6.730 Physics for Solid State Applications

Lecture 13: Electrons in a Periodic Solid

Outline

- Review Electronic Bandstructure Calculations
- Example: 1-D Crystals with Two Atomic Functions
- Example: 1-D Crystals with Two Atom Basis

Overview

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

$2N$ electrons

Tight-binding and Lattice Wave Formalism

Electrons (LCAO)

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

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

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

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

Lattice Waves

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

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

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

Energy for LCAO Bands

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

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

$$\widetilde{H}(n,m) = \langle\phi(\mathbf{r} - \mathbf{n}\mathbf{a}\mathbf{i}_\mathbf{x})|\hat{\mathcal{H}}|\phi(\mathbf{r} - \mathbf{m}\mathbf{a}\mathbf{i}_\mathbf{x})\rangle$$

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

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

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

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

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

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

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

$$\equiv E_s$$

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

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

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

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

Energy Band for 1-D Lattice

Single orbital, single atom basis

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

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

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

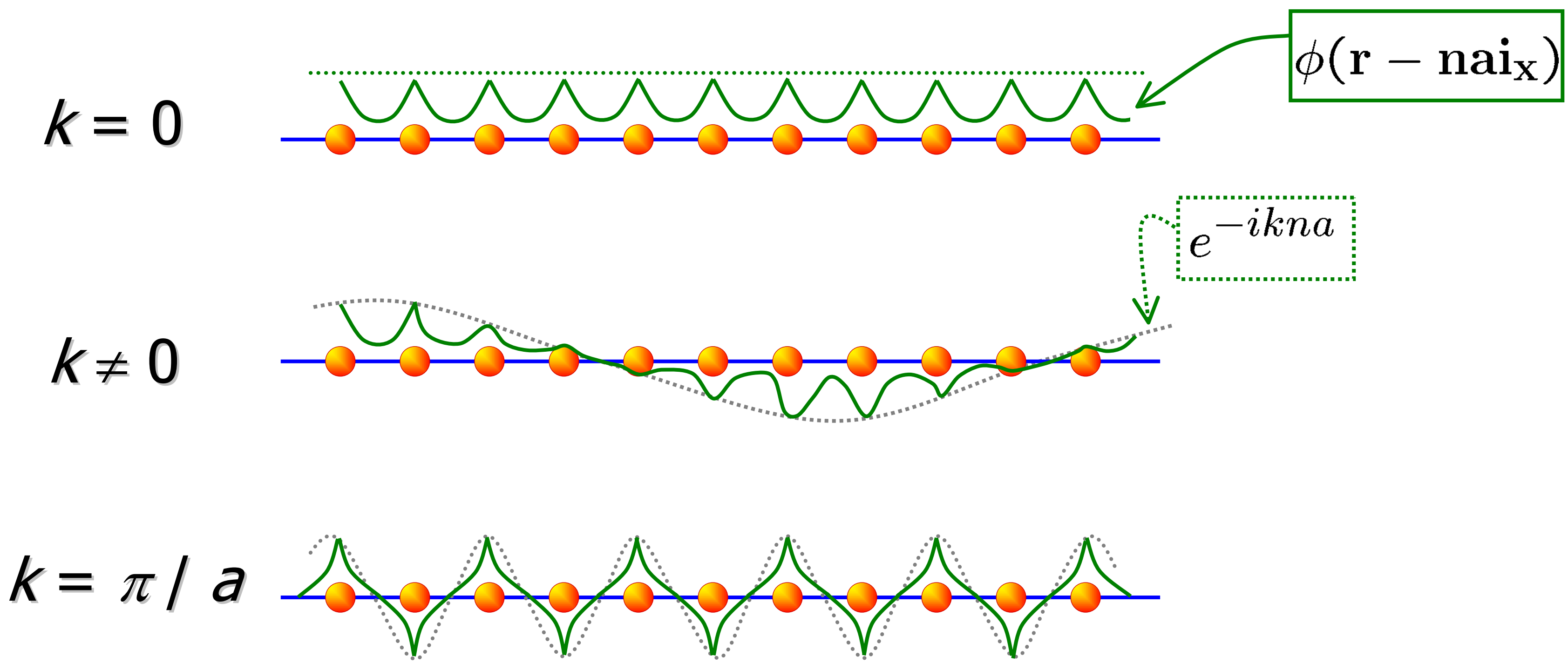
$$|\widetilde{S}(1)| \ll 1$$

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

LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

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



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

Energy Band for 1-D Lattice
Two orbital, single atom basis

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

2*N* electrons

Energy Band for 1-D Lattice

Two orbital, single atom basis

$$\alpha = 2s,\ 2p_x$$

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

$$\sum_{\alpha} \sum_{m=-\infty}^{\infty} \widetilde{\mathbf{H}}_{\beta,\alpha}(n,m)c_{\alpha}[m] = E \sum_{\alpha} \sum_{p=-\infty}^{\infty} \widetilde{\mathbf{S}}_{\beta,\alpha}(n,p)c_{\alpha}[p]$$

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

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

$$\mathbf{c}[\mathbf{n}] = \begin{pmatrix} c_{2s}[n] \\ c_{2p_x}[n] \end{pmatrix}$$

Energy Band for 1-D Lattice

Two orbital, single atom basis

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

$$\mathbf{c}[\mathbf{n}+\mathbf{1}] = \mathbf{e}^{\mathbf{ika}}\mathbf{c}[\mathbf{n}] \qquad \mathbf{c}[\mathbf{n}] = \mathbf{e}^{\mathbf{ikna}}\tilde{\epsilon}$$

Reduced Hamiltonian and Overlap Matrices:

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

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

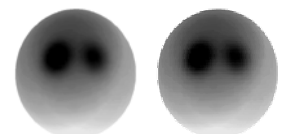
$$\mathbf{S}(\mathbf{k}) = \sum_{\mathbf{m}=-\infty}^{\infty} \tilde{\mathbf{S}}(\mathbf{n},\mathbf{m})\mathbf{e}^{\mathbf{ika}(\mathbf{m}-\mathbf{n})} = \sum_{\mathbf{p}=-\infty}^{\infty} \tilde{\mathbf{S}}(\mathbf{p})\mathbf{e}^{-\mathbf{ikpa}}$$

Energy Band for 1-D Lattice

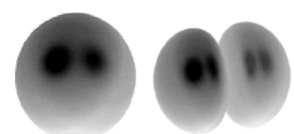
Two orbital, single atom basis
Hamiltonian Matrix

$$E_s = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r}) \rangle \qquad E_p = \langle \phi_p(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p}}(\mathbf{r}) \rangle$$

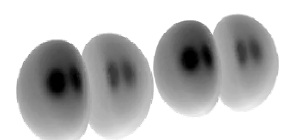
$$V_{ss\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) \rangle$$

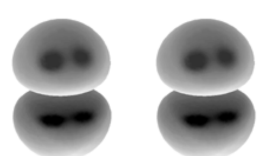


$$V_{sp\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) \rangle$$



$$V_{pp\sigma} = \langle \phi_{p_x}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) \rangle$$





$$V_{pp\pi} = \langle \phi_{p_y}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_y}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) \rangle$$

Energy Band for 1-D Lattice

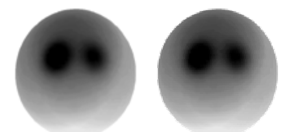
Two orbital, single atom basis

Overlap Matrix

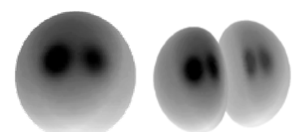
$$1 = \langle \phi_p(\mathbf{r}) | \phi_{\mathbf{p}}(\mathbf{r}) \rangle$$

$$1 = \langle \phi_s(\mathbf{r}) | \phi_{\mathbf{s}}(\mathbf{r}) \rangle$$

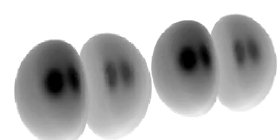
$$S_{ss\sigma} = \langle \phi_s(\mathbf{r}) | \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$

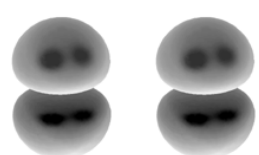


$$S_{sp\sigma} = \langle \phi_s(\mathbf{r}) | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$



$$S_{pp\sigma} = \langle \phi_{p_x}(\mathbf{r}) | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$





$$S_{pp\pi} = \langle \phi_{p_y}(\mathbf{r}) | \phi_{\mathbf{p_y}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$

Energy Band for 1-D Lattice

Two orbital, single atom basis

$$\mathbf{H}(\mathbf{k}) = \begin{array}{c|cc} & |\phi_s\rangle & |\phi_{p_x}\rangle \\ \hline \langle\phi_s| & E_s + V_{ss\sigma}\left(e^{ika} + e^{-ika}\right) & V_{sp\sigma}\left(e^{-ika} - e^{ika}\right) \\ \langle\phi_{p_x}| & V_{sp\sigma}\left(e^{ika} - e^{-ika}\right) & E_p + V_{pp\sigma}\left(e^{ika} + e^{-ika}\right) \end{array}$$

$$\mathbf{S}(\mathbf{k}) = \begin{array}{c|cc} & |\phi_s\rangle & |\phi_{p_x}\rangle \\ \hline \langle\phi_s| & 1 + S_{ss\sigma}\left(e^{ika} + e^{-ika}\right) & S_{sp\sigma}\left(e^{-ika} - e^{ika}\right) \\ \langle\phi_{p_x}| & S_{sp\sigma}\left(e^{ika} - e^{-ika}\right) & 1 + S_{pp\sigma}\left(e^{ika} + e^{-ika}\right) \end{array}$$

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

$$\begin{pmatrix} E_s + 2V_{ss\sigma}\cos ka & -i2V_{sp\sigma}\sin ka \\ i2V_{sp\sigma}\sin ka & E_{p_x} + 2V_{pp\sigma}\cos ka \end{pmatrix} \begin{pmatrix} \epsilon_{2s} \\ \epsilon_{2p_x} \end{pmatrix} = E(k) \begin{pmatrix} \epsilon_{2s} \\ \epsilon_{2p_x} \end{pmatrix}$$

Energy Band for 1-D Lattice

Two orbital, single atom basis

Solutions

$$E_{1,2}(k) = \frac{E_1 + E_2}{2} \pm \frac{1}{2}\left\{(E_2 - E_1)^2 + 4V^2\right\}^{1/2}$$

$$E_1 = E_s + 2V_{ss\sigma}\cos ka \qquad E_2 = E_p + 2V_{pp\sigma}\cos ka \qquad V = 2V_{sp\sigma}\sin ka$$

At k=0:

$$E_1(0) = E_s - 2|V_{ss\sigma}| \qquad \text{with} \qquad \vec{\epsilon}_{1,0} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$ pure s

$$\psi_{1,0}(\mathbf{r}) = \epsilon_{\mathbf{1,0}}\left[\cdots + \phi_{\mathbf{s}}(\mathbf{r} + \mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{s}}(\mathbf{r}) + \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{2a}\mathbf{i}_{\mathbf{x}}) + \ldots\right]$$

$$E_2(0) = E_p + 2|V_{pp\sigma}| \qquad \text{with} \qquad \vec{\epsilon}_{2,0} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$ pure p

$$\psi_{2,0}(\mathbf{r}) = \epsilon_{\mathbf{2,0}}\left[\cdots + \phi_{\mathbf{p_x}}(\mathbf{r} + \mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{p_x}}(\mathbf{r}) + \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) + \ldots\right]$$

Energy Band for 1-D Lattice
Two orbital, single atom basis
Solutions

At k=π/a:

$$E_1(\pi/a) = E_s + 2|V_{ss\sigma}| \qquad \text{with} \qquad \vec{\epsilon}_2(0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$ pure s

$$\psi_{1,\pi/a}(\mathbf{r}) = \epsilon_{1,\pi/\mathbf{a}}\left[\cdots - \phi_{\mathbf{s}}(\mathbf{r}+\mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{s}}(\mathbf{r}) - \phi_{\mathbf{s}}(\mathbf{r}-\mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{s}}(\mathbf{r}-\mathbf{2a}\mathbf{i}_{\mathbf{x}}) - \ldots\right]$$

$$E_2(\pi/a) = E_p - 2|V_{pp\sigma}| \qquad \text{with} \qquad \vec{\epsilon}_{2,0} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$ pure p

$$\psi_{2,\pi/a}(\mathbf{r}) = \epsilon_{2,\pi/\mathbf{a}}\left[\cdots - \phi_{\mathbf{p_x}}(\mathbf{r}+\mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{p_x}}(\mathbf{r}) - \phi_{\mathbf{p_x}}(\mathbf{r}-\mathbf{a}\mathbf{i}_{\mathbf{x}}) + \phi_{\mathbf{p_x}}(\mathbf{r}-\mathbf{2a}\mathbf{i}_{\mathbf{x}}) - \ldots\right]$$

For k away from zone center and zone boundary, bands are mixture of s and p but will have a dominant s-like or p-like character….

At high symmetry points tight-binding returns pure orbitals…

Energy Band for 1-D Lattice

Two orbital, single atom basis

Solutions

$$\psi_{2,0}(\mathbf{r}) = \epsilon_{\mathbf{2,0}} \left[\cdots + \phi_{\mathbf{p_x}}(\mathbf{r} + \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{p_x}}(\mathbf{r}) + \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) + \ldots\right]$$

$$\boxed{E_2(0) = E_p + 2|V_{pp\sigma}|}$$

$$\psi_{2,\pi/a}(\mathbf{r}) = \epsilon_{\mathbf{2},\pi/\mathbf{a}} \left[\cdots - \phi_{\mathbf{p_x}}(\mathbf{r} + \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{p_x}}(\mathbf{r}) - \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{2a}\mathbf{i_x}) - \ldots\right]$$

$$\boxed{E_2(\pi/a) = E_p - 2|V_{pp\sigma}|}$$

$$\psi_{1,\pi/a}(\mathbf{r}) = \epsilon_{1,\pi/\mathbf{a}} \left[\cdots - \phi_{\mathbf{s}}(\mathbf{r} + \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{s}}(\mathbf{r}) - \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{2a}\mathbf{i_x}) - \ldots\right]$$

$$\boxed{E_1(\pi/a) = E_s + 2|V_{ss\sigma}|}$$

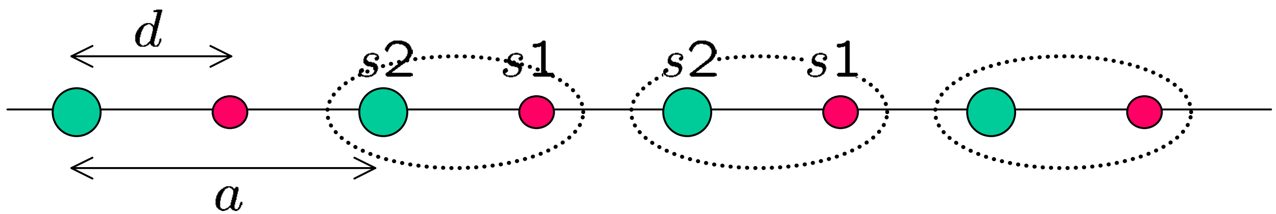
$$\psi_{1,0}(\mathbf{r}) = \epsilon_{1,0} \left[\cdots + \phi_{\mathbf{s}}(\mathbf{r} + \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{s}}(\mathbf{r}) + \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) + \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{2a}\mathbf{i_x}) + \ldots\right]$$

$$\boxed{E_1(0) = E_s - 2|V_{ss\sigma}|}$$

Energy Band for 1-D Lattice

Single orbital, two atom basis

$$\alpha = s1,\ s2$$



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

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

$$E_s = \langle \phi_{s1}(\mathbf{r})|\hat{\mathcal{H}}|\phi_{\mathbf{s1}}(\mathbf{r})\rangle \qquad E_s = \langle \phi_{s2}(\mathbf{r})|\hat{\mathcal{H}}|\phi_{\mathbf{s2}}(\mathbf{r})\rangle$$

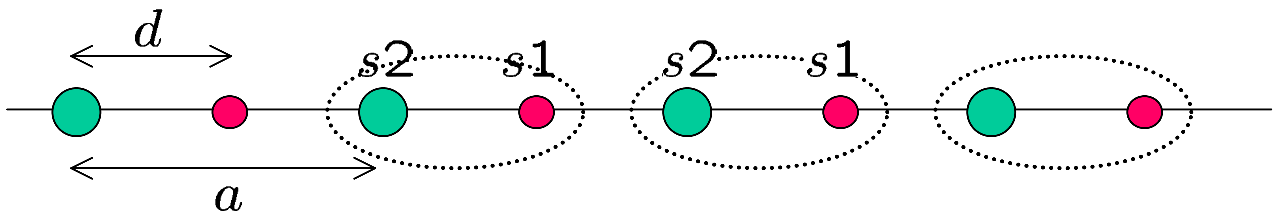
$$V_{s,d} = \langle \phi_{s1}(\mathbf{r})|\hat{\mathcal{H}}|\phi_{\mathbf{s2}}(\mathbf{r})\rangle$$

$$V_{s,a-d} = \langle \phi_{s2}(\mathbf{r})|\hat{\mathcal{H}}|\phi_{\mathbf{s1}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}})\rangle \qquad V_{s,a-d} = \langle \phi_{s1}(\mathbf{r})|\hat{\mathcal{H}}|\phi_{\mathbf{s2}}(\mathbf{r} + \mathbf{a}\mathbf{i}_{\mathbf{x}})\rangle$$

Energy Band for 1-D Lattice

Single orbital, two atom basis

$$\alpha = s1,\ s2$$



$$\mathbf{H}(\mathbf{k}) = \begin{array}{c} \\ \langle\phi_{s1}| \\ \langle\phi_{s2}| \end{array} \begin{array}{cc} |\phi_{s1}\rangle & |\phi_{s2}\rangle \\ \end{array} \begin{pmatrix} E_s & V_{s,d} + V_{s,a-d}e^{ika} \\ V_{s,d} + V_{s,a-d}e^{-ika} & E_s \end{pmatrix}$$

$$\mathbf{S}(\mathbf{k}) = \mathbf{1}$$

$$E_{1,2} = E_s \pm \left\{ V_{s,d}^2 + V_{s,a-d}^2 + 2V_{s,d}V_{s,a-d}\cos ka \right\}^{1/2}$$

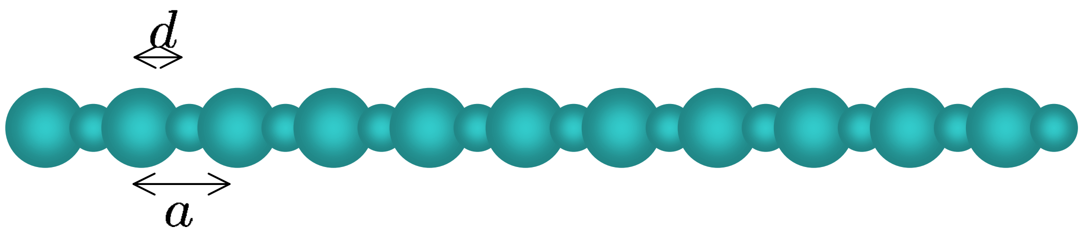
Energy Band for 1-D Lattice

Single orbital, two atom basis

At k=0:

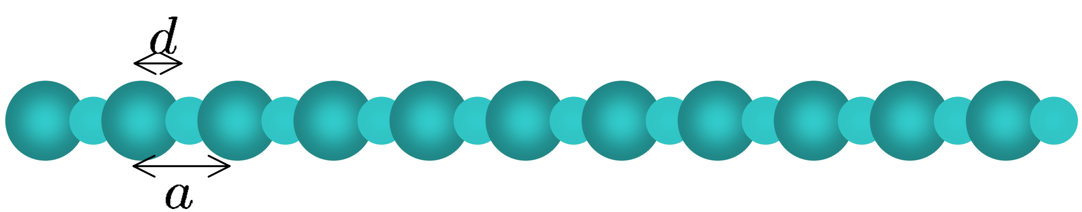
$$E_1(0) = E_s + (V_{s,d} + V_{s,a-d}) \qquad \text{with} \qquad \vec{\epsilon}_{1,0} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\psi_{1,0}(\mathbf{r}) = \epsilon_{\mathbf{1,0}} \{ \cdots + \phi_{\mathrm{s}}(\mathbf{r}) + \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{d}\mathbf{i_x}) + \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) + \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{d}\mathbf{i_x} - \mathbf{a}\mathbf{i_x}) + \dots \}$$



$$E_2(0) = E_s - (V_{s,d} + V_{s,a-d}) \qquad \text{with} \qquad \vec{\epsilon}_{2,0} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\psi_{2,0}(\mathbf{r}) = \epsilon_{\mathbf{2,0}} \{ \cdots + \phi_{\mathrm{s}}(\mathbf{r}) - \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{d}\mathbf{i_x}) + \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{a}\mathbf{i_x}) - \phi_{\mathrm{s}}(\mathbf{r} - \mathbf{d}\mathbf{i_x} - \mathbf{a}\mathbf{i_x}) + \dots \}$$



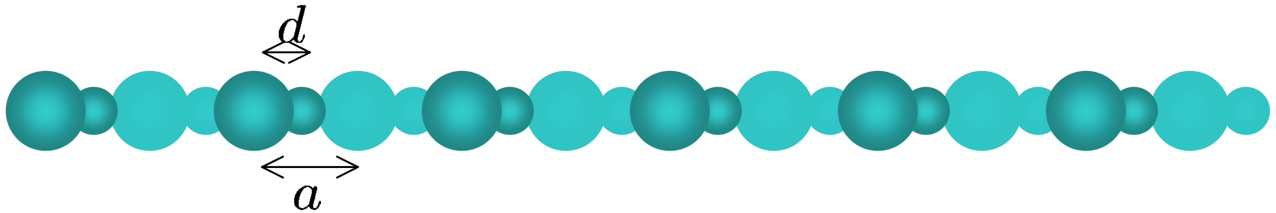
Energy Band for 1-D Lattice

Single orbital, two atom basis

At k=π/a:

$$E_1(\pi/a) = E_s + (V_{s,d} - V_{s,a-d}) \quad \text{with} \quad \vec{\epsilon}_{1,\pi/a} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\psi_{2,\pi/a}(\mathbf{r}) = \epsilon_{\mathbf{1},\pi/\mathbf{a}}\{\cdots + \phi_\mathrm{s}(\mathbf{r}) + \phi_\mathrm{s}(\mathbf{r} - \mathbf{d}\mathbf{i}_\mathrm{x}) - \phi_\mathrm{s}(\mathbf{r} - \mathbf{a}\mathbf{i}_\mathrm{x}) - \phi_\mathrm{s}(\mathbf{r} - \mathbf{d}\mathbf{i}_\mathrm{x} - \mathbf{a}\mathbf{i}_\mathrm{x}) + \ldots\}$$



$$E_2(\pi/a) = E_s - (V_{s,d} - V_{s,a-d}) \quad \text{with} \quad \vec{\epsilon}_{2,0} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\psi_{2,\pi/a}(\mathbf{r}) = \epsilon_{\mathbf{2},\pi/\mathbf{a}}\{\cdots + \phi_\mathrm{s}(\mathbf{r}) - \phi_\mathrm{s}(\mathbf{r} - \mathbf{d}\mathbf{i}_\mathrm{x}) - \phi_\mathrm{s}(\mathbf{r} - \mathbf{a}\mathbf{i}_\mathrm{x}) + \phi_\mathrm{s}(\mathbf{r} - \mathbf{d}\mathbf{i}_\mathrm{x} - \mathbf{a}\mathbf{i}_\mathrm{x}) - \ldots\}$$