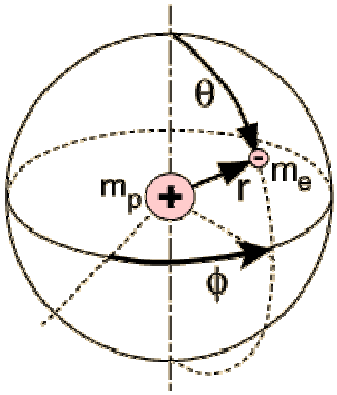
Atoms

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

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\,\underbrace{Y_\ell^m(\theta,\phi)}_{\text{spherical harmonics}}$$

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

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

Energy levels of the hydrogen atom

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

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

Ground state of hydrogen atom

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

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

Ground state energy

Ground state wave function

$$\psi_{100} = R_{10}(r)\,\underbrace{Y_0^0(\theta,\phi)}_{1/\sqrt{4\pi}} = \frac{1}{\sqrt{\pi a^3}}\,e^{-r/a}$$

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

2. Yes.

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

$\ell = 0, 1$

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

$\ell = 0 \quad m = 0$

$\ell = 1 \quad m = -1, 0, 1$ } 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:

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

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

$Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\phi}$

$\psi_{210} = R_{21} Y_1^0$

$\psi_{211} = R_{21} Y_1^1$

$\psi_{21-1} = R_{21} Y_1^{-1}$

Review: hydrogenic atoms (these are called ions since they are charged).

A hydrogenic (or hydrogen-like) atom consists of a single electron orbiting a nucleus with Z protons. What are the corresponding energies?

Potential changes from $V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$ to $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$

so we just need to make substitution $e^2 \to Ze^2$ in all results.

Question for the class:
What is the ground state energy of hydrogen-like helium Z=2)?

Answer:

$$E = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \xrightarrow{e^2\to Ze^2} E = -\left[\frac{m_e}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$E = -\underbrace{\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]}_{E_1 = 13.6\,eV}\frac{Z^2}{n^2} \qquad Z=2,\ n=1 \Rightarrow E = -13.6\times 4\,eV = -54.4\,eV$$

Bohr radius $a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} \to a = \frac{4\pi\epsilon_0\hbar^2}{Zme^2} = \frac{a_0}{Z} \Rightarrow$

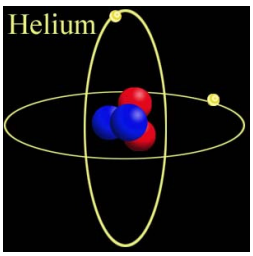
now put "0" label

Ground state wave function is

(H) $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$ $\longrightarrow$ H-like He $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\sqrt{Z^3}\, e^{-rZ/a_0}$

$Z=2$ $\psi_{100} = \frac{2\sqrt{2}}{\sqrt{\pi a_0^3}}\, e^{-2r/a_0}$

Neutral Helium (Z=2), two electrons



^4He

Hamiltonian

$$H = \left\{ -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\}$$

(Z = 2)

Two hydrogenic Hamiltonians (with Z=2), one for electron 1 and one for electron 2.

$$+ \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Term that describes repulsion of two electrons.

What can we do to get some wave functions and energies?

In the lowest approximation, we can start by simply ignoring the second term. Then, the solution can be written simply as product of two hydrogen-like wave functions with Z=2:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\,\psi_{n\ell m}(\vec{r}_2).$$

Questions for the class:

Write ground state wave function of helium ignoring electron repulsion term in the Hamiltonian.

What is its energy?

Answer: The ground state is

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) =$$

$$= \frac{\sqrt{8}}{\sqrt{\pi a_0^3}} e^{-2r_1/a_0} \frac{\sqrt{8}}{\sqrt{\pi a_0^3}} e^{-2r_2/a_0}$$

$$= \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}$$

, a_0 is Bohr radius

The energy is just the sum of the energies of two electrons in this approximation:

$$E = 2\left(-13.6\,eV\,\frac{Z^2}{n^2}\right) = -109\,eV$$

($n=1$, $Z=2$)

The actual experimentally determined energy is -78.975 eV, so while we got some reasonable number in this approximation, the interaction term is quite large. We will learn how to account for the interaction term later in this course.

Now, we need to include spin in our description.

Electrons have spin $1/2$ and; therefore, are fermions. Total wave function has to be antisymmetric.

Review: addition of two spins $1/2$.

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 $1/2$

$s=\frac{1}{2}$, therefore $m_s=\pm\frac{1}{2}$ and there are two eigenstates $|sm_s\rangle = |\frac{1}{2}\ \frac{1}{2}\rangle$,

$|sm_s\rangle = |\frac{1}{2}\ (-\frac{1}{2})\rangle$.

We will call them spin up $\uparrow\ |\frac{1}{2}\ \frac{1}{2}\rangle$ ($\leftarrow m_s=\frac{1}{2}$) and spin down $\downarrow\ |\frac{1}{2}\ -\frac{1}{2}\rangle$ ($\leftarrow m_s=-\frac{1}{2}$).

↑ I will omit ( ).

Addition of angular momenta

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

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

$$\boxed{m = m_1 + m_2}$$. (I omit subscript "s" from now on $m_s \rightarrow m$)

There are four possible combinations:

$m_1=\frac{1}{2}$ $m_2=\frac{1}{2}$ $\uparrow\uparrow$ $m=1$

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

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

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

(first arrow corresponds to the spin of electron 1 and second arrow corresponds to the spin of electron 2)

We can sort out four states as follows:

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

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

This is called a **triplet** configuration.

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

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

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.

Now we can go back to helium

Questions for the class

Is ground state of helium triplet, singlet, or can be either one and can not be determined from the given information?

The helium excited states have form $\psi_{100}\,\psi_{n\ell m}$,

one electron in the ground state and one electron in the excited state.

Do these states have to be singlet, triplet states, or can be both?

Answers:

The total wave function has to be antisymmetric. The spatial wave function that we wrote before is symmetric:

$$\psi(\vec{r}_1,\vec{r}_2) = \frac{8}{\pi a_0^3}\, e^{-2(r_1+r_2)/a_0} \qquad \psi(r_1,r_2) = \psi(\bar{r}_2,\bar{r}_1).$$

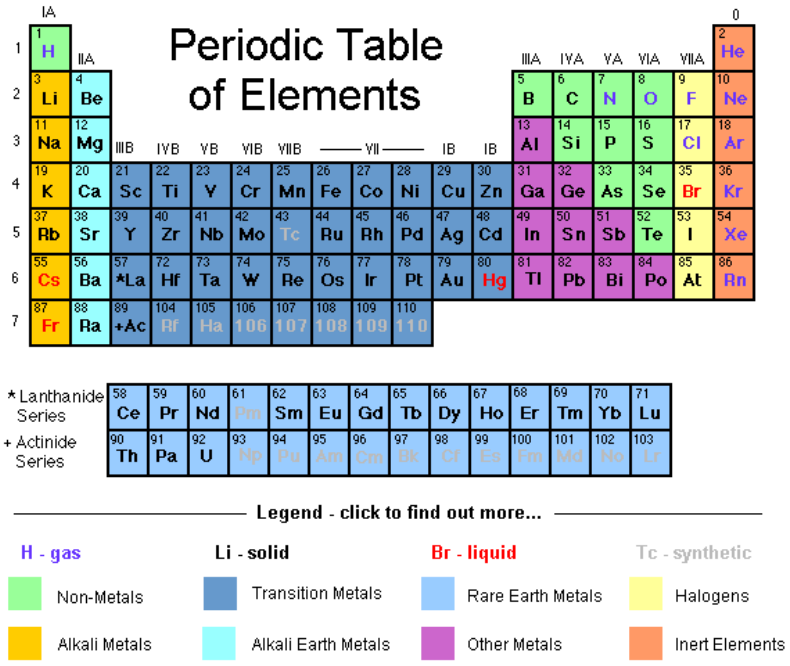
Therefore, spin state has to be a singlet since it is antisymmetric since total wave function must be antisymmetric.

$$\chi = |0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \Rightarrow \quad \chi(2,1) = \frac{1}{\sqrt{2}}(\downarrow\uparrow - \uparrow\downarrow) = -\chi(1,2)$$

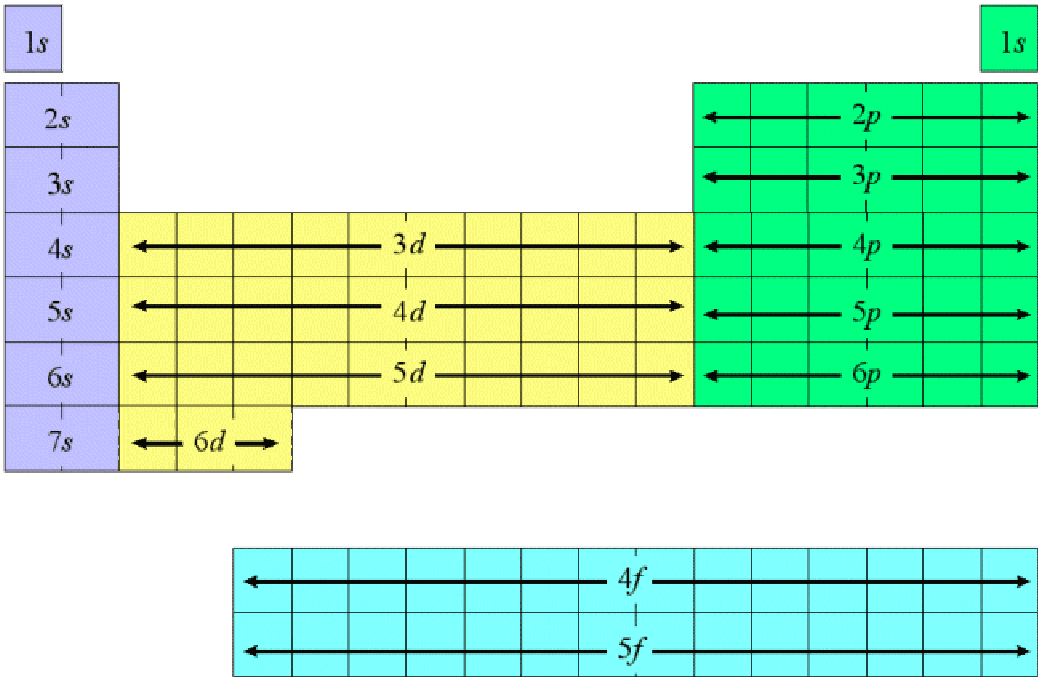
The excited state can be both triplet or singlet state since the electrons are in different states. We can constrict both symmetric and antisymmetric spatial wave functions. Symmetric spatial wave function will go with singlet spin state (parahelium) and antisymmetric one will be triplet (orthohelium).

Note: If your try to put both electrons in excited states, one of them will drop to the ground state and the released energy with be enough to ionize the other one. You will be left with helium ion He^+ (hydrogen-like helium) with one electron.

Periodic table



Periodic table: filling of shells



http://www.colorado.edu/physics/2000/applets/a2.html