

An electron is in an  $\ell = 1$  state of a hydrogen atom. It experience a spin orbit interaction

$$V_{so} = \alpha \vec{L} \cdot \vec{S}$$

and feels a uniform external magnetic field

$$V_b = \mu \vec{B} \cdot (\vec{L} + 2\vec{S})$$

Calculate the eigenvalues of the Hamiltonian in the  $|JM\rangle$  basis.

Calculate the Clebsch-Gordan coefficients.

$$J_- |J, M\rangle = \hbar \sqrt{(J+M)(J-M+1)} |J, M-1\rangle$$

$$S_- |s, m_s\rangle = \hbar \sqrt{(s+m_s)(s-m_s+1)} |s, m_s-1\rangle$$

$$L_- |\ell, m_\ell\rangle = \hbar \sqrt{(\ell+m_\ell)(\ell-m_\ell+1)} |\ell, m_\ell-1\rangle$$

$$\boxed{\left| J = \frac{3}{2}, M = \frac{3}{2} \right\rangle = \left| m_\ell = 1, m_s = \frac{1}{2} \right\rangle}$$

$$J_- \left| J = \frac{3}{2}, M = \frac{3}{2} \right\rangle = (S_- + L_-) \left| m_\ell = 1, m_s = \frac{1}{2} \right\rangle$$

$$\hbar\sqrt{3} \left| J = \frac{3}{2}, M = \frac{1}{2} \right\rangle = \hbar \left| m_\ell = 1, m_s = -\frac{1}{2} \right\rangle + \hbar\sqrt{2} \left| m_\ell = 0, m_s = \frac{1}{2} \right\rangle$$

$$\boxed{\left| J = \frac{3}{2}, M = \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| m_\ell = 1, m_s = -\frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| m_\ell = 0, m_s = \frac{1}{2} \right\rangle}$$

by orthogonality (switch the coefficients and make one negative):

$$\boxed{\left| J = \frac{1}{2}, M = \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| m_\ell = 1, m_s = -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| m_\ell = 0, m_s = \frac{1}{2} \right\rangle}$$

etc...

$$\boxed{\left| J = \frac{3}{2}, M = -\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| m_\ell = -1, m_s = \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| m_\ell = 0, m_s = -\frac{1}{2} \right\rangle}$$

$$\boxed{\left| J = \frac{1}{2}, M = -\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| m_\ell = -1, m_s = \frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| m_\ell = 0, m_s = -\frac{1}{2} \right\rangle}$$

$$\boxed{\left| J = \frac{3}{2}, M = -\frac{3}{2} \right\rangle = \left| m_\ell = -1, m_s = -\frac{1}{2} \right\rangle}$$

We can use these relations to form a matrix that transforms a  $|m_\ell, m_s\rangle$  state into a  $|JM\rangle$  state.

$$\begin{pmatrix} |\frac{3}{2}, \frac{3}{2}\rangle \\ |\frac{3}{2}, \frac{1}{2}\rangle \\ |\frac{1}{2}, \frac{1}{2}\rangle \\ |\frac{3}{2}, -\frac{1}{2}\rangle \\ |\frac{1}{2}, -\frac{1}{2}\rangle \\ |\frac{3}{2}, -\frac{3}{2}\rangle \end{pmatrix} = \begin{pmatrix} 1 & & & & & \\ & \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & & & \\ & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} & & & \\ & & & \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & \\ & & & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} & \\ & & & & & 1 \end{pmatrix} \begin{pmatrix} |1, \frac{1}{2}\rangle \\ |1, -\frac{1}{2}\rangle \\ |0, \frac{1}{2}\rangle \\ |-1, \frac{1}{2}\rangle \\ |0, -\frac{1}{2}\rangle \\ |-1, -\frac{1}{2}\rangle \end{pmatrix}$$

$$|\psi^{(J)}\rangle = C |\psi^{(\ell s)}\rangle$$

Any permutation of this matrix also works, as long as the basis vectors are adjusted accordingly. Since the Clebsch-Gordan coefficients are real (by convention), the transpose of this matrix is its inverse.

$$C^T = C^{-1}$$

This can be demonstrated by solving for the  $|m_\ell, m_s\rangle$  states in terms of the  $|JM\rangle$  states. In this case,

$$C = C^T = C^{-1}$$

but this is not true in general.

Now we write down the Hamiltonian. The spin-orbit component is diagonal in the  $|JM\rangle$  basis.

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \Rightarrow \frac{\hbar^2}{2} (J(J+1) - \ell(\ell+1) - s(s+1))$$

$$\left\langle \frac{3}{2}, \frac{3}{2} \left| V_{so} \right| \frac{3}{2}, \frac{3}{2} \right\rangle = \left\langle \frac{3}{2}, \frac{1}{2} \left| V_{so} \right| \frac{3}{2}, \frac{1}{2} \right\rangle = \left\langle \frac{3}{2}, -\frac{1}{2} \left| V_{so} \right| \frac{3}{2}, -\frac{1}{2} \right\rangle = \left\langle \frac{3}{2}, -\frac{3}{2} \left| V_{so} \right| \frac{3}{2}, -\frac{3}{2} \right\rangle = \frac{\alpha \hbar^2}{2}$$

$$\left\langle \frac{1}{2}, \frac{1}{2} \left| V_{so} \right| \frac{1}{2}, \frac{1}{2} \right\rangle = \left\langle \frac{1}{2}, -\frac{1}{2} \left| V_{so} \right| \frac{1}{2}, -\frac{1}{2} \right\rangle = -\alpha \hbar^2$$

All off-diagonal matrix elements give zero.

$$V_{so}^{(J)} = \frac{\alpha \hbar^2}{2} \begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & -2 & & \\ & & & 1 & \\ & & & & -2 \\ & & & & & 1 \end{pmatrix}$$

In contrast, the component due to the magnetic field is diagonal in the  $|m_\ell, m_s\rangle$  basis.

$$\begin{aligned} \langle 1, \frac{1}{2} | V_b | 1, \frac{1}{2} \rangle &= 2\mu \hbar B & \langle 1, -\frac{1}{2} | V_b | 1, -\frac{1}{2} \rangle &= 0 & \langle 0, \frac{1}{2} | V_b | 0, \frac{1}{2} \rangle &= \mu \hbar B \\ \langle -1, \frac{1}{2} | V_b | -1, \frac{1}{2} \rangle &= 0 & \langle 0, -\frac{1}{2} | V_b | 0, -\frac{1}{2} \rangle &= -\mu B & \langle -1, -\frac{1}{2} | V_b | -1, -\frac{1}{2} \rangle &= -2\mu \hbar B \end{aligned}$$

$$V_b^{(\ell_s)} = \mu\hbar B \begin{pmatrix} 2 & & & & & \\ & 0 & & & & \\ & & 1 & & & \\ & & & 0 & & \\ & & & & -1 & \\ & & & & & -2 \end{pmatrix}$$

We perform a transformation to the  $|JM\rangle$  basis using the matrix of Clebsch-Gordan coefficients.

$$V_b^{(J)} = CV_b^{(\ell_s)}C^T = \mu\hbar B \begin{pmatrix} 2 & & & & & \\ & \frac{2}{3} & -\frac{\sqrt{2}}{3} & & & \\ & -\frac{\sqrt{2}}{3} & \frac{1}{3} & & & \\ & & & -\frac{2}{3} & \frac{\sqrt{2}}{3} & \\ & & & \frac{\sqrt{2}}{3} & -\frac{1}{3} & \\ & & & & & -2 \end{pmatrix}$$

Behold:

$$H^{(J)} = V_{so}^{(J)} + V_b^{(J)}$$

$$= \begin{pmatrix} \frac{\alpha\hbar^2}{2} + 2\mu\hbar B & & & & & \\ & \frac{\alpha\hbar^2}{2} + \frac{2}{3}\mu\hbar B & -\frac{\sqrt{2}}{3}\mu\hbar B & & & \\ & -\frac{\sqrt{2}}{3}\mu\hbar B & -\alpha\hbar^2 + \frac{1}{3}\mu\hbar B & & & \\ & & & \frac{\alpha\hbar^2}{2} - \frac{2}{3}\mu\hbar B & \frac{\sqrt{2}}{3}\mu\hbar B & \\ & & & \frac{\sqrt{2}}{3}\mu\hbar B & -\alpha\hbar^2 - \frac{1}{3}\mu\hbar B & \\ & & & & & \frac{\alpha\hbar^2}{2} - 2\mu\hbar B \end{pmatrix}$$

By choosing unit vectors such that the matrix of Clebsch-Gordan coefficients is block-diagonal, the eigenvalues are easily calculated:

$$E = \begin{cases} \frac{\alpha\hbar^2}{2} \pm 2\mu\hbar B \\ \frac{\mu\hbar B}{2} - \frac{\alpha\hbar^2}{4} \pm \sqrt{\left(\frac{\alpha\hbar^2}{4} + \frac{\mu\hbar B}{2}\right)^2 + \frac{\alpha^2\hbar^4}{2}} \\ -\frac{\mu\hbar B}{2} - \frac{\alpha\hbar^2}{4} \pm \sqrt{\left(\frac{\alpha\hbar^2}{4} - \frac{\mu\hbar B}{2}\right)^2 + \frac{\alpha^2\hbar^4}{2}} \end{cases}$$