6.730 Physics for Solid State Applications

Lecture 15: Electrons in a Periodic Solid

Outline

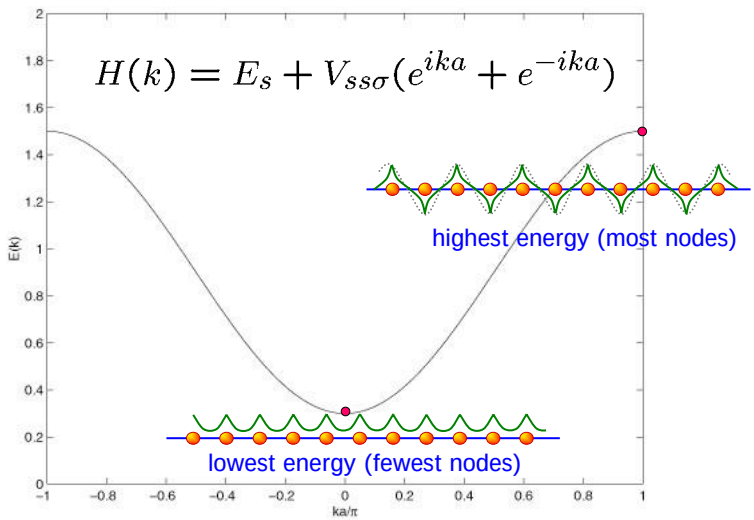
- Review LCAO for 1-D Crystals
- Preview Problem for 2-D Crystal
- 2-D and 3-D Tight-binding
- Example: 2-D Crystal, single atom basis, 4 orbitals

March 8, 2004

Energy Band for 1-D Lattice

Single orbital, single atom basis

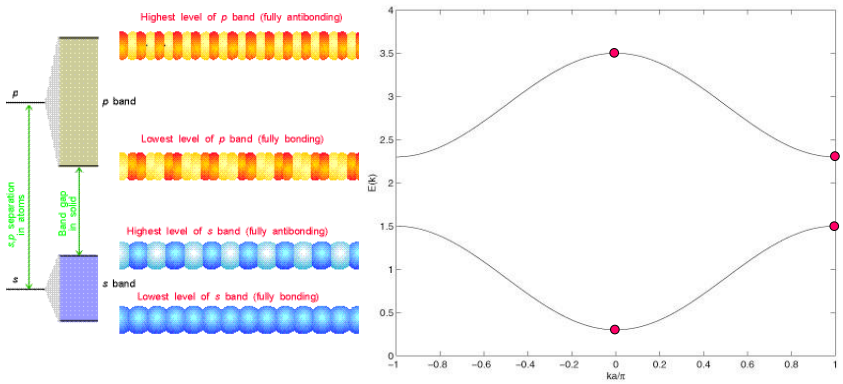
$$H(k) = E_s + V_{ss\sigma}(e^{ika} + e^{-ika})$$



Energy Band for 1-D Lattice

Two orbital, single atom basis

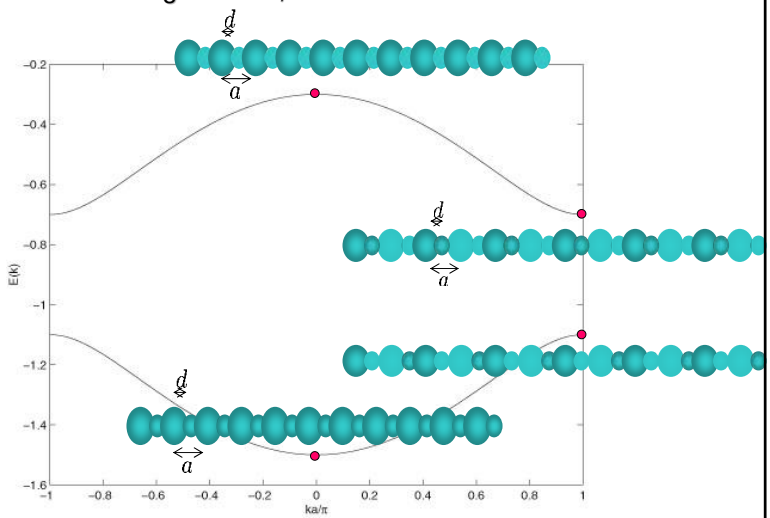
$$\mathbf{H(k)} = \begin{array}{c} \\ \langle\phi_s| \\ \langle\phi_{p_x}| \end{array} \begin{array}{c} \begin{array}{cc} |\phi_s\rangle & |\phi_{p_x}\rangle \end{array} \\ \begin{pmatrix} E_s + V_{ss\sigma}\left(e^{ika} + e^{-ika}\right) & V_{sp\sigma}\left(e^{-ika} - e^{ika}\right) \\ V_{sp\sigma}\left(e^{ika}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



E_s= - 12 eV, E_p= - 6 eV, $V_{ss\sigma}$= - 1 eV, $V_{pp\sigma} = V_{pp\pi}$ = + 1 eV

Energy Band for 1-D Lattice

Single orbital, two atom basis



E_s= - 0.9 eV, $V_{s,a}$= - 0.4 eV, $V_{s,a\text{-}d}$ = - 0.2 eV

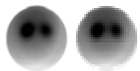
Energy Band for 1-D Lattice

Two orbital, single atom basis

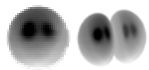
Hamiltonian Matrix

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

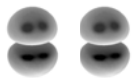
$$V_{ss\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a i_x}) \rangle$$



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



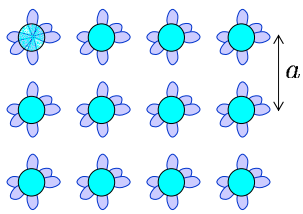
$$V_{pp\sigma} = \langle \phi_{p_x}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a i_x}) \rangle$$



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

Preview Problem: 2D Monatomic Square Crystals

$$\mathbf{c}[\mathbf{R_n}] = \begin{pmatrix} c_s \\ c_{p_x} \\ c_{p_y} \\ c_{p_z} \end{pmatrix}$$



$$\mathbf{H(k)} = \sum_{\mathbf{R_p}} \widetilde{\mathbf{H}}(\mathbf{R_p}) \mathbf{e}^{-\mathbf{ik}\cdot\mathbf{R_p}}$$

$$\mathbf{H(k)} = \begin{array}{c} \\ \langle\phi_s| \\ \langle\phi_{p_x}| \\ \langle\phi_{p_y}| \\ \langle\phi_{p_z}| \end{array} \begin{array}{c} \begin{array}{cccc} |\phi_s\rangle & |\phi_{p_x}\rangle & |\phi_{p_y}\rangle & |\phi_{p_z}\rangle \end{array} \\ \begin{pmatrix} E_s + V_{ss\sigma} g_o & ? & ? & ? \\ V_{sp\sigma} g_1^* & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix} \end{array}$$

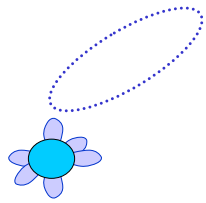
$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a}$$

$$g_1 = e^{-ik_x a} - e^{ik_x a} \qquad g_2 = -e^{-ik_y a} + e^{+ik_y a}$$

$$g_3 = e^{-ik_y a} + e^{ik_y a} \qquad g_4 = e^{-ik_x a} + e^{ik_x a}$$

LCAO Basis for FCC Crystals

$$\psi(\mathbf{r}) = \sum_{\alpha} \sum_{\mathbf{n}=\mathbf{R}_\ell} \mathbf{c}_\alpha[\mathbf{R}_\ell]\phi_\alpha(\mathbf{r}-\mathbf{R}_\ell)$$



Ga: [Ar]3d^{10} 4s^2 4p^1

As: [Ar]3d^{10} 4s^2 4p^3

$$\mathbf{c}[\mathbf{R_n}] = \begin{pmatrix} c_{s1} \\ c_{p_{x1}} \\ c_{p_{y1}} \\ c_{p_{z1}} \\ c_{s2} \\ c_{p_{x2}} \\ c_{p_{y2}} \\ c_{p_{z2}} \end{pmatrix}$$

Tight-binding for 3-D Crystals

$$\psi(\mathbf{r}) = \sum_{\alpha} \sum_{\mathbf{n}=\mathbf{R}_\ell} \mathbf{c}_\alpha[\mathbf{R}_\ell]\phi_\alpha(\mathbf{r}-\mathbf{R}_\ell)$$

Best estimate for energy with LCAO basis....

$$\sum_{\alpha} \sum_{\mathbf{R_m}} \widetilde{\mathbf{H}}_{\beta,\alpha}(\mathbf{R_n},\mathbf{R_m})\mathbf{c}_\alpha[\mathbf{R_m}] = \mathbf{E} \sum_{\alpha} \sum_{\mathbf{R_p}} \tilde{\mathbf{S}}_{\beta,\alpha}(\mathbf{R_n},\mathbf{R_p})\mathbf{c}_\alpha[\mathbf{R_p}]$$

Hamiltonian matrix....

$$\widetilde{\mathbf{H}}_{\beta,\alpha}(\mathbf{R_n},\mathbf{R_m}) = \langle \phi_\beta(\mathbf{r}-\mathbf{R_n}) | \hat{\mathcal{H}} | \phi_\alpha(\mathbf{r}-\mathbf{R_m}) \rangle$$

Overlap matrix....

$$\tilde{\mathbf{S}}_{\beta,\alpha}(\mathbf{R_n},\mathbf{R_p}) = \langle \phi_\beta(\mathbf{r}-\mathbf{R_n}) | \phi_\alpha(\mathbf{r}-\mathbf{R_p}) \rangle$$

Tight-binding for 3-D Crystals

$$\psi(\mathbf{r}) = \sum_{\alpha} \sum_{\mathbf{n}=\mathbf{R}_\ell} \mathbf{c}_\alpha[\mathbf{R}_\ell]\phi_\alpha(\mathbf{r}-\mathbf{R}_\ell)$$

Since the probability of finding electrons at each lattice site is equal...

$$\mathbf{c}[\mathbf{R}_\mathbf{n}+\mathbf{R}_\ell] = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_\ell}\mathbf{c}[\mathbf{R}_\mathbf{n}] \qquad \mathbf{c}[\mathbf{R}_\mathbf{n}] = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_\mathbf{n}}\tilde{\epsilon}$$

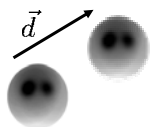
Consequently...

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

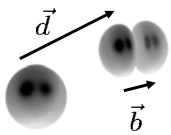
$$\mathbf{H}(\mathbf{k}) = \sum_{\mathbf{R}_\mathbf{p}} \widetilde{\mathbf{H}}(\mathbf{R}_\mathbf{p})\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}_\mathbf{p}} \qquad \mathbf{S}(\mathbf{k}) = \sum_{\mathbf{R}_\mathbf{p}} \tilde{\mathbf{S}}(\mathbf{R}_\mathbf{p})\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}_\mathbf{p}}$$

Orbital Overlaps for 3-D Crystals

$$\langle\phi_{s1}|\hat{\mathcal{H}}|\phi_{s2}\rangle = V_{ss\sigma}$$

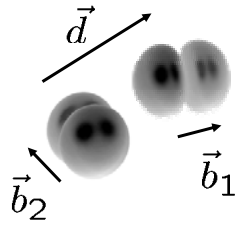


$$\langle\phi_{s1}|\hat{\mathcal{H}}|\phi_{p_2}\rangle = V_{sp\sigma}\hat{\mathbf{d}}\cdot\hat{\mathbf{b}}$$



$\vec{b}$ distance from positive to negative lobe of p-orbital

Orbital Overlaps for 3-D Crystals



$$\langle \phi_{p1} | \hat{\mathcal{H}} | \phi_{p2} \rangle = (\hat{\mathbf{d}}\cdot\hat{\mathbf{b}}_1)(\hat{\mathbf{d}}\cdot\hat{\mathbf{b}}_2)\, V_{pp\sigma} + [\hat{\mathbf{b}}_1 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{d}})]\cdot[\hat{\mathbf{b}}_2 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{d}})]\, V_{pp\pi}$$

$V_{pp\sigma}$ $V_{pp\pi}$

Orbital Overlaps for 3-D Crystals

Diamond and Zincblende

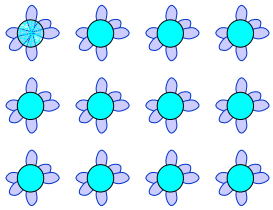
$$V_{\ell\ell' m} = \eta_{\ell\ell' m} \frac{\hbar^2}{2md^2}$$

$\eta_{ss\sigma} = -1.40 \approx -9\pi^2/64$ $\eta_{pp\sigma} = 3.24$

$\eta_{sp\sigma} = 1.84$ $\eta_{pp\pi} = -0.81$

2D Monatomic Square Crystals

$$\mathbf{c}[\mathbf{R_n}] = \begin{pmatrix} c_s \\ c_{p_x} \\ c_{p_y} \\ c_{p_z} \end{pmatrix}$$



$$\mathbf{H(k)} = \begin{array}{c} \\ \langle\phi_s| \\ \langle\phi_{p_x}| \\ \langle\phi_{p_y}| \\ \langle\phi_{p_z}| \end{array} \begin{array}{c} \begin{array}{cccc} |\phi_s\rangle & |\phi_{p_x}\rangle & |\phi_{p_y}\rangle & |\phi_{p_z}\rangle \end{array} \\ \begin{pmatrix} E_s + V_{ss\sigma} g_o & V_{sp\sigma} g_1 & V_{sp\sigma} g_2^* & 0 \\ V_{sp\sigma} g_1^* & E_p + V_{pp\pi} g_3 + V_{pp\sigma} g_4 & 0 & 0 \\ V_{sp\sigma} g_2 & 0 & E_p + V_{pp\pi} g_4 + V_{pp\sigma} g_3 & 0 \\ 0 & 0 & 0 & E_p + V_{pp\pi} g_o \end{pmatrix} \end{array}$$

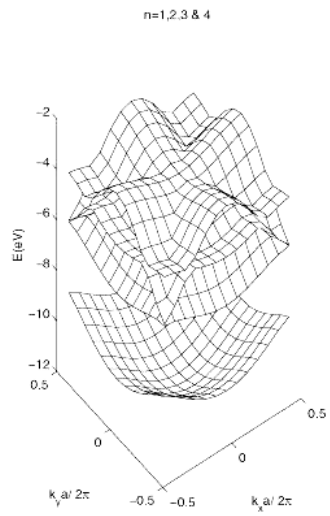
$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a}$$

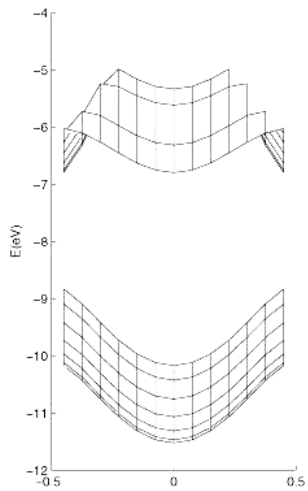
$$g_1 = e^{-ik_x a} - e^{ik_x a} \qquad g_2 = -e^{-ik_y a} + e^{+ik_y a}$$

$$g_3 = e^{-ik_y a} + e^{ik_y a} \qquad g_4 = e^{-ik_x a} + e^{ik_x a}$$

2D Monatomic Square Crystals

Dispersion Relations





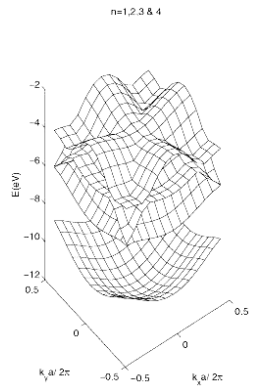
E_s= - 10.11 eV

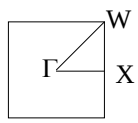
E_p= - 4.86 eV

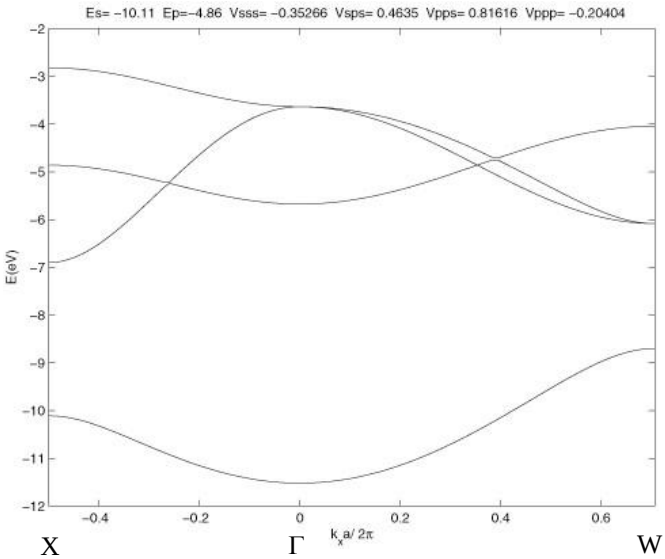
a = 5.5 A

2D Monatomic Square Crystals

Dispersion Relations







2D Monatomic Square Crystals

Dispersion Relations at Γ=0

$$\mathbf{H(k)} = \begin{array}{c} \\ \langle\phi_s| \\ \langle\phi_{p_x}| \\ \langle\phi_{p_y}| \\ \langle\phi_{p_z}| \end{array} \begin{array}{c} \begin{array}{cccc} |\phi_s\rangle & |\phi_{p_x}\rangle & |\phi_{p_y}\rangle & |\phi_{p_z}\rangle \end{array} \\ \begin{pmatrix} E_s + V_{ss\sigma} g_o & V_{sp\sigma} g_1 & V_{sp\sigma} g_2^* & 0 \\ V_{sp\sigma} g_1^* & E_p + V_{pp\pi} g_3 + V_{pp\sigma} g_4 & 0 & 0 \\ V_{sp\sigma} g_2 & 0 & E_p + V_{pp\pi} g_4 + V_{pp\sigma} g_3 & 0 \\ 0 & 0 & 0 & E_p + V_{pp\pi} g_o \end{pmatrix} \end{array}$$

$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a} \rightarrow 4$$

$$g_1 = e^{-ik_x a} - e^{ik_x a} \rightarrow 0$$

$$g_2 = -e^{-ik_y a} + e^{+ik_y a} \rightarrow 0$$

$$g_3 = e^{-ik_y a} + e^{ik_y a} \rightarrow 2$$

$$g_4 = e^{-ik_x a} + e^{ik_x a} \rightarrow 2$$

2D Monatomic Square Crystals

Dispersion Relations at Γ=0

$$\mathbf{H}(\Gamma) = \begin{pmatrix} E_s + 4V_{ss\sigma} & 0 & 0 & 0 \\ 0 & E_p + 2V_{pp\pi} + 2V_{pp\sigma} & 0 & 0 \\ 0 & 0 & E_p + 2V_{pp\pi} + 2V_{pp\sigma} & 00 \\ 0 & 0 & 0 & E_p + 4V_{pp\pi} \end{pmatrix}$$

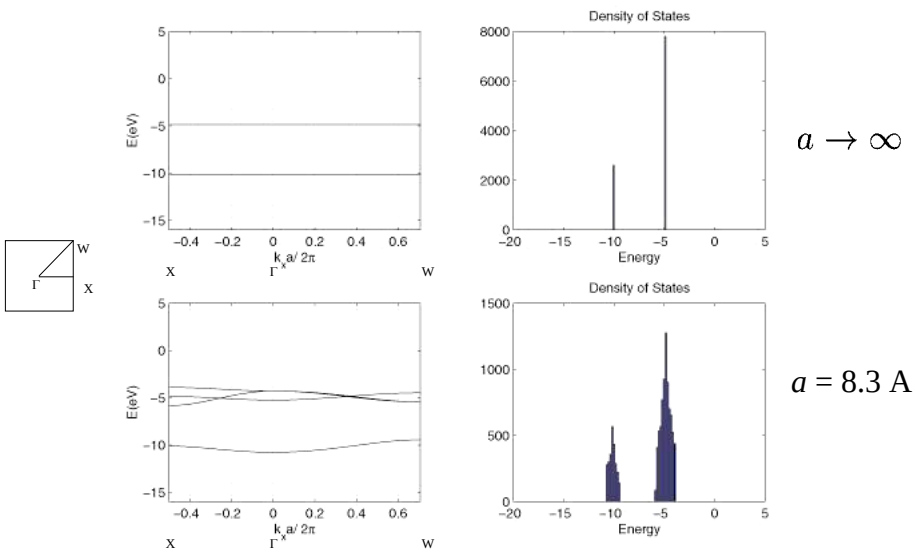
$$E_1(\Gamma) = E_s + 4V_{ss\sigma} \qquad \vec{\epsilon}_1(\Gamma) = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{\epsilon}_3(\Gamma) = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$E_2(\Gamma) = E_p + 4V_{pp\pi}$$

$$E_3(\Gamma) = E_4(\Gamma) = E_p + 2V_{pp\pi} + 2V_{pp\sigma} \qquad \vec{\epsilon}_4(\Gamma) = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad \vec{\epsilon}_2(\Gamma) = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

2D Monatomic Square Crystals

Variations with Lattice Constant

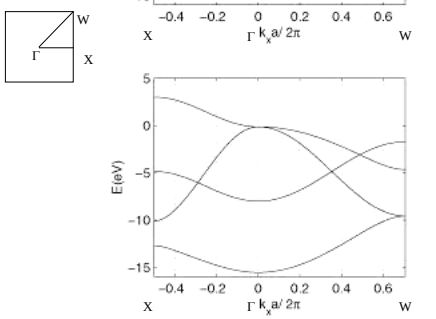


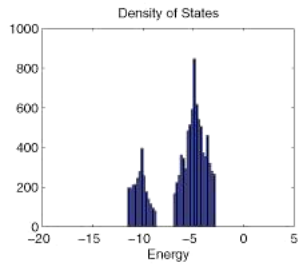
$a \to \infty$

a = 8.3 A

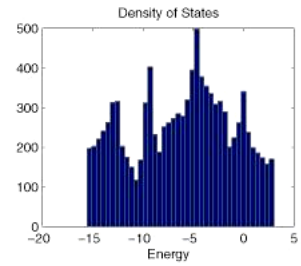
2D Monatomic Square Crystals

Dispersion Relations





a = 5.5 A



a = 2.8 A

2D Monatomic Square Crystals

Fermi Energy

How many states per band ?

$$2 \cdot \frac{\text{Area of BZ}}{\text{Area per state}} = \frac{2 \cdot \left(\frac{2\pi}{a}\right)^2}{\left(\frac{2\pi}{L}\right)^2} = 2n$$

where n is the areal density of atoms

To estimate Fermi energy we need to know the number of outermost valence electrons each atom has...

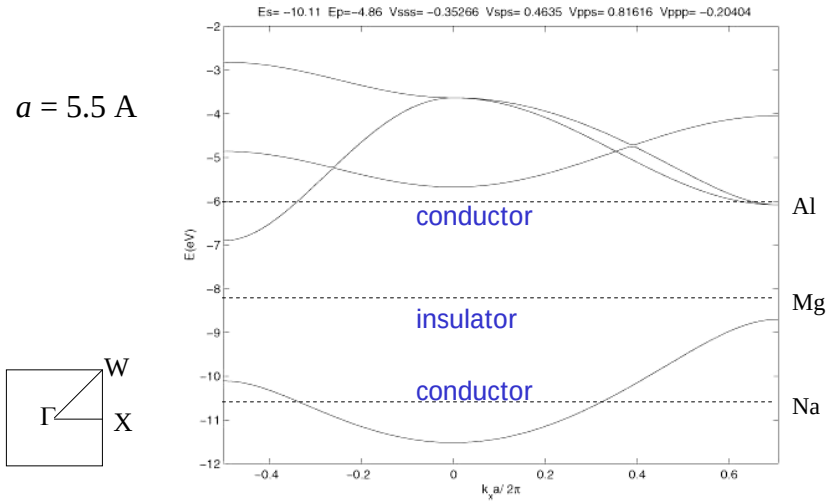
I	II
11 Na	12 Mg

III	IV	V	VI	VII	VIII
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

2D Monatomic Square Crystals

Dispersion Relations

a = 5.5 A



Reducing a, makes Mg a conductor !

I	II	III	IV	V	VI	VII	VIII
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

Name: _____

$$\mathbf{H(k)} = \begin{array}{c} \\ \langle\phi_s| \\ \langle\phi_{p_x}| \\ \langle\phi_{p_y}| \\ \langle\phi_{p_z}| \end{array} \begin{array}{c} \begin{array}{cccc} |\phi_s\rangle & |\phi_{p_x}\rangle & |\phi_{p_y}\rangle & |\phi_{p_z}\rangle \end{array} \\ \begin{pmatrix} E_s + V_{ss\sigma} g_o & ? & ? & ? \\ V_{sp\sigma} g_1^* & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix} \end{array}$$

Matrix element (s-p_x) _____

Matrix element (s-p_y) _____

Matrix element (p_x -p_x) _____

Matrix element (p_x - p_y) _____