Handout 12

Energy Bands in Group IV and III-V Semiconductors

In this lecture you will learn:

- The tight binding method (contd…)
- The energy bands in group IV and group III-V semiconductors with FCC lattice structure
- Spin-orbit coupling effects in solids

FCC Lattice: A Review

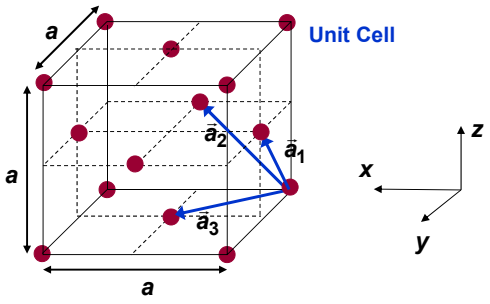
Most group VI and group III-V semiconductor, such as Si, Ge, GaAs, InP, etc have FCC lattices with a two-atom basis

Face Centered Cubic (FCC) Lattice:

$$\vec{a}_1 = \frac{a}{2}\left(\hat{y} + \hat{z}\right)$$

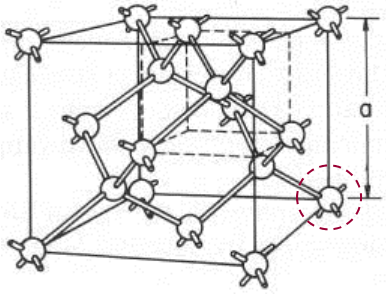
$$\vec{a}_2 = \frac{a}{2}\left(\hat{x} + \hat{z}\right)$$

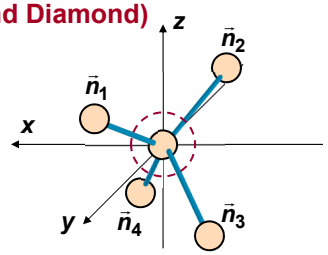
$$\vec{a}_3 = \frac{a}{2}\left(\hat{x} + \hat{y}\right)$$



Lattices of Group IV Semiconductors (Silicon, Germanium, and Diamond)

Diamond lattice (Si, Ge, and Diamond)





Basis vectors

$$\vec{d}_1 = 0 \qquad \vec{d}_2 = \frac{a}{4}(1,1,1)$$

Nearest neighbor vectors

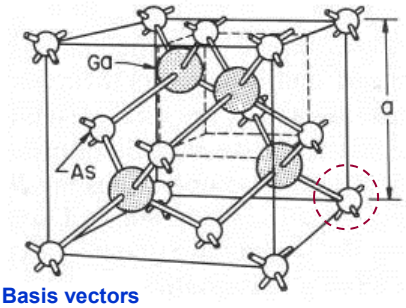
$$\vec{n}_1 = \frac{a}{4}(1,1,1) \qquad \vec{n}_2 = \frac{a}{4}(-1,-1,1)$$

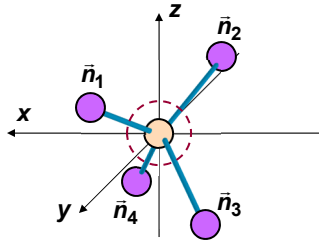
$$\vec{n}_3 = \frac{a}{4}(-1,1,-1) \qquad \vec{n}_4 = \frac{a}{4}(1,-1,-1)$$

- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis.
- Each atom is covalently bonded to four other atoms (and vice versa) via sp3 bonds in a tetrahedral configuration

Lattices of III-V Binaries (GaAs, InP, InAs, AlAs, InSb, etc)

Zincblende lattice (GaAs, InP, InAs)





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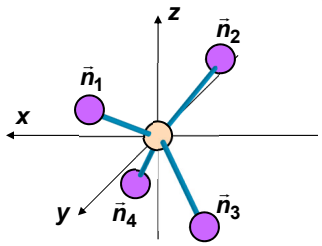
- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis. In contrast to the diamond lattice, the two atoms in the basis of zincblende lattice are different – one belongs to group III and one belongs to group V
- Each Group III atom is covalently bonded to four other group V atoms (and vice versa) via sp3 bonds in a tetrahedral configuration

Example: Tight Binding Solution for GaAs

• Each Ga atom contributes one 4s-orbital and three 4p-robitals

• Each As atom also contributes one 4s-orbital and three 4p-robitals

⇒ Each primitive cell contributes a total of eight orbitals that participate in bonding



1	$\phi_{SG}(\vec{r})$	$\leftrightarrow$ E_{SG}	5	$\phi_{SA}(\vec{r})$	$\leftrightarrow$ E_{SA}
2	$\phi_{PxG}(\vec{r})$	$\leftrightarrow$ E_{PG}	6	$\phi_{PxA}(\vec{r})$	$\leftrightarrow$ E_{PA}
3	$\phi_{PyG}(\vec{r})$	$\leftrightarrow$ E_{PG}	7	$\phi_{PyA}(\vec{r})$	$\leftrightarrow$ E_{PA}
4	$\phi_{PzG}(\vec{r})$	$\leftrightarrow$ E_{PG}	8	$\phi_{PzA}(\vec{r})$	$\leftrightarrow$ E_{PA}

One can write the trial tight-binding solution for wavevector $\vec{k}$ as:

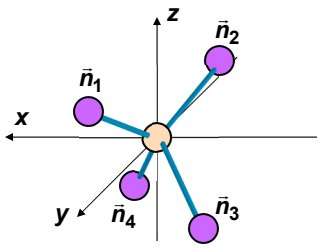
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[\sum_{j=1}^{4} c_j \left| \phi_j(\vec{r} - \vec{R}_m) \right\rangle + e^{i\,\vec{k}\,.\,\vec{d}_2} \sum_{j=5}^{8} c_j \left| \phi_j(\vec{r} - \vec{R}_m - \vec{d}_2) \right\rangle \right]$$

Example: Tight Binding Solution for GaAs

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[\sum_{j=1}^{4} c_j \left| \phi_j(\vec{r} - \vec{R}_m) \right\rangle + e^{i\,\vec{k}\,.\,\vec{d}_2} \sum_{j=5}^{8} c_j \left| \phi_j(\vec{r} - \vec{R}_m - \vec{d}_2) \right\rangle \right]$$

Plug the solution above into the Schrodinger equation to get:

$$H \begin{bmatrix} c_1(\vec{k}) \\ c_2(\vec{k}) \\ c_3(\vec{k}) \\ c_4(\vec{k}) \\ c_5(\vec{k}) \\ c_6(\vec{k}) \\ c_7(\vec{k}) \\ c_8(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_1(\vec{k}) \\ c_2(\vec{k}) \\ c_3(\vec{k}) \\ c_4(\vec{k}) \\ c_5(\vec{k}) \\ c_6(\vec{k}) \\ c_7(\vec{k}) \\ c_8(\vec{k}) \end{bmatrix}$$



Tight Binding Solution for GaAs: The Matrix

$H =$

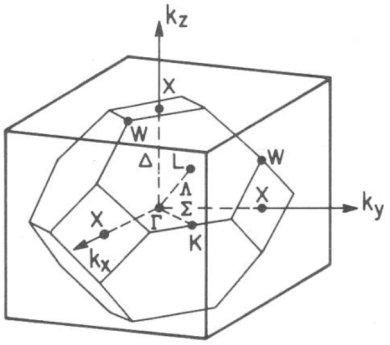
E_{SG}	0	0	0	$-V_{ss\sigma}g_0(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}}g_1(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}}g_2(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}}g_3(\vec{k})$
0	E_{PG}	0	0	$-\frac{V_{sp\sigma}}{\sqrt{3}}g_1(\vec{k})$	$V_1\, g_0(\vec{k})$	$V_2\, g_3(\vec{k})$	$V_2\, g_2(\vec{k})$
0	0	E_{PG}	0	$-\frac{V_{sp\sigma}}{\sqrt{3}}g_2(\vec{k})$	$V_2\, g_3(\vec{k})$	$V_1\, g_0(\vec{k})$	$V_2\, g_1(\vec{k})$
0	0	0	E_{PG}	$-\frac{V_{sp\sigma}}{\sqrt{3}}g_3(\vec{k})$	$V_2\, g_2(\vec{k})$	$V_2\, g_1(\vec{k})$	$V_1\, g_0(\vec{k})$
				E_{SA}	0	0	0
	Hermitian			0	E_{PA}	0	0
				0	0	E_{PA}	0
				0	0	0	E_{PA}

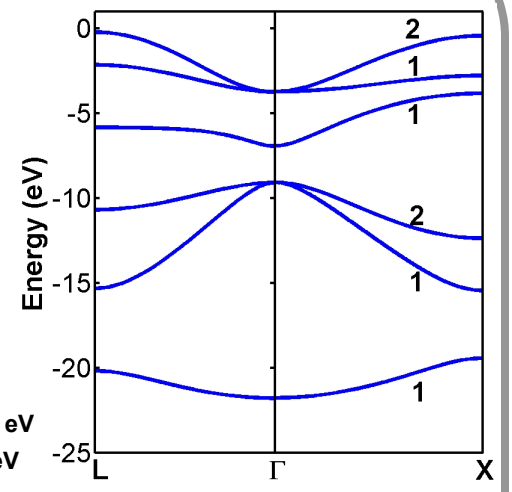
$$g_0(\vec{k}) = e^{i\vec{k}\cdot\vec{n}_1} + e^{i\vec{k}\cdot\vec{n}_2} + e^{i\vec{k}\cdot\vec{n}_3} + e^{i\vec{k}\cdot\vec{n}_4} \qquad g_2(\vec{k}) = e^{i\vec{k}\cdot\vec{n}_1} - e^{i\vec{k}\cdot\vec{n}_2} + e^{i\vec{k}\cdot\vec{n}_3} - e^{i\vec{k}\cdot\vec{n}_4}$$

$$g_1(\vec{k}) = e^{i\vec{k}\cdot\vec{n}_1} - e^{i\vec{k}\cdot\vec{n}_2} - e^{i\vec{k}\cdot\vec{n}_3} + e^{i\vec{k}\cdot\vec{n}_4} \qquad g_3(\vec{k}) = e^{i\vec{k}\cdot\vec{n}_1} + e^{i\vec{k}\cdot\vec{n}_2} - e^{i\vec{k}\cdot\vec{n}_3} - e^{i\vec{k}\cdot\vec{n}_4}$$

$$V_1 = \frac{1}{3}V_{pp\sigma} - \frac{2}{3}V_{pp\pi} \qquad V_2 = \frac{1}{3}V_{pp\sigma} + \frac{1}{3}V_{pp\pi}$$

Tight Binding Solution for GaAs





Tight Binding Solution

Parameter values for GaAs:

$E_{SG} = -11.37$ eV $\quad E_{SA} = -17.33$ eV

$E_{PG} = -4.90$ eV $\quad E_{PA} = -7.91$ eV

$V_{ss\sigma} = 1.70$ eV $\quad V_{pp\sigma} = 3.44$ eV

$V_{sp\sigma} = 2.15$ eV $\quad V_{pp\pi} = 0.89$ eV

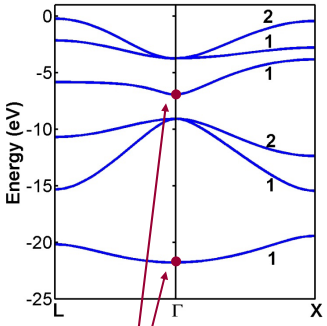
Tight Binding Solution for GaAs: States at the Γ-Point

At the Γ-point:

$$g_0(\vec{k}=0)=4$$

$$g_1(\vec{k})=g_2(\vec{k})=g_3(\vec{k})=0$$

⇒ **Energy eigenvalues can be found analytically**



Two of the eigenvalues at the Γ-point are:

$$E_{\substack{5\\1}}(\vec{k}=0)=\left(\frac{E_{SG}+E_{SA}}{2}\right)\pm\sqrt{\left(\frac{E_{SG}-E_{SGA}}{2}\right)^2+(4V_{ss\sigma})^2}$$

The Bloch function of the lowest energy band and of the conduction band at Γ-point are made up of ONLY s-orbitals from the Ga and As atoms

$$\psi_{c,\vec{k}=0}(\vec{r})=\sum_m\frac{1}{\sqrt{N}}\left[c_1\left|\phi_1(\vec{r}-\vec{R}_m)\right\rangle+c_5\left|\phi_5(\vec{r}-\vec{R}_m-\vec{d}_2)\right\rangle\right]$$

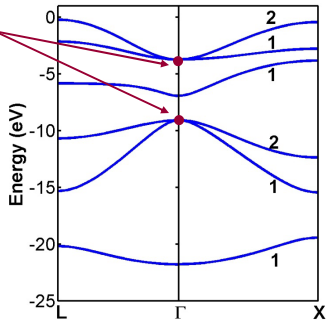
Tight Binding Solution for GaAs: States at the Γ-Point

Six remaining eigenvalues at the Γ-point are:

$$E_{\substack{678\\234}}(\vec{k}=0)=\left(\frac{E_{PG}+E_{PA}}{2}\right)\pm\sqrt{\left(\frac{E_{PG}-E_{PA}}{2}\right)^2+(4V_1)^2}$$

Each eignevalue above is triply degenerate

The Bloch function of the highest three energy bands and of the three valence bands at Γ-point are made up of ONLY p-orbitals from the Ga and As atoms



$$\psi_{v,\vec{k}=0}(\vec{r})=\sum_m\frac{1}{\sqrt{N}}\left[\begin{array}{l}\sum_{j=2}^{4}c_j\left|\phi_j(\vec{r}-\vec{R}_m)\right\rangle\\+\sum_{j=6}^{8}c_j\left|\phi_j(\vec{r}-\vec{R}_m-\vec{d}_2)\right\rangle\end{array}\right]$$

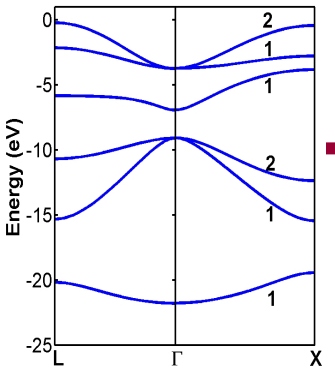
Improved Tight Binding Approaches

- Need to include the effect of spin-orbit-coupling on the valence bands

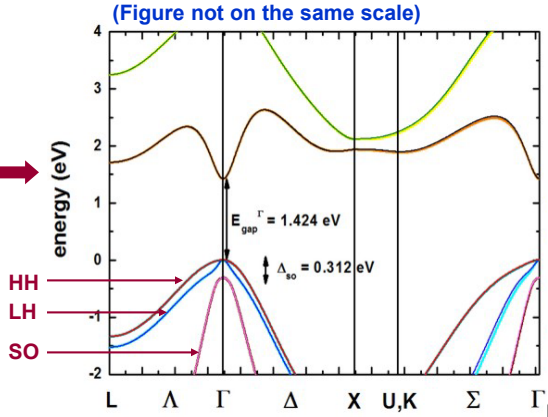
Spin orbit coupling lifts the degeneracy of the valence bands

- Need to include more orbitals (20 per primitive cell as opposed to 8 per primitive cell)
- Use better parameter values

Simplest TB Approach



Improved TB Approach with SO-Coupling
(Figure not on the same scale)



Spin-Orbit Interaction in Solids

An electron moving in an electric field sees an effective magnetic field given by:

$$\vec{B}_{eff} = \frac{\vec{E} \times \vec{P}}{2mc^2}$$

The additional factor of 2 is coming from Thomas precession

The electron has a magnetic moment $\vec{\mu}$ related to its spin angular momentum $\vec{S}$ by:

$$\vec{\mu} = -g\frac{\mu_B}{\hbar}\vec{S} \longrightarrow \hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \qquad \mu_B = \frac{e\hbar}{2m} \quad g \approx 2 \longrightarrow \hat{\vec{\mu}} = -\mu_B\hat{\vec{\sigma}}$$

$$\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z}$$

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The interaction between the electron spin and the effective magnetic field adds a new term to the Hamiltonian:

$$\hat{H}_{so} = -\vec{\mu}.\vec{B}_{eff} = \mu_B\hat{\vec{\sigma}}.\vec{B}_{eff} = \mu_B\hat{\vec{\sigma}}.\frac{1}{2mc^2}\left[\frac{\nabla V(\hat{\vec{r}})}{e} \times \hat{\vec{P}}\right] = \frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}.\left[\nabla V(\hat{\vec{r}}) \times \hat{\vec{P}}\right]$$

Spin-Orbit Interaction in Solids: Simplified Treatment

Near an atom, where electrons spend most of their time, the potential varies mostly only in the radial direction away from the atom. Therefore:

$$\hat{H}_{so} = \frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla V(\hat{\vec{r}})\times\hat{\vec{P}}\right] = \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{\sigma}}\cdot\left[\hat{\vec{r}}\times\hat{\vec{P}}\right]$$
$$= \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{\sigma}}\cdot\hat{\vec{L}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{S}}\cdot\hat{\vec{L}}$$

$\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{P}}$ is the orbital angular momentum of an electron near an atom

Recall from quantum mechanics that the total angular momentum $\hat{\vec{J}}$ is:

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$
$$\Rightarrow \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\vec{S}}.\hat{\vec{L}}$$
$$\Rightarrow \hat{\vec{S}}.\hat{\vec{L}} = \frac{1}{2}\left[\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right]$$

Therefore:

$$\hat{H}_{so} = \frac{1}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\left[\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right]$$

Spin-Orbit Interaction in Solids: Simplified Treatment

For an electron in a p-orbital:

$$\left\langle \phi_p(\vec{r})\left|\hat{L}^2\right|\phi_p(\vec{r})\right\rangle = \hbar^2\ell(\ell+1) = 2\hbar$$

For an electron in a s-orbital:

$$\left\langle \phi_s(\vec{r})\left|\hat{L}^2\right|\phi_s(\vec{r})\right\rangle = \hbar^2\ell(\ell+1) = 0$$

And we always have for an electron:

$$\left\langle \hat{S}^2\right\rangle = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2$$

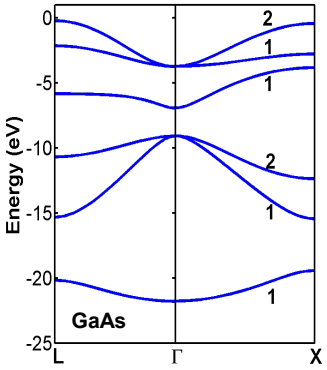
If the electron is in s-orbital then: $\left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\rangle = 0 \quad \Rightarrow \quad \left\langle \hat{H}_{so}\right\rangle = 0$

If the electron is in p-orbital then: $\left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\rangle \neq 0 \quad \Rightarrow \quad \left\langle \hat{H}_{so}\right\rangle \neq 0$

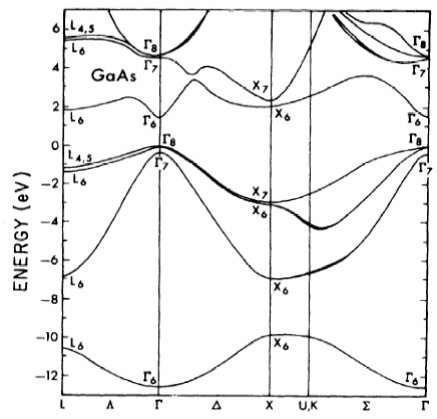
$\Rightarrow$ The energies of the Bloch states made up of p-orbitals (like in the case of the three degenerate valence bands at the Γ point in GaAs) will be most affected by spin-orbit coupling

Tight Binding Vs Pseudopotential Technique

Simplest TB Approach

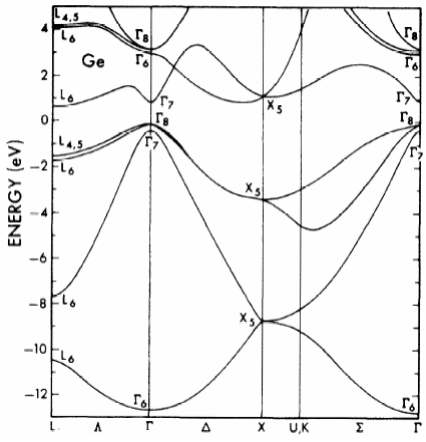


A Little More Sophisticated Approach
Nonlocal Pseudopotential Method

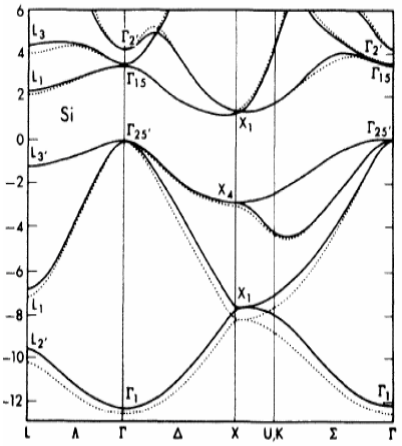


GaAs Energy Bands
(Chelikowski and Cohen, 1976)

Energy Bands of Silicon and Germanium



Germanium Energy Bands
(Chelikowski and Cohen, 1976)



Silicon Energy Bands
(Chelikowski and Cohen, 1976)