6.730 Physics for Solid State Applications

Lecture 13: Electrons in a Periodic Solid

Outline

- Brillouin-Zone and Dispersion Relations
- Introduce Electronic Bandstructure Calculations
- Example: Tight-Binding Method for 1-D Crystals

March 3, 2003

Approaches to Calculating Electronic Bandstructure

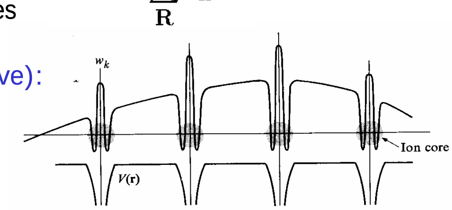
Nearly Free Electron Approximation:

- Superposition of a few plane waves

$$\psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

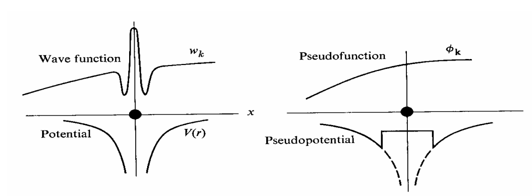
Cellular Methods (Augmented Plane Wave):

- Plane wave between outside r_s
- Atomic orbital inside r_s (core)



Pseudopotential Approximation:

- Superposition of plane waves coupled by pseudopotential



k.p:

- Superposition of bandedge (k=0) wavefunctions

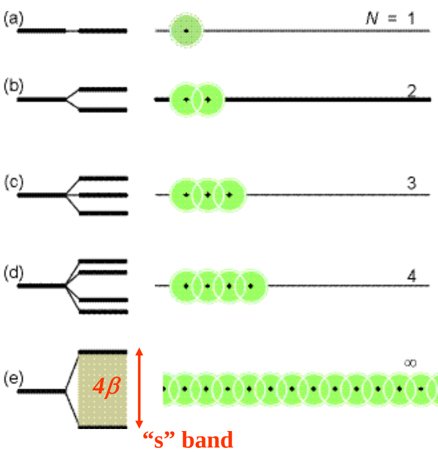
Tight-binding Approximation (LCAO):

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]} \phi_\alpha(r - \mathbf{R}_n)$$

- Superposition of atomic orbitals

Band Formation in 1-D Solid

◆ Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).



When the chain is extended:

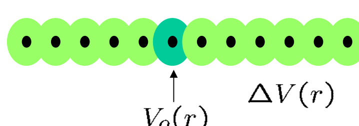
➔ The ***range of energies*** covered by the MOs is ***spread***

➔ This range of energies is filled in with ***more and more orbitals***

➔ The ***width of the*** range of energies of the MOs is ***finite***, while the number of molecular orbitals is ***infinite***: This is called a ***band*** .

Tight-binding (LCAO) Band Theory

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V(r)\right]\psi_l(r) = E_l\psi_l(r)$$



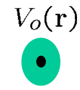
$$V(r) = V_o(r) + \Delta V(r)$$

$$\left[\underbrace{-\frac{\hbar^2\nabla^2}{2m} + V_o(r)}_{\text{atomic}} + \Delta V(r)\right]\psi_l(r) = E_l\psi_l(r)$$

$$\Delta V(\mathbf{r}) = \sum_{\mathbf{R_n}\neq 0} V_0(\mathbf{r}+\mathbf{R_n}) \qquad V(\mathbf{r}) = \sum_{\mathbf{R_j}} V_0(\mathbf{r}+\mathbf{R_j})$$

LCAO Wavefunction

$$\hat{\mathcal{H}} = \frac{\hat{\mathbf{p}}^2}{2m} + V_0(\mathbf{r}) + \Delta V(\mathbf{r})$$



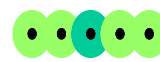
$$\frac{\hat{\mathbf{p}}^2}{2m}\phi_i(\mathbf{r}) + V_0(\mathbf{r})\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

Write general LCAO: Sum over types of orbitals (α = 1s, 2s, 2p, etc.) within a unit cell and sum over unit cells

$$\psi_i(\mathbf{r}) = \sum_{\alpha}\sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]}\phi_\alpha(r - \mathbf{R}_n)$$

Special case: take only one type of s-orbital per unit cell

$$\psi(\mathbf{r}) = \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{c[n]}\phi(\mathbf{r} - \mathbf{nai_x})$$



Energy for LCAO Bands with one-orbital per unit cell

Finite-basis set approximation gives:

$$\sum_{m=-\infty}^{\infty} \widetilde{H}(n,m)c[m] = E \sum_{p=-\infty}^{\infty} \widetilde{S}(n,p)c[p]$$

$$\widetilde{H}(n,m) = \langle\phi(\mathbf{r} - \mathbf{nai_x})|\hat{\mathcal{H}}|\phi(\mathbf{r} - \mathbf{mai_x})\rangle$$

$$\widetilde{S}(n,p) = \langle\phi(\mathbf{r} - \mathbf{nai_x})|\phi(\mathbf{r} - \mathbf{pai_x})\rangle$$

Z-transform, just like lattice waves!

$$c[p+1] = c[p]z^{-1} \quad \text{and} \quad c[p] = c[0]z^{-p}$$

$$\left(\sum_{m=-\infty}^{\infty} \widetilde{H}(n,m)e^{-ik(n-m)a}\right)\epsilon = E\left(\sum_{p=-\infty}^{\infty} \widetilde{S}(n,p)e^{-ik(n-p)a}\right)\epsilon$$

Energy for LCAO Bands

$$\left(\sum_{m=-\infty}^{\infty} \widetilde{H}(n,m)e^{-ik(n-m)a}\right)\epsilon = E\left(\sum_{p=-\infty}^{\infty} \widetilde{S}(n,p)e^{-ik(n-p)a}\right)\epsilon$$

$$\widetilde{H}(n,m) = \widetilde{H}^*(m,n) = \widetilde{H}(n-m)$$ and

$$\widetilde{S}(n,m) = \widetilde{S}^*(m,n) = \widetilde{S}(n-m)$$

Reduced Hamiltonian Matrix:

$$H(k) = \sum_{p=-\infty}^{\infty} \widetilde{H}(p)e^{-ikpa}$$

Reduced Overlap Matrix:

$$S(k) = \sum_{p=-\infty}^{\infty} \widetilde{S}(p)e^{-ikpa}$$

$$H(k)\,\epsilon = E\,S(k)\,\epsilon$$

$$E(k) = \frac{H(k)}{S(k)}$$

Reduced an NxN eigen value problem to a 1x1

Reduced Overlap Matrix for 1-D Lattice

Single s-orbital, single atom basis

$$S(k) = \sum_{p=-\infty}^{\infty} \widetilde{S}(p)e^{-ikpa}$$

$$\widetilde{S}(0) = \langle\phi(r)|\phi(r)\rangle = 1$$

$$\widetilde{S}(1) = \langle\phi(\mathbf{r}-\mathbf{a}\mathbf{i}_\mathbf{x})|\phi(\mathbf{r})\rangle$$

$$\widetilde{S}(1) = \widetilde{S}(-1)$$

$$S(k) = 1 + \widetilde{S}(1)(e^{ika} + e^{-ika})$$

Reduced Hamiltonian Matrix for 1-D Lattice

Single s-orbital, single atom basis

$$H(k) = \sum_{p=-\infty}^{\infty} \widetilde{H}(p) e^{-ikpa}$$

$$\widetilde{H}(0) = \langle \phi(r) | \frac{\hat{p}^2}{2m} + V_0 + \Delta V(r) | \phi(r) \rangle$$

$$= E_s^0 + \langle \phi(r) | \Delta V(r) | \phi(r) \rangle$$

$$\equiv E_s$$

$$\widetilde{H}(1) = \langle \phi(\mathbf{r} - \mathbf{a}\mathbf{i}_\mathbf{x}) | \frac{\hat{\mathbf{p}}^2}{2\mathbf{m}} + \mathbf{V_0} + \mathbf{\Delta V(r)} | \phi(\mathbf{r}) \rangle$$

$$\equiv V_{ss\sigma}$$

$$= \widetilde{H}(-1)$$

$$H(k) = E_s + V_{ss\sigma}(e^{ika} + e^{-ika})$$

Energy Band for 1-D Lattice

Single orbital, single atom basis

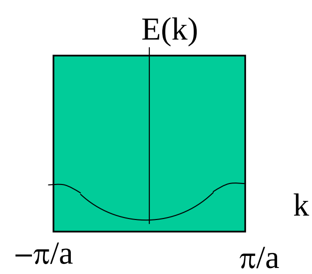
$$H(k)\,\epsilon = E\,S(k)\,\epsilon$$

$$E(k) = \frac{H(k)}{S(k)} = \frac{E_s + V_{ss\sigma}(e^{ika} + e^{-ika})}{1 + \widetilde{S}(1)(e^{ika} + e^{-ika})}$$

$$E(k) = E(k + n2\pi/a)$$

$$|\widetilde{S}(1)| \ll 1$$

$$E(k) \approx E_s + 2\,V_{ss\sigma} \cos ka$$



LCAO Wavefunction for 1-D Lattice

Single s-orbital, single atom basis

$$\psi(\mathbf{r}) = \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{c}[\mathbf{n}]\phi(\mathbf{r} - \mathbf{n}a\mathbf{i}_\mathbf{x})$$

$$c[n] = \epsilon e^{-ikna}$$

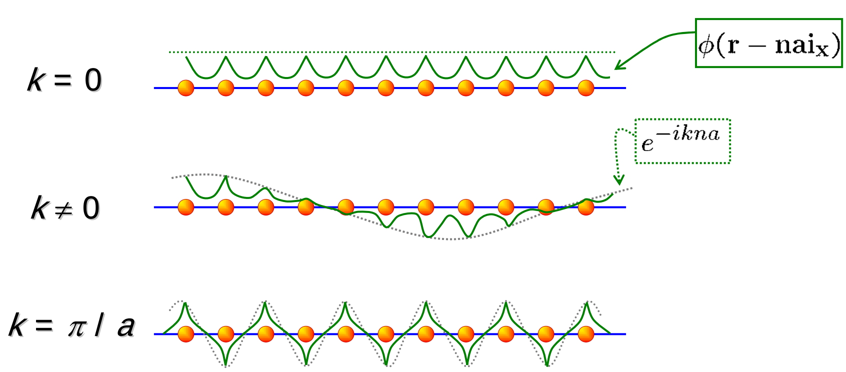
$$\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}}\phi(\mathbf{r} - \mathbf{n}a\mathbf{i}_\mathbf{x})$$

$$\psi_k(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{K}_\ell}(\mathbf{r})$$

LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

$$\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}}\phi(\mathbf{r} - \mathbf{n}a\mathbf{i}_\mathbf{x})$$



$k = 2\pi p/(Na)$

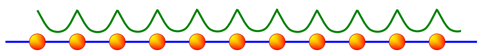
LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

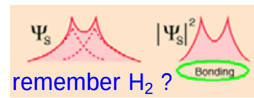
$$\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}} \phi(\mathbf{r} - \mathbf{nai_x})$$

$k = 0$

$$\psi_{k=0}(\mathbf{r}) = \epsilon\,[\cdots + \phi(\mathbf{r} + \mathbf{ai_x}) + \phi(\mathbf{r}) + \phi(\mathbf{r} - \mathbf{ai_x}) + \phi(\mathbf{r} - \mathbf{2ai_x}) + \phi(\mathbf{r} - \mathbf{3ai_x}) + \ldots]$$

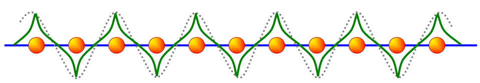


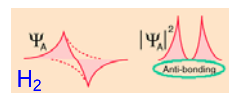
lowest energy (fewest nodes)



$k = \pi/a$

$$\psi_{k=\pi/a}(\mathbf{r}) = \epsilon\,[\cdots - \phi(\mathbf{r} + \mathbf{ai_x}) + \phi(\mathbf{r}) - \phi(\mathbf{r} - \mathbf{ai_x}) + \phi(\mathbf{r} - \mathbf{2ai_x}) - \phi(\mathbf{r} - \mathbf{3ai_x}) + \ldots]$$





highest energy (most nodes)

Bloch's Theorem

LCAO gives: $\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}} \phi(\mathbf{r} - \mathbf{nai_x})$

Translation of wavefunction by a lattice constant...

$$\psi_k(\mathbf{r} + \mathbf{ai_x}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{\mathbf{ikna}} \phi(\mathbf{r} + \mathbf{ai_x} - \mathbf{nai_x})$$

$$= e^{i\mathbf{ka}}\,\epsilon \sum_{n=-\infty}^{\infty} e^{i\mathbf{k(n-1)a}} \phi(\mathbf{r} - (\mathbf{n}-\mathbf{1})\mathbf{ai_x})$$

...yields the original wavefunction multiplied by a phase factor

$$\psi_k(\mathbf{r} + \mathbf{ai_x}) = \mathbf{e}^{\mathbf{ika}} \psi_{\mathbf{k}}(\mathbf{r})$$

Consistent that the probability density is equal at each lattice site

This is not a proof of Bloch's theorem, only showing that LCAO satisfies Bloch's Theorem

Wavefunction Normalization

Using periodic boundary conditione for a crystal
with N lattice sites between boundaries…

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{Na}} \mathrm{e}^{\mathrm{ikx}} \mathrm{u_k}(\mathbf{r})$$

$$1 = \int_{V_{\text{box}}} \psi_k^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r})\, \mathbf{d}^3\mathbf{r}$$

$$= \frac{1}{Na} \int_{V_{\text{box}}} u_k^*(\mathbf{r}) \mathbf{u_k}(\mathbf{r})\, \mathbf{d}^3\mathbf{r} = \frac{1}{\mathbf{a}} \int_{\text{unit cell}} \mathbf{u_k^*}(\mathbf{r}) \mathbf{u_k}(\mathbf{r})\, \mathbf{d}^3\mathbf{r}$$

Counting Number of States in a Band

Combining periodic boundary condition…

$$\psi_k(\mathbf{r} + \mathbf{Na}\mathbf{i_x}) = \psi_{\mathbf{k}}(\mathbf{r})$$

…with Bloch's theorem…

$$\psi_k(\mathbf{r} + \mathbf{Na}\mathbf{i_x}) = \mathrm{e}^{\mathrm{ikNa}} \psi_{\mathbf{k}}(\mathbf{r})$$

…yields a discrete set of k-vectors

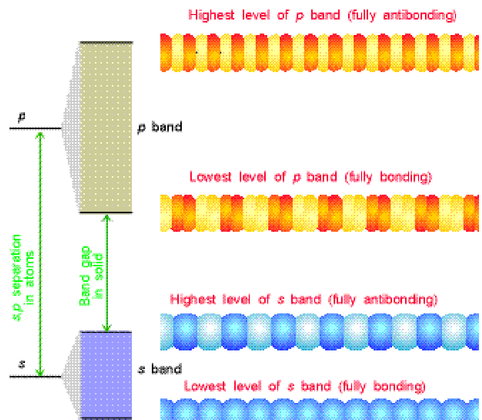
$$k = m\frac{2\pi}{Na} \qquad \text{where} \qquad m = 0, \pm 1, \pm 2, \cdots$$

Within the 1st Brillouin Zone there are *N* states or 2*N* electrons

Overview

$2N$ electrons each for p_x,p_y,p_z

$2N$ electrons



Tight-binding and Lattice Wave Formalism

Electrons (LCAO)

$$(\tilde{\mathbf{S}}^{-1}(\mathbf{k})\,\mathbf{H}(\mathbf{k})\,)\tilde{\epsilon} = \mathbf{E}\,\tilde{\epsilon}$$

$$\mathbf{H}_{\beta,\alpha}(\mathbf{k}) =$$

$$\sum_{\mathbf{R_p}} \langle \phi_\beta(\mathbf{r}-\mathbf{R_s}-\mathbf{R_p})|\hat{\mathcal{H}}|\phi_\alpha(\mathbf{r}-\mathbf{R_s})\rangle \mathbf{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{R_p}}$$

$$S_{\beta,\alpha}(\mathbf{k}) =$$

$$\sum_{\mathbf{R_p}} \langle \phi_\beta(\mathbf{r}-\mathbf{R_s}-\mathbf{R_p})|\phi_\alpha(\mathbf{r}-\mathbf{R_s})\rangle \mathbf{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{R_p}}$$

$$E(k) = E(k + n2\pi/a)$$

Lattice Waves

$$\left(\mathbf{M}^{-1}\mathbf{D}(\mathbf{k})\right)\vec{\epsilon} = \omega^2\vec{\epsilon}$$

$$\mathbf{D_{i,j}}(\mathbf{k}) =$$

$$\sum_{\mathbf{R_p}} \left(\frac{\partial^2 V}{\partial u_i[\mathbf{R_s}+\mathbf{R_p},\mathbf{t}]\,\partial \mathbf{u_j}[\mathbf{R_s},\mathbf{t}]}\right)_{\text{eq}} e^{-i\mathbf{k}\cdot\mathbf{R_p}}$$

$$\omega(k) = \omega(k + n2\pi/a)$$