

Evaluation of model parameters

This task is intended to show the simplest examples of tight-binding models based on LDA band structures. Tight-binding fits provide hopping parameters that can be further introduced into model hamiltonians and applied to the derivation of various quantities. The task includes several problems. The first problem deals with a very basic model, while further tasks suggest extensions of this model and show possible extensions/complications of the fitting procedure.

In all the problems, we consider the (effective) one-band Hubbard model for the $t \ll U_{\text{eff}}$ regime. Then, the low-lying excitations can be mapped onto the Heisenberg model, and the transfer integrals t_i allow to find the exchange integrals $J_i^{\text{AFM}} = 4t_i^2/U_{\text{eff}}$. The exchange integrals define magnetic interactions in the system under investigation. For all the calculations, take $U_{\text{eff}} = 4$ eV that should be a reasonable estimate for Cu-containing materials.

I. Chain of edge-sharing copper plaquettes

1. Create a new directory and run **fedit**. Enter the following structural data for CuCl_2 (for simplicity, we made a fictitious crystal structure; the real structure of CuCl_2 can be found in task III):
 - Space group: $Pmmm$
 - Lattice parameters: $a = 8.0 \text{ \AA}$, $b = 3.3 \text{ \AA}$, $c = 8.0 \text{ \AA}$
 - Atoms: Cu(0, 0, 0) and Cl(0, 0.5, 0.193)
2. Start the self-consistent calculation (convergence time – 2 min)
3. While the calculation is running, get familiar with the crystal structure. You should find that Cu atoms are surrounded by four chlorines. The resulting CuCl_4 plaquettes share edges and form chains along the b direction. Find the local coordinate system for Cu atoms: the z axis should be perpendicular to the $[\text{CuCl}_4]$ plane, the x axis should run along one of the Cu–Cl bonds.
4. After the calculation is converged, run **fedit** once again. Go to the (B)andplot menu and put a cross against the "(B)andstructure plot" option. Add the number of the Cu position to "Local (D)OS sites" and setup the proper local coordinate system ["X-(A)xis" and "(Z)-axis" options]. To change the local coordinate system, put a cross against the "(T)ransform local axes" option. Note that the \mathbf{x} and \mathbf{z} vectors should be given in cartesian coordinates. To find the number of the Cu position, have a look at the **out** file.
5. Run **fplo** once again to calculate the density of states and the bands.
6. Plot the total and atomic-resolved DOS. You should find one isolated band near the Fermi level. Plot the orbital-resolved DOS for Cu d orbitals (+ldos.site001.nl005) and find the origin of this band. Compare the result with the intuitive crystal field considerations. You should find that the states near the Fermi level originate from the Cu $d_{x^2-y^2}$ orbital (once the proper local coordinate system is found). If this is not the case, check your

local coordinate system. Note that the $d_{x^2-y^2}$ and d_{xy} orbitals can be interchanged by changing the \mathbf{x} axis.

Hint – FPLO uses the following notation for individual d orbitals: $m = -2$ (d_{xy}), $m = -1$ (d_{yz}), $m = 0$ ($d_{3z^2-r^2}$), $m = 1$ (d_{xz}), $m = 2$ ($d_{x^2-y^2}$).

7. Run `fedit` with the "-bandplot" option. Use DOS plots to find the reasonable energy window for plotting the bands. Plot the band near the Fermi level.
8. Dispersion of the band shows hoppings along different directions. To analyze these hoppings quantitatively, construct a simple tight-binding model and consider the nearest-neighbor and next-nearest-neighbor hoppings along the structural chains (b direction). Write the general tight-binding hamiltonian (i.e, the $\varepsilon(\mathbf{k})$ dependence) and derive the energies at Γ and Y points. You will also have to take one point between Γ and Y – for example, $\Delta(0, \pi/2b, 0)$.

Hint: FPLO provides reasonable sets of \mathbf{k} points for most of the space groups. You can find this list in the "(B)andstructure plot" menu (the coordinates of individual points are given in Cartesian coordinates in units of $2\pi/a$). In general, one has to plot the bands along the coordinate axes in the reciprocal space ($\Gamma X, \Gamma Y$, and ΓZ directions) and along the edges of the first Brillouin zone.

9. Find the band energies at the Γ, Y , and Δ points. You can roughly estimate the energies from the plot. Alternatively, have a look at the +band file. It contains the coordinates of each \mathbf{k} point (Cartesian system, $2\pi/a$ units) followed by the list of energies for all the bands. The energies are given in eV.
10. Now, you have three equations for band energies at the Γ, Y , and Δ points. These equations include three variables: the orbital energy ε_0 and the two hoppings, t_1 and t_2 . By solving these linear equations, you find t_1 and t_2 . Then, you can also calculate J_1 and J_2 as $4t_i^2/U_{\text{eff}}$. These numbers show the energies of the respective magnetic interactions in the system. Note that the next-nearest-neighbor interaction exceeds the nearest-neighbor one. J_1 is a 90° Cu–Cl–Cu superexchange that has weak AFM contribution. In contrast, J_2 is the Cu–Cl–Cl–Cu interaction mediated by the strong hybridization between the Cu and Cl orbitals.

II. Layer of copper plaquettes – the case of hybridization

1. Setup the calculation for CaCuO_2 :
 - Space group: $P4/mmm$
 - Lattice parameters: $a = 3.86 \text{ \AA}$, $c = 3.2 \text{ \AA}$
 - Atoms: $\text{Ca}(0.5, 0.5, 0.5)$, $\text{Cu}(0, 0, 0)$, and $\text{O}(0.5, 0, 0)$
2. Run the calculation similar to the previous case (convergence time – 3 min). Plot atomic-resolved and orbital-resolved density of states. Plot also the bands near the Fermi level.

3. In CaCuO_2 , you will find wide valence bands with sizable hybridizations. There is no unique, isolated band near the Fermi level. To select the bands for the tight-binding model, calculate bandweights [”(W)eights” option in the ”(B)andplot” menu] and plot the $d_{x^2-y^2}$ orbital character for the valence bands. Now, you can identify proper band energies at each \mathbf{k} point. However, the resulting band is discontinuous, and the fit with the continuous $\varepsilon(\mathbf{k})$ function should be ambiguous.
4. Construct a model for nearest-neighbor interactions t_1 along $[100]$ and $[010]$. Try to fit the parameters of this model (ε_0 and t_1) using band energies at several couples of points (Γ and X , Γ and M , X and M). Any choice of the points gives sizable t_1 , but the absolute numbers are rather different. You can also calculate $J_1 = 4t_1^2/U_{\text{eff}}$ and compare it to the result of the LSDA+ U calculation (see the previous task).
5. To improve the model, try to add further interactions (e.g., along $[110]$). Note however that there is no unique way of the fitting, because only the isolated bands can be unambiguously mapped onto the tight-binding model.

III. Real crystal structure of CuCl_2 – the complex shape of the Brillouin zone (advanced problem)

In the first task, we considered a simplified structure of copper chloride. In fact, this compound has a C -centered monoclinic unit cell that complicates the fitting.

1. Setup the calculation for the real crystal structure of CuCl_2 :
 - Space group: $C2/m$
 - Lattice parameters: $a = 6.9038 \text{ \AA}$, $b = 3.2995 \text{ \AA}$, $c = 6.824 \text{ \AA}$, $\beta = 122.20^\circ$
 - Atoms: $\text{Cu}(0, 0, 0)$ and $\text{Cl}(0.5048, 0, 0.2294)$
2. Run the calculation (convergence time – 4 min), plot and analyze density of states. You will find that the real and simplified crystal structures yield similar results. The only difference between the two structures is the different packing of Cu–Cl chains, while the electronic structure near the Fermi level is mainly determined by the local environment of copper.
3. For the $C2/m$ space group, FPLO gives a set of \mathbf{k} points that do not necessarily lie on the faces of the first Brillouin zone. Moreover, the C -centering of the lattice changes the shape of the Brillouin zone – it is not a simple parallelepiped anymore. To get the exchange couplings along the b direction, consider the dispersion of the band along the k_y axis. Basically, any segment along the k_y axis should be sufficient to calculate t_1 and t_2 . However, be careful while considering the coordinates of the \mathbf{k} points. Remember that FPLO uses the Cartesian coordinate system and the $2\pi/a$ units. The t_1 and t_2 values for the real and simplified structures should be similar (i.e., $t_2 > t_1$ and $t_2 \simeq 0.1 \text{ eV}$).

Solutions for the Evaluation of model parameters

I. Chain of edge-sharing copper plaquettes

- Local coordinate system: $\mathbf{x} = (0, 0.5, 0.5)$ and $\mathbf{z} = (1, 0, 0)$. One can also take $\mathbf{x} = (0, 0, 1)$. Then, the band at the Fermi level will have the d_{xy} origin.

- The tight-binding hamiltonian: $\varepsilon = \varepsilon_0 - 2t_1 \cos(k_y b) - 2t_2 \cos(2k_y b)$

$$\varepsilon_\Gamma = \varepsilon_0 - 2t_1 + 2t_2 = 0.396 \text{ eV}$$

$$\varepsilon_Y = \varepsilon_0 + 2t_1 - 2t_2 = 0.179 \text{ eV}$$

$$\varepsilon_\Delta = \varepsilon_0 + 2t_2 = -0.225 \text{ eV}$$

This yields $\varepsilon_0 = 0.032 \text{ eV}$, $t_1 = -0.054 \text{ eV}$, and $t_2 = -0.128 \text{ eV}$. The resulting exchanges are $J_1^{\text{AFM}} = 34 \text{ K}$ and $J_2^{\text{AFM}} = 191 \text{ K}$. (1 eV = 11.7 K; 1 K = 0.085 eV).

II. Layer of copper plaquettes – the case of hybridization

- The tight-binding hamiltonian: $\varepsilon = \varepsilon_0 - 2t_1(\cos(k_x a) + \cos(k_y b))$

$$\varepsilon_\Gamma = \varepsilon_0 - 4t_1 = -1.98 \text{ eV}$$

$$\varepsilon_X = \varepsilon_0 = -0.85 \text{ eV}$$

$$\varepsilon_M = \varepsilon_0 + 4t_1 = 2.18 \text{ eV}$$

Γ and X yield $\varepsilon_0 = -0.85 \text{ eV}$ and $t_1 = 0.28 \text{ eV}$; Γ and M yield $\varepsilon_0 = 0.1 \text{ eV}$ and $t_1 = 1.04 \text{ eV}$; X and M yield $\varepsilon_0 = -0.85 \text{ eV}$ and $t_1 = 0.76 \text{ eV}$.

- Let's include the next-nearest-neighbor coupling along [110]: $\varepsilon = \varepsilon_0 - 2t_1(\cos(k_x a) + \cos(k_y b)) - 2t_2(\cos[(k_x + k_y)a] + \cos[(k_x - k_y)a])$

$$\varepsilon_\Gamma = \varepsilon_0 - 4t_1 - 4t_2 = -1.98 \text{ eV}$$

$$\varepsilon_X = \varepsilon_0 + 4t_2 = -0.85 \text{ eV}$$

$$\varepsilon_M = \varepsilon_0 + 4t_1 - 4t_2 = 2.18 \text{ eV}$$

This yields $\varepsilon_0 = -0.375 \text{ eV}$, $t_1 = 0.52 \text{ eV}$ ($J_1^{\text{AFM}} = 3150 \text{ K}$), and $t_2 = -0.12 \text{ eV}$ ($J_2^{\text{AFM}} = 168 \text{ K}$)

III. Real crystal structure of CuCl_2 – the complex shape of the Brillouin zone

- Local coordinate system: to keep things simple, one should select $\mathbf{x} = (0, 1, 0)$ and $\mathbf{z} = (1, 0, 0)$. Then, the band at the Fermi level has d_{xy} origin.

- The k_y axis matches the y axis of the Cartesian coordinate system. Therefore, one can use the Y point, as suggested by FPLO: $(0, 1.04619, 0)$. The issue is to setup the calculation along ΓY , because this segment is absent in the default setting. Further considerations are similar to task I:

$$\varepsilon_\Gamma = \varepsilon_0 - 2t_1 + 2t_2 = 0.394 \text{ eV}$$

$$\varepsilon_Y = \varepsilon_0 + 2t_1 - 2t_2 = 0.327 \text{ eV}$$

$$\varepsilon_{\Delta} = \varepsilon_0 + 2t_2 = -0.005 \text{ eV}$$

This yields $\varepsilon_0 = 0.178 \text{ eV}$, $t_1 = -0.017 \text{ eV}$, and $t_2 = -0.091 \text{ eV}$. The resulting exchanges are $J_1^{\text{AFM}} = 3 \text{ K}$ and $J_2^{\text{AFM}} = 97 \text{ K}$.