

9.2.2. Density functional theory

As a motivation why we need density functional theory to understand electrons in solids we introduce the Bernevig-Haegher-Zhang model for two-dimensional topological insulators.

9.2.2.1 The BHZ model

Electrons in solids occupy certain atomic orbitals and have a spin $S = \pm \frac{1}{2}$. The rotationally invariant orbitals get reduced to orbitals that reflect the symmetry of the lattice (like C_{4v} , D_{4h} , etc. rather than $SO(3)$). For a specific semiconductor structure (HgTe, CdTe heterostructures) the relevant orbitals are

$$\begin{aligned} \mathcal{H}_+ & \begin{cases} |E1, +\frac{1}{2}\rangle \\ |H1, +\frac{3}{2}\rangle \end{cases} & \text{where } E1 \text{ is built from } s\text{-type orbitals and} \\ \mathcal{H}_- & \begin{cases} |E1, -\frac{1}{2}\rangle \\ |H1, -\frac{3}{2}\rangle \end{cases} & H1 \text{ is built from } p\text{-type } \{x \pm iy, z\} \text{ orbitals.} \end{aligned}$$

The $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$ reflect the m_j quantum number. The Hilbert-spaces \mathcal{H}_+ and \mathcal{H}_- are connected by time reversal symmetry and are frozen only on \mathcal{H}_+ in the following. In the low-energy physics of HgTe / CdTe heterostructures, one can neglect their coupling.

Note that $|E1\rangle$ and $|H1\rangle$ differ by one quantum of orbital angular momentum (s- vs. p-type). Therefore couplings between them need to be **odd** by standard selection rules. \Rightarrow

$$H \approx \begin{pmatrix} * & k_x - ik_y \\ k_x + ik_y & * \end{pmatrix}.$$

Matrix elements within $E1$ or $H1$ should be **even**. \Rightarrow

$$H \approx \begin{pmatrix} m - 2 + k_x^2 + k_y^2 & k_x - ik_y \\ k_x + ik_y & -m + 2 - k_x^2 - k_y^2 \end{pmatrix}$$

We drop potential terms $\propto \pi$ as they don't contribute anything interesting. In the full Hilbert space we could have

$$H_{full} = \begin{pmatrix} H & G \\ 0 & H^* \end{pmatrix}.$$

As we want to deal with a lattice model, we need it to be periodic in k_x, k_y . The simplest way to do so is to take

$$k \rightarrow \sin(k) \quad ; \quad 1 - k^2 \rightarrow \cos(k)$$

With this we get

$$H = \begin{pmatrix} m + \cos(k_x) + \cos(k_y) & \sin(k_x) - i\sin(k_y) \\ \sin(k_x) + i\sin(k_y) & -m - \cos(k_x) - \cos(k_y) \end{pmatrix}$$

$$= \sum_i d_i(k) \sigma_i \quad \text{with}$$

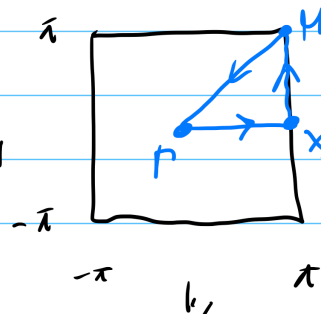
$$\vec{d}(k) = (\sin k_x, \sin k_y, m + \cos(k_x) + \cos(k_y)).$$

We can now observe two different scenarios:

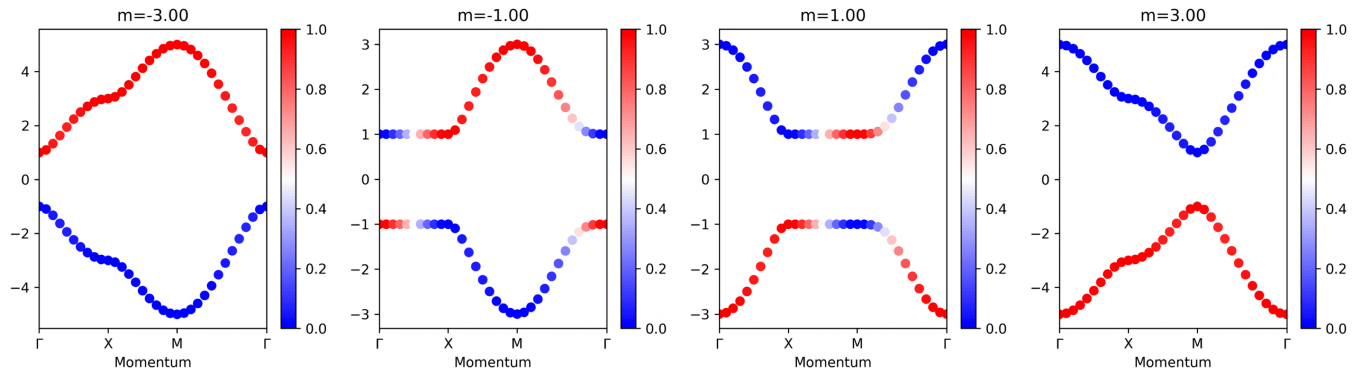
(i) $|m| \gg 1$: The s- and p-type orbitals are largely detuned. Despite their mixing, the eigenstates will be largely of one type throughout the Brillouine zone.

(ii) $|m| < 2$: The s- and p-type orbitals are close in energy and mixed. The Bloch-bands change their character throughout the Brillouine zone.

The numerical solution of the Bloch Hamiltonian can answer this question. In the following we diagonalize H along the path given here, and we color the graph with the orbital polarization:

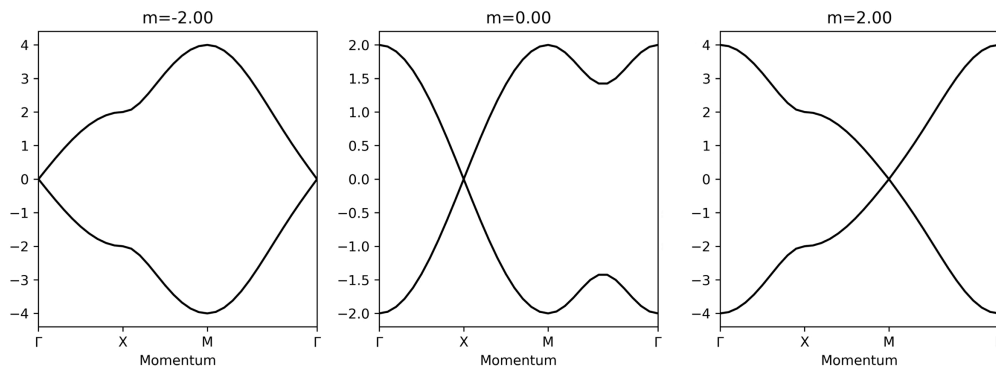


$$H \begin{pmatrix} \psi_s^\pm(\vec{k}) \\ \psi_p^\pm(\vec{k}) \end{pmatrix} = \epsilon_s(\vec{k}) \begin{pmatrix} \psi_s^\pm(\vec{k}) \\ \psi_p^\pm(\vec{k}) \end{pmatrix} \Rightarrow \rho^\pm = |\psi_s^\pm(\vec{k})|^2 \in [0, 1]$$

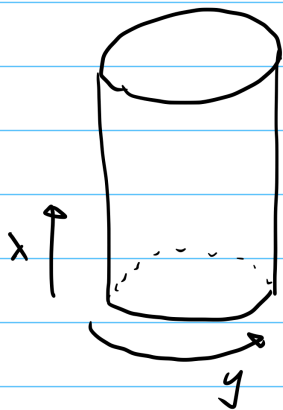


↑ always p or s ↑ changes from s- to p!

This of course goes hand-in-hand with a gap-closing:



The question that now arises is the following: Does anything interesting happen due to this characteristic from $\Gamma \rightarrow M$? The answer is an affirmative *yes* and is revealed if one considers a system with boundaries. Let us take a *spin*:



We still have k_y as a good quantum number. The hopping in x , however, we need to write in real-space. We know from the last lecture that

$$\cos(k_x) = \frac{1}{2}(e^{ik_x} + e^{-ik_x}) \quad \text{and}$$

$$\text{hop} = \begin{pmatrix} 0 & \frac{1}{2} & & & * \\ \frac{1}{2} & 0 & \frac{1}{2} & & \\ & \frac{1}{2} & 0 & \frac{1}{2} & \\ & & \frac{1}{2} & 0 & \ddots \\ * & & & \ddots & \ddots \end{pmatrix}$$

if $* = \frac{1}{2} \Rightarrow$
we add periodicity also in x -direction

For $\sin(k_x) = \frac{1}{2}(-ie^{ik_x} + ie^{-ik_x})$ we have similarly

$$\text{hop}_y = \begin{pmatrix} 0 & -\frac{i}{2} & & & * \\ \frac{i}{2} & 0 & -\frac{i}{2} & & \\ & \frac{i}{2} & 0 & -\frac{i}{2} & \\ & & \frac{i}{2} & 0 & \ddots \\ * & & & \ddots & \ddots \end{pmatrix}$$

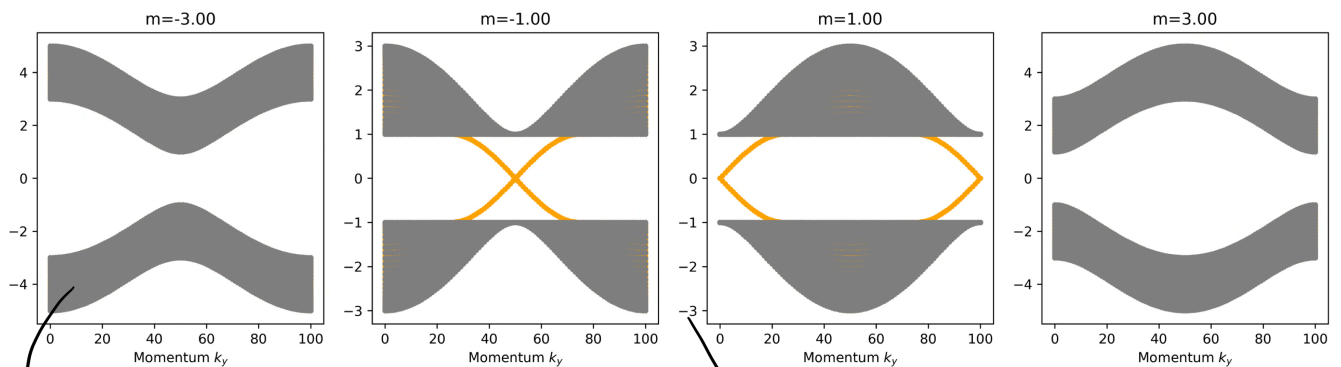
if $* = \frac{i}{2}$ we add periodicity also in x -direction

With this write for the Hamiltonian

$$H = \text{hop} \otimes \sigma_x + \Pi \otimes \sin k_y \sigma_y + [(m + \cos(k_y))\Pi + \text{hop}_y] \otimes \sigma_z$$

We now diagonalize this Hamiltonian for $k_y \in [-\pi, \pi]$. Each time we deal with a $(2 \times L_x) \times (2 \times L_x)$ Hamiltonian. We do this once with periodic boundary conditions (gray)

and once on the open cylinder (yellow)



in the bulk, the gray (periodic) dots fully cover the yellow dots

when the bulk bands change throughout the Brillouin zone edge states appear on the cylinder!

But m , our tuning parameter, was just arbitrarily chosen! And who told us that the orbitals E1 and H1 are relevant? In order to find their simple model observations to realistic materials, we need the machinery of density functional theory! Of course DFT serves a much broader audience than this motivating example.

9.2.2.2. Theoretical background

Walter Kohn was awarded the Nobel prize for the following idea: In DFT, the many-body wave function of \mathbb{R}^{3N} coordinates is replaced by the electron density which lives in \mathbb{R}^3 . DFT, or mean-field theory, reduces the many-body problem to a single particle one. In contrast to

Hartree-Fock theory it could be - in principle - exact! However, there is a bit of an obstruction also here: the unknown *exchange-correlation functional*. But let's develop the theory from the beginning.

DFT is based on two theorems by Hohenberg and Kohn which we will prove in the exercise class.

The first theorem states that the ground-state energy E_0 of an electronic system in an external potential V is a *functional* of the electron density

$$E_0 = E[\rho] = \int d\vec{r}^3 V(\vec{r})\rho(\vec{r}) + F[\rho]$$

with a universal functional $F[\rho]$

The second theorem states that the density $\rho_0(\vec{r})$ of the ground state

$$\rho_0(\vec{r}) = \langle \Psi_0 | \hat{\rho}(\vec{r}) | \Psi_0 \rangle$$

minimizes $F[\rho]$.

These two theorems make our lives very easy: We only have to minimize $F[\rho]$ and we get E_0 and ρ_0 ! And all of this is actually exact! Where is the problem? While $F[\rho]$ is universal, it is also *unknown*. We therefore have to approximate $F[\rho]$. One typically starts from

$$F[\rho] = E_h[\rho] + E_k[\rho] + E_{xc}[\rho]$$

The Hartree form is given by

$$E_h[\rho] = \frac{e^2}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}.$$

The kinetic part $E_k[\rho]$ is given by the expression of a free electron gas with the same density $\rho(\vec{r})$. We relegated all unknowns to $E_{xc}[\rho]$... we will come back to it later.

To calculate $\rho_0(\vec{r})$ we have to minimize the energy, solving a variational problem

$$0 = \delta E[\rho] = \int d\vec{r} \rho(\vec{r}) \left[V(\vec{r}) + e^2 \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_k[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \right]$$

subject to the constraint (the electron number is conserved)

$$\int d\vec{r} \delta \rho(\vec{r}) = 0.$$

Comparing this variational equation to the one for non-interacting systems

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \phi_\mu(\vec{r}) = \epsilon_\mu \phi_\mu(\vec{r}),$$

we realize that they are the same if we define the potential as

$$V_{\text{eff}}(\vec{r}) = V(\vec{r}) + e^2 \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}(\vec{r})$$

where

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}.$$

The above equation arises because we separated the kinetic energy of the non-interacting electron system from the functional.

The non-linear equation is again solved iteratively, making an ansatz using $\frac{N}{2}$ normalized single-electron wave functions

$$\rho(\vec{r}) = 2 \sum_{\substack{\mu=1 \\ \text{spin}}}^{N/2} |\phi_{\mu}(\vec{r})|^2$$

9.2.2.3 Local density approximation (LDA)

Apart from restricting the basis set, everything was exact so far. As we don't know $E_{xc}[\rho]$ and thus $V_{xc}(\vec{r})$, we need to make approximations.

The simplest approximation is the LDA, which replaces V_{xc} by that of a uniform electron gas with the same density. Instead of taking a functional $E[\rho]$ which could contain

$$\rho(\vec{r}), \nabla \rho(\vec{r}), \nabla^2 \rho(\vec{r}), \text{ etc.}$$

we ignore all gradient terms and write

$$E_{xc}[\rho] = E_{LDA}(\rho).$$

Using $r_s^{-1} = a_B \left(\frac{4\pi}{3\rho} \right)^{1/3}$,

the exchange correlations are given by

$$V_{xc} = -\frac{e^2}{a_B} \left(\frac{3}{2\pi}\right)^{2/3} \frac{1}{r_s} \left[1 + \underbrace{0.0545 r_s}_{\text{filling QMC}} \log\left(1 + \frac{11.6}{r_s}\right) \right].$$

free gas

Of course there are more refined approximations on the market which we don't cover here.

9.3 Car-Parinello molecular dynamics

In the lecture on "Computational statistical physics" you have learned about molecular dynamics methods, in which atoms move on classical trajectories under forces like the Lennard-Jones potential, which have been previously calculated in quantum mechanical simulations. It would be nicer and more accurate, to use a full quantum mechanical force calculation at every time-step!

Roberto Car and Michele Parinello have combined PFT with molecular dynamics to do just that. Their method, Car-Parinello molecular dynamics (CPMD) allows much better simulations of molecular vibration spectra and chemical reactions.

The atomic nuclei are propagated using classical molecular dynamics, but the electronic forces which move them are estimated using PFT:

$$M_n \frac{d^2 \vec{R}_n}{dt^2} = \frac{\partial E[\rho(\vec{r}, t), \vec{R}_n]}{\partial \vec{R}_n},$$

here M_n and \vec{R}_n are the masses and coordinates of the n 'th

atomic nucleus. As the solution of the full electronic problem at every time step is very time intensive we don't start from scratch each time. Instead CPMD uses the previous $\{\phi_\mu\}$ of the DFT calculation and evolves them to the ground state of the current $\{\mathbf{R}_n\}$. Hence, both $\{\mathbf{R}_n\}$ and $\{\phi_\mu\}$ evolve in the same molecular dynamics scheme. The electronic degrees are updated using an artificial dynamics

$$m \frac{d^2 \phi_\mu(\mathbf{r}, t)}{dt^2} = -\zeta \frac{\delta E[\phi(\mathbf{r}, t), \mathbf{R}_n]}{\delta \phi_\mu^*(\mathbf{r}, t)} + \sum_\nu \Lambda_{\nu\mu} \phi_\nu(\mathbf{r}, t),$$

where m is an artificial mass m that needs to be much lighter than all M_n . The Lagrange multipliers $\Lambda_{\nu\mu}$ need to be chosen to ensure normalization of $\{\phi_\mu\}$.

Since the exact form of the artificial dynamics of the electronic structure does not matter, we can evolve the expansion coefficients $d_{\mu n}$ of an expansion of ϕ_μ in terms of some basis functions. This gives equations of the form

$$m \ddot{d}_{\mu n} = - \frac{\partial E}{\partial d_{\mu n}} + \sum_\nu \Lambda_{\nu\mu} \sum_l \int d\mathbf{r} \dots$$