Tight-Binding Method:

I. Motivation: $H_{at}\,\psi_n = E_n\,\psi_n$ (single atom; single atom w.f.)

$H = H_{at} + \Delta U(r)$ with $\Delta U(r)$ small

see Fig. 10.2

There is a set of approximate solutions:

$$\langle r | n, R \rangle = \psi_n(r - R).$$

Individually these do not satisfy Bloch's Thm; however, there is a linear combination which does:

$$\psi_{nk}(r) = \sum_{R'} e^{ik\cdot R'} \psi_n(r - R')$$

$$\psi_{nk}(r + R) = \sum_{R'} e^{ik\cdot R'} \psi_n(r - R' + R) \quad ; \; R'' = R' - R, \; R' = R'' + R$$

$$= \sum_{R''} e^{ik\cdot(R''+R)} \psi_n(r - R'')$$

$$= e^{ik\cdot R}\,\psi_{nk}(r) \;//$$

II. Derivation: Look for $\psi_{nk}(r)$ (depends on k) of the form (of tight binding)

$$|\psi\rangle = \sum_R e^{ik\cdot R} \sum_n b_n |n, R\rangle$$

$$= \sum_{R,n} e^{ik\cdot R} b_n |n, R\rangle$$

$$= \sum_n b_n |n, \vec{0}\rangle + \sum_{R\neq 0, n} e^{ik\cdot R} b_n |n, R\rangle$$

Solve for the b_n:

only small for w.f. centered about the origin

$$H|\psi\rangle = (Hat + \Delta U)|\psi\rangle$$

① $= Hat \sum b_n |n, \vec{0}\rangle$

② $+ \Delta U \sum^{n} b_n |n, \vec{0}\rangle$

③ $+ Hat \sum^{n}{}' e^{ik\cdot R} b_n |n, \vec{R}\rangle$ $\quad \Sigma'$ means $R \neq 0$

④ $+ \Delta U \sum^{n,R}_{n,R}{}' e^{ik\cdot R} b_n |n, \vec{R}\rangle$

⑤ $= \mathcal{E} \sum_n b_n |n, \vec{0}\rangle$

⑥ $+ \mathcal{E} \sum^{n}_{n,R}{}' e^{ik\cdot R} b_n |n, \vec{R}\rangle$

Act on the LHS with $\langle m, \vec{0}|$. All the Hat become E_m:

⑤ ① ⑥ ③

$$(\mathcal{E} - E_m) b_m = -(\mathcal{E} - E_m) \sum_n b_n \left(\sum_R{}' e^{ik\cdot R} \langle m, \vec{0} | n, \vec{R} \rangle \right)$$

$$+ \quad ② \sum_n b_n \langle m, \vec{0} | \Delta U | n, \vec{0} \rangle$$

$$+ \quad ④ \sum_n b_n \left(\sum_R{}' e^{ik\cdot R} \langle m, \vec{0} | \Delta U | n, \vec{R} \rangle \right)$$

small

III. Application to single s-level:

$$(\mathcal{E} - E_s) = -(\mathcal{E} - E_s) \left(\sum_R{}' e^{ik\cdot R} \langle s, \vec{0} | s, \vec{R} \rangle \right) \quad \leftarrow \alpha(R)$$

$$+ \quad \langle s, \vec{0} | \Delta U | s, \vec{0} \rangle \quad \leftarrow -\beta$$

$$+ \quad \left(\sum_R{}' e^{ik\cdot R} \langle s, \vec{0} | \Delta U | s, \vec{R} \rangle \right) \quad \leftarrow -\gamma(R)$$

$$\Rightarrow \mathcal{E} - E_s = -\frac{\beta + \sum_R{}' e^{ik\cdot R} \gamma(R)}{1 + \sum_R{}' e^{ik\cdot R} \alpha(R)} \approx -\beta - \sum_R{}' e^{ik\cdot R} \gamma(R)$$

Make the further approximation that the sum is only over nearest neighbors: $\gamma(R) \to \gamma$.

$$\boxed{\mathcal{E} = E_s - \beta - \gamma \sum_{R \in n.n.} e^{i k \cdot R}}$$

A. Simple cubic lattice: $R = \pm a\hat{x}, \pm a\hat{y}, \pm a\hat{z}$

$$\mathcal{E} = E_s - \beta - 2\gamma(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$

For small k this is approximately

$$\mathcal{E} = E_s - \beta - 6\gamma + \gamma a^2 (k_x^2 + k_y^2 + k_z^2).$$

B. BCC lattice: $R = \frac{a}{2}(\pm\hat{x} \pm \hat{y} \pm \hat{z})$

$$\mathcal{E} = E_s - \beta - 8\gamma \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)$$

C. FCC lattice: $R = \frac{a}{2}(\pm\hat{x} \pm \hat{y}), \frac{a}{2}(\pm\hat{y} \pm \hat{z}), \frac{a}{2}(\pm\hat{z} \pm \hat{x})$

$$\mathcal{E} = E_s - \beta - 4\gamma\left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right)\cos\left(\frac{k_x a}{2}\right)\right)$$

? plot K3Dsurf ?

Remarks on tight binding:

1. More atomic levels
   3×3 p
   5×5 d
   Plotted in direction of symmetry

2. Localized level → narrow band
   Too wide → T.B. not work

3. Traveling wave even though constructed of localized levels

4. Lattice w/ basis → even only "s" bands have multiple bands (graphene example)

5. Spin-orbit coupling → spin & spatial together

6. Indep. electron (discuss later)

Always of form $\sum_R e^{ik\cdot R}\psi_n(r-R) = \psi_{nk}(r)$

IV. Wannier functions: Periodicity in k-space

$\psi_{n(k+K)}(r) = \psi_{nk}(r) \rightarrow \psi_{nk}(r) = \sum_R f_{n,r}(R)\, e^{iR\cdot k}$,
(periodic in K)

where $f_{nr}(R) = \frac{1}{V}\int_{1BZ} d^3k\, e^{-iR\cdot k}\psi_{nk}(r)$. V = volume in 1BZ (k-space)

$$f_{n(r+R_0)}(R+R_0) = \frac{1}{V}\int_{1BZ} d^3k\, e^{-i(R+R_0)\cdot k}\psi_{nk}(r+R_0)$$

$$= \frac{1}{V}\int_{1BZ} d^3k\, e^{-i(R+R_0)\cdot k} e^{ik\cdot R_0}\psi_{nk}(r)$$

$$= f_{nr}(R)$$

$\rightarrow f_{nr}(R) = \phi_n(r-R)$.

& $\psi_{nk}(r) = \sum_R e^{ik\cdot R}\phi_n(r-R)$ //