Física de Semiconductores

Lección 8

Beyond free electrons: pseudopotentials

- We want to calculate $U_{\boldsymbol{K}} = \frac{1}{v_c} \int_{\text{unit cell}} d\boldsymbol{r}\, V\left(\boldsymbol{r}\right) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}$

We assume $V\left(\boldsymbol{r}\right) = \sum_j V_j\left(\boldsymbol{r}\right)$ and if we define new potentials centered at each atom in the unit cell

$$V\left(\boldsymbol{r}\right) = \sum_j U_j\left(\boldsymbol{r} - \boldsymbol{d}_j\right)$$

so

$$U_{\boldsymbol{K}} = \frac{1}{v_c} \int_{\text{unit cell}} d\boldsymbol{r} \left[\sum_j U_j\left(\boldsymbol{r} - \boldsymbol{d}_j\right)\right] e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}$$

$$= \frac{1}{v_c} \sum_j e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_j} \int_{\text{unit cell}} d\boldsymbol{r}'\, U_j\left(\boldsymbol{r}'\right) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}'} = \sum_j e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_j} U_{j\boldsymbol{K}}$$

Two atom cells

- For a two atom cell, I can always choose $\boldsymbol{d}_A = -\boldsymbol{d}_B$

so $$U_{\boldsymbol{K}} = \sum_j e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_j} U_{j\boldsymbol{K}} = e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_A} U_{A\boldsymbol{K}} + e^{+i\boldsymbol{K}\cdot\boldsymbol{d}_A} U_{B\boldsymbol{K}} =$$

$$= \cos\left(\boldsymbol{K}\cdot\boldsymbol{d}_A\right)\left(U_{A\boldsymbol{K}} + U_{B\boldsymbol{K}}\right) - i\sin\left(\boldsymbol{K}\cdot\boldsymbol{d}_A\right)\left(U_{B\boldsymbol{K}} - U_{A\boldsymbol{K}}\right)$$

if the atoms are identical

$$U_{\boldsymbol{K}} = \sum_j e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_j} U_{j\boldsymbol{K}} = e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_A} U_{A\boldsymbol{K}} + e^{+i\boldsymbol{K}\cdot\boldsymbol{d}_A} U_{B\boldsymbol{K}} =$$

$$U_{\boldsymbol{K}} = 2\cos\left(\boldsymbol{K}\cdot\boldsymbol{d}_A\right) U_{A\boldsymbol{K}}$$

Form factors

$$U_{j\boldsymbol{K}} = \int_{\text{unit cell}} d\boldsymbol{r}\, U_j\left(\boldsymbol{r}\right) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}$$

Assume central potential

$$U_{j\boldsymbol{K}} = \int_{\text{unit cell}} d\boldsymbol{r}\, U_j\left(r\right) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} = \iiint d\varphi\, d\theta\, dr r^2 \sin\theta U_j\left(r\right) e^{-iKr\cos\theta}$$

$$= 2\pi \int dr r^2 U_j\left(r\right) \int_0^{\pi} d\theta \sin\theta e^{-iKr\cos\theta} = 2\pi \int dr r^2 U_j\left(r\right) \int_{-1}^{1} du e^{-iKru}$$

$$= 2\pi \int dr r^2 U_j\left(r\right) \left.\frac{e^{-iKru}}{-iKr}\right|_{-1}^{1} = 2\pi \int dr r^2 U_j\left(r\right) \frac{e^{-iKr} - e^{iKr}}{-iKr} =$$

$$= 4\pi \int dr r^2 U_j\left(r\right) \frac{\sin Kr}{Kr}$$

Depends only on magnitude of K

Ranking of reciprocal lattice vectors by magnitude

$$\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3, -\boldsymbol{b}_1, -\boldsymbol{b}_2, -\boldsymbol{b}_3, \boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3, -\boldsymbol{b}_1 - \boldsymbol{b}_2 - \boldsymbol{b}_3 \Rightarrow V_3$$

$$\boldsymbol{b}_1 + \boldsymbol{b}_2, \boldsymbol{b}_1 + \boldsymbol{b}_3, \boldsymbol{b}_2 + \boldsymbol{b}_3, -\boldsymbol{b}_1 - \boldsymbol{b}_2, -\boldsymbol{b}_1 - \boldsymbol{b}_3, -\boldsymbol{b}_2 - \boldsymbol{b}_3 \Rightarrow V_4$$

$$\boldsymbol{b}_1 - \boldsymbol{b}_2, \boldsymbol{b}_1 - \boldsymbol{b}_3, \boldsymbol{b}_2 - \boldsymbol{b}_3, \boldsymbol{b}_2 - \boldsymbol{b}_1, \boldsymbol{b}_3 - \boldsymbol{b}_1, \boldsymbol{b}_3 - \boldsymbol{b}_2 \Rightarrow V_8$$

$$2\boldsymbol{b}_1 + \boldsymbol{b}_2, 2\boldsymbol{b}_2 + \boldsymbol{b}_3, 2\boldsymbol{b}_3 + \boldsymbol{b}_1, -2\boldsymbol{b}_1 - \boldsymbol{b}_2,$$

$$-2\boldsymbol{b}_2 - \boldsymbol{b}_3, -2\boldsymbol{b}_3 - \boldsymbol{b}_1 \Rightarrow V_{11}$$

Diamond structure factors for b_1

$$\cos\left(\boldsymbol{K}\cdot\boldsymbol{d}_A\right)=\cos\left[-\tfrac{1}{8}\left(K_x+K_y+K_z\right)a\right]$$

$$\cos\left(\boldsymbol{b}_1\cdot\boldsymbol{d}_A\right)=\cos\left[-\tfrac{1}{8}\left(-\frac{2\pi}{a}\right)a\right]=\cos\left[\frac{\pi}{4}\right]=\sqrt{2}/2$$

Same for $\boldsymbol{b}_2,\boldsymbol{b}_3,-\boldsymbol{b}_1,-\boldsymbol{b}_2,-\boldsymbol{b}_3$

$$\cos\left(\left(\boldsymbol{b}_1+\boldsymbol{b}_2+\boldsymbol{b}_3\right)\cdot\boldsymbol{d}_A\right)=\cos\left[-\tfrac{1}{8}\left(-\frac{6\pi}{a}\right)a\right]=\cos\left[\frac{3\pi}{4}\right]=-\sqrt{2}/2$$

Same for $-\boldsymbol{b}_1-\boldsymbol{b}_2-\boldsymbol{b}_3$

Diamond structure factors for b_1+b_2

$$\cos\left(\boldsymbol{K}\cdot\boldsymbol{d}_A\right)=\cos\left[-\tfrac{1}{8}\left(K_x+K_y+K_z\right)a\right]$$

$$\cos\left(\left(\boldsymbol{b}_1+\boldsymbol{b}_2\right)\cdot\boldsymbol{d}_A\right)=\cos\left[-\tfrac{1}{8}\left(-\frac{4\pi}{a}\right)a\right]=\cos\left[\frac{\pi}{2}\right]=0$$

Same for all other combinations of the form (2,0,0)

Form factors

- We thus have

$$U_{\boldsymbol{K}} =$$

$$= \frac{1}{v_c}\sum_{\boldsymbol{R}}\int_{\text{unit cell}} d\boldsymbol{r}\sum_{\boldsymbol{R}}\left[V_A\left(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{d}_A\right)+V_B\left(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{d}_B\right)\right]e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}$$

$$= \frac{1}{v_c}\sum_{\boldsymbol{R}}\int_{\text{unit cell}} d\boldsymbol{r}V_A\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\left(\boldsymbol{r}'+\boldsymbol{R}+\boldsymbol{d}_A\right)}+\frac{1}{v_c}\sum_{\boldsymbol{R}}\int_{\text{unit cell}} d\boldsymbol{r}V_B\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\left(\boldsymbol{r}'+\boldsymbol{R}\right.}$$

$$= \frac{N}{v_c}\int_{\text{unit cell}} d\boldsymbol{r}V_A\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\left(\boldsymbol{r}'+\boldsymbol{d}_A\right)}+\frac{N}{v_c}\int_{\text{unit cell}} d\boldsymbol{r}V_B\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\left(\boldsymbol{r}'+\boldsymbol{d}_B\right)}$$

$$= \frac{N}{v_c}e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_A}\int_{\text{unit cell}} d\boldsymbol{r}V_A\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\boldsymbol{r}'}+\frac{N}{v_c}e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_B}\int_{\text{unit cell}} d\boldsymbol{r}V_B\left(\boldsymbol{r}'\right)e^{-i\boldsymbol{K}\cdot\boldsymbol{r}'}$$

$$= V_A\left(\boldsymbol{K}\right)e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_A}+V_B\left(\boldsymbol{K}\right)e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_B}$$

Spin

- Electrons have spin with eigenvalues ½ and -½ , and two component eigenfunctions in spin-space of the form

$$\chi_{1/2} \equiv \chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \chi_{-1/2} \equiv \chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- Therefore, the complete wavefunction for an electron must be a two-component spinor of the form

$$\begin{pmatrix} \varphi\left(\boldsymbol{r}, \uparrow\right) \\ \varphi\left(\boldsymbol{r}, \downarrow\right) \end{pmatrix}$$

Hamiltonian

- Any hermitian matrix in spinor space must be a linear combination of Pauli spin matrices

$$\begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix} = \left(\frac{a+b}{2}\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + c\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + d\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} + \left(\frac{a-b}{2}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix};$$

$$I \qquad \sigma_x \qquad \sigma_y \qquad \sigma_z$$

- A hamiltonian must be invariant under rotations, so it must be of the form

$$H(\boldsymbol{r},\boldsymbol{s}) = H_0(\boldsymbol{r})\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + H_x(\boldsymbol{r})\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + H_y(\boldsymbol{r})\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} + H_z(\boldsymbol{r})\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix};$$

Spin-independent hamiltonian

- If the hamiltonian is independent of spin

$$H(\boldsymbol{r},\boldsymbol{s})\varphi_\lambda(\boldsymbol{r},s)=$$

$$=H_0(\boldsymbol{r})\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}\varphi_\lambda(\boldsymbol{r},\uparrow)\\\varphi_\lambda(\boldsymbol{r},\downarrow)\end{pmatrix}=\begin{pmatrix}H_0(\boldsymbol{r})&0\\0&H_0(\boldsymbol{r})\end{pmatrix}\begin{pmatrix}\varphi_\lambda(\boldsymbol{r},\uparrow)\\\varphi_\lambda(\boldsymbol{r},\downarrow)\end{pmatrix}=E_\lambda\begin{pmatrix}\varphi_\lambda(\boldsymbol{r},\uparrow)\\\varphi_\lambda(\boldsymbol{r},\downarrow)\end{pmatrix}$$

- Let

$$H_0\varphi_\nu(\boldsymbol{r})=E_\nu\varphi_\nu(\boldsymbol{r})$$

- Then I can choose as the solutions

$$\begin{pmatrix}\varphi_\lambda(\boldsymbol{r},\uparrow)\\\varphi_\lambda(\boldsymbol{r},\downarrow)\end{pmatrix}=\varphi_\nu(\boldsymbol{r})\begin{pmatrix}1\\0\end{pmatrix}\equiv\varphi_\nu(\boldsymbol{r})\uparrow;\quad\begin{pmatrix}\varphi_\lambda(\boldsymbol{r},\uparrow)\\\varphi_\lambda(\boldsymbol{r},\downarrow)\end{pmatrix}=\varphi_\nu(\boldsymbol{r})\begin{pmatrix}0\\1\end{pmatrix}\equiv\varphi_\nu(\boldsymbol{r})\downarrow$$

Spin-dependent hamiltonian

- If the hamiltonian is spin-dependent, it will be of the form

$$\begin{pmatrix} H_0 + H_z & H_x + iH_y \\ H_x - iH_y & H_0 - H_z \end{pmatrix}$$

- If the off-diagonal terms are not zero, then the spinor wave functions will mix up- and down spins.

Origin of spin

- En mecánica cuántica $H \to ih\frac{\partial}{\partial t}; \boldsymbol{p} \to -i\hbar\boldsymbol{\nabla}$
- Entonces,

$$H = \frac{p^2}{2m} \Rightarrow ih\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\Psi$$

- Pero la energía relativista es $H = \sqrt{c^2p^2 + m_0^2c^4}$
- If we square to eliminate radical

$$H^2 = c^2p^2 + m_0^2c^4 \Rightarrow -\hbar^2\frac{\partial^2\Psi}{\partial t^2} = -c^2\hbar^2\frac{\partial^2\Psi}{\partial x^2} + m_0^2c^4\Psi$$

$$\frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = \hbar^2\frac{\partial^2\Psi}{\partial x^2} - \frac{m_0^2c^2}{\hbar^2}\Psi$$

- This is the Klein-Gordon equation. It is not an evolution equation. It would imply different postulates for relativistic quantum mechanics.

Dirac equation

We propose $\left[c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta m_0 c^2\right]\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}$

And we demand:

$$\left[c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta m_0 c^2\right]\left[c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta m_0 c^2\right] = c^2p^2 + m_0^2c^4$$

This requires

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$$

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_x\alpha_z + \alpha_z\alpha_x =$$

$$= \alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0$$

This can only be satisfied if the α's and β are 4x4 matrices.

Dirac equation

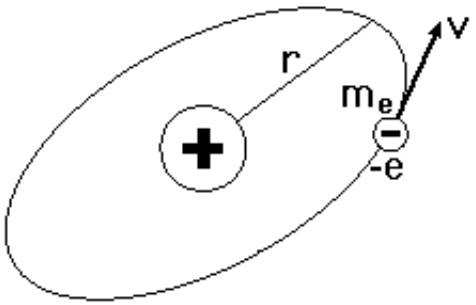
$$\left[c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta m_0 c^2\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}; \quad \beta = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix}$$

Thus the wave function is a four-component vector that contains the electron with spin up and down, and the positron with spin up and down. Expansion of Dirac equation in series of v/c gives non-relativistic Schrödinger equation plus other terms, including spin-orbit interaction.

Magnetic moment

- The magnetic moment of a loop current is defined as mu = IA. Applying this to an electron orbiting a nucleus:



$$\mu = \frac{(-e)v}{2\pi r}\left(\pi r^2\right) = -\frac{evr}{2}$$

$$= -\frac{emvr}{2m} = -\frac{eL}{2m}$$

$$\boldsymbol{\mu} = -\frac{e\boldsymbol{L}}{2m}$$

Spin

- We might expect to have a magnetic moment associated with the electron spin given by

$$\boldsymbol{\mu} = -\frac{e\boldsymbol{S}}{2m}$$

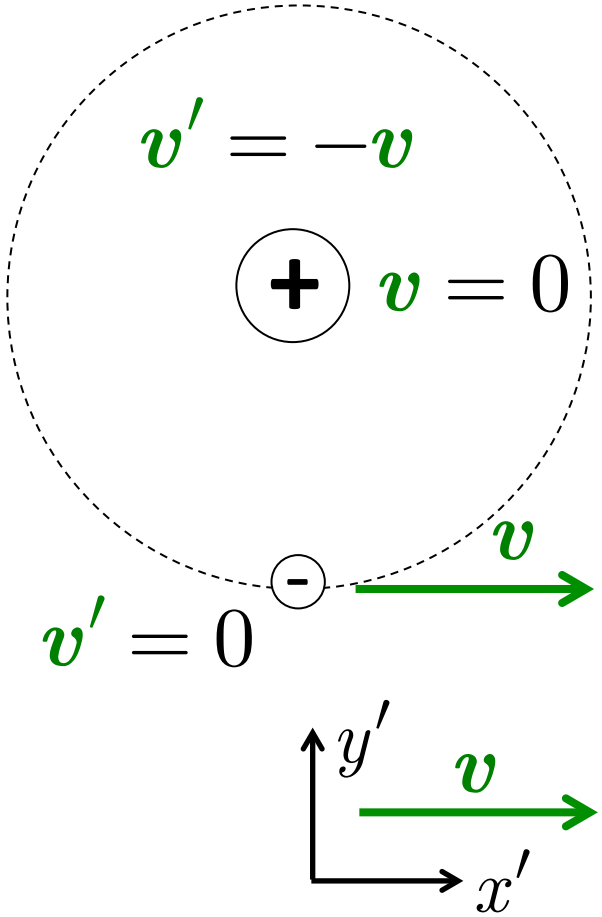
- but the actual expression is

$$\boldsymbol{\mu} = -g_s \frac{e\boldsymbol{S}}{2m}$$

- Here g_s is the so-called Landé g-factor. From the Dirac equation it is g_s =2, but from QED it is g_s =2.0023

Electron rest frame

- Let us consider an inertial reference frame in which the electron is instantaneously at rest

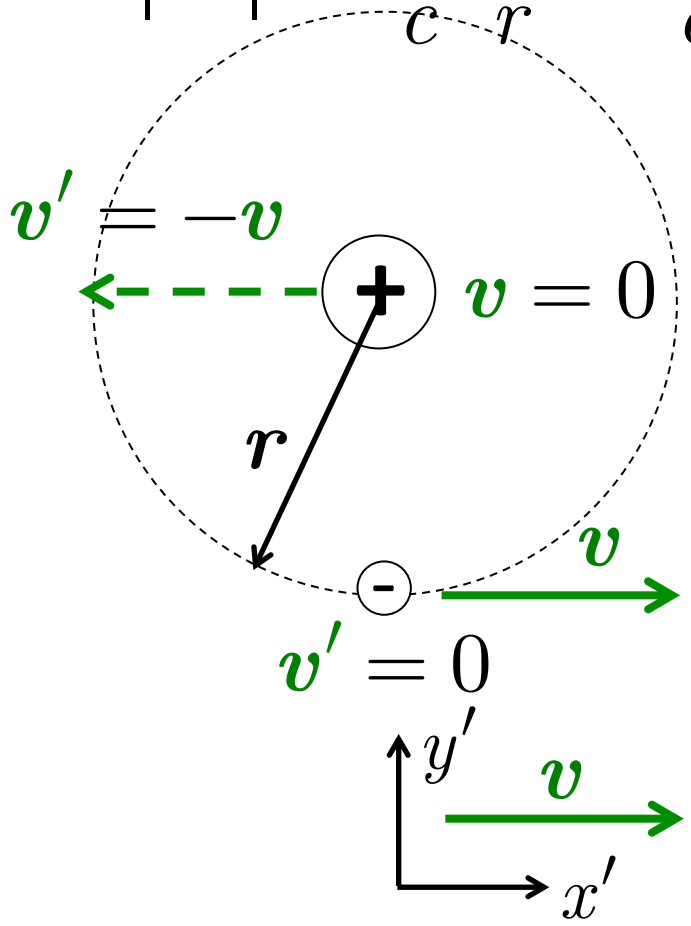


En este sistema, existe un campo magnético en la posición del electrón debido al movimiento del núcleo hacia la izquierda.

B in electron rest frame

- From Biot-Savart's law

$$\left|\boldsymbol{B}'\right| = \frac{2\pi}{c}\frac{I}{r} = \frac{2\pi}{c}\frac{Ze}{Tr} = \frac{2\pi}{c}\frac{Zev}{\left(2\pi r\right)r} = \frac{Ze}{c}\frac{v}{r^2}$$



$$\boldsymbol{B}' = -\frac{Ze}{c}\frac{\boldsymbol{v}\times\boldsymbol{r}}{r^3}$$

$$= -\frac{\boldsymbol{v}}{c}\times\frac{Ze\boldsymbol{r}}{r^2}\left(\frac{\boldsymbol{r}}{r}\right) = -\frac{\boldsymbol{v}\times\boldsymbol{E}}{c}$$

Donde E es el campo eléctrico producido por el núcleo.

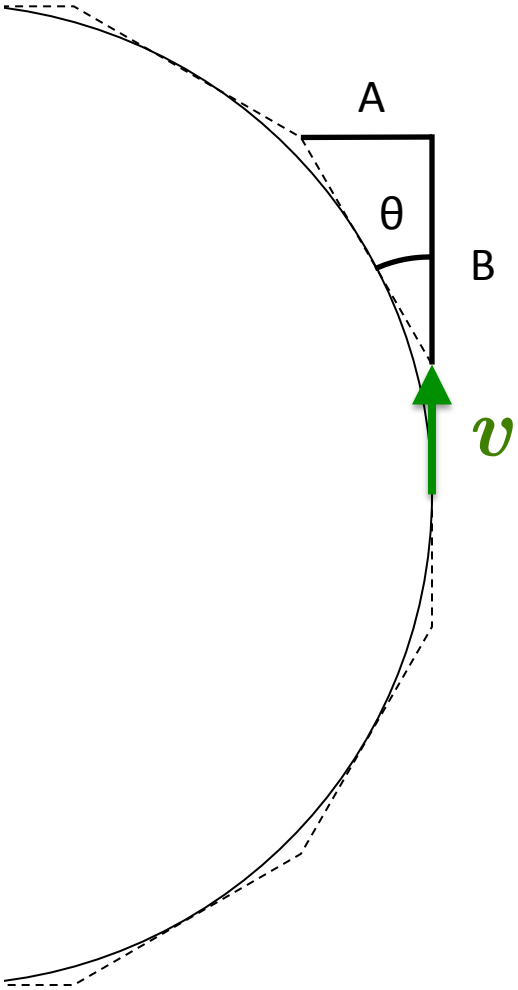
Torque

- Because of the field *B'*, there is a torque on the spin, so that

$$\frac{d\boldsymbol{s}}{dt} = \frac{\boldsymbol{\mu} \times \boldsymbol{B}'}{c}$$

- Classically $d\boldsymbol{s}/dt$ is the same whether computed in the lab frame (proton) or in the frame where the electron is instantaneously at rest. But relativistically this is not true because the sytems are rotating relative to each other...

Thomas precession (I)



Assume object flying in a circle. Approximate large circular orbit by N-side polygon. N very large. For each segment, angle changes by 2π/N ~A/B. But in rest frame of object, B is contracted by γ, so angle is γA/B . After circle, angle measured in lab frame is obviously 2π, but angle accumulated on rest frames is γ2π. Therefore

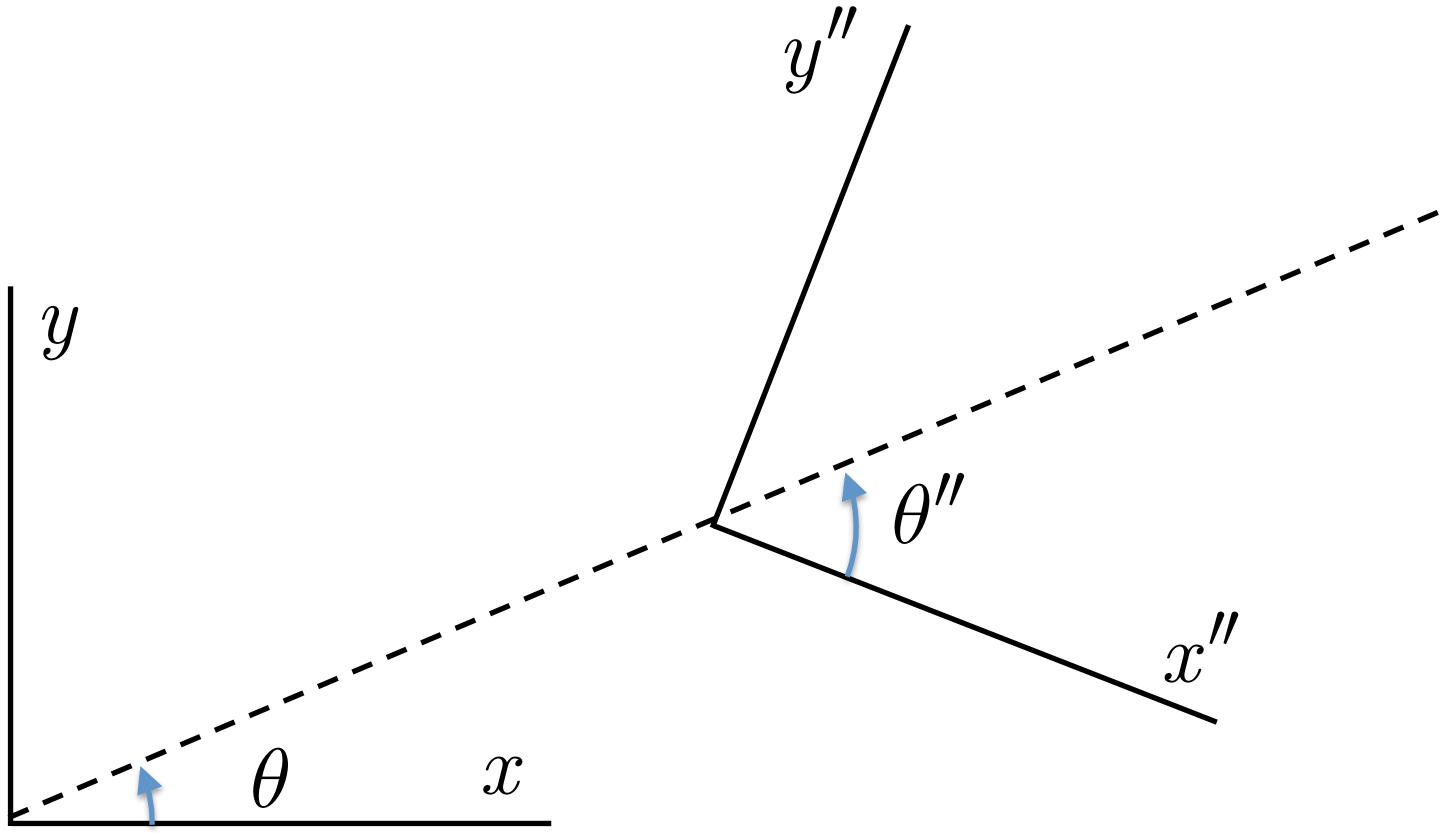
$$\Delta\theta = 2\pi\left(\gamma - 1\right)$$

Dividing by T $\quad \omega_P = \omega\left(\gamma - 1\right)$

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$$

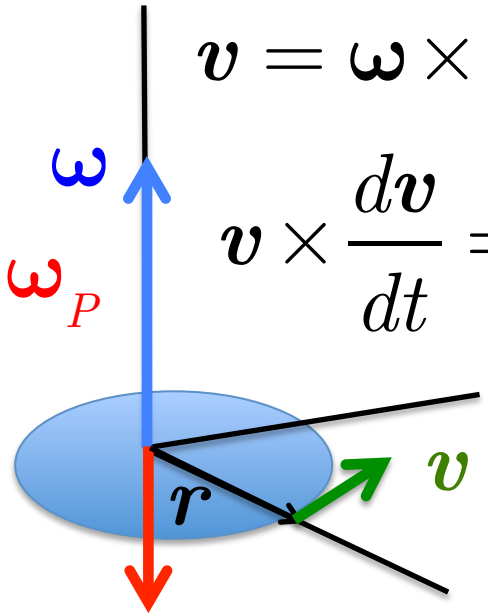
Rotation sign

For θ''>θ, double-primed system is rotated clockwise with respect to unprimed system



Thomas precession 3D

We want to eliminate the angular velocity from our expression, hoping that it will generalize to general, non-circular motion



$$\boldsymbol{v} = \boldsymbol{\omega} \times \boldsymbol{r} \Rightarrow \frac{d\boldsymbol{v}}{dt} = \boldsymbol{\omega} \times \boldsymbol{v}$$

$$\boldsymbol{v} \times \frac{d\boldsymbol{v}}{dt} = \boldsymbol{v} \times \left(\boldsymbol{\omega} \times \boldsymbol{v} \right) = \boldsymbol{\omega}\left(\boldsymbol{v} \cdot \boldsymbol{v} \right) - \boldsymbol{v}\left(\boldsymbol{v} \cdot \boldsymbol{\omega} \right) = v^2 \boldsymbol{\omega}$$

$$\omega_P = \omega\left(\gamma - 1 \right) \sim \frac{1}{2}\left(\frac{v}{c} \right)^2 \omega$$

$$\boldsymbol{\omega}_P = -\frac{1}{2c^2}\, \boldsymbol{v} \times \frac{d\boldsymbol{v}}{dt}$$

Lab frame vs electron frame

$$\left.\frac{d\boldsymbol{S}}{dt}\right|_{\text{lab frame}} = \left.\frac{dS}{dt}\right|_{\text{inst frame}} + \boldsymbol{\omega}_P \times \boldsymbol{S}$$

$$= \boldsymbol{\mu} \times \boldsymbol{B}' + \frac{m}{e}\boldsymbol{\omega}_P \times \boldsymbol{\mu} = \boldsymbol{\mu} \times \left(\boldsymbol{B}' - \frac{m}{e}\boldsymbol{\omega}_P \right)$$

$$= \boldsymbol{\mu} \times \left(-\boldsymbol{v} \times \boldsymbol{E}/c^2 - \frac{m}{2c^2 e}\boldsymbol{v} \times \frac{d\boldsymbol{v}}{dt} \right) =$$

$$= \boldsymbol{\mu} \times \left(-\boldsymbol{v} \times \boldsymbol{E}/c - \frac{1}{2c^2 e}\boldsymbol{v} \times \left(-e\boldsymbol{E} \right) \right)$$

$$= \boldsymbol{\mu} \times \left(-\boldsymbol{v} \times \boldsymbol{E}/c^2 + \frac{1}{2c^2}\boldsymbol{v} \times \boldsymbol{E} \right) = \boldsymbol{\mu} \times \left(-\frac{1}{2c^2}\boldsymbol{v} \times \boldsymbol{E} \right)$$

Magnetic energy

- If torque is given by $\boldsymbol{\mu} \times \left(-\frac{1}{2c^2} \boldsymbol{v} \times \boldsymbol{E} \right)$, the energy is

$$U = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2} \boldsymbol{v} \times \boldsymbol{E} \right)$$

- The electric field is $E = -\frac{\partial V}{\partial r} \frac{\boldsymbol{r}}{r}$, so

$$U = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2 r} \frac{\partial V}{\partial r} \boldsymbol{v} \times \boldsymbol{r} \right) = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2 m r} \frac{\partial V}{\partial r} \boldsymbol{p} \times \boldsymbol{r} \right)$$

$$= -\boldsymbol{\mu} \cdot \left(\frac{1}{2c^2 m r} \frac{\partial V}{\partial r} \boldsymbol{L} \right) = \frac{e}{2c^2 m^2} \frac{1}{r} \frac{\partial V}{\partial r} \boldsymbol{S} \cdot \boldsymbol{L}$$

Magnetic energy

- If torque is given by $\boldsymbol{\mu} \times \left(-\frac{1}{2c^2} \boldsymbol{v} \times \boldsymbol{E} \right)$, the energy is

$$U = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2} \boldsymbol{v} \times \boldsymbol{E} \right)$$

- The electric field is $E = -\frac{\partial V}{\partial r} \frac{\boldsymbol{r}}{r}$, so

$$U = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2 r} \frac{\partial V}{\partial r} \boldsymbol{v} \times \boldsymbol{r} \right) = -\boldsymbol{\mu} \cdot \left(-\frac{1}{2c^2 m r} \frac{\partial V}{\partial r} \boldsymbol{p} \times \boldsymbol{r} \right)$$

$$= -\boldsymbol{\mu} \cdot \left(\frac{1}{2c^2 m r} \frac{\partial V}{\partial r} \boldsymbol{L} \right) = \frac{e}{2c^2 m^2} \frac{1}{r} \frac{\partial V}{\partial r} \boldsymbol{S} \cdot \boldsymbol{L}$$

Hydrogenic wave functions

$$\left|1,0,0\right\rangle = \left|1s\right\rangle = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\left|2,0,0\right\rangle = \left|2s\right\rangle = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$$\left|2,1,0\right\rangle = \left|2p_0\right\rangle = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z}{a_0}e^{-Zr/2a_0} r\cos\theta \propto \left|2p_z\right\rangle$$

$$\left|2,1,1\right\rangle = \left|2p_1\right\rangle = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z}{a_0}e^{-Zr/2a_0} r\sin\theta e^{i\phi} = \frac{\left|2p_x\right\rangle + i\left|2p_y\right\rangle}{\sqrt{2}}$$

$$\left|2,1,-1\right\rangle = \left|2p_{-1}\right\rangle = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z}{a_0}e^{-Zr/2a_0} r\sin\theta e^{-i\phi} = \frac{\left|2p_x\right\rangle - i\left|2p_y\right\rangle}{\sqrt{2}}$$

New notation for p-states

$$p_x \Leftrightarrow X$$

$$p_y \Leftrightarrow Y$$

$$p_z \Leftrightarrow Z$$

Spin-orbit Interaction

- Because the radial part is the same for all p-functions, I can write

$$H_{SO} = \lambda \boldsymbol{L} \cdot \boldsymbol{S} = \lambda \left(J^2 - L^2 - S^2 \right) \Big/ 2; \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

- Accordingly, the SO interaction is diagonalized by simultaneous eigenfunctions of J^2, L^2, and S^2.

Eigenfunctions of J^2, J_z

$$\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle = \left|1,1\right\rangle\uparrow \quad = \left(X+iY\right)\uparrow/\sqrt{2}$$

$$\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle = \left|1,-1\right\rangle\downarrow = \left(X-iY\right)\downarrow/\sqrt{2}$$

$$\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|1,1\right\rangle\downarrow - \sqrt{\frac{2}{3}}\left|1,0\right\rangle\uparrow = \frac{1}{\sqrt{6}}\left(X+iY\right)\downarrow - \sqrt{\frac{2}{3}}Z\uparrow$$

$$\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|1,0\right\rangle\downarrow + \sqrt{\frac{1}{3}}\left|1,-1\right\rangle\uparrow = \sqrt{\frac{2}{3}}Z\downarrow + \sqrt{\frac{1}{6}}\left(X-iY\right)\uparrow$$

$$\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|1,0\right\rangle\uparrow - \sqrt{\frac{2}{3}}\left|1,1\right\rangle\downarrow = \frac{1}{\sqrt{3}}Z\uparrow - \sqrt{\frac{1}{3}}\left(X+iY\right)\downarrow$$

$$\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\left|1,0\right\rangle\downarrow - \sqrt{\frac{2}{3}}\left|1,-1\right\rangle\uparrow = -\sqrt{\frac{1}{3}}\left(X-iY\right)\uparrow + \sqrt{\frac{1}{3}}Z\downarrow$$

Transformation matrix

	$X\uparrow$	$Y\uparrow$	$Z\downarrow$	$X\downarrow$	$Y\downarrow$	$Z\uparrow$
$\frac{3}{2},\frac{3}{2}$	$1/\sqrt{2}$	$i/\sqrt{2}$	0	0	0	0
$\frac{3}{2},-\frac{1}{2}$	$1/\sqrt{6}$	$-i/\sqrt{6}$	$\sqrt{2/3}$	0	0	0
$\frac{1}{2},-\frac{1}{2}$	$-\sqrt{1/3}$	$i\sqrt{1/3}$	$\sqrt{1/3}$	0	0	0
$\frac{3}{2},-\frac{3}{2}$	0	0	0	$1/\sqrt{2}$	$-i/\sqrt{2}$	0
$\frac{3}{2},\frac{1}{2}$	0	0	0	$1/\sqrt{6}$	$i/\sqrt{6}$	$\sqrt{2/3}$
$\frac{1}{2},\frac{1}{2}$	0	0	0	$-\sqrt{1/3}$	$-i\sqrt{1/3}$	$1/\sqrt{3}$

Inverse transformation

$$\left|X\uparrow\right\rangle = \frac{1}{\sqrt{2}}\left|\frac{3}{2},\frac{3}{2}\right\rangle + \frac{1}{\sqrt{6}}\left|\frac{3}{2},-\frac{1}{2}\right\rangle - \frac{1}{\sqrt{3}}\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

$$\left|Y\uparrow\right\rangle = \frac{-i}{\sqrt{2}}\left|\frac{3}{2},\frac{3}{2}\right\rangle + \frac{i}{\sqrt{6}}\left|\frac{3}{2},-\frac{1}{2}\right\rangle - \frac{i}{\sqrt{3}}\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

$$\left|Z\downarrow\right\rangle = \sqrt{\frac{2}{3}}\left|\frac{3}{2},-\frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

$$\left|X\downarrow\right\rangle = \frac{1}{\sqrt{2}}\left|\frac{3}{2},-\frac{3}{2}\right\rangle + \frac{1}{\sqrt{6}}\left|\frac{3}{2},\frac{1}{2}\right\rangle - \frac{1}{\sqrt{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

$$\left|Y\downarrow\right\rangle = \frac{i}{\sqrt{2}}\left|\frac{3}{2},-\frac{3}{2}\right\rangle - \frac{i}{\sqrt{6}}\left|\frac{3}{2},\frac{1}{2}\right\rangle + \frac{i}{\sqrt{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

$$\left|Z\uparrow\right\rangle = \sqrt{\frac{2}{3}}\left|\frac{3}{2},\frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

Operator *LS*

$$J^2\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle=\tfrac{15}{4}\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle;\quad L^2\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle=2\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle;\quad S^2\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle$$

$$J^2\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle=\tfrac{15}{4}\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle;\quad L^2\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle=2\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle;\quad S^2\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle$$

$$J^2\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle=\tfrac{15}{4}\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle;\quad L^2\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle=2\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle;\quad S^2\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle$$

$$J^2\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle=\tfrac{15}{4}\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle;\quad L^2\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle=2\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle;\quad S^2\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle$$

$$J^2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle;\quad L^2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle=2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle;\quad S^2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle$$

$$J^2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle;\quad L^2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle=2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle;\quad S^2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle=\tfrac{3}{4}\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$$

$$\tfrac{1}{2}\left(J^2-L^2-S^2\right)\left|\tfrac{3}{2},\ldots\right\rangle=\tfrac{1}{2}\left(\tfrac{15}{4}-2-\tfrac{3}{4}\right)\left|\tfrac{3}{2},\ldots\right\rangle=\tfrac{1}{2}\left|\tfrac{3}{2},\ldots\right\rangle$$

$$\tfrac{1}{2}\left(J^2-L^2-S^2\right)\left|\tfrac{1}{2},\ldots\right\rangle=\tfrac{1}{2}\left(\tfrac{3}{4}-2-\tfrac{3}{4}\right)\left|\tfrac{3}{2},\ldots\right\rangle=-\left|\tfrac{3}{2},\ldots\right\rangle$$

Matrix elements of H_{SO}

$$\left\langle \tfrac{3}{2},\tfrac{3}{2}\right| H_{SO} \left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle = \lambda/2$$

$$\left\langle \tfrac{3}{2},\tfrac{3}{2}\right| H_{SO} \left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle = \lambda/2$$

$$\left\langle \tfrac{1}{2},\tfrac{3}{2}\right| H_{SO} \left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle = \lambda/2$$

$$\left\langle -\tfrac{1}{2},\tfrac{3}{2}\right| H_{SO} \left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle = \lambda/2$$

$$\left\langle \tfrac{1}{2},\tfrac{1}{2}\right| H_{SO} \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = -\lambda$$

$$\left\langle \tfrac{1}{2},-\tfrac{1}{2}\right| H_{SO} \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = -\lambda$$

H_{SO} matrix elements of p-states

$$\left\langle X\uparrow\middle|H_{SO}\middle|Y\uparrow\right\rangle =$$

$$= -\frac{i}{2}\left\langle \tfrac{3}{2},\tfrac{3}{2}\middle|H_{SO}\middle|\tfrac{3}{2},\tfrac{3}{2}\right\rangle + \frac{i}{6}\left\langle \tfrac{-1}{2},\tfrac{3}{2}\middle|H_{SO}\middle|\tfrac{3}{2},\tfrac{-1}{2}\right\rangle + \frac{i}{3}\left\langle \tfrac{-1}{2},\tfrac{1}{2}\middle|H_{SO}\middle|\tfrac{1}{2},\tfrac{-1}{2}\right\rangle$$

$$= -\frac{i}{2}\left(\frac{\lambda}{2}\right) + \frac{i}{6}\left(\frac{\lambda}{2}\right) + \frac{i}{3}\left(-\lambda\right) = -i\left(\frac{\lambda}{2}\right)$$

$$\left\langle X\uparrow\middle|H_{SO}\middle|Z\uparrow\right\rangle = 0; \quad \left\langle X\uparrow\middle|H_{SO}\middle|X\downarrow\right\rangle = 0; \quad \left\langle X\uparrow\middle|H_{SO}\middle|Y\downarrow\right\rangle = 0$$

$$\left\langle X\uparrow\middle|H_{SO}\middle|Z\downarrow\right\rangle = \lambda/2; \left\langle Y\uparrow\middle|H_{SO}\middle|Z\downarrow\right\rangle = -i\,\lambda/2; \left\langle Y\uparrow\middle|H_{SO}\middle|X\downarrow\right\rangle = 0$$

$$\left\langle Y\uparrow\middle|H_{SO}\middle|Y\downarrow\right\rangle = 0; \quad \left\langle Y\uparrow\middle|H_{SO}\middle|Z\uparrow\right\rangle = 0; \quad \left\langle Z\downarrow\middle|H_{SO}\middle|X\downarrow\right\rangle = 0$$

$$\left\langle Z\downarrow\middle|H_{SO}\middle|Y\downarrow\right\rangle = 0; \quad \left\langle Z\downarrow\middle|H_{SO}\middle|Z\uparrow\right\rangle = 0; \quad \left\langle X\downarrow\middle|H_{SO}\middle|Y\downarrow\right\rangle = i\,\lambda/2$$

$$\left\langle X\downarrow\middle|H_{SO}\middle|Z\uparrow\right\rangle = \lambda/2; \quad \left\langle Y\downarrow\middle|H_{SO}\middle|Z\uparrow\right\rangle = i\,\lambda/2$$

16x16 matrix

- If we use the base of s and p functions, the matrix elements we just calculated imply that we need to solve a 16x16 problem.
- However, in the case of diamond-structure materials with inversion symmetry, the states are all double-degenerate, so it would in principle be possible to reduce the problem to a 8x8 matrix by taking appropriate symmetric and antisymmetric combinations.