6.730 Physics for Solid State Applications

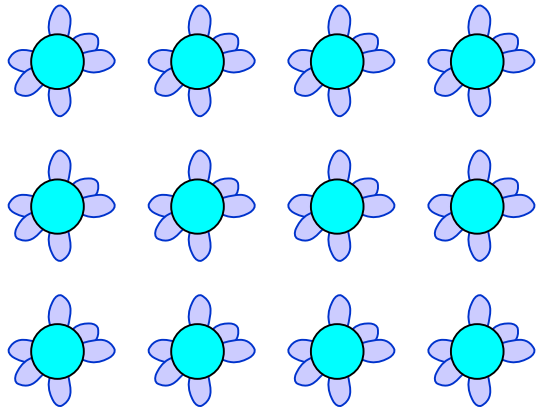
Lecture 15: Electrons in a Periodic Solid

Outline

- Review 2-D Tight-binding
- 3-D Tight-binding
- Semiconductor Fermi Energy
- Silicon Bandstructure

2D Monatomic Square Crystals

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



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

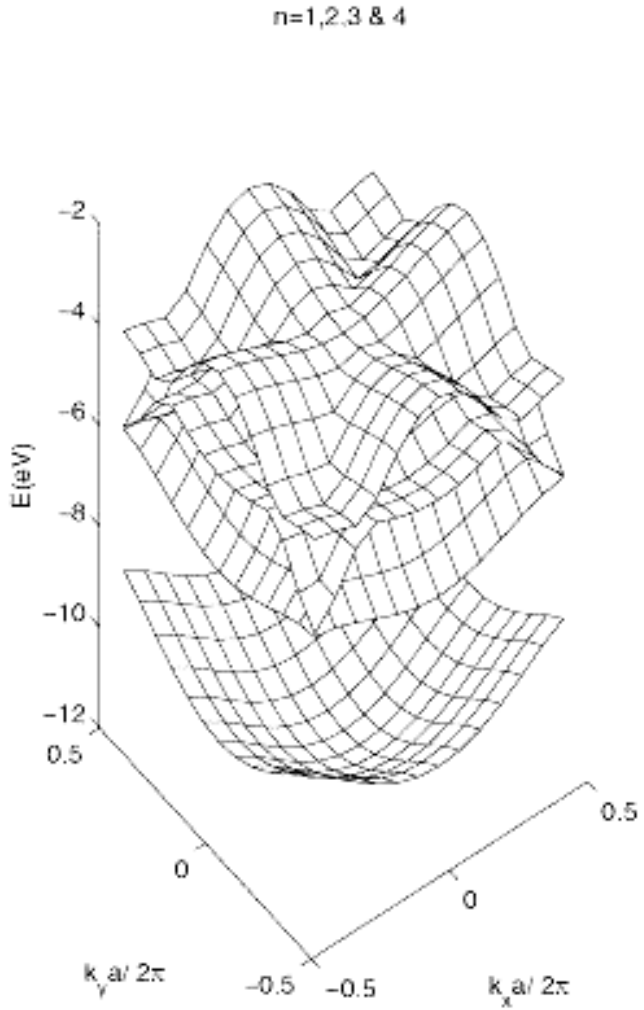
$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a}$$

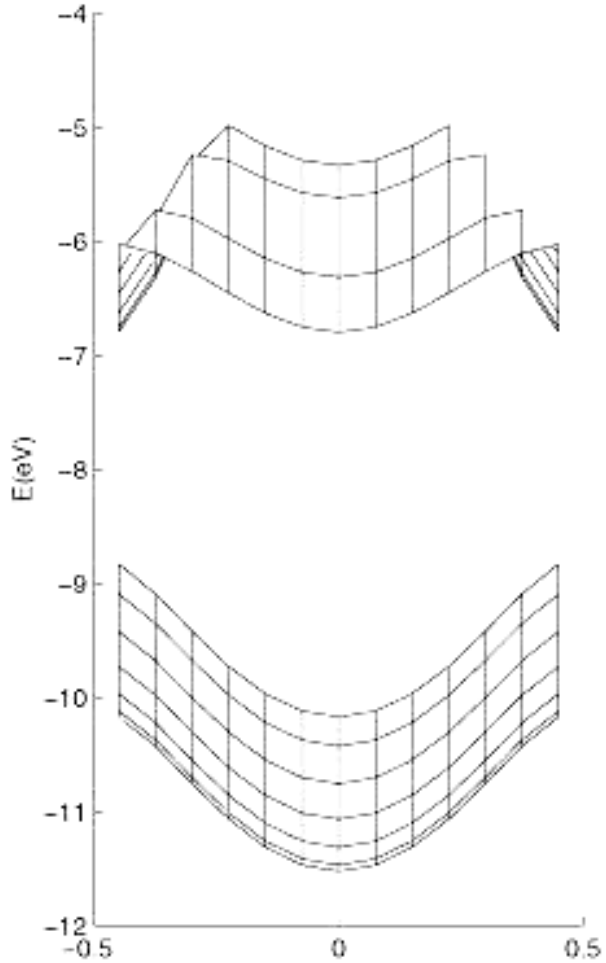
$$g_1 = e^{-ik_x a} - e^{ik_x a} \qquad g_2 = -e^{-ik_y a} + e^{+ik_y a}$$

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

2D Monatomic Square Crystals

Dispersion Relations





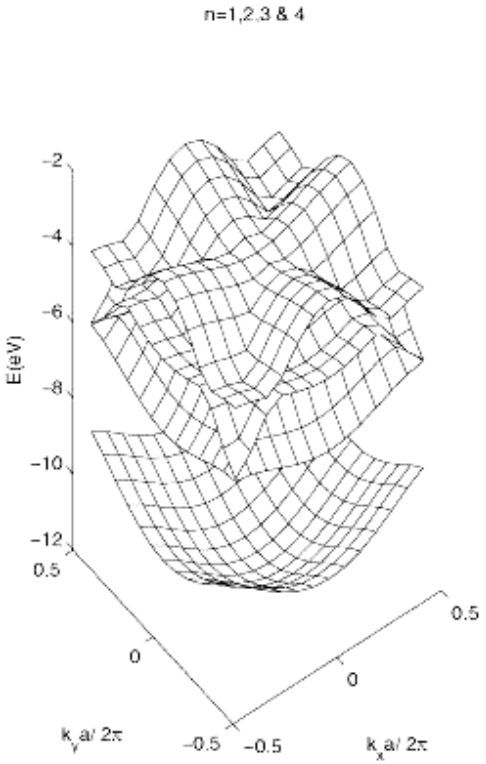
E_s = - 10.11 eV

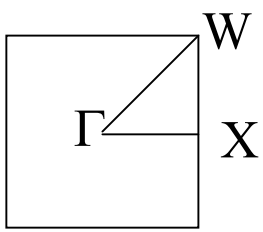
E_p = - 4.86 eV

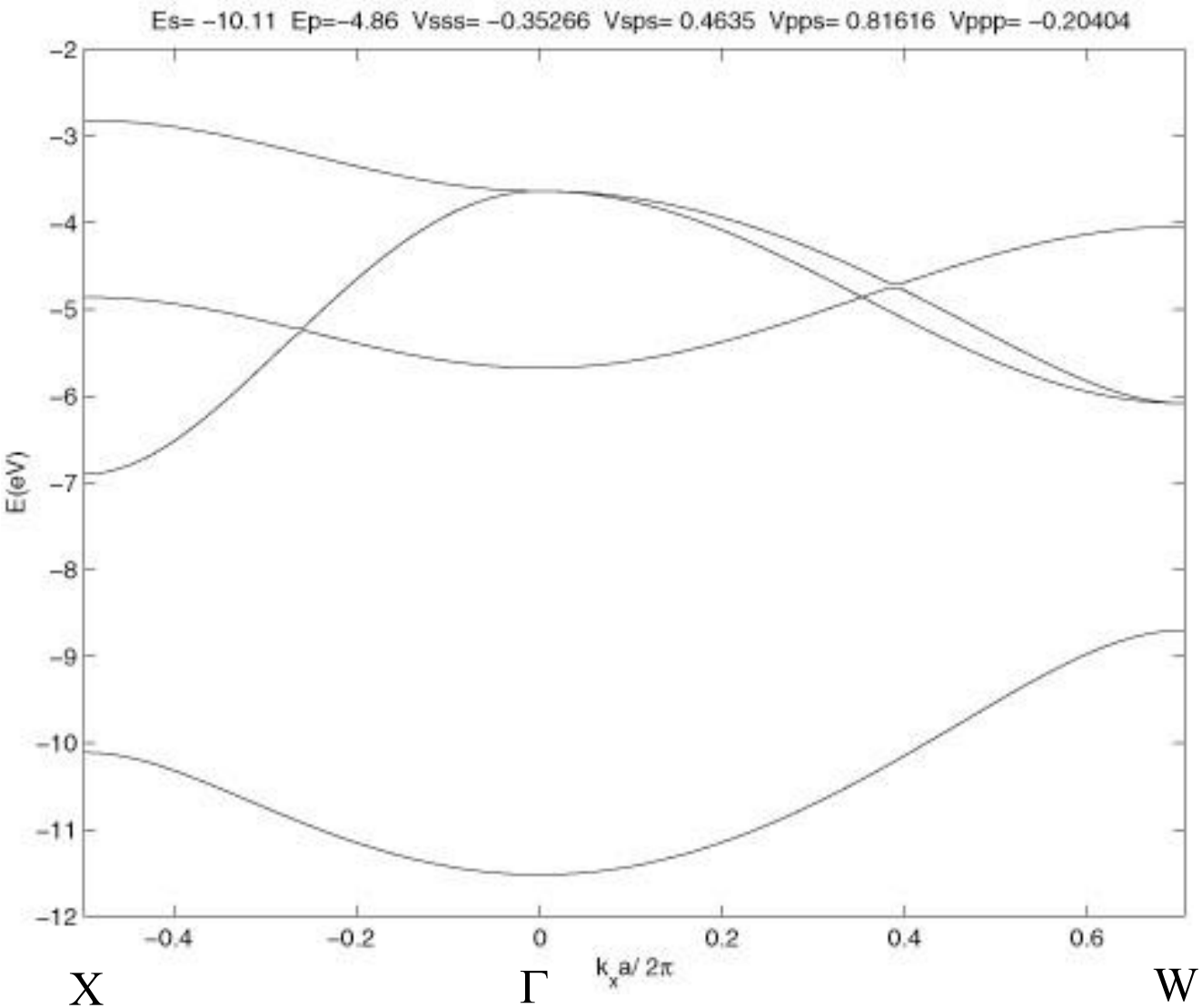
a = 5.5 A

2D Monatomic Square Crystals

Dispersion Relations

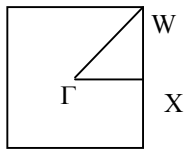


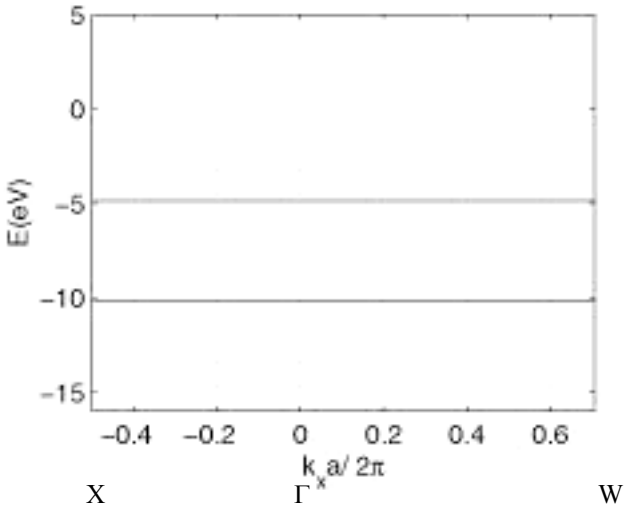


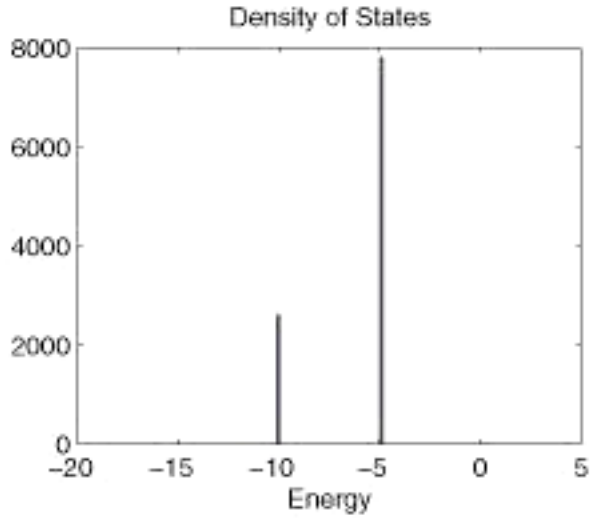


2D Monatomic Square Crystals

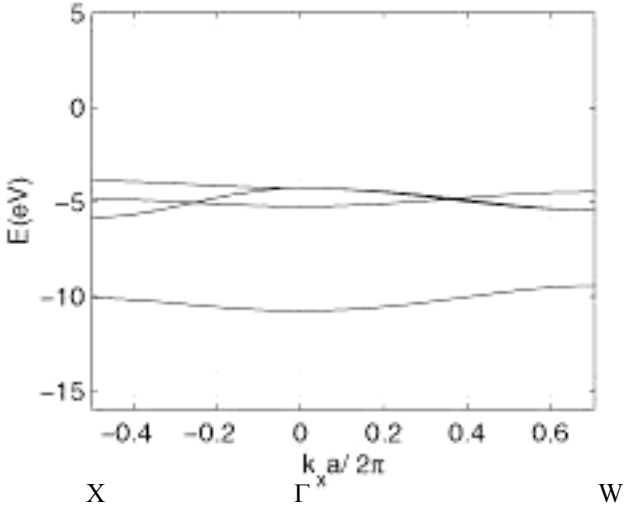
Variations with Lattice Constant

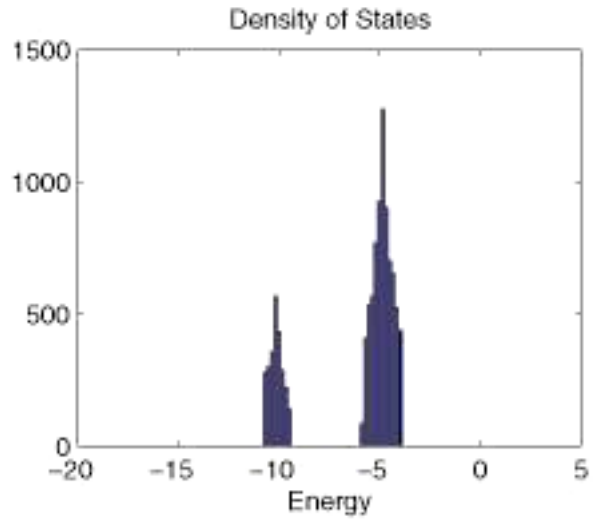






$a \to \infty$

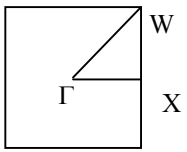


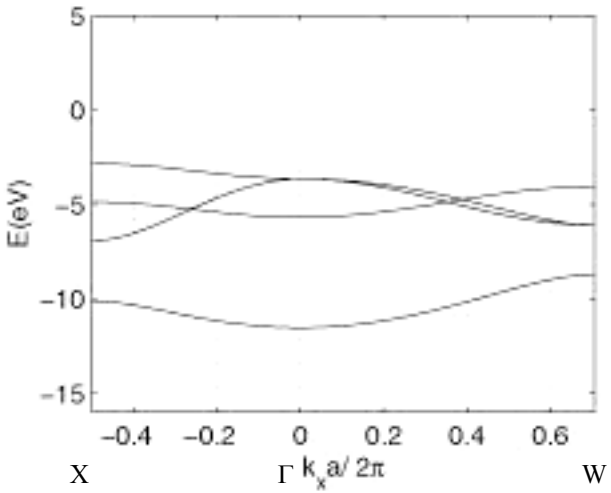


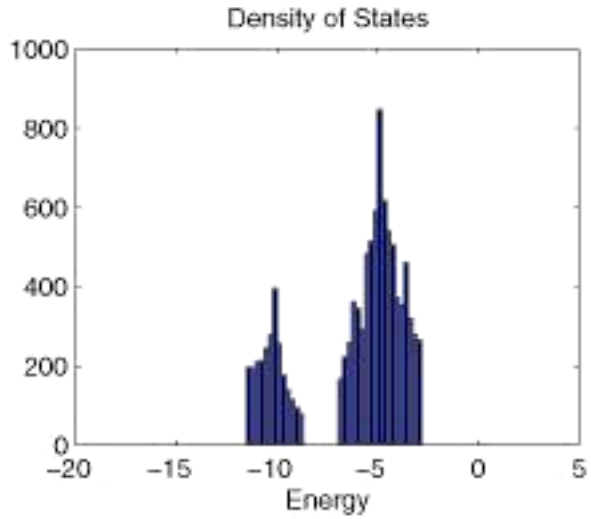
$a = 8.3$ A

2D Monatomic Square Crystals

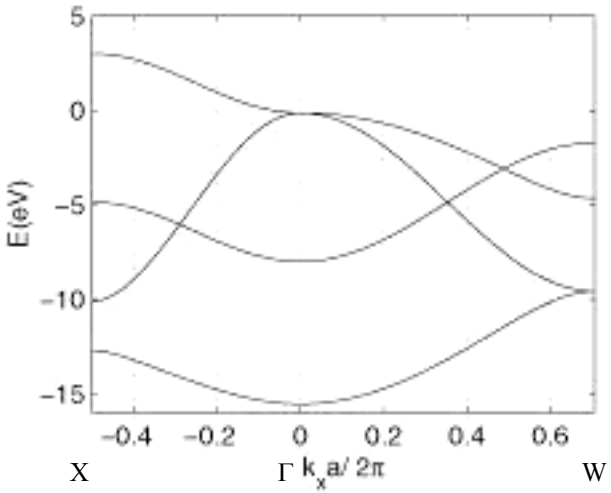
Dispersion Relations

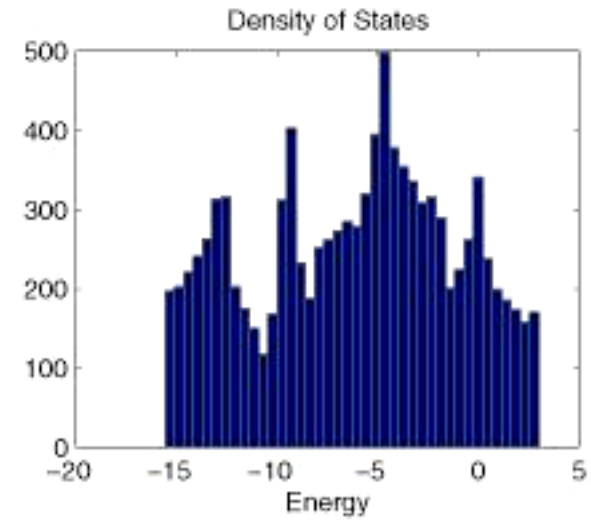






$a = 5.5$ A





$a = 2.8$ 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

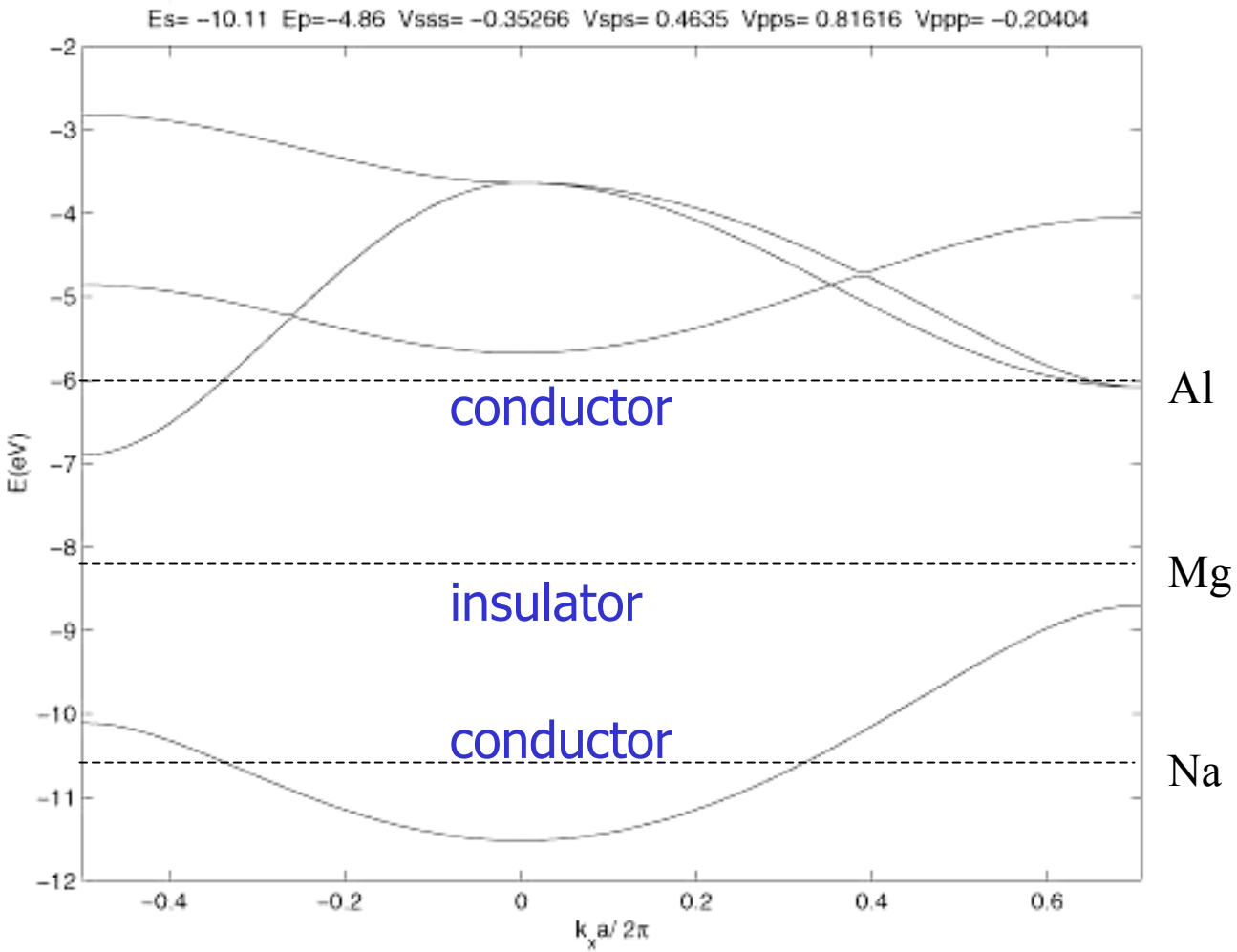
To estimate Fermi energy we need to know the number of outermost valence electrons each atom has…

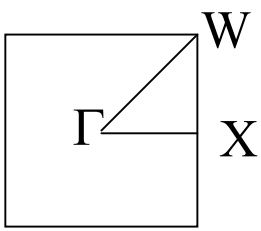
I	II	III	IV	V	VI	VII	VIII
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

2D Monatomic Square Crystals

Dispersion Relations

$a = 5.5$ A



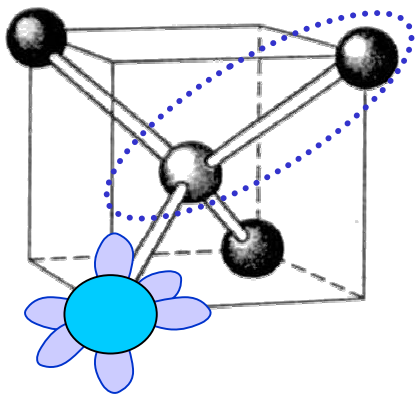


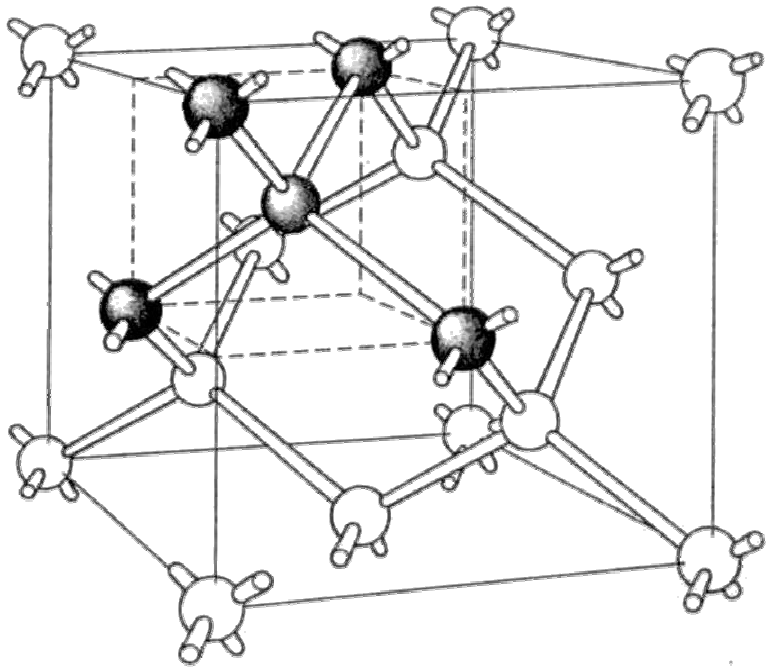
Reducing *a*, makes Mg a conductor (semimetal) !

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

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

$$\mathbf{c}[\mathbf{R_n}] = \begin{pmatrix} c_{s1} \\ c_{p_x 1} \\ c_{p_y 1} \\ c_{p_z 1} \\ c_{s2} \\ c_{p_x 2} \\ c_{p_y 2} \\ c_{p_z 2} \end{pmatrix}$$

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….

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

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….

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

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…

$$\mathbf{c}[\mathbf{R_n}+\mathbf{R}_\ell] = \mathbf{e}^{\mathbf{ik}\cdot\mathbf{R}_\ell}\mathbf{c}[\mathbf{R_n}] \qquad \mathbf{c}[\mathbf{R_n}] = \mathbf{e}^{\mathbf{ik}\cdot\mathbf{R_n}}\tilde{\epsilon}$$

Consequently…

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

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

Energy Band for 1-D Lattice

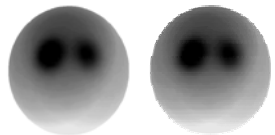
Two orbital, single atom basis

Hamiltonian Matrix

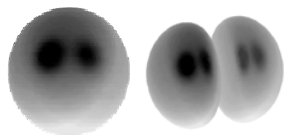
$$E_s = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r}) \rangle$$

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

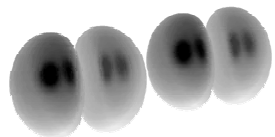
$$V_{ss\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$

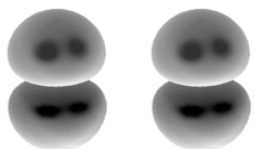


$$V_{sp\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$



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

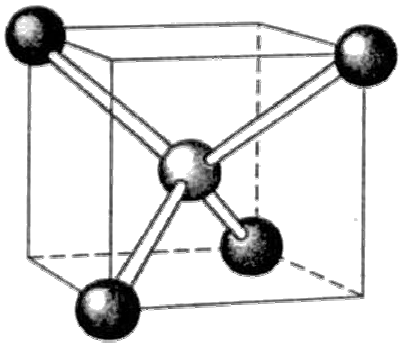


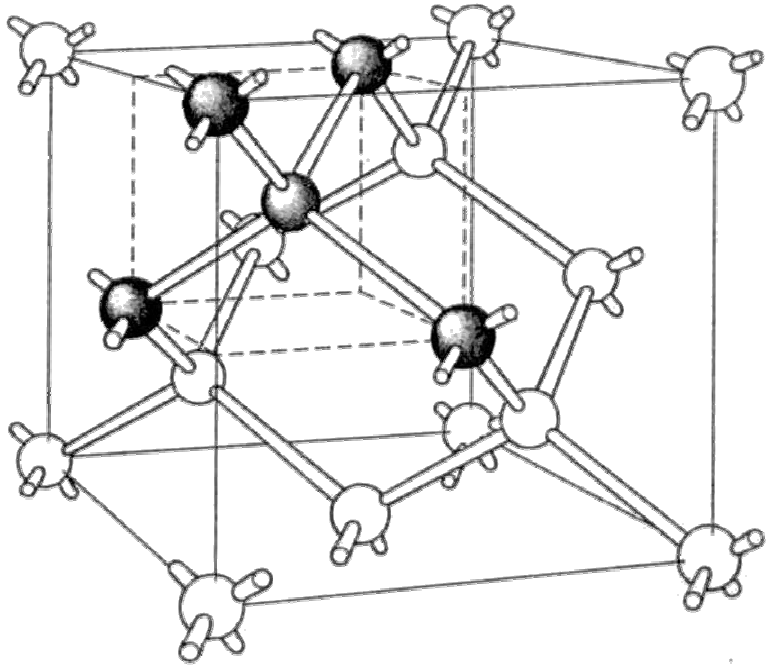


$$V_{pp\pi} = \langle \phi_{p_y}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_y}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$

Orbital Overlaps for 3-D Crystals

Diamond and Zincblende





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

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

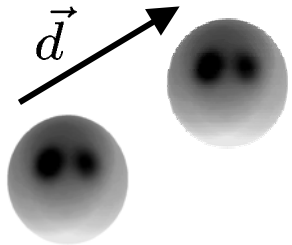
$$\eta_{pp\sigma} = \quad 3.24$$

$$\eta_{sp\sigma} = 1.84$$

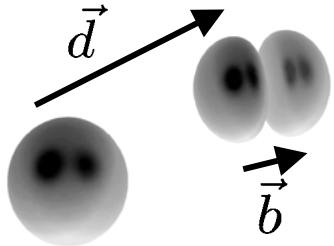
$$\eta_{pp\pi} = -0.81$$

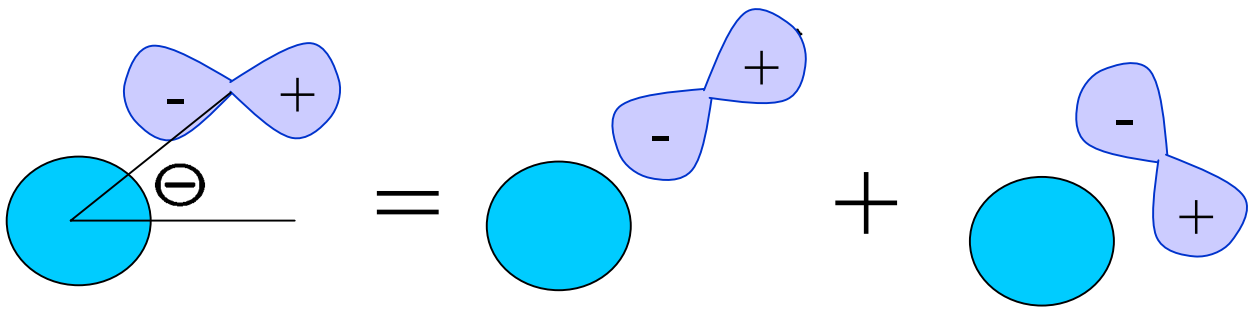
Orbital Overlaps for 3-D Crystals

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



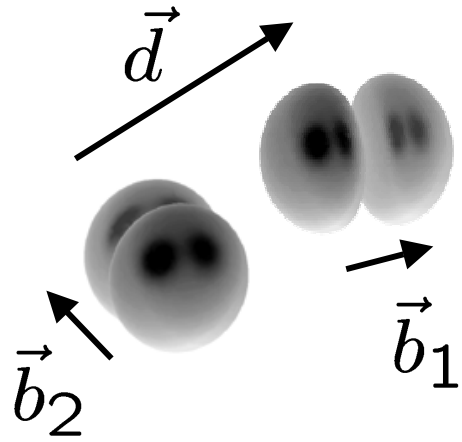
$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_2} \rangle = V_{sp\sigma} \hat{\mathbf{d}} \cdot \hat{\mathbf{b}}$$



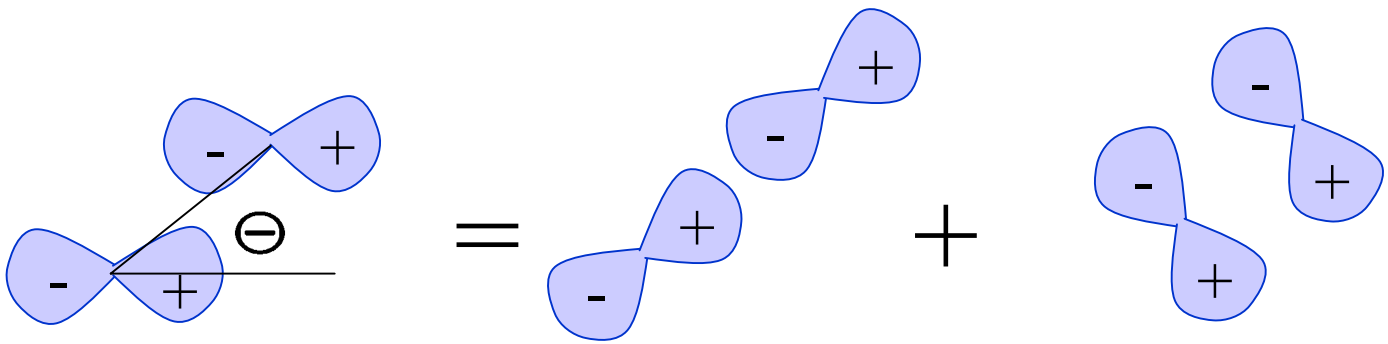


$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_{y2}} \rangle = V_{sp\sigma} cos\Theta + 0\, sin\Theta$$

Orbital Overlaps for 3-D Crystals



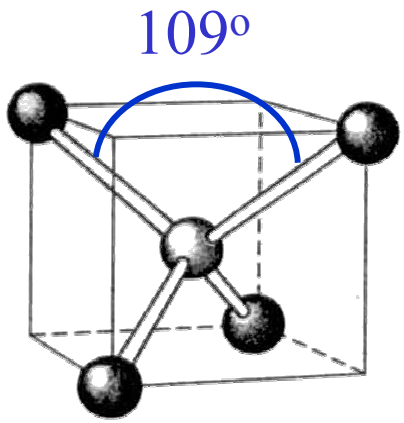
$$\langle \phi_{p1} | \hat{\mathcal{H}} | \phi_{p2} \rangle = (\hat{\mathbf{d}}\cdot\hat{\mathbf{b}}_1)(\hat{\mathbf{d}}\cdot\hat{\mathbf{b}}_2)\, V_{pp\sigma} + [\hat{\mathbf{b}}_1 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_1\cdot\hat{\mathbf{d}})]\cdot[\hat{\mathbf{b}}_2 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_2\cdot\hat{\mathbf{d}})]\,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

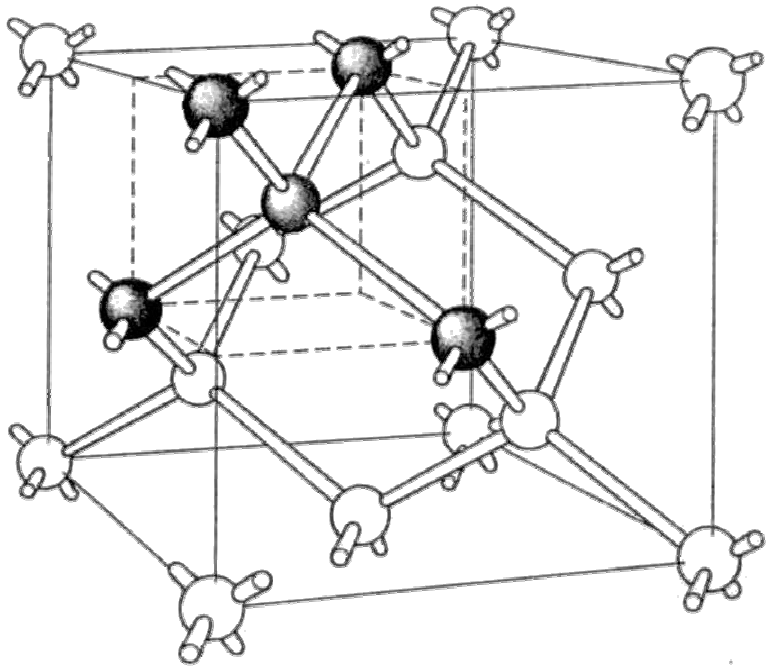


$$\langle \phi_{p_{y1}} | \hat{\mathcal{H}} | \phi_{p_{y2}} \rangle = V_{pp\sigma} cos^2\Theta + V_{pp\pi} sin^2\Theta$$

Orbital Overlaps for 3-D Crystals

Diamond and Zincblende





$$\Theta = \frac{109^o}{2}$$

$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_{y2}} \rangle = V_{sp\sigma} cos\Theta = V_{sp\sigma} \frac{1}{\sqrt{3}}$$

$$\langle \phi_{p_{y1}} | \hat{\mathcal{H}} | \phi_{p_{y2}} \rangle = V_{pp\sigma} cos^2\Theta + V_{pp\pi} sin^2\Theta = V_{pp\sigma} \frac{1}{3} + V_{pp\pi} \frac{2}{3}$$

Zincblende LCAO Bands

Reduced Hamiltonian Matrix

$$
\begin{array}{c}
 \\
\langle\phi_{s1}| \\
\langle\phi_{p_x1}| \\
\langle\phi_{p_y1}| \\
\langle\phi_{p_z1}| \\
\langle\phi_{s2}| \\
\langle\phi_{p_x2}| \\
\langle\phi_{p_y2}| \\
\langle\phi_{p_z2}|
\end{array}
\begin{array}{c}
\begin{array}{cccccccc}
|\phi_{s1}\rangle & |\phi_{p_x1}\rangle & |\phi_{p_y1}\rangle & |\phi_{p_z1}\rangle & |\phi_{s2}\rangle & |\phi_{p_x2}\rangle & |\phi_{p_y2}\rangle & |\phi_{p_z2}\rangle
\end{array} \\
\left(\begin{array}{cccccccc}
E_s & 0 & 0 & 0 & E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\
0 & E_p & 0 & 0 & -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\
0 & 0 & E_p & 0 & -E_{sp}g_2 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\
0 & 0 & 0 & E_p & -E_{sp}g_3 & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\
E_{ss}g_0^* & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & E_s & 0 & 0 & 0 \\
E_{sp}g_1^* & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & 0 & E_p & 0 & 0 \\
E_{sp}g_2^* & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & 0 & E_p & 0 \\
E_{sp}g_3^* & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & 0 & E_p
\end{array}\right)
\end{array}
$$

$$E_{ss} = V_{ss\sigma} \qquad E_{sp} = -\frac{1}{\sqrt{3}}V_{sp\sigma}$$

$$E_{xy} = \frac{1}{3}V_{pp\sigma} - \frac{1}{3}V_{pp\pi} \qquad E_{xx} = \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi}$$

Zincblende LCAO Bands

Nearest Neighbors

$$\mathbf{R}_2 = -\frac{\mathbf{a}}{\mathbf{2}}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{R}_3 = -\frac{\mathbf{a}}{\mathbf{2}}(\hat{\mathbf{z}} + \hat{\mathbf{x}})$$

$$\mathbf{R}_4 = -\frac{\mathbf{a}}{\mathbf{2}}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

Zincblende LCAO Bands

Reduced Hamiltonian Matrix

$$
\begin{array}{c}
 \\
\langle\phi_{s1}| \\
\langle\phi_{p_x1}| \\
\langle\phi_{p_y1}| \\
\langle\phi_{p_z1}| \\
\langle\phi_{s2}| \\
\langle\phi_{p_x2}| \\
\langle\phi_{p_y2}| \\
\langle\phi_{p_z2}|
\end{array}
\begin{array}{c}
\begin{array}{cccccccc}
|\phi_{s1}\rangle & |\phi_{p_x1}\rangle & |\phi_{p_y1}\rangle & |\phi_{p_z1}\rangle & |\phi_{s2}\rangle & |\phi_{p_x2}\rangle & |\phi_{p_y2}\rangle & |\phi_{p_z2}\rangle
\end{array} \\
\left(\begin{array}{cccccccc}
E_s & 0 & 0 & 0 & E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\
0 & E_p & 0 & 0 & -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\
0 & 0 & E_p & 0 & -E_{sp}g_2 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\
0 & 0 & 0 & E_p & -E_{sp}g_3 & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\
E_{ss}g_0^* & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & E_s & 0 & 0 & 0 \\
E_{sp}g_1^* & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & 0 & E_p & 0 & 0 \\
E_{sp}g_2^* & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & 0 & E_p & 0 \\
E_{sp}g_3^* & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & 0 & E_p
\end{array}\right)
\end{array}
$$

$$g_0 = 1 + e^{-i\mathbf{k}\cdot\mathbf{R_2}} + e^{-i\mathbf{k}\cdot\mathbf{R_3}} + e^{-i\mathbf{k}\cdot\mathbf{R_4}}$$

$$g_1 = 1 + e^{-i\mathbf{k}\cdot\mathbf{R_2}} - e^{-i\mathbf{k}\cdot\mathbf{R_3}} - e^{-i\mathbf{k}\cdot\mathbf{R_4}}$$

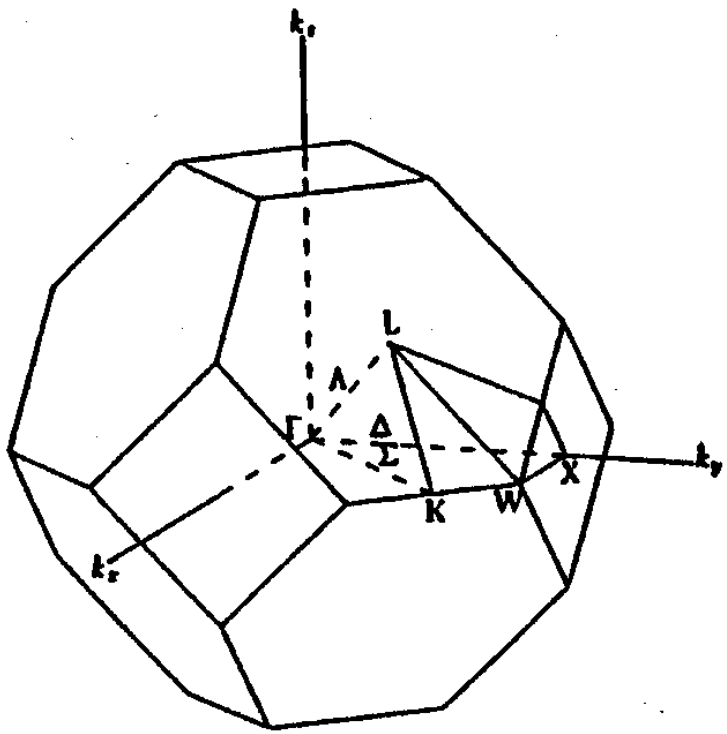
$$g_3 = 1 - e^{-i\mathbf{k}\cdot\mathbf{R_2}} + e^{-i\mathbf{k}\cdot\mathbf{R_3}} - e^{-i\mathbf{k}\cdot\mathbf{R_4}}$$

$$g_4 = 1 - e^{-i\mathbf{k}\cdot\mathbf{R_2}} - e^{-i\mathbf{k}\cdot\mathbf{R_3}} + e^{-i\mathbf{k}\cdot\mathbf{R_4}}$$

Silicon Bandstructure

Si: [Ne] $3s^2\ 3p^2$

4 e- per silicon atom
2 silicon atoms per lattice site
total: 8 electrons at each site



Silicon and Germanium Bandstructure

Si: [Ne] $3s^2\ 3p^2$

Ge: [Ar]$3d^{10}\ 4s^2\ 4p^2$

LCAO and Nearly Free Electron Bandstructure

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]} \phi_\alpha(r - \mathbf{R}_n) \qquad \psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{kr}}$$