

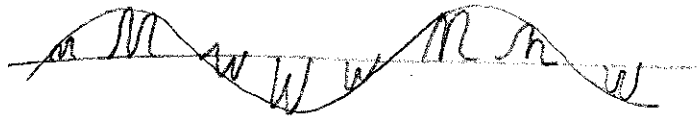
Other Methods for Calculating Band Structure

- * Many advances since book was written.
- * Focus on underlying physics, which has not changed.

Simply Fourier transforming is not a good idea because

1. $U_k \sim \text{Rydberg (13.6eV)}$, large
2. Many coefficients needed:

core ψ :



Valence ψ : even more wiggles

Problem statement

Solve Schrodinger Eq. in a primitive unit cell with the boundary condition at the sides:

$$\psi(r) = e^{-ik \cdot R} \psi(r+R) \quad \dots \psi \text{ continuous}$$

$$\hat{n}(r) \cdot \vec{\nabla} \psi = -e^{-ik \cdot R} \hat{n}(r+R) \cdot \vec{\nabla} \psi(r+R) \dots \nabla \psi \text{ too}$$

Common approx.

- * Replace $U(r)$ (full potential) by atomic $V(r)$.
- * Replace $U(r) = V(|r-R|)$ when $|r-R| < r_0$
 $= 0$ when $|r-R| > r_0$
muffin-tin potential ↴

Even the muffin-tin potential is not easy to solve. Two methods:

Augmented Plane-Wave (APW)

- * Interstitial region: $e^{ik \cdot r}$
- * Atomic region: solutions to Schrodinger Eq at E_k
- * ψ continuous at boundary ($r=r_0$)
- * Take linear combination of these plane waves to get full ψ (variational calc.)

Green's Function Method (KKR)

* Write Schrodinger Eq. in integral form

$$\psi_k(r) = \int d^3r' G_{E_k}(r-r') U(r') \psi_k(r')$$

↑ Green fnt. contains E_k & kinetic energy - not U .

* Still boundary condition at r_0 .

Orthogonalized Plane Wave (OPW)

Basis: $\phi_{\mathbf{k}}^{(r)} = e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_c b_c \psi_{\mathbf{k}}^c(r)$

\uparrow core \uparrow core wave functions with wave vector \mathbf{k}

Orthogonal to core:

$$\langle \psi_{\mathbf{k}}^c | \phi_{\mathbf{k}} \rangle = 0 = \int d^3r \psi_{\mathbf{k}}^{c*}(r) e^{i\mathbf{k}\cdot\mathbf{r}} + b_c \quad \dots \text{over 1 unit cell/atom}$$

$$\rightarrow b_c = -\int d^3r \psi_{\mathbf{k}}^{c*}(r) e^{i\mathbf{k}\cdot\mathbf{r}}$$

Use this basis to construct eigenstates:

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}}$$

- * In $\phi_{\mathbf{k}}$ basis matrix elements of U are smaller.
- * In general nearly free electron $E_{\mathbf{k}}$ does not mean free electron wave functions. Actual ψ could be quite complicated as shown by OPW.
- * Sometimes the U 's are fit experimentally: for cases that look like the nearly free electron $E_{\mathbf{k}}$.

Pseudopotential

* Large topic. Entire review articles on pseudopotential.

* Do only simplest case here based on OPW. ↘

$$\phi_k = e^{i\mathbf{k}\cdot\mathbf{r}} - \sum_c \left(\int d^3r' \psi_k^{c*}(r') e^{i\mathbf{k}\cdot\mathbf{r}'} \right) \psi_k^c(r)$$

$$\psi_k = \sum_K c_K \phi_{k+K}$$

$$= \sum_K c_K e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

$$- \sum_c \left(\int d^3r' \psi_k^{c*}(r') \sum_K c_K e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}'} \right) \psi_k^c(r)$$

need $\psi_{k+K}^c = \psi_k^c$

$\phi_k^v \equiv \sum_K c_K \phi_{k+K}$ is smooth

$$\psi_k = \phi_k^v(r) - \sum_c \left(\int d^3r' \psi_k^{c*}(r') \phi_k^v(r') \right) \psi_k^c(r)$$

$$H \psi_k = E_k \psi_k \rightarrow$$

$$H \phi_k^v - \sum_c \left(\int d^3r' \psi_k^{c*} \phi_k^v \right) (H \psi_k^c) = E_k^c \psi_k^c$$

$$= E_k^v \left(\phi_k^v - \sum_c \left(\int d^3r' \psi_k^{c*} \phi_k^v \right) \psi_k^c \right)$$

$$\rightarrow H \phi_k^v + \boxed{\sum_c (E_k^v - E_c) \left(\int d^3r' \psi_k^{c*}(r') \phi_k^v(r') \right) \psi_k^c(r)} = E_k^v \phi_k^v$$

↗ new, non-local operator on ϕ_k^v
 $\equiv V^R$

$$H + V^R = -\frac{\hbar^2}{2m} \nabla^2 + V^{\text{pseudo}}$$

Since ϕ_k^\vee are smooth, expect V^{pseudo} to be small. V^R partially cancels U .