Application of Tight-Binding Method to Case of an s-band arising from a single atomic s-level

* all coefficients $b = 0$ except the one for the single atomic s-level

$$\Rightarrow \left(\varepsilon(\vec{k}) - E_s\right) b_s = -\left(\varepsilon(\vec{k}) - E_s\right)\left(\sum_{R\neq 0} \int \psi_s^*(\vec{r})\,\psi_s(\vec{r}-\vec{R})\, e^{i\vec{k}\cdot\vec{R}}\, d\vec{r}\right) b_s$$

$$+ \left(\int \psi_s^*(\vec{r})\,\Delta U(\vec{r})\,\psi_s(\vec{r})\, d\vec{r}\right) b_s$$

$$+ \left(\sum_{R\neq 0} \int \psi_s^*(\vec{r})\,\Delta U(\vec{r})\,\psi_s(\vec{r}-\vec{R})\, e^{i\vec{k}\cdot\vec{R}}\, d\vec{r}\right) b_s$$

b_s cancels

$$\Rightarrow \quad \varepsilon(\vec{k}) - E_s = -\left(\varepsilon(\vec{k}) - E_s\right)\left(\sum_{R\neq 0} \alpha(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}\right)$$

$$- \beta$$

$$- \sum_{R\neq 0} \gamma(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

with

$$\alpha(\vec{R}) = \int \psi_s^*(\vec{r})\,\psi_s(\vec{r}-\vec{R})\, d\vec{r}$$

$$\beta = -\int \psi_s^*(\vec{r})\,\Delta U(\vec{r})\,\psi_s(\vec{r})\, d\vec{r} = \int \Delta U(\vec{r})\,|\psi_s(\vec{r})|^2\, d\vec{r}$$

$$\gamma(\vec{R}) = -\int \psi_s^*(\vec{r})\,\Delta U(\vec{r})\,\psi_s(\vec{r}-\vec{R})\, d\vec{r}$$

So,

$$\left(\mathcal{E}(\vec{k}) - E_s\right)\left[1 + \sum \alpha(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}\right] = -\beta - \sum \gamma(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

$$\Rightarrow \quad \mathcal{E}(\vec{k}) - E_s = \frac{-\beta - \sum \gamma(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}}{1 + \sum \alpha(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}}$$

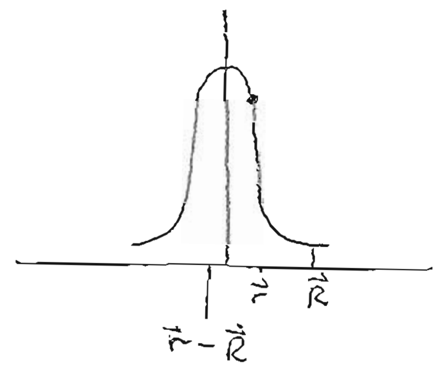
$$\Rightarrow \quad \boxed{\mathcal{E}(\vec{k}) = E_s - \frac{\beta + \sum \gamma(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}}{1 + \sum \alpha(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}}}$$

Since ψ is an s-level, $\psi(\vec{r})$ is real

and $\psi(\vec{r}) = f(|\vec{r}|)$ = a function of the magnitude of $\vec{r}$

$$\Rightarrow \psi(\vec{r}) = \psi(-\vec{r})$$

Thus, $\alpha(-\vec{R}) = \int \psi_s^*(\vec{r})\, \psi_s(\vec{r} - (-\vec{R}))\, d\vec{r}$



$$= \int \psi(\vec{r})\, \psi(\vec{r} + \vec{R})\, d\vec{r}$$

$$= \int \psi(-\vec{r})\, \psi(-(\vec{r} + \vec{R}))\, d\vec{r}$$

$$= \int_a^b \psi(-\vec{r})\, \psi(-\vec{r} - \vec{R})\, d\vec{r}$$

then change variables $\vec{r}' = -\vec{r}$

$$= -\int_b^a \psi(\vec{r}')\, \psi(\vec{r}' - \vec{R})\, d\vec{r}'$$

$$= \int_a^b \psi(\vec{r})\, \psi(\vec{r} - \vec{R})\, d\vec{r} = \alpha(\vec{R})$$

So, $\boxed{\alpha(-\vec{R}) = \alpha(\vec{R})}$

also assume the inversion symmetry of Bravais lattice

$$\Rightarrow \quad \Delta U(-\vec{r}) = \Delta U(\vec{r})$$

$$\Rightarrow \gamma(-\vec{R}) = -\int \psi(\vec{r})\, \Delta U(\vec{r})\, \psi(\vec{r} - -\vec{R})\, d\vec{r}$$

$$= -\int_a^b \psi(-\vec{r})\, \Delta U(-\vec{r})\, \psi(-\vec{r} - \vec{R})\, d\vec{r}$$

again, let $\vec{r}\,' = -\vec{r}$

$d\vec{r}\,' = -d\vec{r}$

$$= +\int_b^a \psi(\vec{r}\,')\, \Delta U(\vec{r}\,')\, \psi(\vec{r}\,' - \vec{R})\, d\vec{r}\,'$$

$$= -\int_a^b \psi(\vec{r})\, \Delta U(\vec{r})\, \psi(\vec{r} - \vec{R})\, d\vec{r} = \gamma(\vec{R})$$

So, $\boxed{\gamma(-\vec{R}) = \gamma(\vec{R})}$

Next, assume that terms in α in denominator (181)

of expression for $\mathcal{E}(\vec{k})$ will be only small corrections to the value of

$$1 + \sum \alpha(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

$$\Rightarrow \quad \cong \quad 1$$

And also assume that only nearest neighbor separations give appreciable overlap integrals

$$\Rightarrow \mathcal{E}(\vec{k}) = E_s - \beta - \sum_{n.n.} \gamma(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

now, $\mathcal{E}(\vec{k})$ must be <u>real</u>

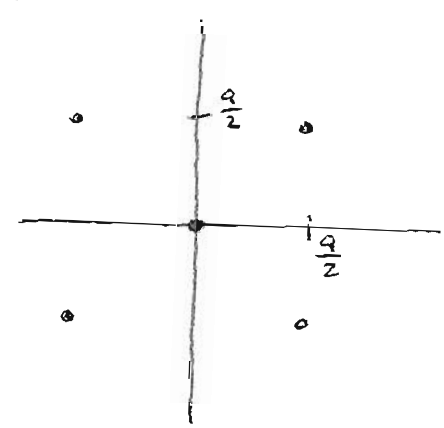
$$\Rightarrow \boxed{\mathcal{E}(\vec{k}) = E_s - \beta - \sum_{n.n.} \gamma(\vec{R}) \cos(\vec{k}\cdot\vec{R})}$$

Now, apply this to case of fcc crystal

$$\vec{R} = \frac{a}{2}(\pm 1, \pm 1, 0),$$

$$\frac{a}{2}(\pm 1, 0, \pm 1),$$

$$\frac{a}{2}(0, \pm 1, \pm 1)$$



$$\vec{k} = (k_x, k_y, k_z)$$

$$\Rightarrow \quad \vec{k}\cdot\vec{R} = \frac{a}{2}(\pm k_x \pm k_y),$$

$$\frac{a}{2}(\pm \cancel{k_x} \cdot \pm k_z),$$

$$\frac{a}{2}(\pm k_y \pm k_z)$$

Next, note that $\Delta U(\vec{r}) = \Delta U(x, y, z)$ has the full cubic symmetry of the lattice

$$\Rightarrow \quad \Delta U(a, b, c) = \Delta U(-a, b, c)$$
$$= \Delta U(a, -b, c)$$
etc.

and $\Delta U(a, b, c) = \Delta U(b, c, a) = \Delta U(c, a, b)$

This implies that $\gamma(\vec{R})$ with

$$\vec{R} = \frac{a}{2}(\pm 1, \pm 1, 0),\ \frac{a}{2}(\pm 1, 0, \pm 1),\ \frac{a}{2}(0, \pm 1, \pm 1)$$

is the same for all these $\vec{R}$'s

$$\Rightarrow \quad \underline{\gamma(\vec{R}) = \gamma}$$

So,

$$\varepsilon(\vec{k}) = E_s - \beta - \sum_{n.n.} \gamma(\vec{R}) \cos(\vec{k}\cdot\vec{R})$$

$$= E_s - \beta - \sum_{n.n.} \gamma \cos(\vec{k}\cdot\vec{R})$$

$$= E_s - \beta - \gamma \sum_{n.n.} \cos(\vec{k}\cdot\vec{R})$$

also note $\cos(x) = \cos(-x)$

$$\Rightarrow \varepsilon(\vec{k}) = E_s - \beta - \gamma\Big[\cos\left(\frac{k_x a}{2} + \frac{k_y a}{2}\right) + \cos\left(-\frac{k_x a}{2} - \frac{k_y a}{2}\right)$$

$$+ \cos\left(-\frac{k_x a}{2} + \frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2} - \frac{k_y a}{2}\right)$$

+ etc.

8 more such terms involving k_x, k_z and k_y, k_z]

~~can show that~~

After some further simplification, can get:

$$\varepsilon(\vec{k}) = E_s - \beta - 4\gamma\Big[\cos\tfrac{1}{2}k_x a \cos\tfrac{1}{2}k_y a + \cos\tfrac{1}{2}k_y a \cos\tfrac{1}{2}k_z a + \cos\tfrac{1}{2}k_z a \cos\tfrac{1}{2}k_x a\Big]$$

therefore,

characteristic feature of the tight-binding

=> bandwidth proportional to the small overlap integral γ

=> tight-binding bands are <u>narrow</u>