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

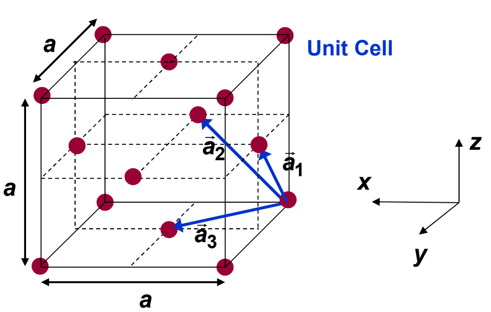
Most group VI and group III-V semiconductor, such as Si, Ge, GaAs, InP, etc have FCC lattices with a two-atom basis

Face Centered Cubic (FCC) Lattice:

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

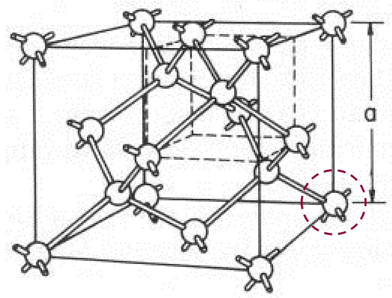
$$\vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z})$$

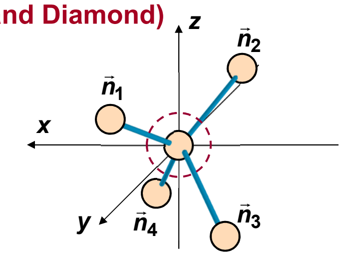
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$



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

Diamond lattice (Si, Ge, and Diamond)





Nearest neighbor vectors

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

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

Basis vectors

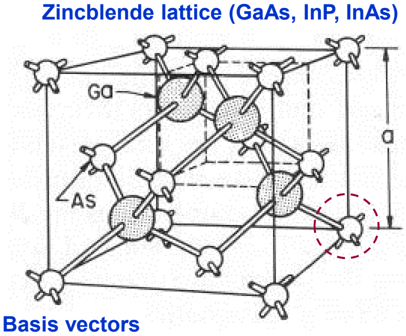
$$\vec{d}_1 = 0 \qquad \vec{d}_2 = \frac{a}{4}(1,1,1)$$

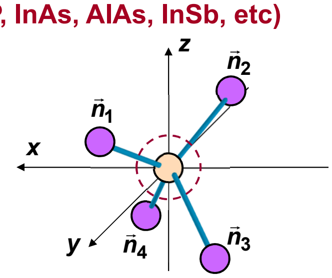
• The underlying lattice is an FCC lattice with a two-point (or two-atom) basis.

• 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)





Nearest neighbor vectors

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

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Basis vectors

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

• 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

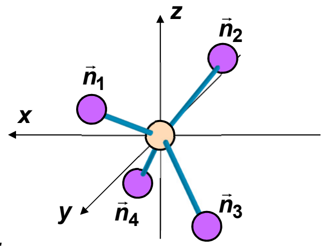
• Each Group III atom is covalently bonded to four other group V atoms (and vice versa) via sp3 bonds in a tetrahedral configuration

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

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

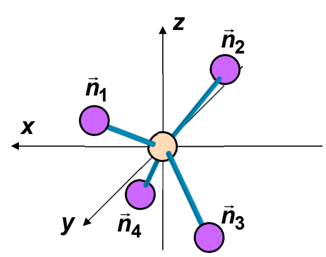
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[\sum_{j=1}^{4} c_j \left|\phi_j(\vec{r}-\vec{R}_m)\right\rangle + e^{i\,\vec{k}\,.\,\vec{d}_2} \sum_{j=5}^{8} c_j \left|\phi_j(\vec{r}-\vec{R}_m-\vec{d}_2)\right\rangle \right]$$

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

$H =$

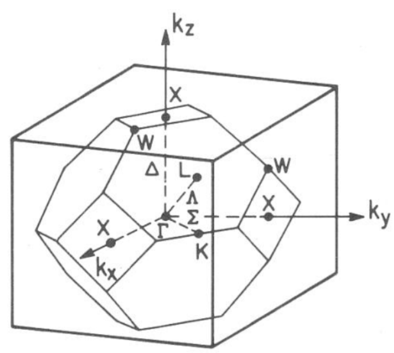
E_{SG}	0	0	0	$-V_{ss\sigma} g_0(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}} g_1(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}} g_2(\vec{k})$	$\frac{V_{sp\sigma}}{\sqrt{3}} g_3(\vec{k})$
0	E_{PG}	0	0	$-\frac{V_{sp\sigma}}{\sqrt{3}} g_1(\vec{k})$	$V_1\, g_0(\vec{k})$	$V_2\, g_3(\vec{k})$	$V_2\, g_2(\vec{k})$
0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

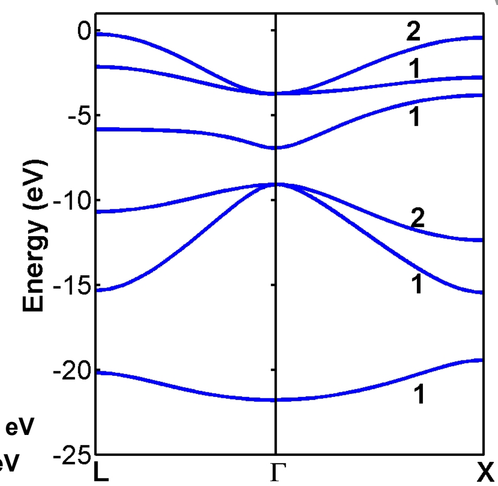
$$g_0(\vec{k}) = e^{i\vec{k}.\vec{n}_1} + e^{i\vec{k}.\vec{n}_2} + e^{i\vec{k}.\vec{n}_3} + e^{i\vec{k}.\vec{n}_4} \qquad g_2(\vec{k}) = e^{i\vec{k}.\vec{n}_1} - e^{i\vec{k}.\vec{n}_2} + e^{i\vec{k}.\vec{n}_3} - e^{i\vec{k}.\vec{n}_4}$$

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

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

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

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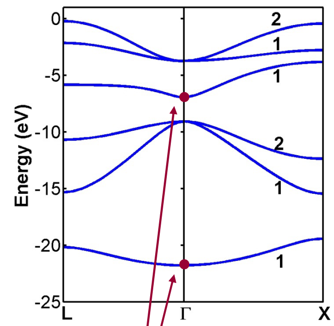
Tight Binding Solution for GaAs: States at the Γ-Point

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

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

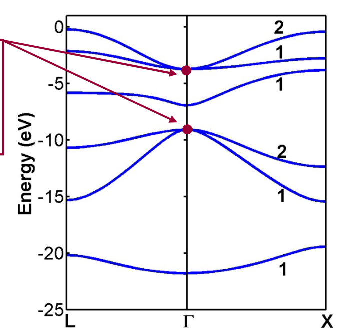
Tight Binding Solution for GaAs: States at the Γ-Point

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



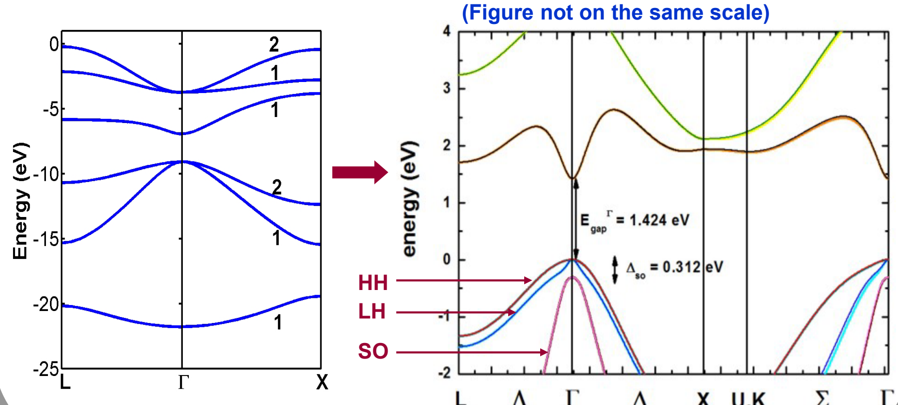
$$\psi_{v,\vec{k}=0}(\vec{r})=\sum_m \frac{1}{\sqrt{N}}\left[\sum_{j=2}^{4} c_j\,|\phi_j(\vec{r}-\vec{R}_m)\rangle+\sum_{j=6}^{8} c_j\,|\phi_j(\vec{r}-\vec{R}_m-\vec{d}_2)\rangle\right]$$

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:

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

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:

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

$$\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{\boldsymbol{x}} + \hat{\sigma}_y\hat{\boldsymbol{y}} + \hat{\sigma}_z\hat{\boldsymbol{z}} \quad \hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

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

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

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:

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

For an electron in a s-orbital:

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

And we always have for an electron:

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

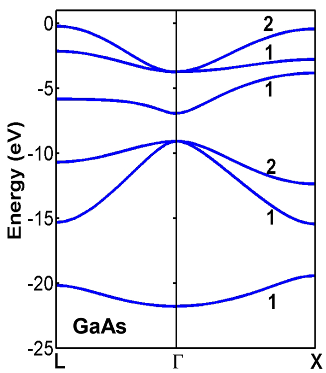
If the electron is in s-orbital then: $\left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\rangle = 0 \Rightarrow \left\langle \hat{H}_{so}\right\rangle = 0$

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

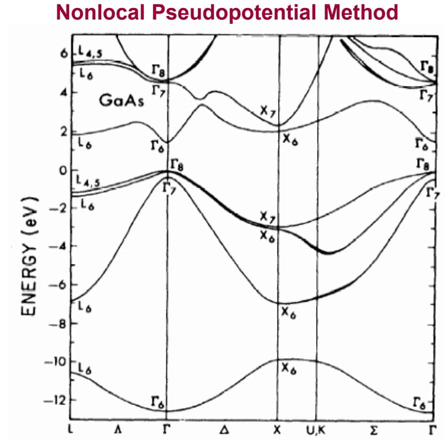
$\Rightarrow$ The energies of the Bloch states made up of p-orbitals (like in the case of the three degenerate valence bands at the Γ point in GaAs) will be most affected by spin-orbit coupling

Tight Binding Vs Pseudopotential Technique

Simplest TB Approach

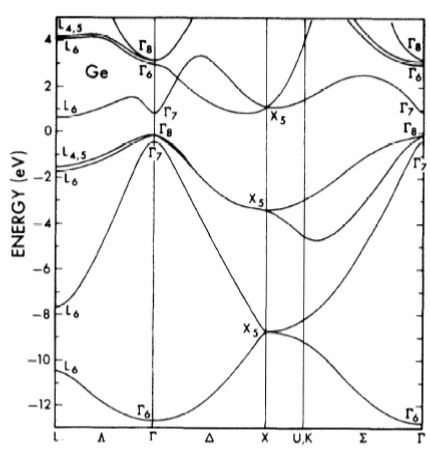


A Little More Sophisticated Approach
Nonlocal Pseudopotential Method

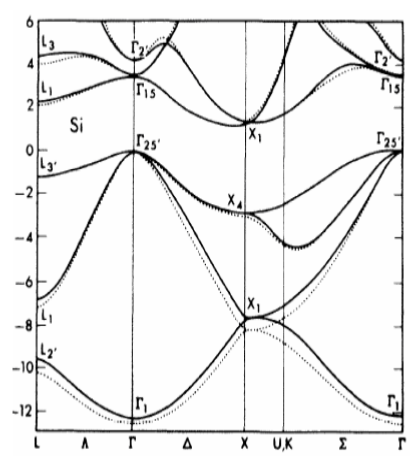


GaAs Energy Bands
(Chelikowski and Cohen, 1976)

Energy Bands of Silicon and Germanium



Germanium Energy Bands
(Chelikowski and Cohen, 1976)



Silicon Energy Bands
(Chelikowski and Cohen, 1976)

Appendix: Spin-Orbit Interaction and Bloch Functions

In the absence of spin-orbit interaction we had:

$$\hat{H}_o \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r})$$

$$\left[-\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r})\right] \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r})$$

Electron states with spin-up and spin-down were degenerate $\Big\{ E_{n,\uparrow}(\vec{k}) = E_{n,\downarrow}(\vec{k})$

In the presence of spin-orbit coupling the Hamiltonian becomes:

$$\hat{H} = \hat{H}_o + \hat{H}_{so}$$

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

Since the Hamiltonian is now spin-dependent, pure spin-up or pure spin-down states are no longer the eigenstates of the Hamiltonian

The eigenstates can be written most generally as a superposition of up and down spin states, or:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r}) |\uparrow\rangle + \beta_{n,\vec{k}}(\vec{r}) |\downarrow\rangle$$

χ =Quantum number for the two spin degrees of freedom, usually taken to be +1 or -1

Appendix: Spin-Orbit Interaction and Bloch Functions

$$\hat{H} \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k}) \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

$$\left\{-\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i \frac{\hbar^2}{4m^2c^2} \hat{\vec{\sigma}} \cdot \left[\nabla_{\vec{r}} V(\hat{\vec{r}}) \times \vec{\nabla}_{\vec{r}}\right]\right\} \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k}) \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

For each wavevector in the FBZ, and for each band index, one will obtain two solutions of the above equation

We label one as χ = +1 and the other with χ = -1 and in general $E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$

These two solutions will correspond to spins pointing in two different directions (usually collinear and opposite directions). Let these directions be specified by $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\, \psi_{n,\vec{k},\chi}(\vec{r}) = +1\, \psi_{n,\vec{k},\chi}(\vec{r})$$

$$\hat{\vec{\sigma}}.\hat{n}\, \psi_{n,\vec{k},-\chi}(\vec{r}) = -1\, \psi_{n,\vec{k},-\chi}(\vec{r})$$

Appendix: Spin-Orbit Interaction and Lattice Symmetries

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

Lattice Translation Symmetry:

$$\psi_{n,\vec{k},\chi}(\vec{r}+\vec{R})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}+\vec{R})\\ \beta_{n,\vec{k}}(\vec{r}+\vec{R})\end{bmatrix}=\begin{bmatrix}e^{i\vec{k}.\vec{R}}\alpha_{n,\vec{k}}(\vec{r})\\ e^{i\vec{k}.\vec{R}}\beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=e^{i\vec{k}.\vec{R}}\psi_{n,\vec{k},\chi}(\vec{r})$$

Rotation Symmetry:

Let $\hat{S}$ be an operator belonging to the rotation subgroup of the crystal point-group, such that:

$$V(\hat{S}\vec{r})=V(\vec{r}) \qquad \left\{\hat{S}^T=\bar{S}^{-1}\Rightarrow \text{unitary}\right.$$

(The case of inversion symmetry will be treated separately)

Appendix: Spin-Orbit Interaction and Rotation Symmetry

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} \quad\Leftrightarrow\quad E_{n,\chi}(\vec{k})$$

We replace $\vec{r}$ by $\hat{S}\vec{r}$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\hat{S}\vec{r}}^2}{2m}+V(\hat{S}\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla_{\hat{S}\vec{r}}V(\hat{S}\hat{\vec{r}})\times\vec{\nabla}_{\hat{S}\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\hat{S}\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}$$

Appendix: Spin-Orbit Interaction and Rotation Symmetry

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\,\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V\left(\hat{\vec r}\right)\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}=E_{n,\chi}\left(\vec k\right)\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}$$

The above equation does not look like the Schrodinger equation!

We define a unitary spin rotation operator $\hat R_{\hat S}$ that operates in the Hilbert space of spins and rotates spin states in the sense of the operator $\hat S$

Consider a spin vector pointing in the $\hat n$ direction:

$$\hat{\vec\sigma}.\hat n\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat{\vec\sigma}.\hat n\hat R_{\hat S}^{-1}\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat R_{\hat S}\hat{\vec\sigma}.\hat n\hat R_{\hat S}^{-1}\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\,\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\left(\hat{\vec\sigma}.\hat S\hat n\right)\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}$$

The spin rotation operators have the property: $\hat R_{\hat S}\left(\hat{\vec\sigma}.\hat n\right)\hat R_{\hat S}^{-1}=\hat{\vec\sigma}.\hat S\hat n$

Appendix: Spin-Orbit Interaction and Point-Group Symmetry

Start from:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\,\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V\left(\hat{\vec r}\right)\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}=E_{n,\chi}\left(\vec k\right)\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}$$

Introduce spin rotation operator $\hat R_{\hat S}$ corresponding to the rotation generated by the matrix $\hat S$:

$$\hat R_{\hat S}^{-1}\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\,\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V\left(\hat{\vec r}\right)\times\vec\nabla_{\vec r}\right]\right\}\hat R_{\hat S}\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}=E_{n,\chi}\left(\vec k\right)\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}$$

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\,\hat{\vec\sigma}\,.\left[\nabla_{\vec r}V\left(\hat{\vec r}\right)\times\vec\nabla_{\vec r}\right]\right\}\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}=E_{n,\chi}\left(\vec k\right)\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}$$

The above equation shows that the new state:

$$\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}\left(\hat S\vec r\right)\\ \beta_{n,\vec k}\left(\hat S\vec r\right)\end{bmatrix}$$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$

Appendix: Spin-Orbit Interaction and Point-Group Symmetry

Since:

$$\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}(\vec{r}+\vec{R})\right)\\ \beta_{n,\vec{k}}\left(\hat{S}(\vec{r}+\vec{R})\right)\end{bmatrix} = e^{i\vec{k}.\hat{S}\vec{R}}\ \hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix} = e^{i\hat{S}^{-1}\vec{k}.\vec{R}}\ \hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

The new state is a Bloch state with wavevector $\hat{S}^{-1}\vec{k}$

Summary:

If $\hat{S}$ is an operator for a point-group symmetry operation then the two states given by:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\psi_{n,\hat{S}^{-1}\vec{k},\chi'}(\vec{r}) = \hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

→ This represents a rotated (in space) version of the original Bloch state. Even the spin is rotated appropriately by the spin rotation operator.

have the same energy:

$$E_{n,\chi'}\left(\hat{S}^{-1}\vec{k}\right) = E_{n,\chi}\left(\vec{k}\right)$$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

Suppose the crystal potential has inversion symmetry:

$$V(-\vec{r}) = V(\vec{r})$$

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\nabla_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} \quad\Leftrightarrow\quad E_{n,\chi}\left(\vec{k}\right)$$

We replace $\vec{r}$ by $-\vec{r}$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{-\vec{r}}^2}{2m} + V(-\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{-\vec{r}}V(-\hat{\vec{r}})\times\nabla_{-\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix} = E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\nabla_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix} = E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

The above equation shows that the new state: $\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Since:

$$\begin{bmatrix}\alpha_{n,\vec{k}}(-(\vec{r}+\vec{R}))\\ \beta_{n,\vec{k}}(-(\vec{r}+\vec{R}))\end{bmatrix}=e^{i(-\vec{k}).\vec{R}}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

the new state is a Bloch state with wavevector $-\vec{k}$

In most cases, the new state: $\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

has the same spin direction as the state: $\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

So we can write: $\psi_{n,-\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

Summary:

If the crystal potential has inversion symmetry then the two states given by:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}\qquad\psi_{n,-\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

have the same energy:

$$E_{n,\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Consider the Bloch function:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r})|\uparrow\rangle + \beta_{n,\vec{k}}(\vec{r})|\downarrow\rangle$$

Suppose the Bloch function corresponds to the spin pointing in the direction of the unit vector $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r}) = \hat{\vec{\sigma}}.\hat{n}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\,\psi_{n,\vec{k},\chi}(\vec{r})$$

What if we want the state with the opposite spin at the same location?

The answer is:

$$-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} -\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Proof:

$$\hat{\vec{\sigma}}.\hat{n}\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right] = -i\left[-\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^*$$

$$= -i\left[-\hat{\sigma}_y\hat{\sigma}_y\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\hat{\sigma}_y\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -i\left[\hat{\sigma}_y\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^*$$

$$= -i\left[\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -1\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right]$$

$$\left\{ \hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \quad \Rightarrow \quad \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}} \right\}$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Suppose we have solved it and found the solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} \Leftrightarrow E_{n,\chi}(\vec{k})$

We complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

It does not look like the original Schrodinger equation!

Note that:

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

$$\Rightarrow \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}}$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av = \lambda v$$

One can always perform a unitary transformation with matrix *T* and obtain:

$$TAT^{-1}Tv = \lambda Tv \qquad B = TAT^{-1}$$
$$\Rightarrow Bu = \lambda u \qquad u = Tv$$

So try a transformation with the unitary matrix $-i\hat{\sigma}_y$ with the equation:

$$\left(-i\hat{\sigma}_y\right)\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^* . \left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}\left(+i\hat{\sigma}_y\right)\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\Rightarrow \left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}} . \left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

We have found a new solution: $\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$

with the same energy $E_{n,\chi}(\vec{k})$ as the original solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Question: What is the physical significance of the new solution?

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Under lattice translation we get for the new solution:

$$\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}+\vec{R}) \\ \alpha^*_{n,\vec{k}}(\vec{r}+\vec{R})\end{bmatrix} = e^{-i\vec{k}.\vec{R}}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

So the new solution is a Bloch state with wavevector $-\vec{k}$

$$\psi_{n,-\vec{k},?}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

Note that the new solution found can also be written as:

$$-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

But as shown earlier, the above state has spin opposite to the state $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Therefore, the new solution is a Bloch state $\psi_{n,-\vec{k},-\chi}(\vec{r})$, i.e.:

$$\psi_{n,-\vec{k},-\chi}(\vec{r}) = -i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And we have also found that its energy is the same as that of the state $\psi_{n,\vec{k},\chi}(\vec{r})$:

$$E_{n,-\chi}(-\vec{k}) = E_{n,\chi}(\vec{k})$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the time-dependent Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\vec r,t)\\ \beta_{n,\vec k}(\vec r,t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec k}(\vec r,t)\\ \beta_{n,\vec k}(\vec r,t)\end{bmatrix}$$

Solution is:

$$\psi_{n,\vec k,\chi}(\vec r,t)=\begin{bmatrix}\alpha_{n,\vec k}(\vec r,t)\\ \beta_{n,\vec k}(\vec r,t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec k}(\vec r)e^{-iE_{n,\chi}(\vec k)t}\\ \beta_{n,\vec k}(\vec r)e^{-iE_{n,\chi}(\vec k)t}\end{bmatrix}=\psi_{n,\vec k,\chi}(\vec r)e^{-iE_{n,\chi}(\vec k)t}$$

Lets see if we can find a solution under time-reversal (i.e. when t is replaced by $-t$):

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\vec r,-t)\\ \beta_{n,\vec k}(\vec r,-t)\end{bmatrix}=-i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec k}(\vec r,-t)\\ \beta_{n,\vec k}(\vec r,-t)\end{bmatrix}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)+i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}^*\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}$$

And it still does not look like the original Schrodinger equation!

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av=\lambda v$$

One can always perform a unitary transformation with matrix T and obtain:

$$TAT^{-1}Tv=\lambda Tv \qquad \Rightarrow Bu=\lambda u \qquad \left\{\begin{aligned}B&=TAT^{-1}\\ u&=Tv\end{aligned}\right.$$

So try a transformation with the unitary matrix $-i\hat\sigma_y$ with the equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)+i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}^*\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}$$

$$\left(-i\hat\sigma_y\right)\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)+i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}^*\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\left(+i\hat\sigma_y\right)\left(-i\hat\sigma_y\right)\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\left(-i\hat\sigma_y\right)\begin{bmatrix}\alpha^*_{n,\vec k}(\vec r,-t)\\ \beta^*_{n,\vec k}(\vec r,-t)\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\cdot\left[\nabla V(\hat{\vec r})\times\vec\nabla\right]\right\}\begin{bmatrix}-\beta^*_{n,\vec k}(\vec r,-t)\\ \alpha^*_{n,\vec k}(\vec r,-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}-\beta^*_{n,\vec k}(\vec r,-t)\\ \alpha^*_{n,\vec k}(\vec r,-t)\end{bmatrix}$$

The above equation now looks like the time-dependent Schrodinger equation

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Summary:

Corresponding to the Bloch state:

$$\psi_{n,\vec{k},\chi}(\vec{r},t)=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \beta_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,\vec{k},\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

with energy:

$$E_{n,\chi}(\vec{k})$$

the time-reversed Bloch state is:

$$\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \alpha^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,-\vec{k},-\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

and the time-reversed state has the same energy as the original state:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Appendix: Crystal Inversion Symmetry and Time Reversal Symmetry

Time reversal symmetry implies:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Inversion symmetry implies:

$$E_{n,\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

In crystals which have inversion and time reversal symmetries the above two imply:

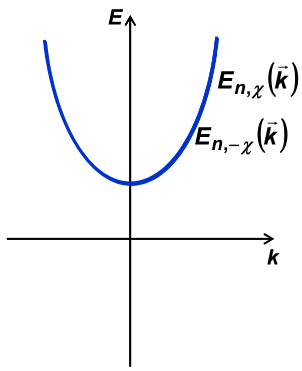
$$E_{n,-\chi}(\vec{k})=E_{n,\chi}(\vec{k})$$ ⟶ There is spin degeneracy!

In crystals which do not have inversion symmetry the above two do not guarantee spin degeneracy. In general:

$$E_{n,-\chi}(\vec{k})\neq E_{n,\chi}(\vec{k})$$ ⟶ Bands with different spins can have different energy dispersion relations

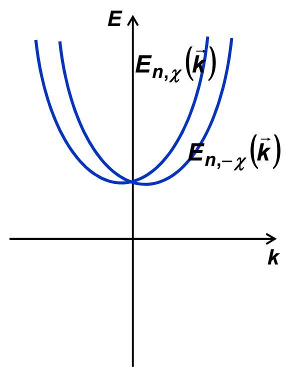
Appendix: Crystal Inversion Symmetry and Time Reversal Symmetry

Cartoon (and much exaggerated) sketches of the conduction bands of Ge and GaAs are shown below:



Ge

$$E_{n,-\chi}(\vec{k}) = E_{n,\chi}(\vec{k})$$



GaAs

$$E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$$