Slater-Koster TB Method & its application to Bi_2Se_3

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Outline

- Review of models to describe electrons' behavior
- Introduction to S-K TB model
- Step-by-step procedure
- Exercise: 1D s-band chain & Graphene
- An example: $Bi_2X_3\ (X=Se,Te)$
- Step further (waitlist)

Introduction to S-K TB model

- What are (conventional) solid state materials?

Bloch theorem for non-interacting electrons in a periodic potential.

In solid state physics, the TB model is an approach to the calculation of electronic band structure using approximation set of wave functions based on superposition of wave functions for isolated atoms located at each atomic site. ——wiki

- Historical development

1928, Robert Mulliken, the idea of a molecular orbital;
1928, B. N. Finklestein et al, the LCAO method for approximating molecular orbitals;
1928, Felix Bloch, extended to solids and called as LCAO-MO approach;
1954, Slater and Koster, the parameterized TB model method with effective interpolation scheme.

- Features

Quantum mechanical model; One-electron model

Like the many other physical models, tight-binding model is a typical and practical one, able to help us understand *why* solids behave as they are.

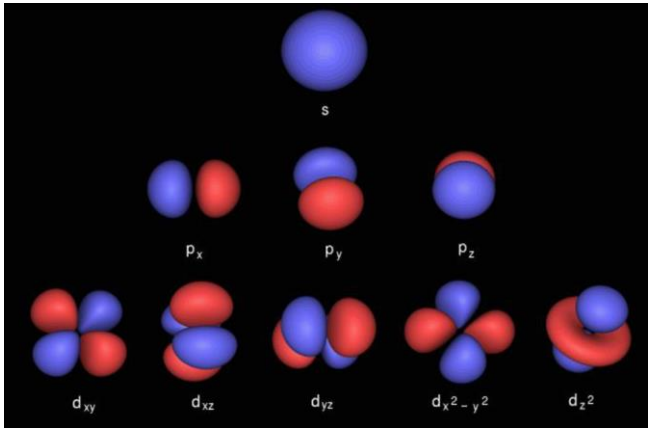
"Building a tight binding Hamiltonian yourself, by hand, is certainly the surest way to learn and understand the method."

Construction of LCAO Hamiltonian

- The LCAO idea is to express one-electron wave functions as a combination of atomic orbitals

We consider a set of atomic-like orbitals located on atomic positions $\vec{R}_i$

$$\psi(\vec{r}) = \sum_{\alpha,i} c_{\alpha,i}\chi_\alpha(\vec{r} - \vec{R}_i)$$



- Construct physical quantities over **atomic** functions

The Hamiltonian matrix elements $H_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = \langle \chi_\alpha \mid H \mid \chi_\beta \rangle = \int d\vec{r}\chi_\alpha(\vec{r} - \vec{R}_i)H\chi_\beta(\vec{r} - \vec{R}_j)$

The overlap matrix elements $S_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = \langle \chi_\alpha \mid \chi_\beta \rangle = \int d\vec{r}\chi_\alpha(\vec{r} - \vec{R}_i)\chi_\beta(\vec{r} - \vec{R}_j)$

- Generalized eigenvalue problem

$$H\psi(\vec{r}) = E\psi(\vec{r}) \Rightarrow \quad H\sum_{\beta,j} c_{\beta,j}\chi_\beta(\vec{r} - \vec{R}_j) = E\sum_{\beta,j} c_{\beta,j}\chi_\beta(\vec{r} - \vec{R}_j)$$

$$\chi_\alpha(\vec{r} - \vec{R}_i)H\sum_{\beta,j} c_{\beta,j}\chi_\beta(\vec{r} - \vec{R}_j) = \chi_\alpha(\vec{r} - \vec{R}_i)E\sum_{\beta,j} c_{\beta,j}\chi_\beta(\vec{r} - \vec{R}_j)$$

$$\sum_{\beta,j} c_{\beta,j}H_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = E\sum_{\beta,j} c_{\beta,j}S_{\alpha\beta}(\vec{R}_i, \vec{R}_j) \Rightarrow \boxed{H_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = ES_{\alpha\beta}(\vec{R}_i, \vec{R}_j)} \quad \boldsymbol{H\psi = ES\psi}$$

Construction of LCAO Hamiltonian

- Take periodicity into consideration, and new set of orbitals can be defined

$$\chi_{\alpha i\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}}\chi_{\alpha}(\vec{r}-(\vec{\tau}_i+\vec{T}))$$

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\alpha,i} c_{n,\alpha,i}(\vec{k})\chi_{ai\vec{k}}(\vec{r})$$

α: index of orbitals
i: index of atoms
$\vec{\tau}_i$: atom position in **unit cell**
$\vec{T}$: translation vector

Note: $\chi_{\alpha i\vec{k}}(\vec{r})$ and $\psi_{n\vec{k}}(\vec{r})$ are functions in k-space, while $\vec{r}$ is just a label fixed with frame of coordinates of lattice.

(Bloch) Hamiltonian becomes

$$\begin{aligned} H_{\alpha\beta ij}(\vec{k}) &= \langle \chi_{\alpha i\vec{k}} \mid H \mid \chi_{\beta j\vec{k}} \rangle \\ &= \left(\frac{1}{\sqrt{N}}\sum_{\vec{T}} e^{-i\vec{k}\cdot\vec{T}} \langle \chi_{\alpha} \mid\right) H(\vec{\tau}_i+\vec{T},\vec{\tau}_j+\vec{T}') \left(\frac{1}{\sqrt{N}}\sum_{\vec{T}'} e^{i\vec{k}\cdot\vec{T}'} \mid \chi_{\beta}\rangle\right) \\ &= \frac{1}{N}\sum_{\vec{T},\vec{T}'} e^{i\vec{k}\cdot(\vec{T}'-\vec{T})} H_{\alpha\beta}(\vec{\tau}_i+\vec{T},\vec{\tau}_j+\vec{T}') \end{aligned}$$

- What's the insight?

1. The so-called electronic materials, are just electrons fly inside periodic lattice. LCAO method presents a very rough way to show that, once the wave function of atoms are known, you just need to pick them up and build blocks as children do.

2. LCAO method is a paradigm to feel the philosophy and methodology of reductionism, though it made relatively little achievements for it is too demanding in terms of calculation.

Two Key Approximations

- Two centers approximation (Slater-Koster)

All overlap terms and Hamiltonian matrix elements involve only orbitals and potentials on two atomic sites.

$$H_{\alpha\beta}(\vec{R}_i,\vec{R}_j) = \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid H \mid \psi_\beta(\vec{r}-\vec{R}_j) \rangle$$
$$= \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid -\frac{\hbar^2}{2m^*}\nabla^2_{\vec{r}} + \sum_{\vec{k}} V_{\vec{k}}(\vec{r}-\vec{R}_k) \mid \psi_\beta(\vec{r}-\vec{R}_j) \rangle$$
$$= \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid -\frac{\hbar^2}{2m^*}\nabla^2_{\vec{r}} \mid \psi_\beta(\vec{r}-\vec{R}_j) \rangle + \boxed{\sum_k \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid V_k(\vec{r}-\vec{R}_k) \mid \psi_\beta(\vec{r}-\vec{R}_j) \rangle}$$

- What does two centers mean?

Keeping only $k = i$ or $k = j$, gives the two-center approximation, or else it is a three center tight-binding model.

- Orthogonal approximation

For overlapping term:

on the same atomic site $S_{\alpha\beta}(\vec{R}_i,\vec{R}_i) = \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid \psi_\beta(\vec{r}-\vec{R}_i) \rangle = \delta_{\alpha\beta}$

on two different sites $S_{\alpha\beta}(\vec{R}_i,\vec{R}_j) = \langle \psi_\alpha(\vec{r}-\vec{R}_i) \mid \psi_\beta(\vec{r}-\vec{R}_j) \rangle \approx \delta_{ij}\delta_{\alpha\beta} \rightarrow \delta_{\alpha\beta}$

Löwdin theorem:

This is not an *orthogonalized* tight-binding where you transform your orbitals to be orthogonal.

$$H_{\alpha\beta}(\vec{R}_i,\vec{R}_j) = ES_{\alpha\beta}(\vec{R}_i,\vec{R}_j) \approx E\delta_{\alpha\beta}$$

$$\boldsymbol{H}\psi = E\boldsymbol{S}\psi \Rightarrow \boldsymbol{H}\psi = E\psi$$

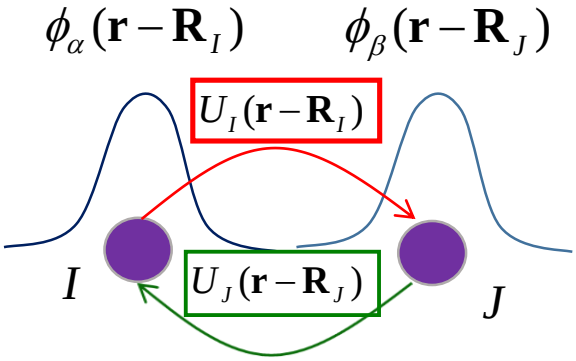
Phys. Rev 94, 1498 (1956); P. O Löwdin, J. Chem. Phys. 18, 365(1950)

Schematics of three kinds of "hopping"

- Onsite terms

Influenced by the presence of neighboring atoms

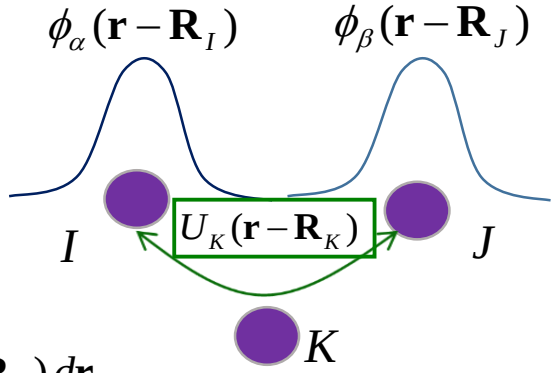
$$H^{II}_{TB,\alpha\beta} = \varepsilon^{I(0)}_{\alpha}\delta_{\alpha\beta} + \sum_{K\neq I}^{P}\int \phi^{*}_{\alpha}(\mathbf{r}-\mathbf{R}_I)U_K(\mathbf{r}-\mathbf{R}_K)\phi_{\beta}(\mathbf{r}-\mathbf{R}_I)\,d\mathbf{r}$$



- Two-center hopping integrals

The electron feels the attraction of both nuclei

$$H^{II}_{TB,\alpha\alpha} = \varepsilon^{I(0)}_{\alpha} = \int \phi^{*}_{\alpha}(\mathbf{r}-\mathbf{R}_I)\left[-\frac{\hbar^2}{2m}\nabla^2 + U_I(\mathbf{r}-\mathbf{R}_I)\right]\phi_{\alpha}(\mathbf{r}-\mathbf{R}_I)d\mathbf{r}$$



- Three-center hopping integrals

The electron between I and J is influenced by the presence of another atom K.

$$H^{IJ}_{TB,\alpha\beta} = \int \phi^{*}_{\alpha}(\mathbf{r}-\mathbf{R}_I)\left[-\frac{\hbar^2}{2m}\nabla^2 + U_I(\mathbf{r}-\mathbf{R}_I) + U_J(\mathbf{r}-\mathbf{R}_J)\right]\phi_{\beta}(\mathbf{r}-\mathbf{R}_J)\,d\mathbf{r}$$

Semi-Empirical Tight-binding

- Key point

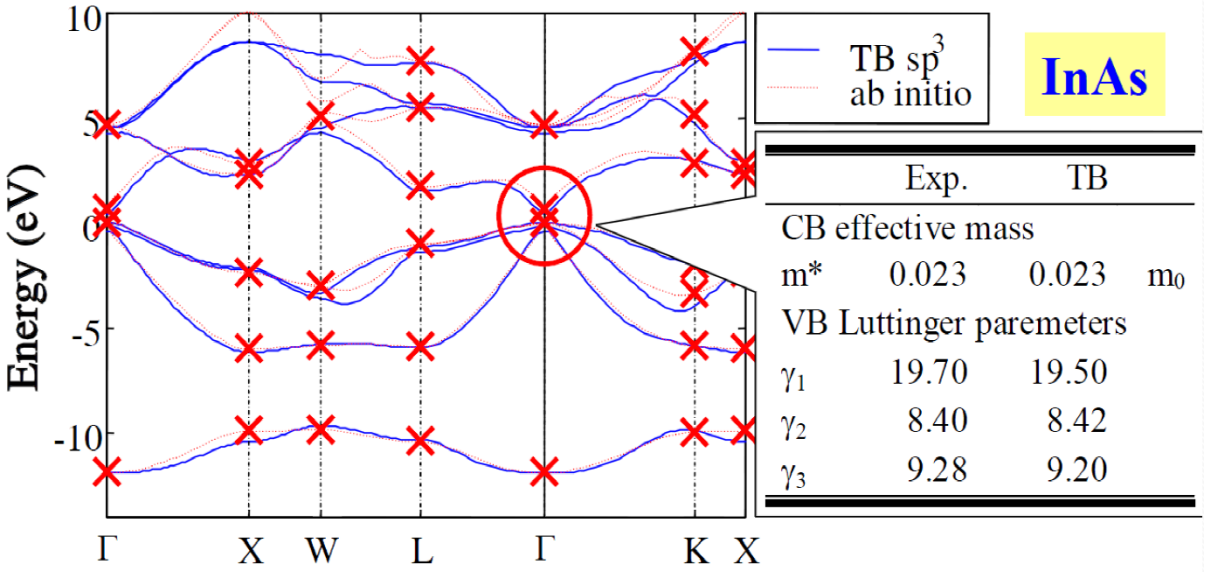
Parameterize the matrix elements $H_{\alpha\beta}(\vec{R},\vec{R}')$ that becomes the tight-binding parameters.

- What is the matter?

1. Orbitals are never defined;
2. Parameters are obtained by fitting or adjusting band structures.

- Ways to obtaining parameters

1. Fitting: Minimization of the discrepancy between the band structures;
2. Adjusting on band structure: the band structure have some points fixed;
3. Analytic expression of values of the band structure at some high symmetry points.



Phys. Rev 94, 1498 (1956)

Step-by-step procedure

- Atomic orbitals χ_α + Lattice $\vec{R} \rightarrow \chi_\alpha(\vec{r} - \vec{R}_i)$

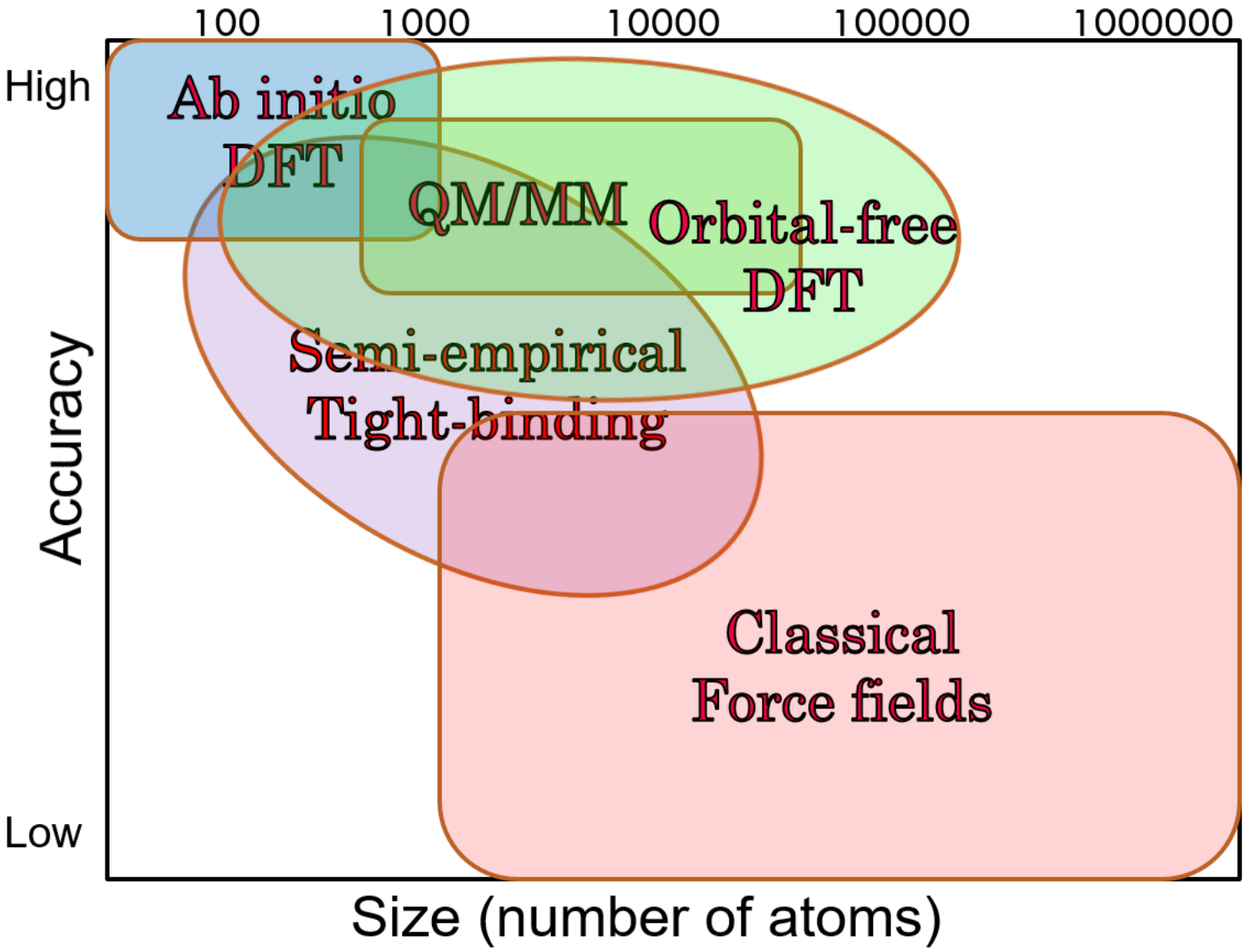
- Hamiltonian: $H_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = \int d\vec{r}\chi_\alpha(\vec{r} - \vec{R}_i)H\chi_\beta(\vec{r} - \vec{R}_j)$
  Correlation function: $S_{\alpha\beta}(\vec{R}_i, \vec{R}_j) = \int d\vec{r}\chi_\alpha(\vec{r} - \vec{R}_i)\chi_\beta(\vec{r} - \vec{R}_j)$
  (just parametrize them)

- Generalized eigenvalue equation
  $$\boldsymbol{H}\psi = E\boldsymbol{S}\psi \Leftrightarrow \det(\boldsymbol{H} - E\boldsymbol{S}) = 0$$

- Two-center approximation: $H_{\alpha\beta ij} = 0$ ($| i - j | > 1$)
  (No overlapping approximation: $\boldsymbol{S} = \mathbb{I}_d$)

- Fitting parameters(for SETB)

Overview



J. Kohanoff, CCMS Summer Institute, 2012

Exercise: 1D s-band

Linear combination of the atomic orbitals:

$$|k\rangle = \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{inka}\,|n\rangle$$

Assuming only nearest neighbor overlap：

$$\langle n|H|n\rangle = E_0, \langle n\pm1|H|n\rangle = t$$

$$\langle n|n\rangle = 1, \langle n\pm1|n\rangle = s$$

To obtain the energy of state $|k\rangle$, we take following steps

$$H|k\rangle = \frac{1}{\sqrt{N}}\sum_{n} e^{inka} H|n\rangle$$

$$\langle k|H|k\rangle = \frac{1}{N}\sum_{n,m} e^{i(n-m)ka}\langle m|H|n\rangle = E_0 + 2t\cos ka$$

and

$$\langle k|k\rangle = \frac{1}{N}\sum_{n,m} e^{i(n-m)ka}\langle m|n\rangle = 1 + 2s\cos(ka)$$

Thus, we arrive at the familiar form of the energy dispersion

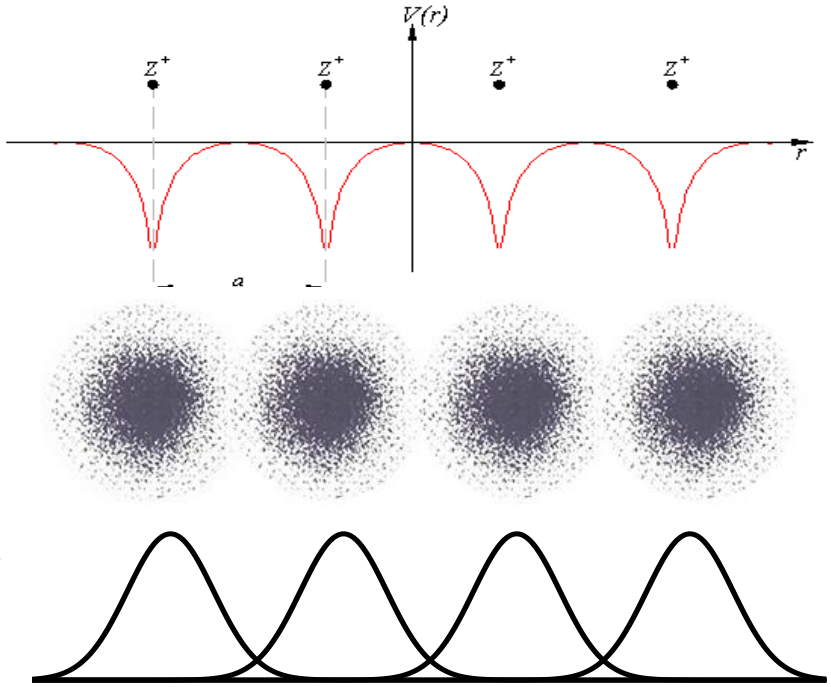
$$E(k) = \frac{E_0 + 2t\cos ka}{1 + 2s\cos ka}$$

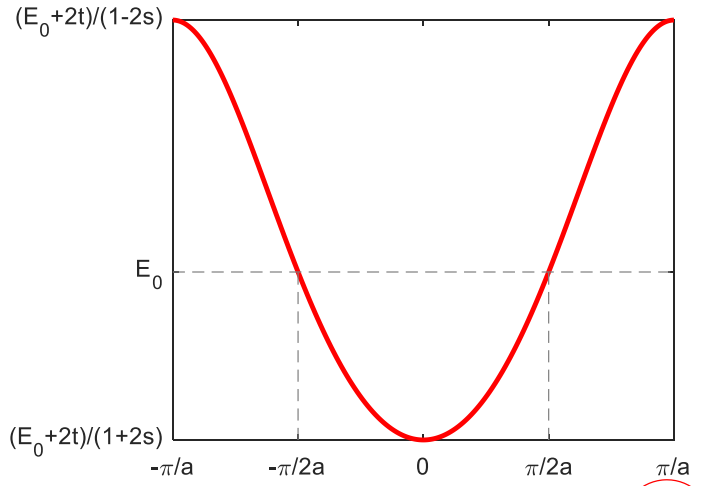
The Physics:

$E(k=0) = \frac{E_0+2t}{1+2s}$, bonding orbitals;

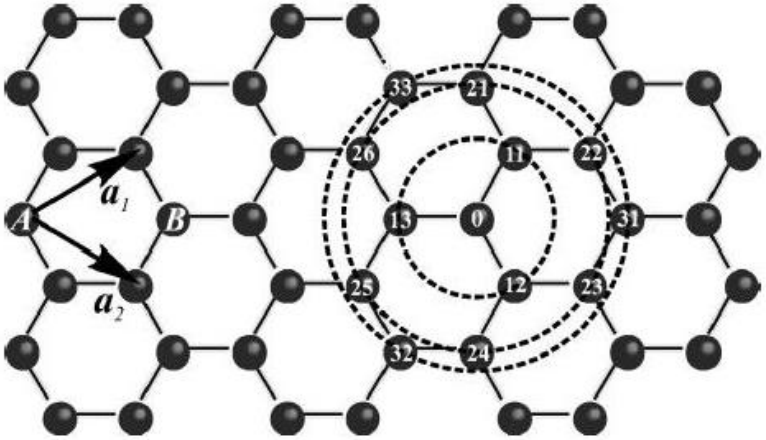
$E\left(k = \pm\frac{\pi}{2a}\right) = E_0$, non-bonding orbitals;

$E\left(k = \pm\frac{\pi}{a}\right) = \frac{E_0-2t}{1-2s}$, anti-bonding orbitals.





Exercise: Graphene



We start from the most general problem for p_z orbital with generalized eigenvalue equation

$$(\boldsymbol{H} - E\boldsymbol{S})\psi = 0$$

$$\begin{vmatrix} H_{AA}(\vec{k}) - E(\vec{k})S_{AA}(\vec{k}) & H_{AB}(\vec{k}) - E(\vec{k})S_{AB}(\vec{k}) \\ H_{AB}^{\dagger}(\vec{k}) - E(\vec{k})S_{AB}^{\dagger}(\vec{k}) & H_{BB}(\vec{k}) - E(\vec{k})S_{BB}(\vec{k}) \end{vmatrix} = 0$$

General solution: $E_{\pm}(\vec{k}) = \dfrac{-(-2E_0 + E_1) \pm \sqrt{(-2E_0 + E_1)^2 - 4E_2E_3}}{2E_3}$

with $E_0 = H_{AA}S_{AA}, E_1 = S_{AB}H_{AB}^{\dagger}, E_2 = H_{AA}^2 - H_{AB}H_{AB}^{\dagger}, E_3 = S_{AA}^2 - S_{AB}S_{AB}^{\dagger}$

- Take tight-binding approximation, namely, limit the sums to the first nearest-neighbors

$$H_{AB} = \frac{1}{N}\sum_{\vec{R}_A}\sum_{\vec{R}_B} e^{i\vec{k}\cdot(\vec{R}_B - \vec{R}_A)}\langle \vec{r} - \vec{R}_A \mid H \mid \varphi(\vec{r} - \vec{R}_B)\rangle = t_1\left(e^{i\vec{k}\cdot\vec{R}_{11}} + e^{i\vec{k}\cdot\vec{R}_{12}} + e^{i\vec{k}\cdot\vec{R}_{13}}\right)$$

Parameter: $t_1 = \langle \varphi_A(\vec{r} - \vec{R}_A) \mid H \mid \varphi_B(\vec{r} - \vec{R}_A - \vec{R}_{1i})\rangle \ (i = 1,2,3)$

$$S_{AB} = s_1\left(e^{i\vec{k}\cdot\vec{R}_{11}} + e^{i\vec{k}\cdot\vec{R}_{12}} + e^{i\vec{k}\cdot\vec{R}_{13}}\right)$$

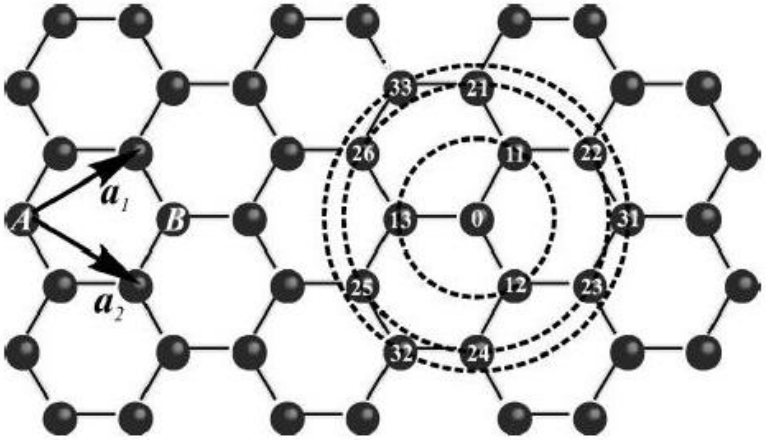
Parameter: $s_1 = \langle \varphi_A(\vec{r} - \vec{R}_A) \mid \varphi_B(\vec{r} - \vec{R}_A - \vec{R}_{1i})\rangle \ (i = 1,2,3)$

$$H_{AA} = \frac{1}{N}\sum_{\vec{R}_A}\langle \vec{r} - \vec{R}_A \mid H \mid \varphi(\vec{r} - \vec{R}_A)\rangle = \mu_A \qquad H_{AA} = \frac{1}{N}\sum_{\vec{R}_B}\langle \vec{r} - \vec{R}_B \mid H \mid \varphi(\vec{r} - \vec{R}_B)\rangle = \mu_B$$

$$S_{AA} = S_{BB} = 1$$

S. Reich, et al. PRB 66, 035412 (2002)

Exercise: Graphene



Now, we arrive at a Slater-Koster Hamiltonian and its eigenvalue equation

$$\begin{pmatrix} \mu_A & t_1\left(e^{i\vec{k}\cdot\vec{R}_{11}}+e^{i\vec{k}\cdot\vec{R}_{12}}+e^{i\vec{k}\cdot\vec{R}_{13}}\right) \\ t_1^*\left(e^{-i\vec{k}\cdot\vec{R}_{11}}+e^{-i\vec{k}\cdot\vec{R}_{12}}+e^{-i\vec{k}\cdot\vec{R}_{13}}\right) & \mu_B \end{pmatrix}\psi = E\begin{pmatrix} 1 & s_1 \\ s_1^* & 1 \end{pmatrix}\psi$$

No overlapping approximation, i.e. orthogonal tight-binding: $s_1 = 0$

$$\begin{pmatrix} \mu_A & t_1\left(e^{i\vec{k}\cdot\vec{R}_{11}}+e^{i\vec{k}\cdot\vec{R}_{12}}+e^{i\vec{k}\cdot\vec{R}_{13}}\right) \\ t_1^*\left(e^{-i\vec{k}\cdot\vec{R}_{11}}+e^{-i\vec{k}\cdot\vec{R}_{12}}+e^{-i\vec{k}\cdot\vec{R}_{13}}\right) & \mu_B \end{pmatrix}\psi = E\psi$$

$$H = \begin{pmatrix} \mu_A & t_1\left(e^{i\vec{k}\cdot\vec{R}_{11}}+e^{i\vec{k}\cdot\vec{R}_{12}}+e^{i\vec{k}\cdot\vec{R}_{13}}\right) \\ t_1^*\left(e^{-i\vec{k}\cdot\vec{R}_{11}}+e^{-i\vec{k}\cdot\vec{R}_{12}}+e^{-i\vec{k}\cdot\vec{R}_{13}}\right) & \mu_B \end{pmatrix}$$
$$= \frac{\mu_A+\mu_B}{2}\sigma_0 + d_i\sigma_i$$

$$d_1 = t_1\left[\cos\left(\vec{k}\cdot\vec{R}_{11}\right)+\cos\left(\vec{k}\cdot\vec{R}_{12}\right)+\cos\left(\vec{k}\cdot\vec{R}_{13}\right)\right]$$
$$d_2 = -t_1\left[\sin\left(\vec{k}\cdot\vec{R}_{11}\right)+\sin\left(\vec{k}\cdot\vec{R}_{12}\right)+\sin\left(\vec{k}\cdot\vec{R}_{13}\right)\right]$$
$$d_3 = \frac{\mu_A-\mu_B}{2}$$

$$E_\pm\left(\vec{k}\right) = d_0 \pm \sqrt{d_1^2+d_2^2+d_3^2}$$

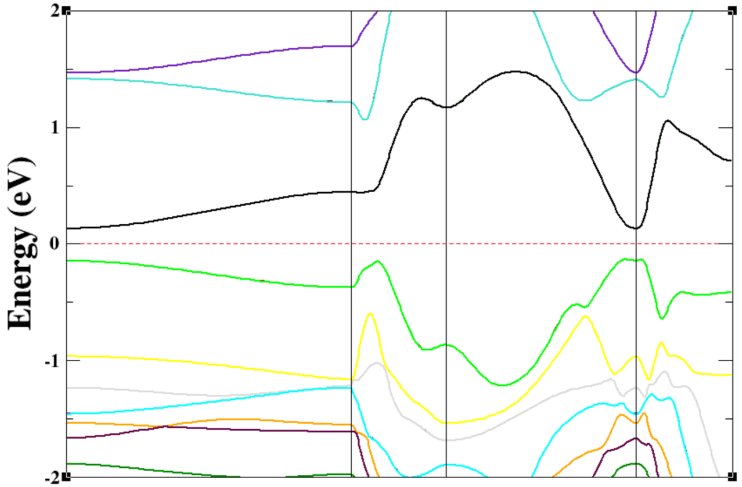
S. Reich, et al. PRB 66, 035412 (2002)

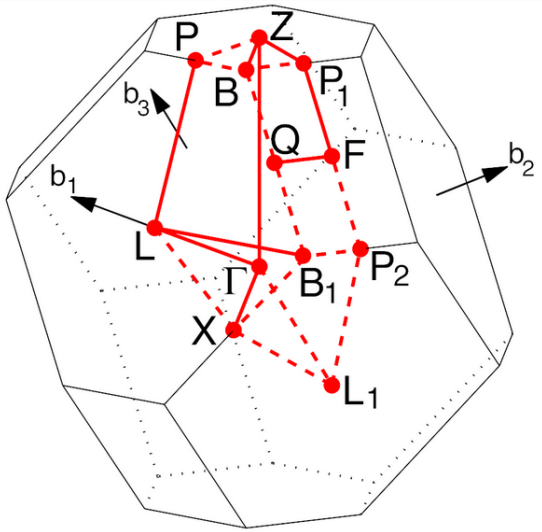
Bi_2Se_3/Bi_2Te_3

- Lattice: ABC-stacked honeycombs

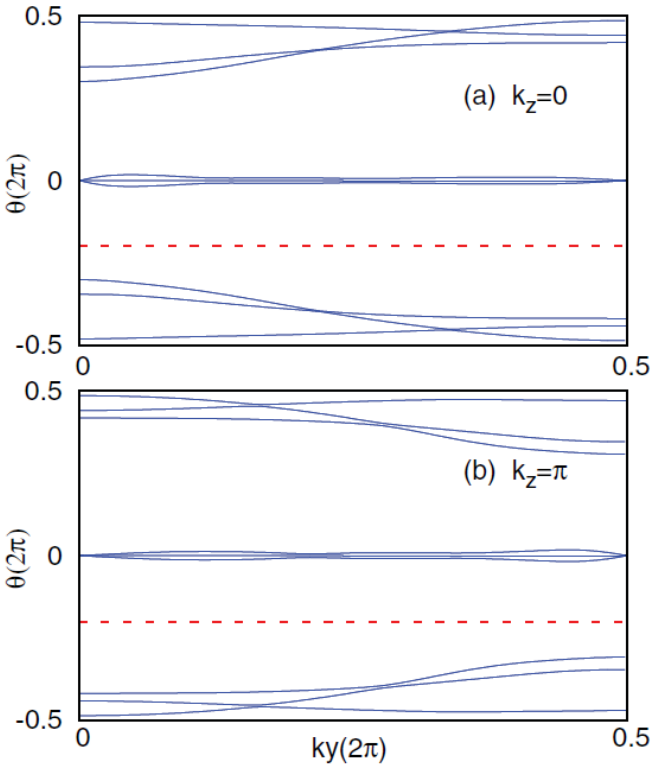
$R\bar{3}m$ (No.166): 36 symmetries, including (-*x*,-*y*,-*z*)

- Band structure





- Wannier center ($\mathbb{Z}_2$)



Assignments:

- Surface state
- Spin texture

Improving the tight-binding model

- Linear-muffin-tin orbitals tight-binding (LMTO-TB)
- Hartree-Fock-based TB
- Ab initio multicenter TB
- DF-based TB (DFTB)

DFT equations + tight-binding approximation

- Self-consistent charge DFTB