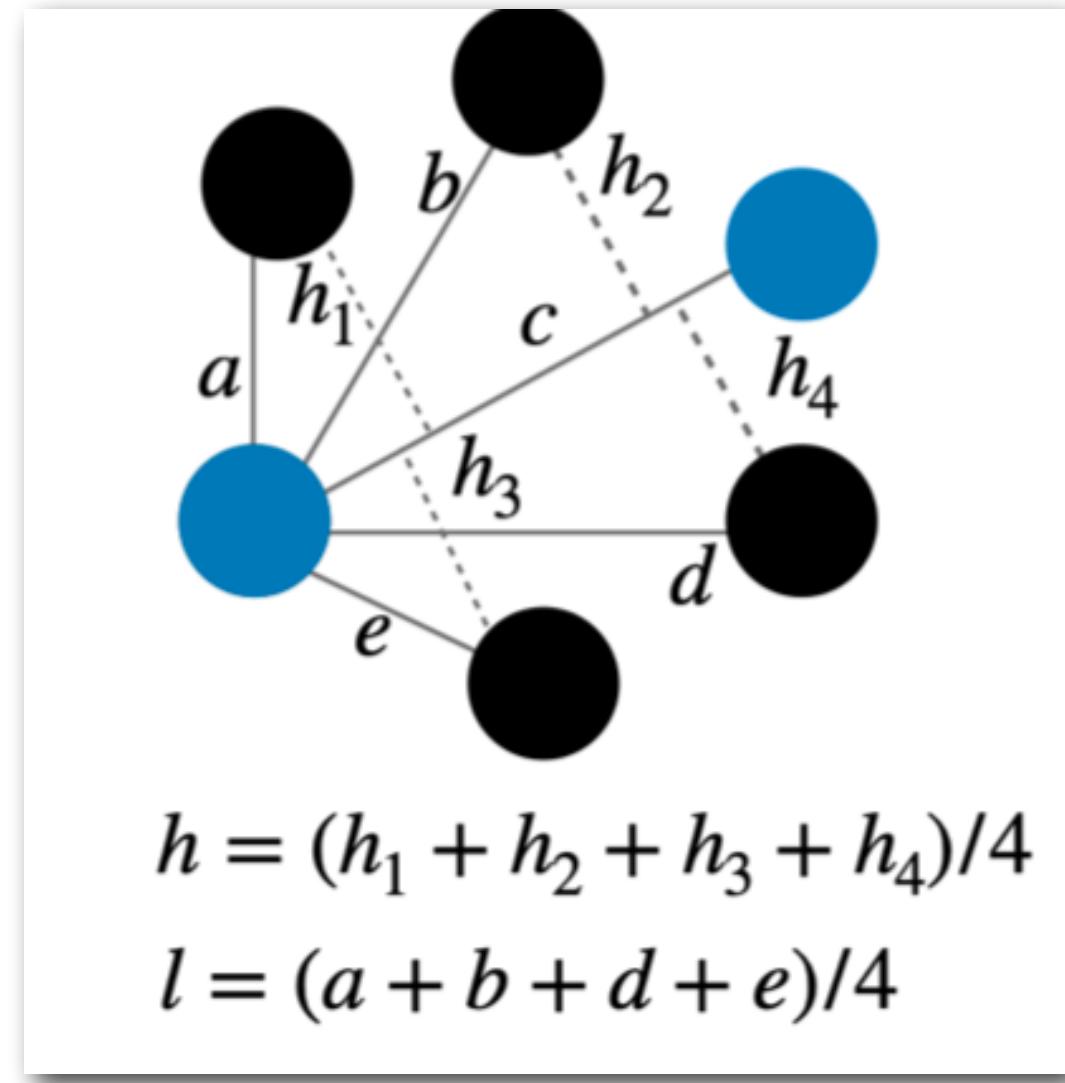
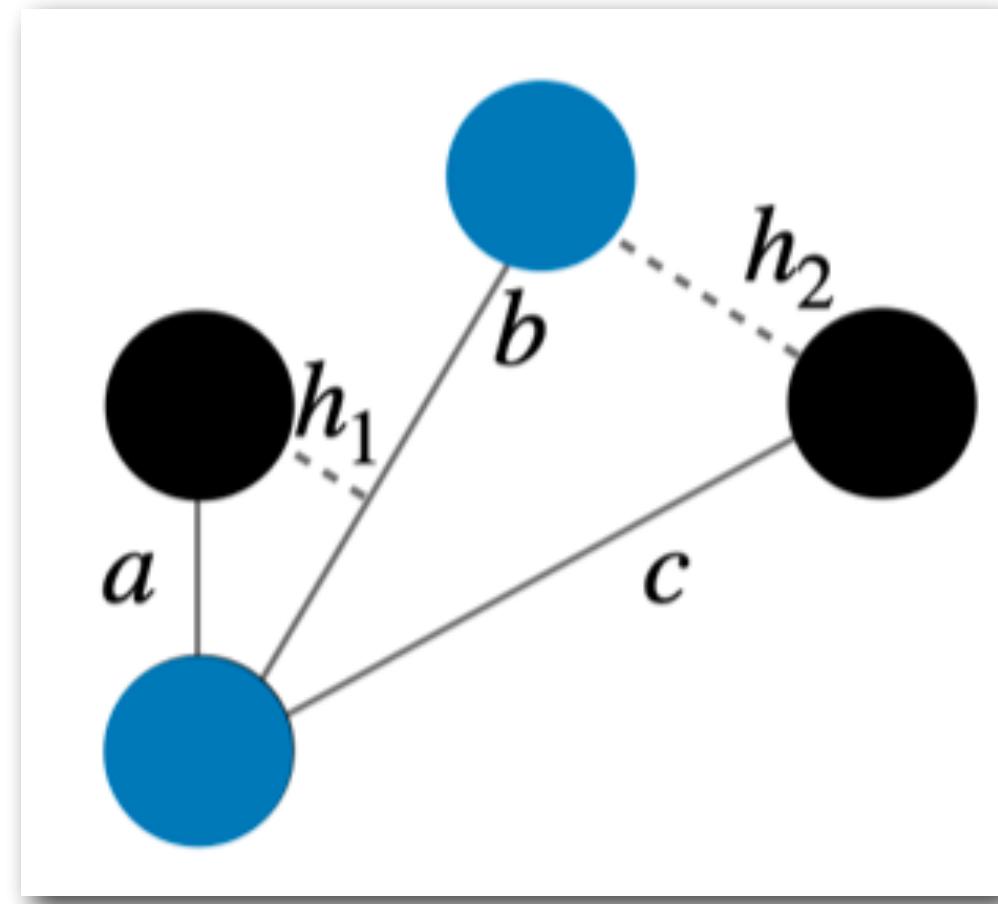
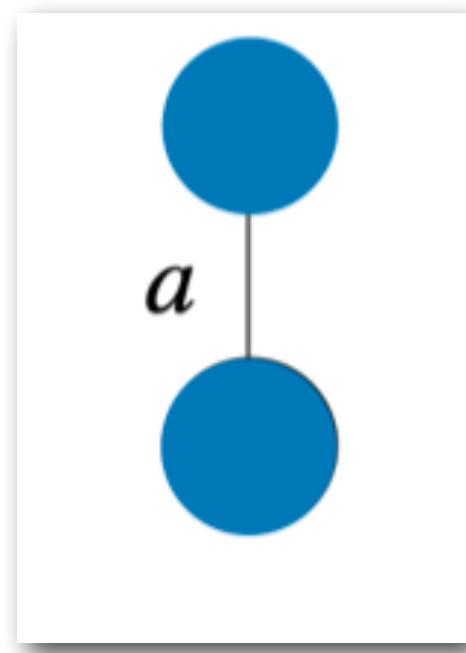
$$H_{KS} = [c_1^\dagger \quad c_2^\dagger] \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix} [c_1 \quad c_2]$$

Example: H2

Example application: local environment tight binding model of graphene



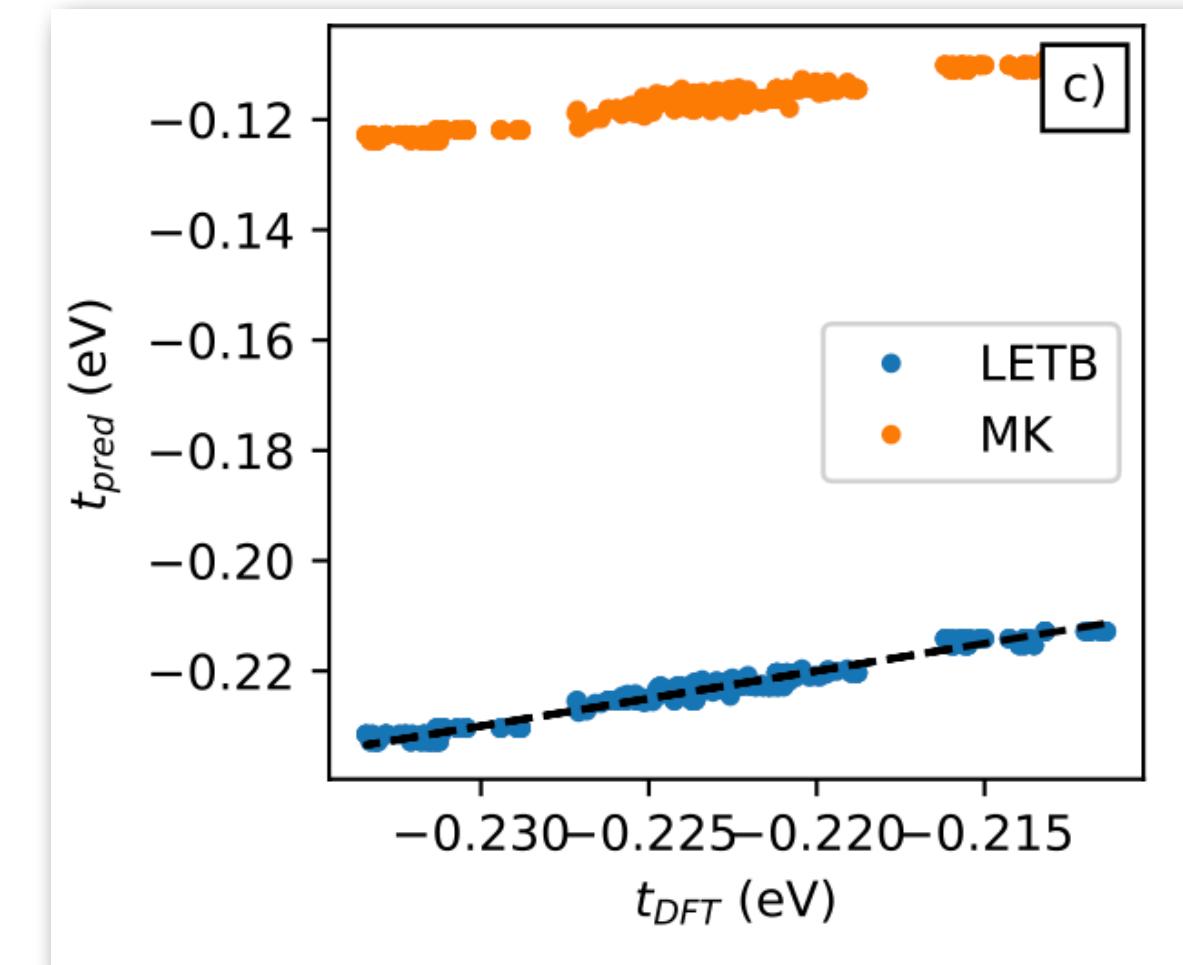
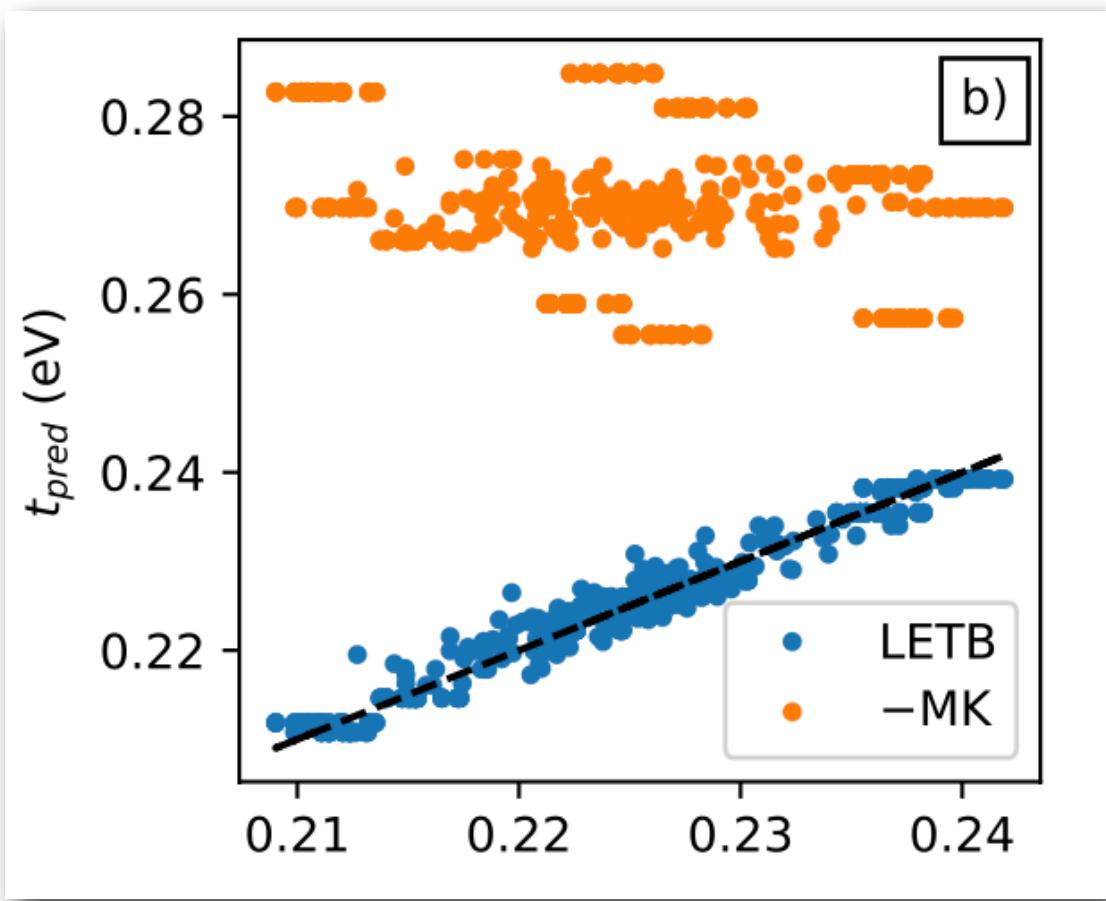
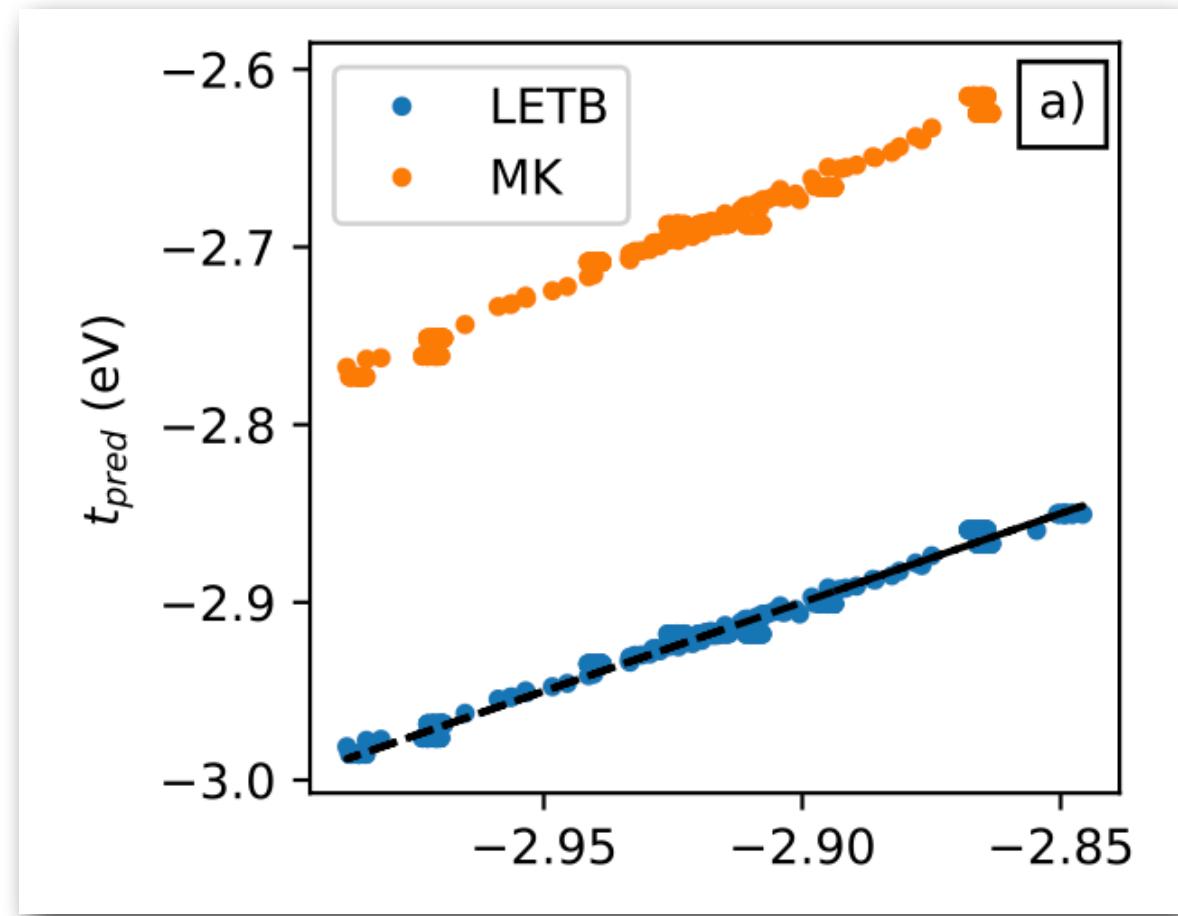
Describing the t's



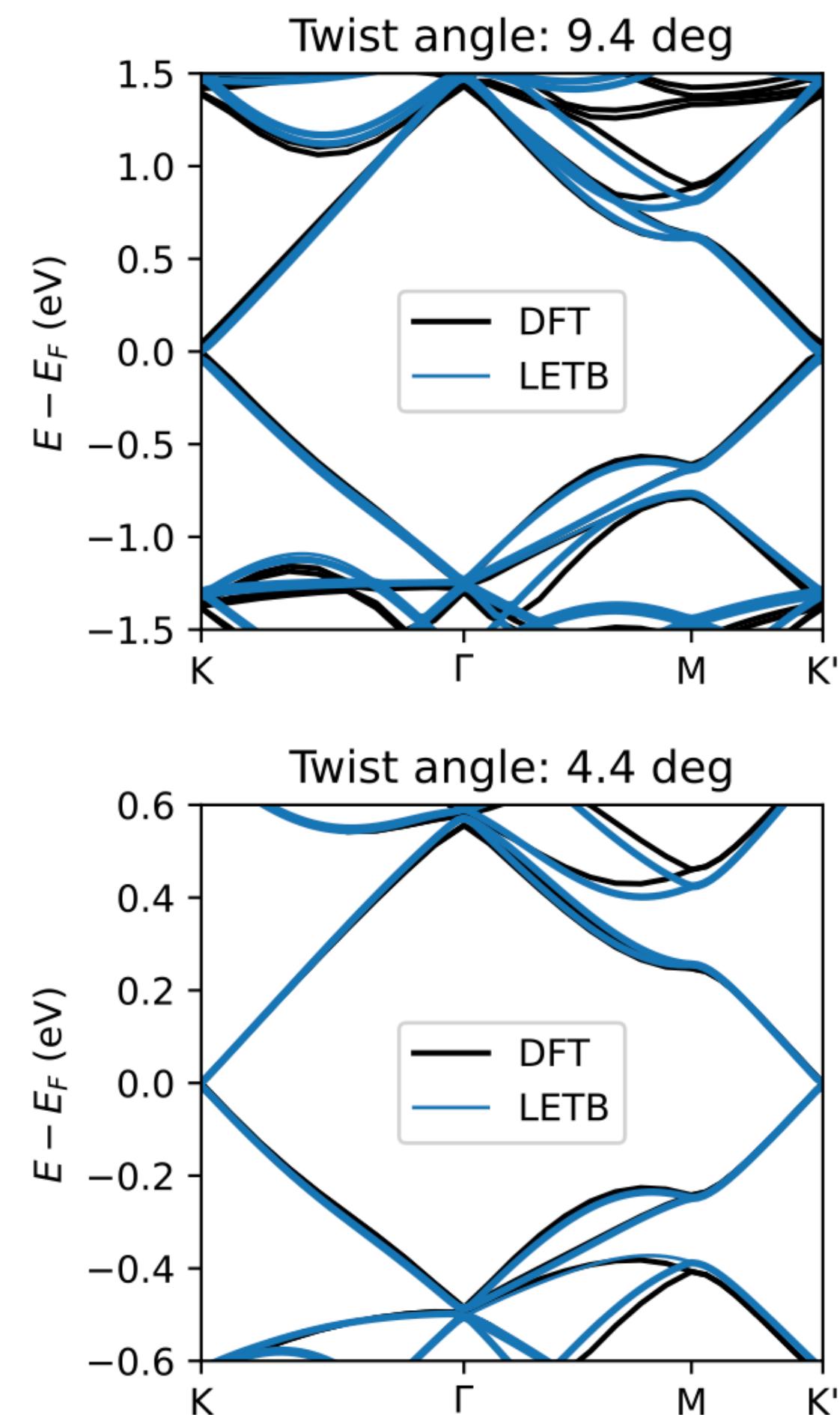
Nearest neighbor:

descriptor is just distance

Nearest-

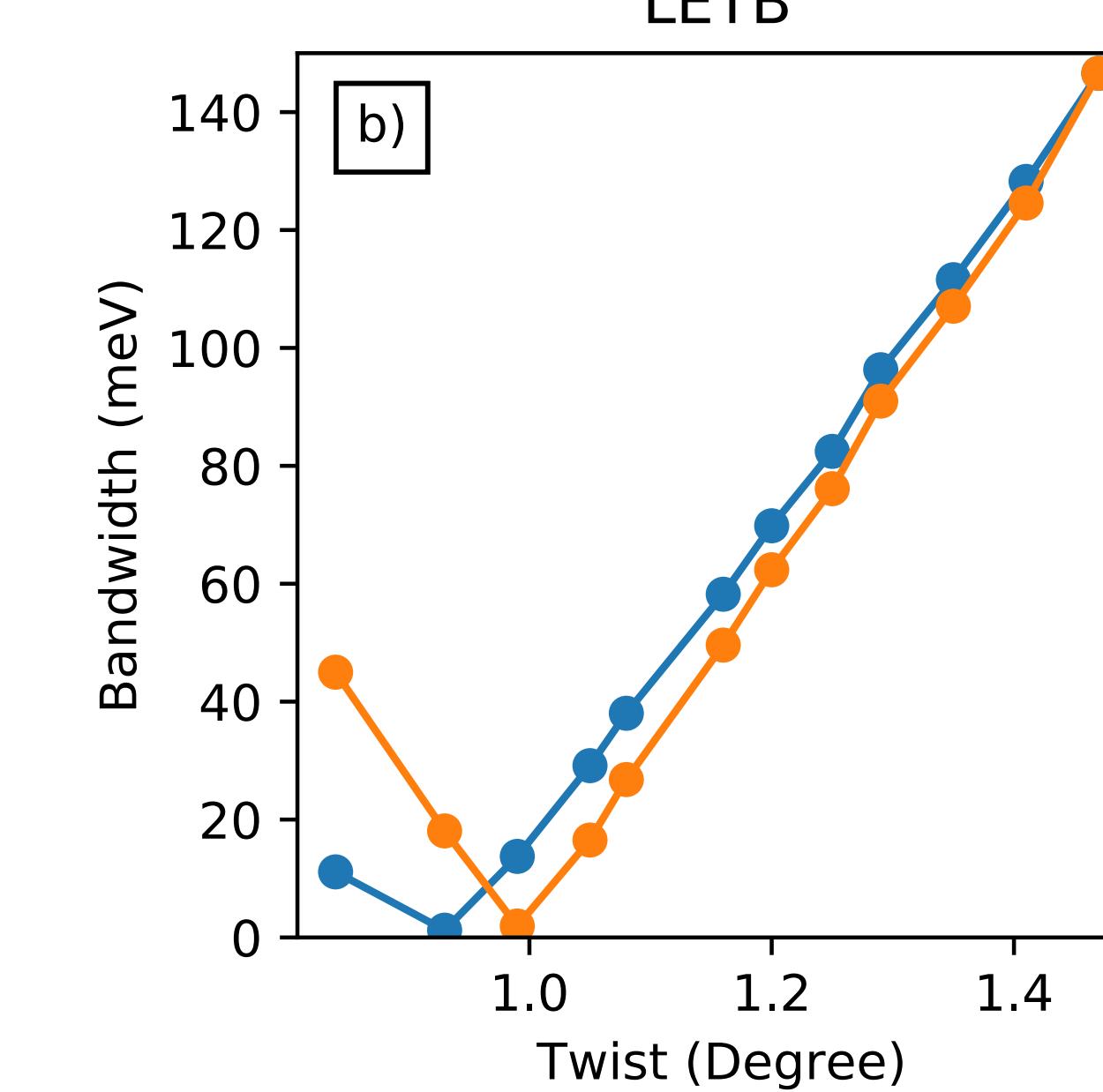
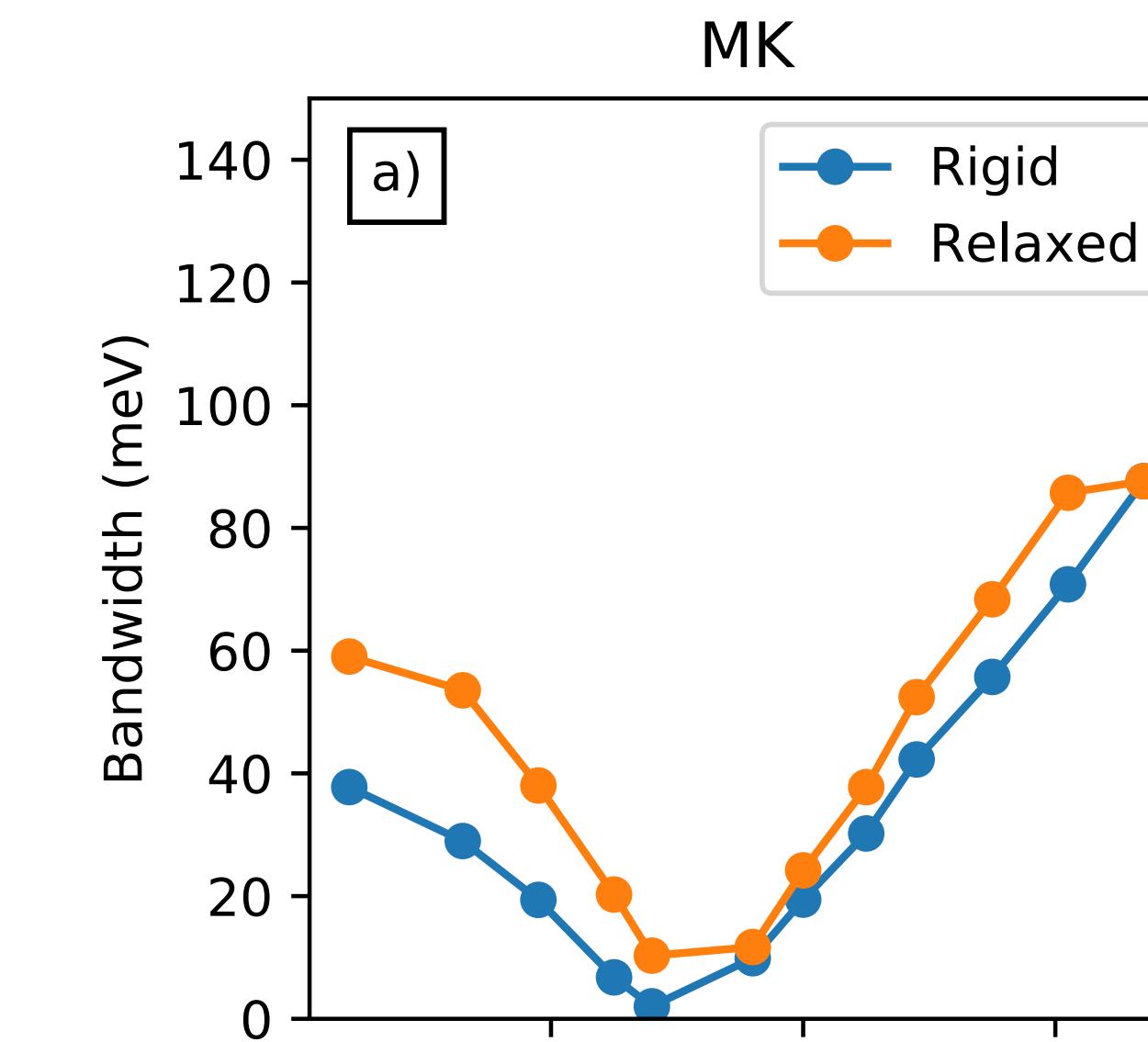
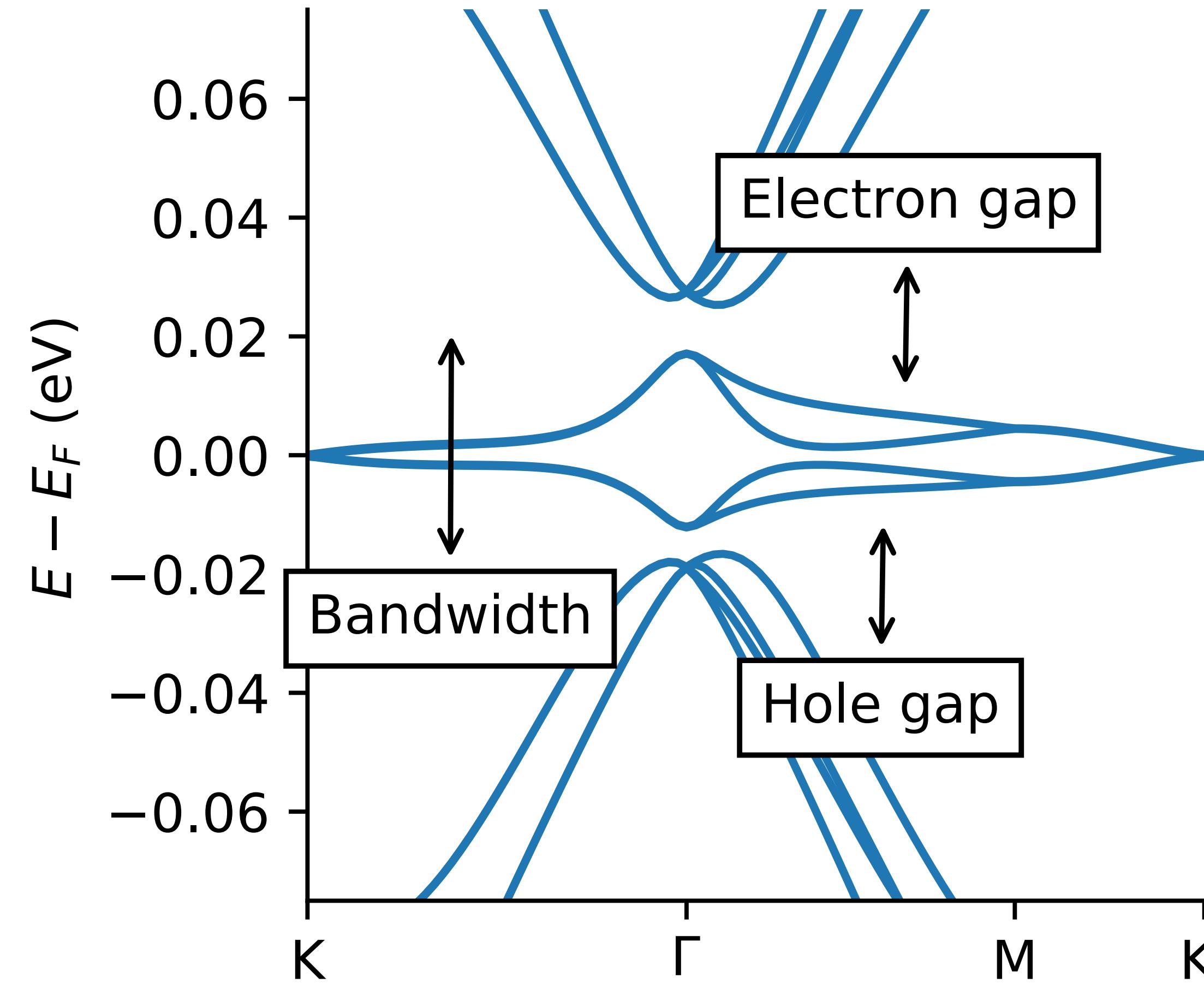


Validation



The model never saw twisted bilayer graphene

Reproduces DFT results on twisted graphene almost perfectly



Summary

1

Divide into high and low energy parts

Born-Oppenheimer

Diagonalize H_{KS} , choose bands

2

Find states within low-energy sector

Quantum chemistry

Diagonalize H_{KS}
(already did it)

3

Compress Hamiltonian within each sector

Fit to $V(x)$

Rewrite in localized basis

Discussion questions

Will improving models always improve agreement with experiment?