The tight-binding method

Consider a solid as a collection of weakly interacting neutral atoms. This is a good assumption when the distance between the atoms is much bigger than the size of the electron orbitals.

In the vicinity of each lattice point the full periodic crystal potential can be approximated by H_{at} of a single atom. Assume that the bound states of H_{at} are well localized.

$$H_{at} \psi_n = E_n \psi_n$$

$\psi_n(r) \to 0$ when r exceeds a distance of the order of the lattice constant. (the "range" of ψ_n)

When $H \neq H_{at}$ only at $r >$ "range" of ψ_n, the wavefunction $\psi_n(r)$ is an excellent approx. to a stationary-state wavefunction of $\mathcal{H}$ with eigenvalue E_n. To calculate corrections

$$\mathcal{H} = \mathcal{H}_{at} + \Delta U(r)$$

But $\Delta U(r)$ vanishes when $\psi_n(r) \neq 0$.

Wavefunctions $\psi_n(\vec{r} - \vec{R})$ are also a solution.

To satisfy the Bloch condition $\psi(r+R) = e^{ikR}\psi(r)$

$$\psi_{nk}(r) = \sum_R e^{ikR} \psi_n(r-R)$$

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

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

The energy bands $\varepsilon_n(k)$ however have little structure $\varepsilon_n(k) \simeq E_n$

A more realistic assumption is that $\psi_n(r)$ is small but non-zero when $\Delta U(r)$ becomes appreciable

$$\psi(r) = \sum_R e^{ikR} \phi(r-R)$$

$$\phi(r) = \sum_n b_n \psi_n(r)$$

$$H\psi = (H_{at} + \Delta U(r))\psi(r) = \varepsilon(k)\psi(r)$$

Multiply by $\psi_m^*(r)$ and integrate

$$\int \psi_m^* H_{at} \psi = \int (H_{at}\psi_m)^* \psi =$$

$$= E_m \int \psi_m^* \psi$$

$$(\varepsilon(k) - E_m)\int \psi_m^* \psi \, dr = \int \psi_m^* \Delta U \cdot \psi$$

Use $\int \psi_m^* \psi_n \, dr = \delta_{mn}$

$$(\mathcal{E}(k) - E_m)\, b_m = -(\mathcal{E}(k) - E_m) \sum_{R \neq 0} \sum_n \int dr\, \psi_m^*(r)\, \psi_n(r-R)\, e^{i\bar{k}\bar{R}}\, b_n$$

$$+ \sum_n \int dr\, \psi_m^*(r)\, \Delta U(r)\, \psi_n(r) \cdot b_n$$

$$+ \sum_n \sum_{R \neq 0} \int dr\, \psi_m^*(r)\, \Delta U(r)\, \psi_n(r-R)\, e^{i\bar{k}\bar{R}}\, b_n$$