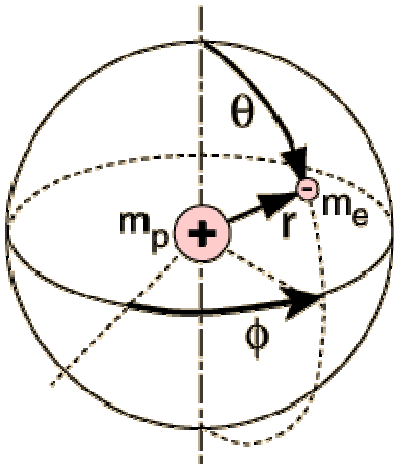## Review of hydrogen atom

Heavy proton (put at the origin), charge e and much lighter electron, charge -e.

Potential energy, from Coulomb's law

$$V(r) = - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r}$$

Potential is spherically symmetric. Therefore, solutions must have form

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) \, Y_\ell^m(\theta, \phi)$$

$$0 \le \ell < n$$
$$-\ell \le m \le \ell$$

spherical harmonics

n is principal quantum number
l is orbital angular momentum quantum number
m is magnetic quantum number

Energy levels of the hydrogen atom

$$E = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \right] \frac{1}{n^2} \longrightarrow \boxed{E = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots}$$

E_1

Note: energy depends only on principal quantum number n in non-relativistic approximation.

Ground state of hydrogen atom

$$n = 1$$
$$\ell = 0$$
$$m = 0$$

$$E_1 = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \right] = -13.6 \, eV$$

Ground state energy

Ground state wave function

$$\Psi_{100} = R_{10}(r) \, Y_0^0(\theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

$$1/\sqrt{4\pi}$$

Excited states

Questions for class

1. What is the energy of the first excited state(s) (in eV)?
2. Is it degenerate?
3. If it is degenerate, how many states have the same energy and what are their quantum numbers ? (ignore spin)

Answers

1. $n = 2$ $\quad E_2 = \dfrac{E_1}{2^2} = \dfrac{-13.6\,eV}{4} = -3.4\,eV$

2. Yes.

3. $n = 2$ $\qquad 0 \le \ell < n \quad$ (integers)

$\ell = 0, 1$

for each ℓ, $\quad -\ell \le m \le \ell \Rightarrow$

$\ell = 0 \quad m = 0$

$\ell = 1 \quad m = -1, 0, 1$ $\qquad \left.\begin{array}{l}\\\\\end{array}\right\}$ 4 levels

Note on spectroscopic notations (they are actually used).

There are letters associated with values of orbital angular momentum. The first few are:

$\ell = 0$	s
$\ell = 1$	p
$\ell = 2$	d
$\ell = 3$	f

For example, state with
$n=1$ $l=0$ is referred to as 1s,
$n=2$ $l=0$ is referred to as 2s,
$n=2$ $l=1$ is referred to as 2p, and so on.

While the energies are the same for the four $n=2$ states, the wave functions are not:

$\boxed{2s}$ $\quad R_{20} = \dfrac{1}{\sqrt{2}} a^{-3/2}\left(1 - \dfrac{r}{a}\right)\exp(-r/2a)$ $\qquad Y_0^0 = \dfrac{1}{\sqrt{4\pi}}$ $\qquad \boxed{\Psi_{200} = R_{20}\,Y_0^0}$

$\boxed{2p}$ $\quad R_{21} = \dfrac{1}{\sqrt{24}} a^{-3/2}\dfrac{r}{a}\exp(-r/2a)$ $\qquad Y_1^0 = \sqrt{\dfrac{3}{4\pi}}\cos\theta$

$\boxed{\begin{array}{l} \Psi_{210} = R_{21}\,Y_1^0 \quad \Psi_{21-1} = R_{21}\,Y_1^{-1} \\ \Psi_{211} = R_{21}\,Y_1^1 \end{array}}$ $\qquad Y_1^{\pm 1} = \mp\sqrt{\dfrac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

Angular momentum: summary

If
$$[L_x, L_y] = i\hbar L_z$$
$$[L_y, L_z] = i\hbar L_x$$
$$[L_z, L_x] = i\hbar L_y \qquad \text{then}$$

Eigenfunctions f_ℓ^m of L^2 and L_z are labeled by m and l:

eigenvalue of L^2 $\qquad$ eigenvalue of L_z

$$L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m, \qquad L_z f_\ell^m = \hbar m f_\ell^m.$$

$\ell = 0, 1, 2, \dots$ (only integer values for orbital angular momentum)

For a given value of l, there are $2l+1$ values of m: $\quad m = -\ell, -\ell+1, \dots, \ell-1, \ell.$

Generally, half-integer values of the angular momentum are also allowed but not for orbital angular moment.

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right].$$

Elementary particles carry intrinsic angular momentum **S** in addition to **L**.
Spin of elementary particles has nothing to do with rotation, does not depend on coordinates θ and ϕ, and is purely a quantum mechanical phenomena.

Spin $\frac{1}{2}$

$S = \frac{1}{2}$, therefore $m = \pm\frac{1}{2}$ and there are two eigenstates $|sm\rangle = |\frac{1}{2} \frac{1}{2}\rangle$,

$|sm\rangle = |\frac{1}{2}\left(-\frac{1}{2}\right)\rangle$.

We will call them spin up $\uparrow$ $|\frac{1}{2} \frac{1}{2}\rangle$ $\overset{m=\frac{1}{2}}{\swarrow}$ and spin down $\downarrow$ $|\frac{1}{2} -\frac{1}{2}\rangle$ $\overset{m=-\frac{1}{2}}{\swarrow}$.

$\uparrow$ I will omit ( ).

Taking these eigenstates to be basis vectors, we can express any spin state of a particle with spin $\frac{1}{2}$ as:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-$$

$\nearrow$ represents Spin up $\uparrow$

$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$\nwarrow$ represents Spin down $\downarrow$

$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

All our spin operators are 2x2 matrixes for spin $\frac{1}{2}$, which we can find out from how they act on our basis set states χ_+ and χ_-.

Raising and lowering operators:

$$S_\pm = S_x \pm i S_y$$

$$\boxed{S_\pm |sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}\, |s\,(m\pm 1)\rangle}$$

Class exercise

The electron in a hydrogen atom occupies the combined spin an position state:

$$\psi = R_{21} \left(\sqrt{1/3} \ Y_1^0 \ \chi_+ \ + \ \sqrt{2/3} \ Y_1^1 \ \chi_- \right)$$

$n=2 \quad \ell=1$

$\ell=1, \ m_\ell=0 \qquad s=\frac{1}{2}, \ m_s=\frac{1}{2}$

$\ell=1, \ m_\ell=1 \qquad s=\frac{1}{2}, \ m_s=-\frac{1}{2}$

Note that $m_\ell + m_s = \frac{1}{2}$ in both cases

(a) If you measure the orbital angular momentum squared L^2, what values might your get and what is the probability of each?

$\ell=1 \qquad L^2 \psi = \ell(\ell+1) \hbar^2 \psi \quad \Rightarrow$

You get $\hbar^2 \ell(\ell+1) = 2\hbar^2$ with probability P=1 (100%).

(b) Same for z component of the orbital angular momentum, L_z.

$$L_z \psi = \hbar m_\ell \psi$$

Possible values of m_ℓ: $m_\ell = 0$ or 1.

$$P = \left(\sqrt{\tfrac{1}{3}} \right)^2 = \frac{1}{3} \quad \text{for} \quad m_\ell = 0$$

$$P = \left(\sqrt{\tfrac{2}{3}} \right)^2 = \frac{2}{3} \quad \text{for} \quad m_\ell = 1.$$

(c) Same for the spin angular momentum squared S^2.

$$S^2 \psi = \hbar^2 s(s+1) \psi \qquad s=\frac{1}{2} \Rightarrow \text{You get} \ \frac{3}{4}\hbar^2 \ \text{with} \ P=1.$$
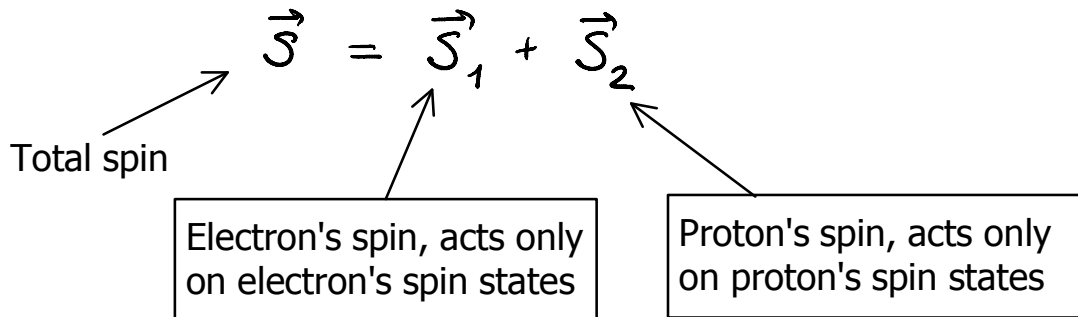
(d) Same for z component of the spin angular momentum S_z.

$$S_z \psi = \hbar m_s \psi \qquad m_s = \frac{1}{2} \ \text{and} \ -\frac{1}{2}$$

$$P = \frac{1}{3} \ \text{for} \ m_s = \frac{1}{2} \ ; \quad P = \frac{2}{3} \ \text{for} \ m_s = -\frac{1}{2}$$

Addition of angular momenta

Let's go back to ground state of hydrogen: it has one proton with spin $\frac{1}{2}$ and one electron with spin $\frac{1}{2}$ (orbital angular momentum is zero). What is the total angular momentum $\vec{S}$ of the hydrogen atom?

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

Total spin

| Electron's spin, acts only on electron's spin states | Proton's spin, acts only on proton's spin states |

$$S_z \, \chi_1 \chi_2 = \left(S_z^{(1)} + S_z^{(2)} \right) \chi_1 \chi_2 =$$

electron's spin state   proton's spin state

$$= \left(S_z^{(1)} \chi_1 \right) \chi_2 + \chi_1 \left(S_z^{(2)} \chi_2 \right) = \hbar m_1 \chi_1 \chi_2 + \hbar m_2 \chi_1 \chi_2$$

$$= \hbar \left(m_1 + m_2 \right) \chi_1 \chi_2$$

Therefore, the z components just add together and quantum number m for the composite system is simply

$$m = m_1 + m_2 \; .$$

There are four possible combinations:

$$m_1 = \tfrac{1}{2} \quad m_2 = \tfrac{1}{2} \quad \uparrow\uparrow \quad m = 1$$

$$m_1 = \tfrac{1}{2} \quad m_2 = -\tfrac{1}{2} \quad \uparrow\downarrow \quad m = 0$$

$$m_1 = -\tfrac{1}{2} \quad m_2 = -\tfrac{1}{2} \quad \downarrow\uparrow \quad m = 0$$

$$m_1 = -\tfrac{1}{2} \quad m_2 = -\tfrac{1}{2} \quad \downarrow\downarrow \quad m = -1$$

(first arrow corresponds to the electron spin and second arrow corresponds to the nuclear spin) .

Well, it appears that we have an extra state!

Let's apply lowering operator to state $\uparrow\uparrow$ to sort this out:

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

$$S_-^{(1)} \uparrow = S_-^{(1)} |\tfrac{1}{2}\tfrac{1}{2}\rangle = \hbar \sqrt{\tfrac{1}{2}\cdot\tfrac{3}{2} - \tfrac{1}{2}(\tfrac{1}{2}-1)} \, |\tfrac{1}{2} -\tfrac{1}{2}\rangle = \hbar\downarrow$$

state with $S=\frac{1}{2}, m=\frac{1}{2}$

state with $S=\frac{1}{2}\;\; m=-\frac{1}{2}$

$$S_-(\uparrow\uparrow) = \left(S_-^{(1)} + S_-^{(2)}\right)\uparrow\uparrow$$

$$= \left(S_-^{(1)}\uparrow\right)\uparrow + \uparrow\left(S_-^{(2)}\uparrow\right) = \hbar\downarrow\uparrow + \hbar\uparrow\downarrow = \hbar\left(\downarrow\uparrow + \uparrow\downarrow\right)$$

(Note: normalization is not preserved here).

So we can sort out four states as follows:

Three states $|s\,m\rangle$ with spin s = 1, m = 1, 0, -1:

$$\begin{cases} |1\,1\rangle = \uparrow\uparrow \\[4pt] |1\,0\rangle = \frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right) \\[4pt] |1\,{-}1\rangle = \downarrow\downarrow \end{cases} \quad S=1$$

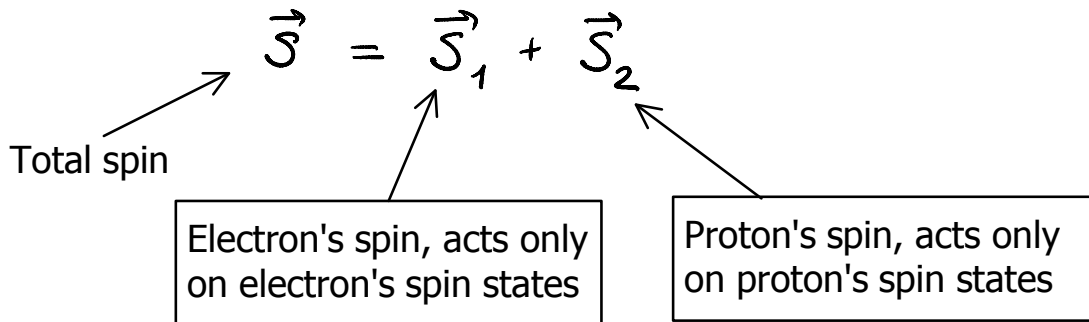This is called a **triplet** configuration.

and one state with spin s = 0, m = 0:

$$\left\{ |0\,0\rangle = \frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right) \right\} \quad S=0$$

This is called a **singlet** configuration.

Summary: Combination of two spin $^1\!/_2$ particles can carry a total spin of s = 1 or s = 0, depending on whether they occupy the triplet or singlet configuration.

Addition of angular momenta

Ground state of hydrogen: it has one proton with spin $\frac{1}{2}$ and one electron with spin $\frac{1}{2}$ (orbital angular momentum is zero). What is the total angular momentum $\vec{S}$ of the hydrogen atom?

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

Total spin

| Electron's spin, acts only on electron's spin states | Proton's spin, acts only on proton's spin states |

The z components just add together and quantum number m for the composite system is simply

$$m = m_1 + m_2 \, .$$

In general, it you combine any angular momentum j_1 and j_2 you get every

value of angular momentum from $|j_1 - j_2|$ to $j_1 + j_2$ in integer steps:

$$j = |j_1 - j_2| , \dots , (j_1 + j_2)$$

It does not matter if it is orbital angular momentum or spin.

Example:

$$j_1 = \frac{3}{2} \qquad j_2 = 3 \quad \Rightarrow$$

$$|j_1 - j_2| = \left| \frac{3}{2} - 3 \right| = \frac{3}{2}$$

$$j_1 + j_2 = \frac{3}{2} + 3 = \frac{9}{2}$$

Total angular momentum j can be $\frac{3}{2}, \frac{5}{2}, \frac{7}{2},$ and $\frac{9}{2}.$

Problem

Quarks carry spin $\frac{1}{2}$. Two quarks (or actually a quark and an antiquark) bind together to make a meson (such as pion or kaon). Three quarks bind together to make a barion (such as proton or neutron). Assume all quarks are in the ground state so the orbital angular momentum is zero).

(1) What spins are possible for mesons?

(2) What spins are possible for baryons?

Solution:

(1) $S_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$ $\Rightarrow$ $\boxed{S = 0 \text{ or } 1.}$

(2) $S_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$ $S_3 = \frac{1}{2}$

$\underbrace{\qquad\qquad\qquad}$

Add these first

$S_{12} = 0 \text{ or } 1$

Now add the third spin: $S_{12} = 0$ $S_3 = \frac{1}{2}$ $\Rightarrow$ $S = \frac{1}{2}$

$S_{12} = 1$ $S_3 = \frac{1}{2}$ $\Rightarrow$ $S = |\frac{1}{2} - 1|, \ldots (\frac{1}{2} + 1) \Rightarrow$

$S = \frac{1}{2} \text{ or } \frac{3}{2}$

$\boxed{S = \frac{1}{2} \text{ or } \frac{3}{2}}$