Quantum Mechanics (P304H)
Part 2 – Lecture 17

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Matrix representation

- The matrix representation of angular momentum:
  - A general angular momentum state can be written as:

$$|\psi\rangle = a_1|l,l\rangle + a_2|l,l-1\rangle + \ldots + a_{2l}|l,-l+1\rangle + a_{2l+1}|l,-l\rangle \qquad (1)$$

  - We can write this "$|ket\rangle$" function as a column matrix:

$$|\psi\rangle = \begin{bmatrix} a_1 \\ \vdots \\ a_{2l+1} \end{bmatrix}$$

  - And the "$\langle bra|$" function as a row matrix:

$$\langle\psi| = \begin{bmatrix} a_1^* & \cdots & a_{2l+1}^* \end{bmatrix}$$

Matrix representation

– An operator acting on the wave function is then represented as a matrix multiplying the vector.

– The eigenvalue equation takes the form:

λ is the eigenvalue

$$\hat{A}|\psi\rangle = \begin{bmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn} \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_n \end{bmatrix} = \lambda \begin{bmatrix} a_1 \\ \vdots \\ a_n \end{bmatrix} \quad \text{with} \quad n = 2l+1$$

which is equivalent to:

$$\begin{vmatrix} A_{11}-\lambda & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn}-\lambda \end{vmatrix} = 0$$

– The Hermitian conjugate of matrix $\hat{A}$ is defined as:

$$\underline{\hat{A}^{+} \triangleq \hat{A}^{*T}} = \begin{bmatrix} A_{11}^{*} & \cdots & A_{n1}^{*} \\ \vdots & \ddots & \vdots \\ A_{1n}^{*} & \cdots & A_{nn}^{*} \end{bmatrix}$$

Complex conjugate, transpose

– Therefore a matrix is called Hermitian if: $\boxed{A_{ij} = A_{ji}^{*}}$

8. Angular Momentum

❑ Spin in matrix form (case $s=½$):

– Spin is an intrinsic angular momentum: a property of elementary particles

– Spin can not be represented by the orbital angular momentum operator $\hat{L}$

– Fermions (*e.g.* e^-, p, n, the d, s, b quarks) have spin $½\hbar$:

$$s = \frac{1}{2} \quad \Rightarrow \quad m_s = +\frac{1}{2}, -\frac{1}{2}$$

where the z component is $s_z = m_s \hbar$

This is not "spin" in the classical sense of a spinning top, but an intrinsic property of the particle! See problem 20 (sheet 3) to show that $L= ½\hbar$ is not allowed classically.

– We denote by χ_{s,m_s} the simultaneous eigenstates of $\hat{S}^2$ and $\hat{S}_z$:

$$\hat{S}^2 \chi_{s,m_s} = s(s+1)\hbar^2 \chi_{s,m_s}$$

$$\hat{S}_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s}$$

– For spin ½, there are only two normalised spin eigenfunctions

$$\chi_{1/2,1/2}, \quad \chi_{1/2,-1/2}$$

'spin up' (↑) 'spin down' (↓)

8. Angular Momentum

– In matrix form, we can introduce the notation

$$\chi_{s,m_s} \doteq \left| s, m_s \right\rangle$$

and the two eigenstates can be written as: $\left| \frac{1}{2}, +\frac{1}{2} \right\rangle, \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$

– Because there are only two states, we can represent these by matrices of size n=2

$$\left| \frac{1}{2}, +\frac{1}{2} \right\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

– Each state is called a *spinor*. As per (1) can write the full wave function as

$$\left| s, m_s \right\rangle = a_{1/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_{-1/2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} a_{1/2} \\ a_{-1/2} \end{bmatrix}$$

$a_{1/2}$ and $a_{-1/2}$ are some coefficients

and the eigenvalues equation is

$$\hat{S}_z \left| s, m_s \right\rangle = m_s \hbar \left| s, m_s \right\rangle \quad \Rightarrow \quad \hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (2)$$

8. Angular Momentum

– It is convenient to introduce the so-called *ladder operators* defined by:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y$$

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y$$

with the property

$$\hat{S}_- = \hat{S}_+^+$$

Exercise: prove these properties

– Then we have:

$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) \qquad \hat{S}_y = \frac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right)$$

$$\left[\hat{S}_z, \hat{S}_+\right] = \left[\hat{S}_z, \hat{S}_x\right] + i\left[\hat{S}_z, \hat{S}_y\right] = i\hbar\hat{S}_y + i(-i\hbar)\hat{S}_x = +\hbar\hat{S}_+$$

$$\left[\hat{S}_z, \hat{S}_-\right] = -\hbar\hat{S}_-$$

The ladder operator S_+ increases eigenvalue of S_z by $\hbar$ and operator S_- lowers it by $\hbar$.

8. Angular Momentum

– One can prove the following relations

These will be revisited in the 4th year Atomic Systems course

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

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

$$\hat{S}_+|s,m_s\rangle = \sqrt{\left(\frac{1}{2}-m_s\right)\left(\frac{1}{2}+m_s+1\right)}\hbar|s,m_s+1\rangle \quad \Rightarrow \quad \hat{S}_+ = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

$$\hat{S}_-|s,m_s\rangle = \sqrt{\left(\frac{1}{2}+m_s\right)\left(\frac{1}{2}-m_s+1\right)}\hbar|s,m_s-1\rangle \quad \Rightarrow \quad \hat{S}_- = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

– And then we have

$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{S}_y = \frac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right) = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad (3)$$

8. Angular Momentum

❑ Pauli Spin Matrices:

– The form of equations (2) and (3) suggests the introduction of the matrices:

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (4)$$

such that we can simply write

$$\underline{\hat{S}} = \frac{\hbar}{2}\underline{\hat{\sigma}}$$

– The 2×2 complex matrices from (4) are Hermitian and unitary. They are called Pauli Spin Matrices and were introduced in 1925 by Wolfgang Pauli.

– One can check commutation relations using the σ-s

$$\left[\hat{S}_x,\hat{S}_y\right] = \frac{1}{4}\hbar^2\left(\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} - \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\right)$$

$$= \frac{1}{4}\hbar^2\left(\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} - \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}\right) = i\hbar\frac{1}{2}\hbar\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = i\hbar\hat{S}_z$$

8. Angular Momentum

– For example, let us calculate the eigenstates of S_z for spin $1/2$:

$$\begin{vmatrix} 1-\lambda & 0 \\ 0 & -1-\lambda \end{vmatrix} = 0 \quad \Rightarrow \quad -(1-\lambda)(1+\lambda)=0 \quad \Rightarrow \quad \lambda = \pm 1$$

$$\Rightarrow \quad \text{the eigenvalues of } \hat{S}_z \text{ are } \pm\frac{1}{2}\hbar$$

$$\frac{1}{2}\hbar\begin{bmatrix} 1-\lambda & 0 \\ 0 & -1-\lambda \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0 \quad \Rightarrow \quad \begin{cases} \left|\frac{1}{2},\frac{1}{2}\right\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} & \text{if } \lambda = 1 \\ \left|\frac{1}{2},-\frac{1}{2}\right\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} & \text{if } \lambda = -1 \end{cases}$$

– The eigenstates of S_x and S_y also give eigenvalues of $\pm½\hbar$ *(show this)*.

– For spin $1/2$ the eigenvalue of S^2 is $S^2=s(s+1)\hbar^2=3/4\hbar^2$ and one can prove that

$$\hat{\underline{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3}{4}\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \Rightarrow \quad \left[\hat{\underline{S}}^2, \hat{S}_x\right] = \left[\hat{\underline{S}}^2, \hat{S}_y\right] = \left[\hat{\underline{S}}^2, \hat{S}_z\right] = 0$$

This is because all matrices commute with the identity matrix.

8. Angular Momentum

❑ Addition relations for angular momenta:

– We can have particles with both orbital angular momentum and intrinsic angular momentum (spin).

– We need to calculate the total angular momentum $\hat{\underline{J}} = \hat{\underline{L}} + \hat{\underline{S}}$

$$\hat{L}^2|l,m_l\rangle = l(l+1)\hbar^2|l,m_l\rangle \qquad \hat{S}^2|s,m_s\rangle = s(s+1)\hbar^2|s,m_s\rangle$$

$$\hat{L}_z|l,m_l\rangle = m_l\hbar|l,m_l\rangle \qquad \hat{S}_z|s,m_s\rangle = m_s\hbar|s,m_s\rangle$$

– If L and S are independent, then any component of L commutes with any component of S, so L^2, L_z, S^2 and S_z form a complete set of observables with eigenstates that will be the *direct product* of the individual eigenstates:

$$|(l,m_l);(s,m_s)\rangle \equiv |j,m\rangle$$

– The total angular momentum will satisfy the eigenvalue equations:

$$\hat{J}^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle$$

$$\hat{J}_z|j,m\rangle = m\hbar|j,m\rangle$$

Note that we use now m_l for the L_z quantum numbers and m for the eigenvalues of J_z !

8. Angular Momentum

– We have the following commutation relations:

$$\left.\begin{array}{l}\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z\\ \left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z\end{array}\right\}\Rightarrow\left[\hat{J}_x,\hat{J}_y\right]=i\hbar\hat{J}_z$$

– Since the operators L and S commute

$$\hat{J}^2=\left(\hat{\underline{L}}+\hat{\underline{S}}\right)^2=\hat{L}^2+\hat{S}^2+2\hat{\underline{L}}\cdot\hat{\underline{S}}\quad\Rightarrow\quad\left[\hat{J}^2,\hat{L}^2\right]=\left[\hat{J}^2,\hat{S}^2\right]=0$$

– But we can not have simultaneous eigenstates of J^2, L_z and S_z:

$$\left[\hat{J}^2,\hat{L}_z\right]=\left[\hat{L}^2+\hat{S}^2+2\hat{\underline{L}}\cdot\hat{\underline{S}},\hat{L}_z\right]=2\left[\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y+\hat{L}_z\hat{S}_z,\hat{L}_z\right]=$$
$$=2\left[\hat{L}_x,\hat{L}_z\right]\hat{S}_x+2\left[\hat{L}_y,\hat{L}_z\right]\hat{S}_y=-2i\hbar\hat{L}_y\hat{S}_x+2i\hbar\hat{L}_x\hat{S}_y\neq0$$

8. Angular Momentum

❑ Addition of two angular momenta: $\hat{\underline{J}}=\hat{\underline{L}}+\hat{\underline{S}}$

– z-projections:

$$m=m_l+m_s$$

– Range of values:

$$m_l=-l,\ldots,0,\ldots,l\quad\Rightarrow\quad 2l+1\text{ values}$$
$$m_s=-s,\ldots,0,\ldots,s\quad\Rightarrow\quad 2s+1\text{ values}$$
$$m=-j,\ldots,0,\ldots,j\quad\Rightarrow\quad 2j+1\text{ values}$$

– The maximum value for j is: $j_{\max}=l+s$

– The minimum value for j is: $j_{\min}=|l-s|$

$$\Rightarrow\quad|l-s|\le j\le l+s$$

Proof: We have the same number of eigenfunctions in both basis sets, and if $l\geq s$ then

$$\sum_{j=|l-s|}^{l+s}(2j+1)=\left[2(l+s)+1+2(l+s+1)+1+\ldots+2(l+s+2s)+1\right]=$$
$$=2(l-s)(2s+1)+2(1+2+\ldots+2s)+2s+1=(2l+1)(2s+1)$$

8. Angular Momentum

Examples:

- Two spin ½ systems: $j=s_1+s_2$, with s_1=1/2 and s_2=1/2
  - Total angular momentum:

$$j=\frac{1}{2}+\frac{1}{2}=1 \quad \Rightarrow \quad m=+1,0,-1 \qquad \textbf{(triplet)}$$

$$j=\frac{1}{2}-\frac{1}{2}=0 \quad \Rightarrow \quad m=0 \qquad \textbf{(singlet)}$$

  - Four states: $(2s_1+1)(2s_2+1)=\left(2\times\frac{1}{2}+1\right)\left(2\times\frac{1}{2}+1\right)=4$

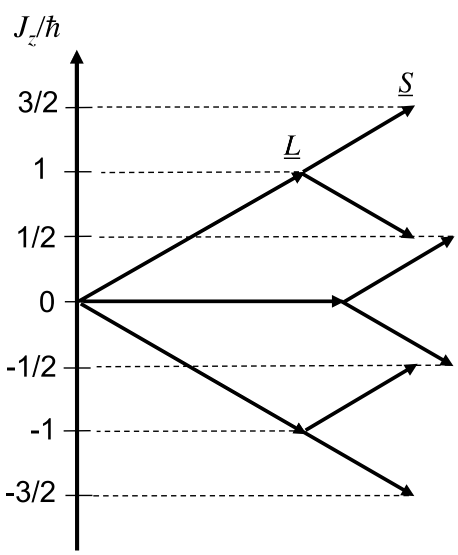
- Electron (s=1/2) with orbital angular momentum l=1:
  - Because $j=l+s$, with l=1 and s=1/2 results in 6 states $(2l+1)(2s+1) = 3\times 2$

$$j=1+\frac{1}{2}=\frac{3}{2} \quad \Rightarrow \quad m=+\frac{3}{2},+\frac{1}{2},-\frac{1}{2},-\frac{3}{2} \qquad \textbf{(quadruplet)}$$

$$j=1-\frac{1}{2}=\frac{1}{2} \quad \Rightarrow \quad m=+\frac{1}{2},-\frac{1}{2} \qquad \textbf{(doublet)}$$

8. Angular Momentum

- The vector interpretation of the addition of angular momentum:
  - For the same example $j=l+s$, with l=1 and s=1/2



- The orbital angular momentum vector $\underline{L}$ has 3 possible orientations.
- The spin $\underline{S}$ can have **2** possible orientations.
- The total angular momentum $\underline{J}$ can then have **6** possible orientations.

- The component J_z can have **4** distinct values:

$$-3/2\hbar,\ -1/2\hbar,\ 1/2\hbar,\ 3/2\hbar$$

8. The Zeeman Effect

- Is the splitting of a spectral line into several components in the presence of a static magnetic field.
- First observed by Pieter Zeeman in 1896, who was awarded the 1902 Nobel Prize for it's discovery.
- When the magnetic interaction is stronger than the spin-orbit interaction (strong field):

$$\Delta E = \mu_B B(m_l + 2m_s)$$

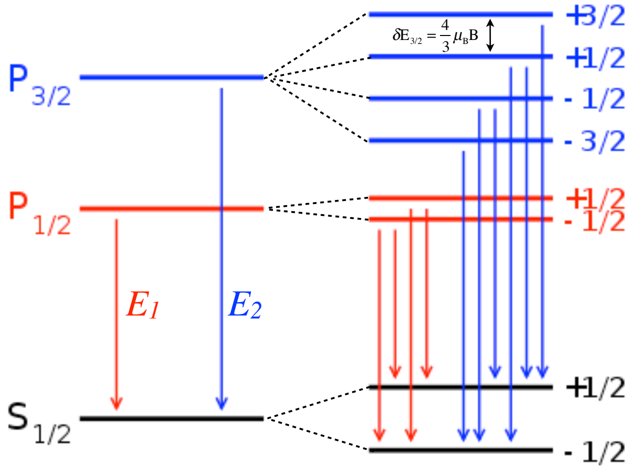
- In the case of a weak magnetic field (when the spin-orbit term dominates):

$$\Delta E_{m_j} = g\mu_B B m_j$$

with the *Landé* g factor given by

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

Referred to as the 'anomalous' Zeeman effect before the electron spin was discovered.



Transitions between the energy levels of atomic hydrogen. The r.h.s. split occurs in the presence of a weak magnetic field