6.730 Physics for Solid State Applications

Lecture 16: Electrons in a Periodic Solid

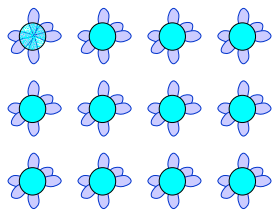
Outline

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

March 10, 2004

2D Monatomic Square Crystals

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



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

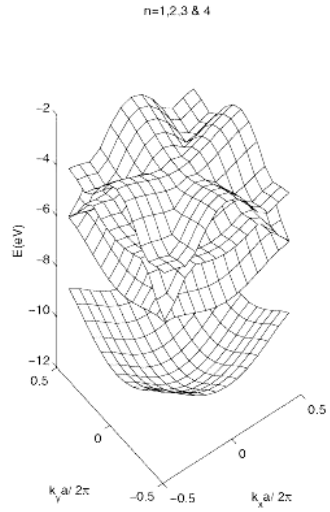
$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a}$$

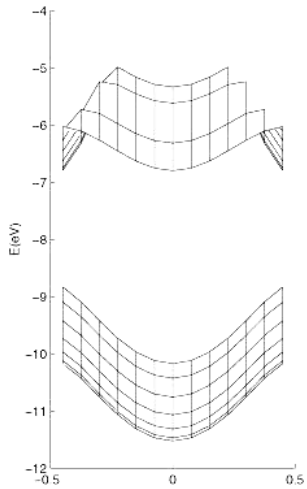
$$g_1 = e^{-ik_x a} - e^{ik_x a} \qquad g_2 = -e^{-ik_y a} + e^{+ik_y a}$$

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

2D Monatomic Square Crystals

Dispersion Relations





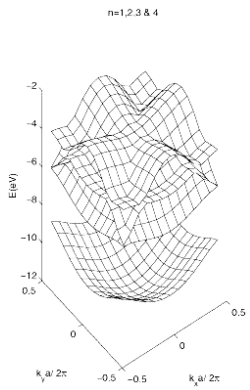
E_s= - 10.11 eV

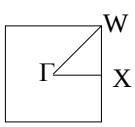
E_p= - 4.86 eV

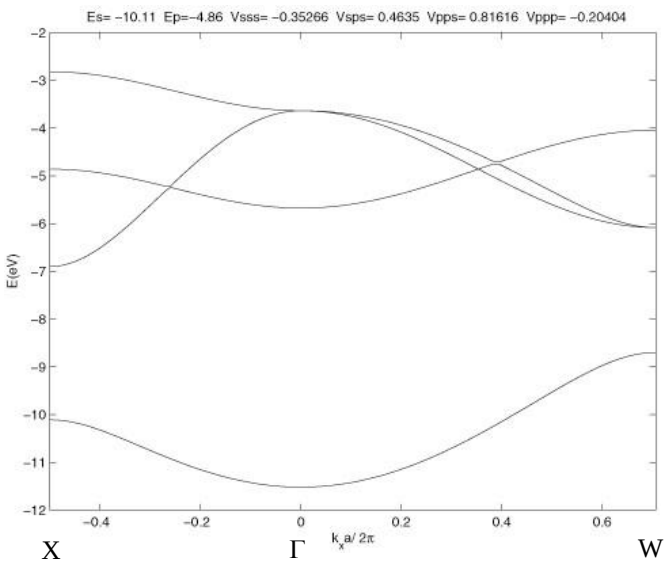
a = 5.5 A

2D Monatomic Square Crystals

Dispersion Relations

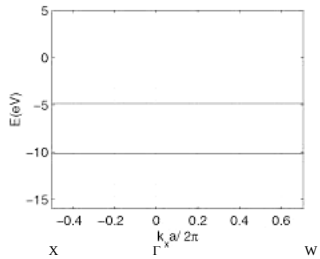


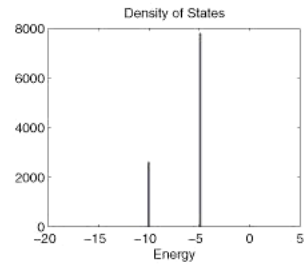




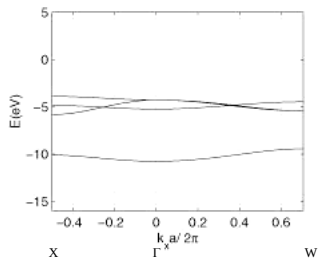
2D Monatomic Square Crystals

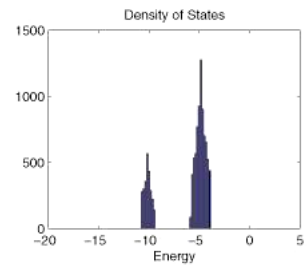
Variations with Lattice Constant





$a \to \infty$

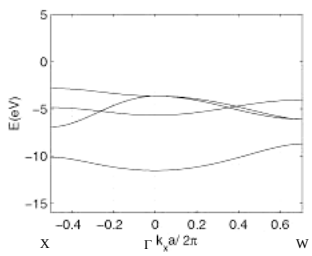


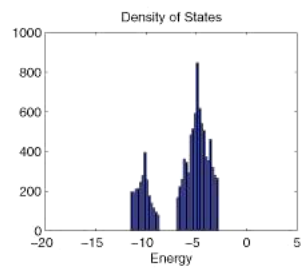


a = 8.3 A

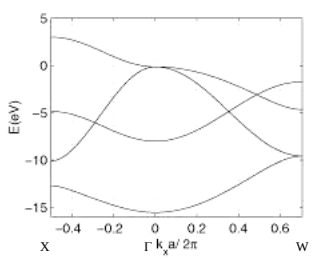
2D Monatomic Square Crystals

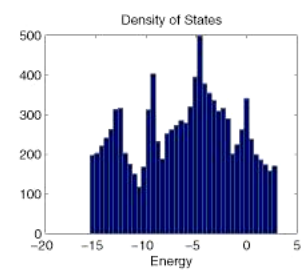
Dispersion Relations





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...

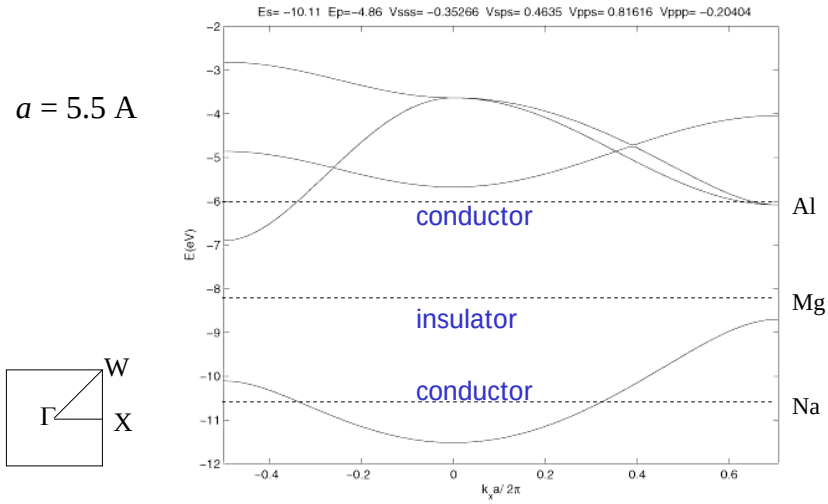
I	II
11 Na	12 Mg

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 (semimetal) !

I	II
11 Na	12 Mg

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

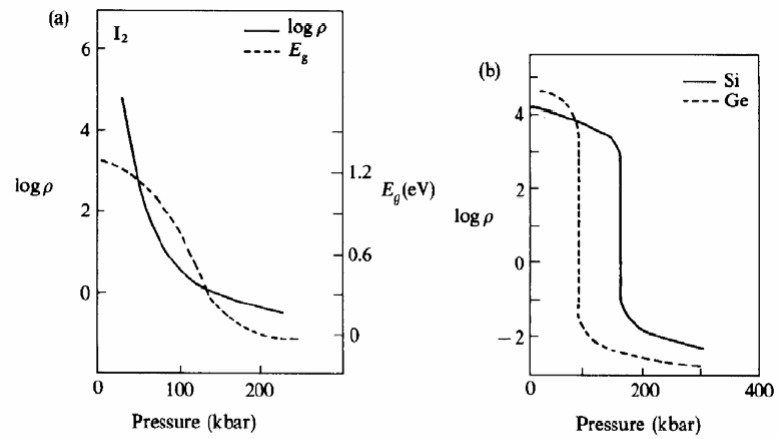
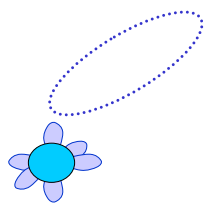


Fig. 5.20 Transitions to metallic state at high pressure. (a) Molecular iodine, showing electrical resistivity and band gap. (b) Electrical resistivity of silicon and germanium. (From H. G. Drickamer and C. W. Frank, *Electronic transitions and the high-pressure chemistry and physics of solids* Chapman and Hall, 1973.)

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...

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

Consequently...

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

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

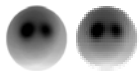
Energy Band for 1-D Lattice

Two orbital, single atom basis

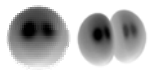
Hamiltonian Matrix

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

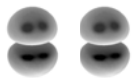
$$V_{ss\sigma} = \langle \phi_s(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{s}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$



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



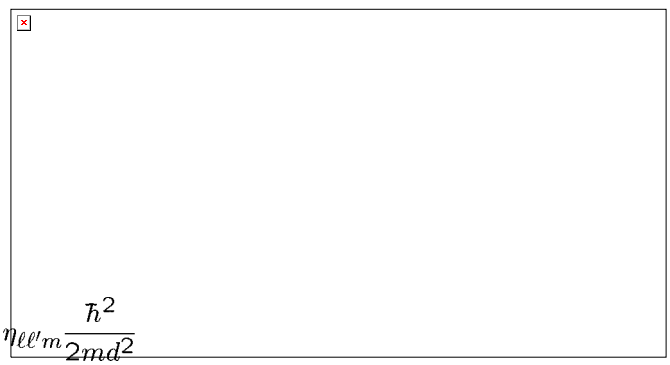
$$V_{pp\sigma} = \langle \phi_{p_x}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{\mathbf{p_x}}(\mathbf{r} - \mathbf{a}\mathbf{i}_{\mathbf{x}}) \rangle$$



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

Orbital Overlaps for 3-D Crystals

Diamond and Zincblende



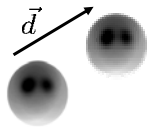
$$V_{\ell\ell' m} = \eta_{\ell\ell' m} \frac{\hbar^2}{2md^2}$$

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

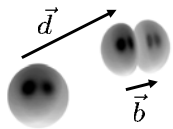
$$\eta_{sp\sigma} = 1.84 \qquad \eta_{pp\pi} = -0.81$$

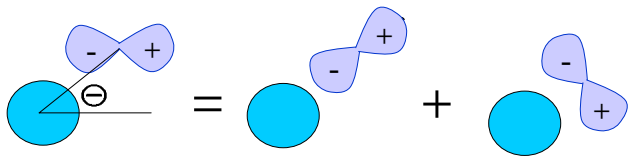
Orbital Overlaps for 3-D Crystals

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



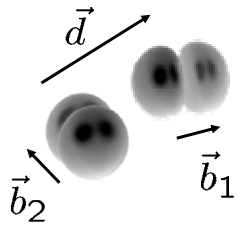
$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_2} \rangle = V_{sp\sigma} \hat{\mathrm{d}} \cdot \hat{\mathrm{b}}$$



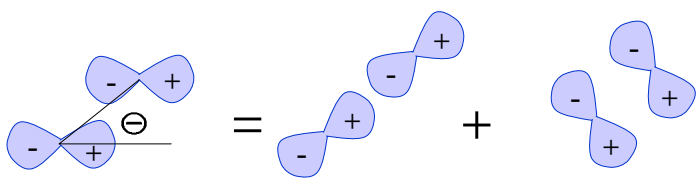


$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_{y2}} \rangle = V_{sp\sigma} cos\Theta + 0\, sin\Theta$$

Orbital Overlaps for 3-D Crystals



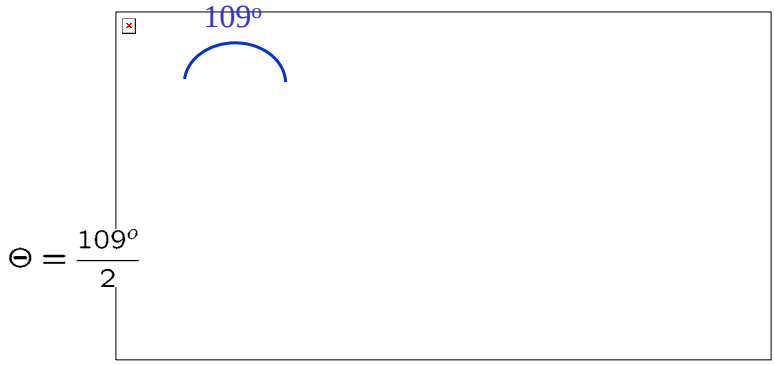
$$\langle \phi_{p1} | \hat{\mathcal{H}} | \phi_{p2} \rangle = (\hat{\mathrm{d}} \cdot \hat{\mathrm{b}}_1)(\hat{\mathrm{d}} \cdot \hat{\mathrm{b}}_2)\, V_{pp\sigma} + [\hat{\mathrm{b}}_1 - \hat{\mathrm{d}}(\hat{\mathrm{b}}_1 \cdot \hat{\mathrm{d}})] \cdot [\hat{\mathrm{b}}_2 - \hat{\mathrm{d}}(\hat{\mathrm{b}}_2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



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

Orbital Overlaps for 3-D Crystals

Diamond and Zincblende



$$\langle \phi_{s1} | \hat{\mathcal{H}} | \phi_{p_y 2} \rangle = V_{sp\sigma} cos\Theta = V_{sp\sigma} \frac{1}{\sqrt{3}}$$

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

Zincblende LCAO Bands

Reduced Hamiltonian Matrix

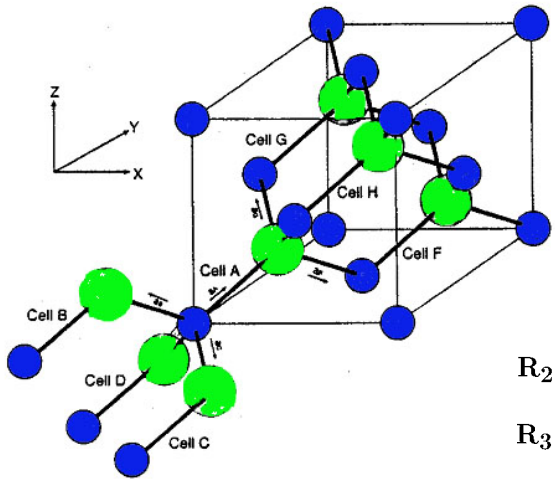
$$\begin{array}{c} \\ \langle\phi_{s1}| \\ \langle\phi_{p_x 1}| \\ \langle\phi_{p_y 1}| \\ \langle\phi_{p_z 1}| \\ \langle\phi_{s2}| \\ \langle\phi_{p_x 2}| \\ \langle\phi_{p_y 2}| \\ \langle\phi_{p_z 2}| \end{array} \begin{array}{c} \begin{array}{cccccccc} |\phi_{s1}\rangle & |\phi_{p_x 1}\rangle & |\phi_{p_y 1}\rangle & |\phi_{p_z 1}\rangle & |\phi_{s2}\rangle & |\phi_{p_x 2}\rangle & |\phi_{p_y 2}\rangle & |\phi_{p_z 2}\rangle \end{array} \\ \begin{pmatrix} E_s & 0 & 0 & 0 & E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ 0 & E_p & 0 & 0 & -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\ 0 & 0 & E_p & 0 & -E_{sp}g_2 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\ 0 & 0 & 0 & E_p & -E_{sp}g_3 & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\ E_{ss}g_0^* & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & E_s & 0 & 0 & 0 \\ E_{sp}g_1^* & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & 0 & E_p & 0 & 0 \\ E_{sp}g_2^* & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & 0 & E_p & 0 \\ E_{sp}g_3^* & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & 0 & E_p \end{pmatrix} \end{array}$$

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

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

Zincblende LCAO Bands

Nearest Neighbors



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

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

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

Zincblende LCAO Bands

Reduced Hamiltonian Matrix

$$\begin{array}{c} \\ \langle\phi_{s1}| \\ \langle\phi_{px}1| \\ \langle\phi_{py}1| \\ \langle\phi_{pz}1| \\ \langle\phi_{s2}| \\ \langle\phi_{px}2| \\ \langle\phi_{py}2| \\ \langle\phi_{pz}2| \end{array} \begin{array}{c} \begin{array}{cccccccc} |\phi_{s1}\rangle & |\phi_{px}1\rangle & |\phi_{py}1\rangle & |\phi_{pz}1\rangle & |\phi_{s2}\rangle & |\phi_{px}2\rangle & |\phi_{py}2\rangle & |\phi_{pz}2\rangle \end{array} \\ \begin{pmatrix} E_s & 0 & 0 & 0 & E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ 0 & E_p & 0 & 0 & -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\ 0 & 0 & E_p & 0 & -E_{sp}g_2 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\ 0 & 0 & 0 & E_p & -E_{sp}g_3 & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\ E_{ss}g_0^* & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & E_s & 0 & 0 & 0 \\ E_{sp}g_1^* & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & 0 & E_p & 0 & 0 \\ E_{sp}g_2^* & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_1^* & 0 & 0 & E_p & 0 \\ E_{sp}g_3^* & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & 0 & E_p \end{pmatrix} \end{array}$$

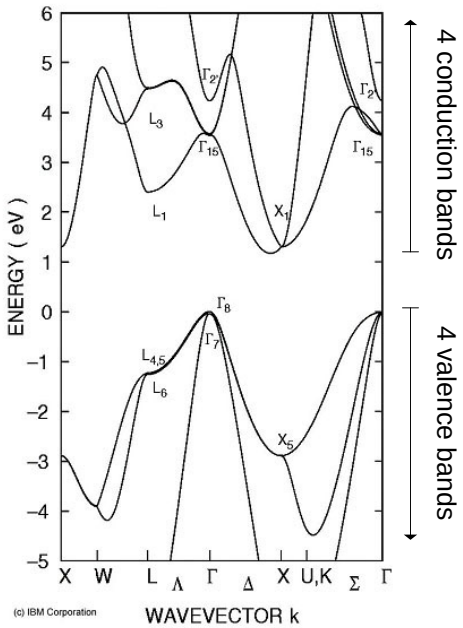
$$g_0 = 1 + e^{-i\mathbf{k}\cdot\mathbf{R}_2} + e^{-i\mathbf{k}\cdot\mathbf{R}_3} + e^{-i\mathbf{k}\cdot\mathbf{R}_4}$$

$$g_1 = 1 + e^{-i\mathbf{k}\cdot\mathbf{R}_2} - e^{-i\mathbf{k}\cdot\mathbf{R}_3} - e^{-i\mathbf{k}\cdot\mathbf{R}_4}$$

$$g_3 = 1 - e^{-i\mathbf{k}\cdot\mathbf{R}_2} + e^{-i\mathbf{k}\cdot\mathbf{R}_3} - e^{-i\mathbf{k}\cdot\mathbf{R}_4}$$

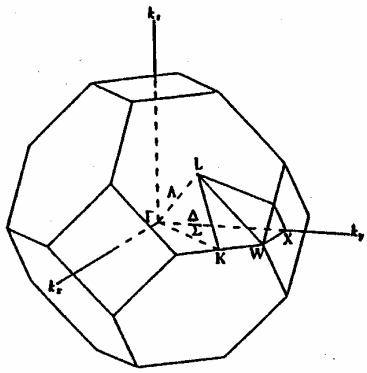
$$g_4 = 1 - e^{-i\mathbf{k}\cdot\mathbf{R}_2} - e^{-i\mathbf{k}\cdot\mathbf{R}_3} + e^{-i\mathbf{k}\cdot\mathbf{R}_4}$$

Silicon Bandstructure

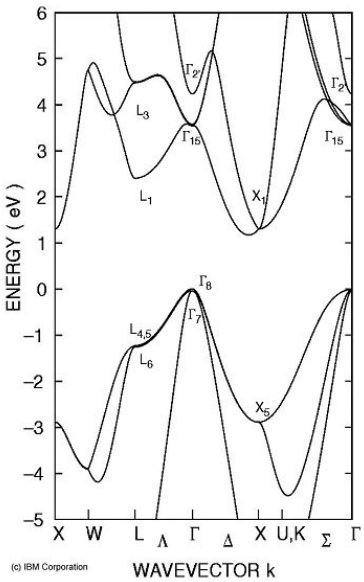


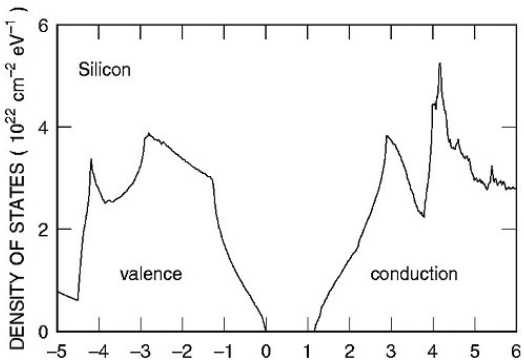
Si: [Ne] $3s^2\ 3p^2$

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



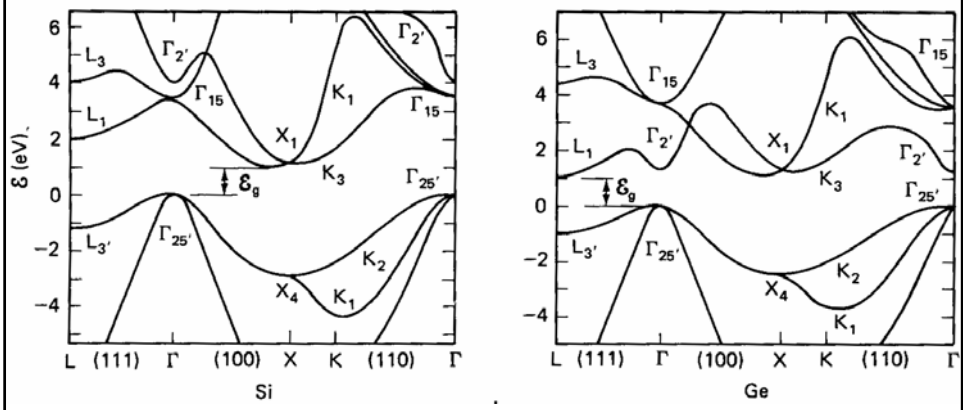
Silicon Bandstructure





http://www.research.ibm.com/DAMOCLES/html_files/phys.html

Silicon and Germanium Bandstructure



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

LCAO and Nearly Free Electron Bandstructure

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

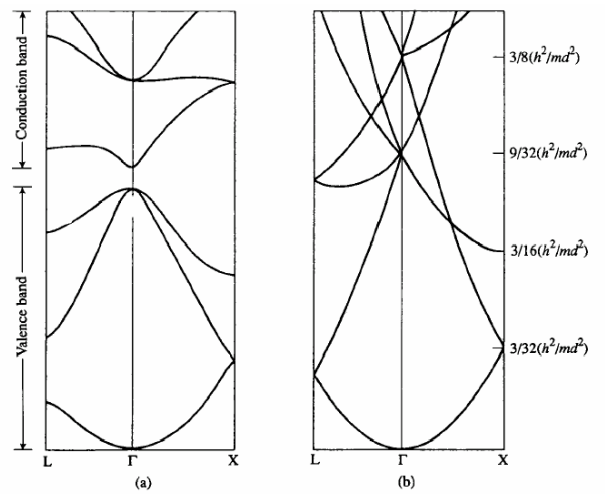


Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp^3 basis, and the free electron bands. From Harrison (1980).