6.730 Physics for Solid State Applications

Lecture 12: Electrons in a Periodic Solid

Outline

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

Solutions of Lattice Equations of Motion

Convert to Difference Equation

$$M\frac{d^2}{dt^2}u[n,t] = -\sum_{m=-\infty}^{\infty}\widetilde{D}(n,m)u[m,t]$$

Time harmonic solutions…

$$\tilde{u}[n,t] = \tilde{U}[n,\omega]e^{-i\omega t}$$

Plugging in, converts equation of motion into coupled difference equations:

$$M\omega^2\tilde{U}[n] = \sum_{m=-\infty}^{\infty}\widetilde{D}(n,m)\tilde{U}[m]$$

Solutions of Lattice Equations of Motion

$$M\omega^2 \tilde{U}[n] = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m)\tilde{U}[m]$$

We can guess solution of the form:

$$\tilde{U}[p+1] = \tilde{U}[p]z^{-1} \qquad \text{and} \qquad \tilde{U}[p] = \tilde{U}[0]z^{-p}$$

This is equivalent to taking the z-transform…

$$M\omega^2 \tilde{U}[0] = \left(\sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) z^{n-m} \right) \tilde{U}[0]$$

$$M\omega^2 = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) z^{n-m}$$

Solutions of Lattice Equations of Motion

Consider Undamped Lattice Vibrations

$$M\omega^2 = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) z^{n-m} \qquad \tilde{U}[p] = \tilde{U}[0] z^{-p}$$

We are going to consider the undamped vibrations of the lattice:

$$|U[m]| = |U[n]|$$

$$|z| = 1$$

$$z = e^{-ika}$$

$$\boxed{\tilde{u}[n,t] = \tilde{U}[0] e^{i(kna - \omega t)}}$$

Solutions of Lattice Equations of Motion

Dynamical Matrix

$$M\omega^2 = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) z^{n-m}$$

$$\tilde{u}[n,t] = \tilde{U}[0] e^{i(kna-\omega t)}$$

$$z = e^{-ika}$$

$$M\omega^2 = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) e^{ika(m-n)} v$$

$$= \sum_{m=-\infty}^{\infty} \widetilde{D}(n-m) e^{ika(m-n)}$$

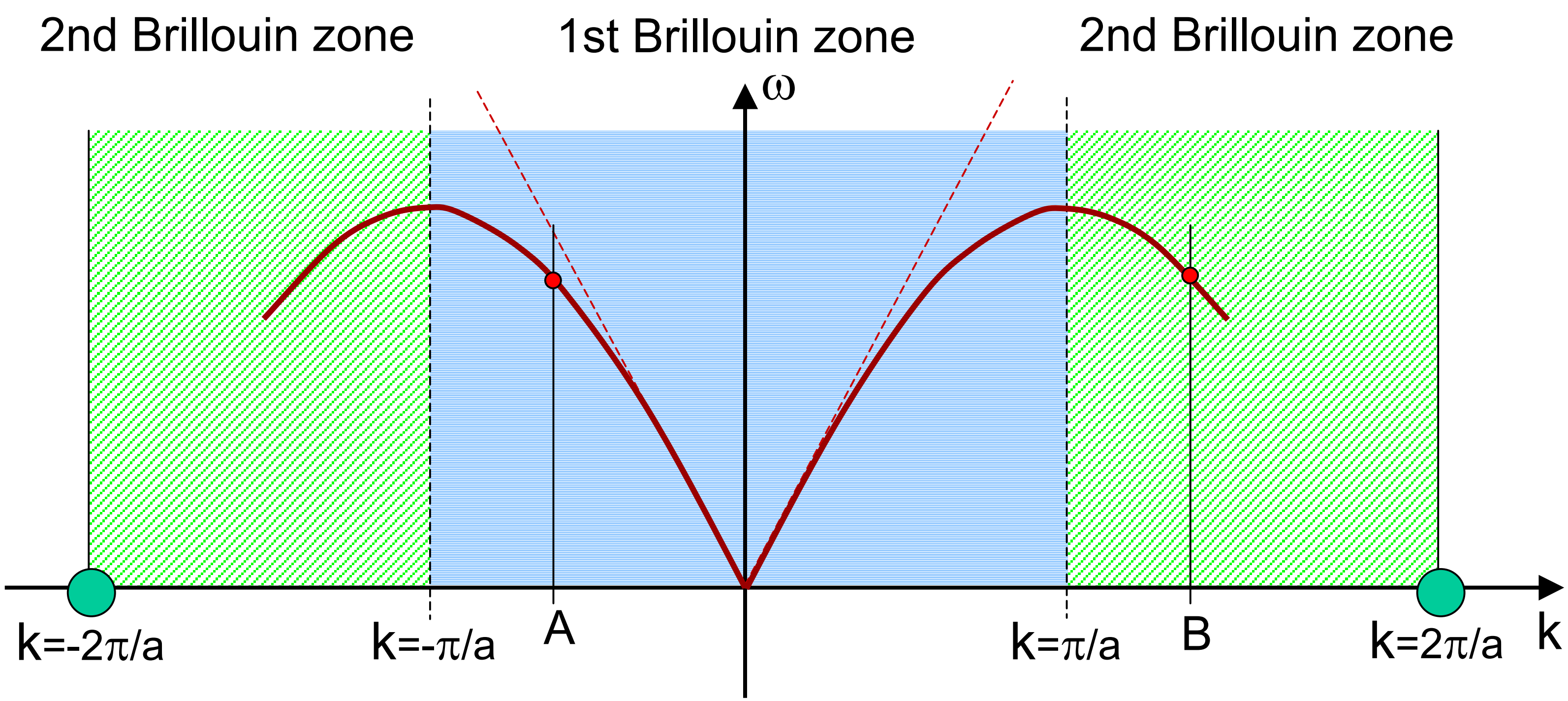
$$= \underbrace{\sum_{p=-\infty}^{\infty} \widetilde{D}(p) e^{-ikap}}_{\text{Dynamical Matrix } D(k)}$$

$$\boxed{\omega = \sqrt{\frac{D(k)}{M}}}$$

Solution of 1-D Lattice Equation of Motion

Example of Nearest Neighbor Interactions

$$\omega = 2\sqrt{\frac{\alpha}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



From what we know about Brillouin zones the points A and B (related by a reciprocal lattice vector) must be identical

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

This implies that the wave form of the vibrating atoms must also be identical.

Solution of 3-D Lattice Equation of Motion

$$\mathbf{U[n+1] = e^{ika}U[n]}$$

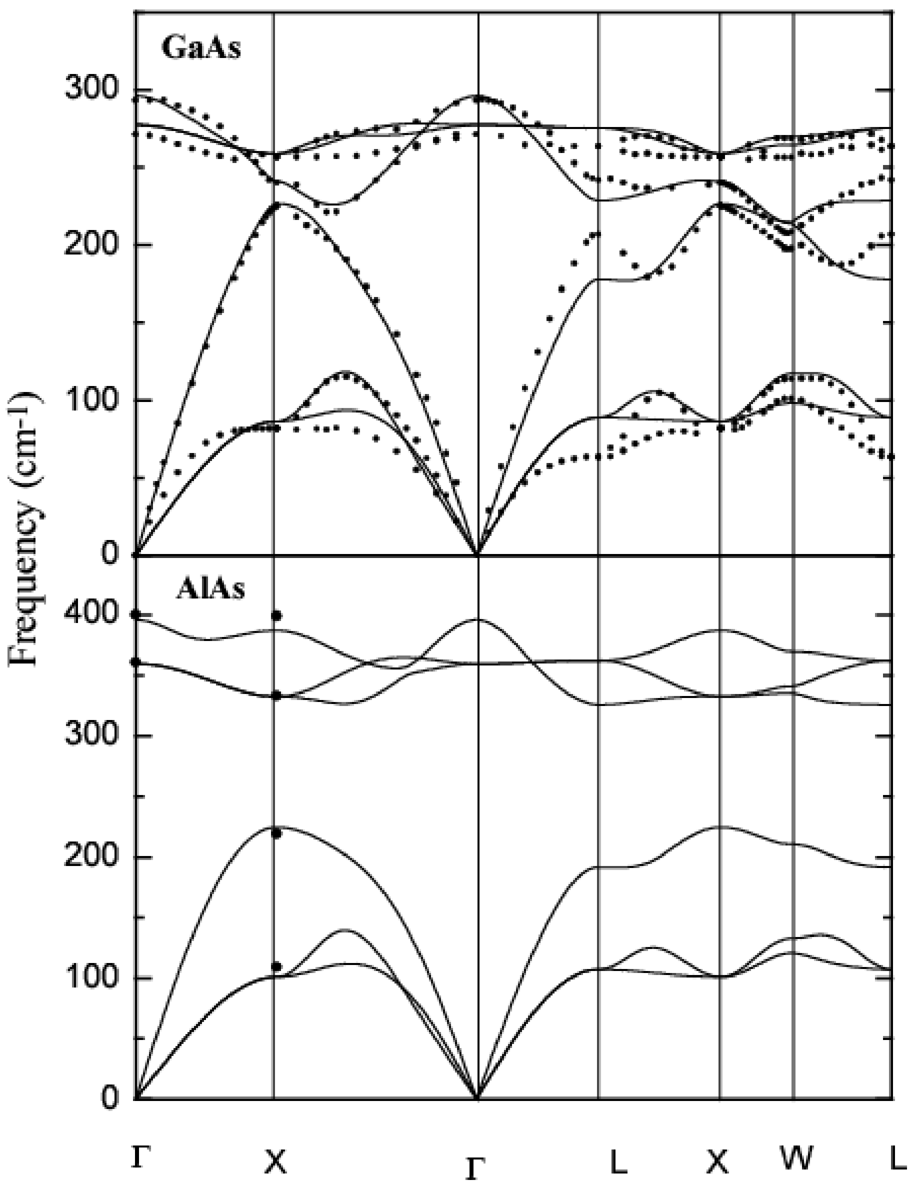
$$\mathbf{U[n] = e^{ikna}U[0] = e^{ikna}}\tilde{\epsilon}$$

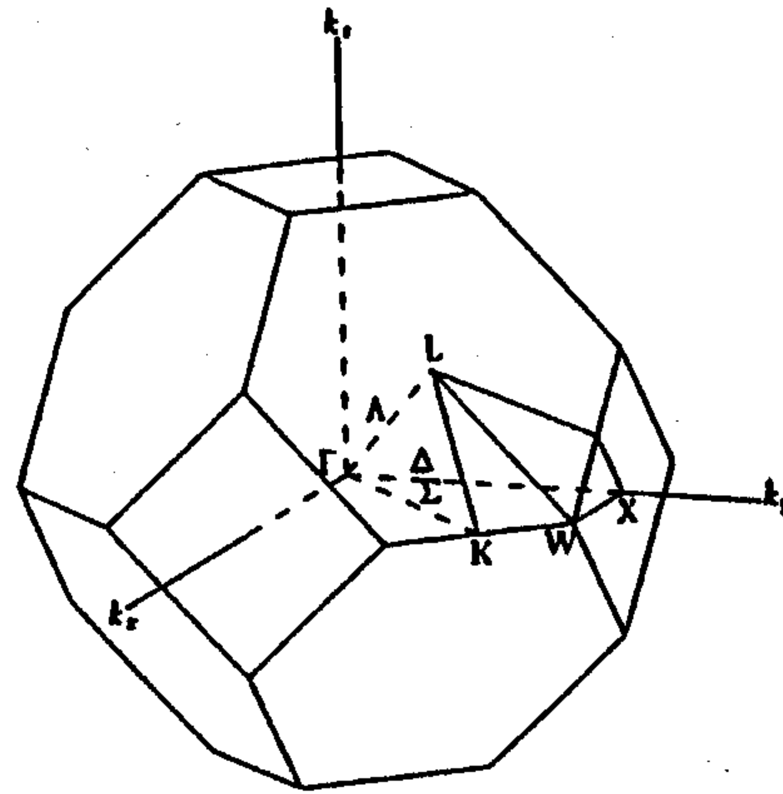
$$\omega^2\mathbf{M}\tilde{\epsilon} = \mathbf{D(k)}\tilde{\epsilon}$$

$$\mathbf{D(k)} = \sum_{\mathbf{m}=-\infty}^{\infty} \widetilde{\mathbf{D}}\mathbf{(n-m)e^{ika(m-n)}} = \sum_{\mathbf{p}=-\infty}^{\infty} \widetilde{\mathbf{D}}\mathbf{(p)e^{-ikpa}}$$

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

Phonon Dispersion in FCC with 2 Atom Basis





http://debian.mps.krakow.pl/phonon/Public/phrefer.html

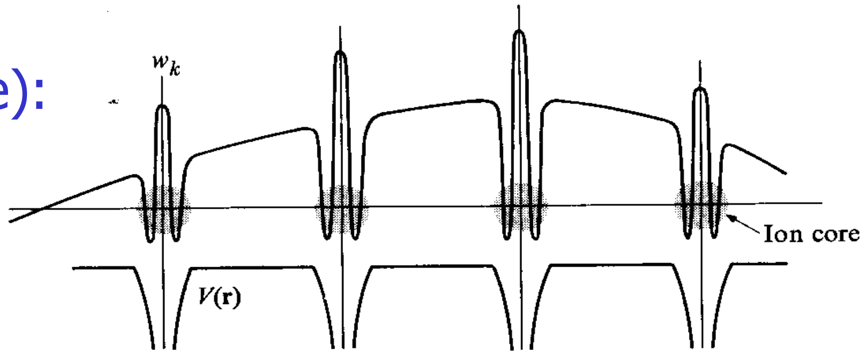
Approaches to Calculating Electronic Bandstructure

Nearly Free Electron Approximation:

- Superposition of a few plane waves

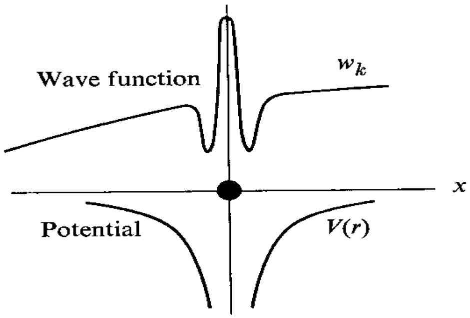
$$\psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

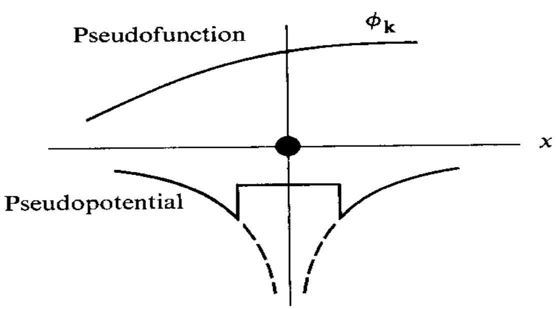
Cellular Methods (Augmented Plane Wave):



- 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

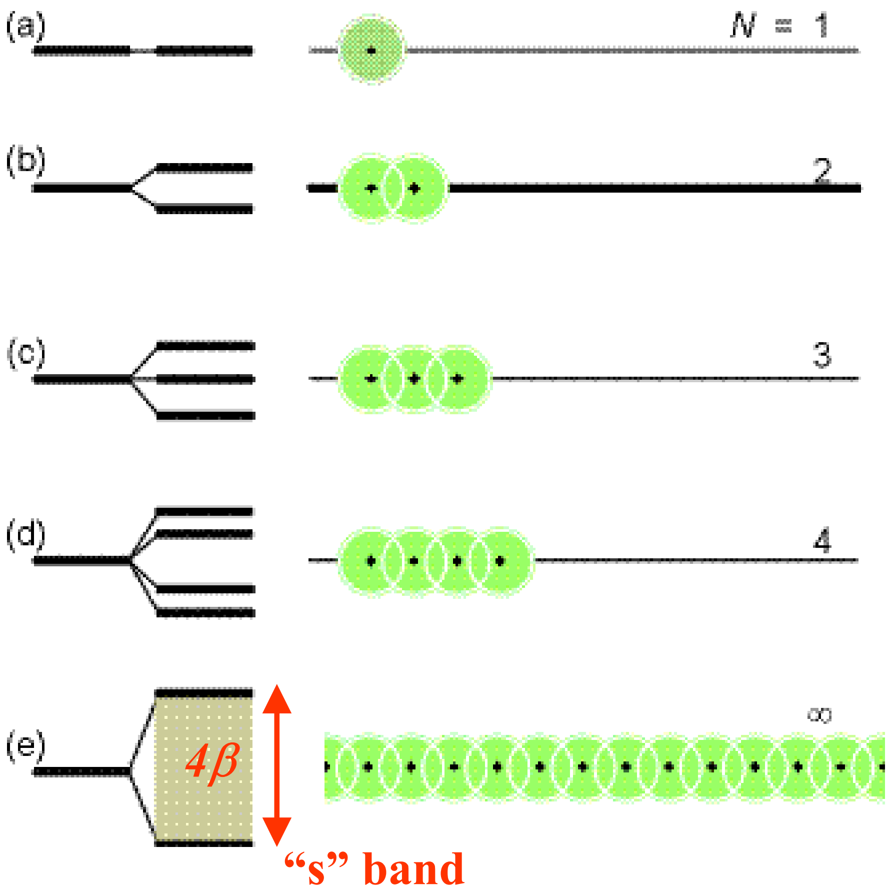
Tight-binding Approximation (LCAO):

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

- 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:

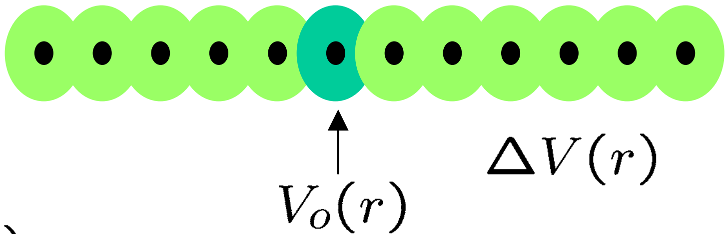
➔ The ***range of energies*** covered by the MOs is ***spread***

➔ 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

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



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

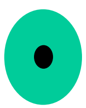
$$\left[\underbrace{-\frac{\hbar^2\nabla^2}{2m} + V_o(r)}_{\text{atomic}} + \Delta V(r)\right]\psi_l(r) = E_l\psi_l(r)$$

$$\Delta V(r) = \sum_{R\neq 0} V_0(r+R) \qquad V(r) = \sum_R V_0(r+R)$$

LCAO Wavefunction

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

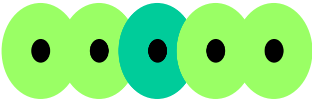
$V_o(r)$



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

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

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



Energy for LCAO Bands

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

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

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

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

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

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 Overlap Matrix for 1-D Lattice

Single orbital, single atom basis

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

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

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

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

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

Reduced Hamiltonian Matrix for 1-D Lattice

Single orbital, single atom basis

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

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

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

$$\equiv E_s$$

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

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

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

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

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 orbital, single atom basis

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

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

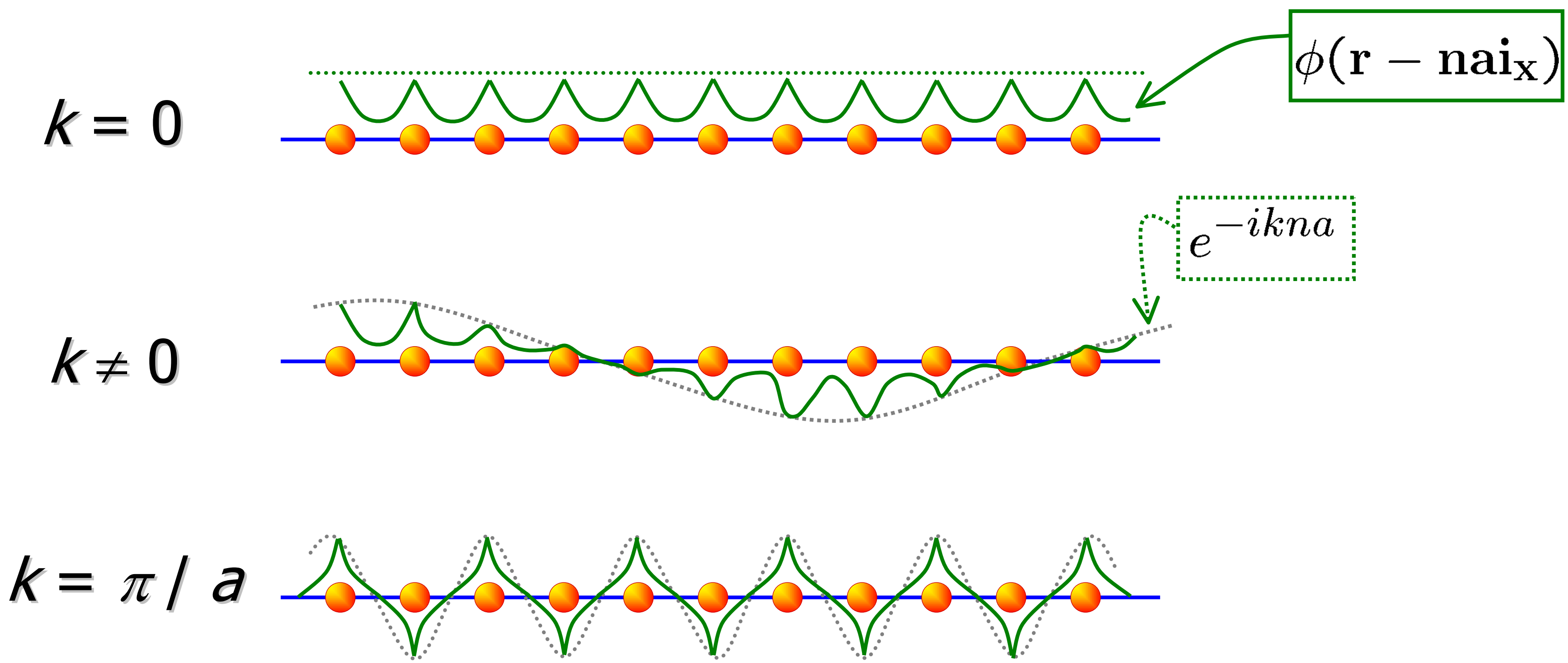
$$\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}}\phi(\mathbf{r} - \mathbf{n}\mathbf{a}\mathbf{i}_{\mathbf{x}})$$

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

LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

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



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

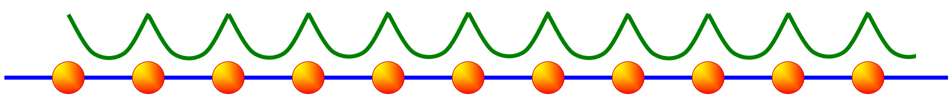
LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

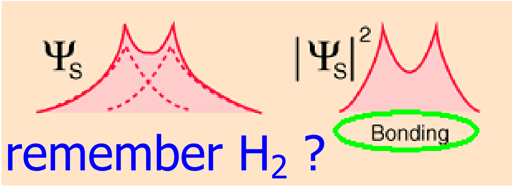
$$\psi_k(\mathbf{r}) = \epsilon \sum_{\mathbf{n}=-\infty}^{\infty} \mathbf{e}^{-\mathbf{ikna}} \phi(\mathbf{r} - \mathbf{nai_x})$$

$k = 0$

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

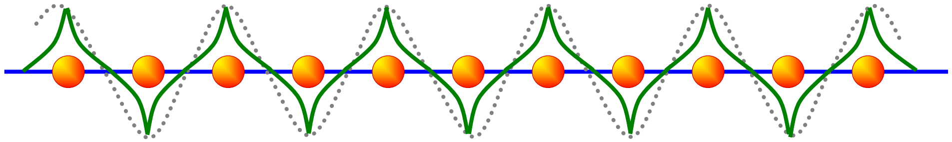


lowest energy (fewest nodes)

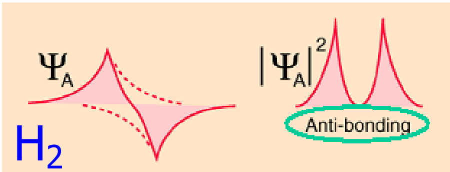


$k = \pi/a$

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



highest energy (most nodes)



Bloch's Theorem

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

Translation of wavefunction by a lattice constant…

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

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

…yields the original wavefunction multiplied by a phase factor

$$\psi_k(\mathbf{r} + \mathbf{a}\mathbf{i}_\mathbf{x}) = \mathbf{e}^{\mathbf{ika}} \psi_\mathbf{k}(\mathbf{r})$$

Consistent that the probability density is equal at each lattice site

Wavefunction Normalization

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

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

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

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

Counting Number of States in a Band

Combining periodic boundary condition…

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

…with Bloch's theorem…

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

…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

Tight-binding and Lattice Wave Formalism

Electrons (LCAO)

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

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

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

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

Lattice Waves

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

$$\widetilde{\mathbf{D}}_{i,j}(p,m) = \left(\frac{\partial^2 V}{\partial u_i[p,t]\,\partial u_j[m,t]}\right)_{\mathrm{eq}}$$

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