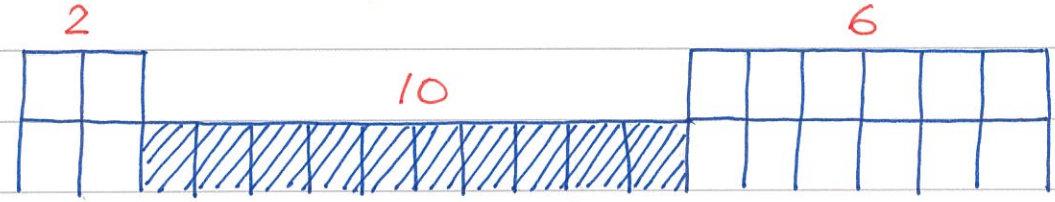
HH0136 Magic Numbers in Periodic Table

Take a closer look at the structure of the periodic table. It is easy to spot the "magic numbers"...



Can Schrödinger equation explain these magic numbers? Let us try to find the solution step by step.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{\sqrt{x^2+y^2+z^2}}\Psi$$

To find the stationary state with energy $E=\hbar\omega$, the wave function acquires a time-dependent phase,

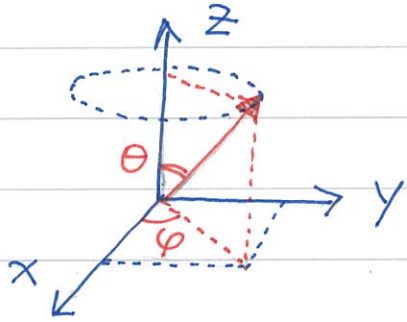
$$\Psi(x,y,z,t) = \phi(x,y,z)\, e^{-i\omega t}$$

← $\phi(x,y,z)$ satisfies the time-independent Schrödinger EQ.

$$-\frac{\hbar^2}{2m}\nabla^2\phi - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{\sqrt{x^2+y^2+z^2}}\phi = E\phi$$

It turns out that the equation becomes easier when transforming to spherical coordinates (r,θ,φ).

① Spherical coordinates. Let us transform (x,y,z) into the spherical coordinates (r,θ,φ).



$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

It shall be clear that the potential energy is simplified.

check. $x^2+y^2+z^2$
$= r^2(\sin^2\theta\cos^2\varphi+\sin^2\theta\sin^2\varphi+\cos^2\theta)$
$\rightarrow x^2+y^2+z^2 = r^2$ ✓

BUT! The kinetic energy becomes rather messy....

Q: for curious cats, you may want to find out...
what is ∇^2 in the spherical coordinates?

To solve the Schrödinger equation in the spherical coordinates is beyond the scope of the class. Thus, I shall just write down the solutions ☺

$\psi_{nem_e}(r,\theta,\varphi)$ $n = 1, 2, 3, \cdots$ principal quantum number.

The other two quantum numbers ℓ, m_ℓ are associated with the angular momentum $\vec{L}$ and satisfy the rules:

$\ell = 0, 1, 2, \cdots, n-1$
$m_\ell = 0, \pm1, \pm2, \cdots, \pm\ell$

The stationary states are labeled by the quantum numbers n, ℓ, m_ℓ.

For hydrogen atom, it is quite remarkable that the quantized energies are given by

$$E_n = -\frac{me^4}{32\pi^2\hbar^2\epsilon_0^2}\frac{1}{n^2} = -\frac{13.6\,eV}{n^2}$$

same as Bohr's model, only depends on n!

① Quantization of angular momentum. Consider a particle rotating around the z axis with constant angular momentum L_z.

$$\phi(x) = e^{ipx/\hbar} \longrightarrow \phi(\theta) = e^{iL_z\theta/\hbar}$$

Making analog with the 1D plane wave, it is reasonable to guess the wave function $\phi(\theta)$ as shown here. However, we expect that the wave function goes back to itself after one complete rotation of 2π.

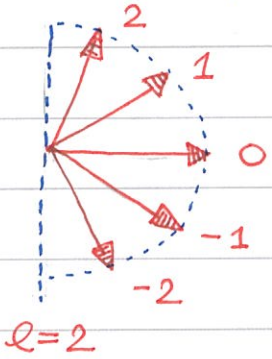
$$\phi(\theta+2\pi) = \phi(\theta) \longrightarrow e^{i2\pi L_z/\hbar} = 1, \quad L_z = n\hbar$$

The angular momentum L_z is quantized! This is cute — the angular range $(0, 2\pi)$ is finite and leads to L_z quantization. Just like the energy/momentum quantization in the infinite potential well.

Rotations in 3D are not as simple. But, since the angles are still compact, quantization is expected.

$\vec{L} = (L_x, L_y, L_z)$ Unlike the linear momentum, once L_z can be pinned down, the other two components L_x, L_y are uncertain.

That is to say, there are uncertainty relations between L_x, L_y, L_z and only one of them can be quantized. The quantization rules turn out to be peculiar,



$$|\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \qquad \ell = 0, 1, 2, \cdots$$

$$L_z = m_\ell \hbar \qquad m_\ell = 0, \pm 1, \pm 2, \cdots, \pm \ell$$

In general, there is no upper bound for ℓ. But, in hydrogen atom, $\ell = 0, 1, 2, \cdots, n-1$.

Ⓓ Ground state of hydrogen atom. The lowest energy state in H atom corresponds to $n=1$. In this case, $\ell = 0$, $m_\ell = 0$.

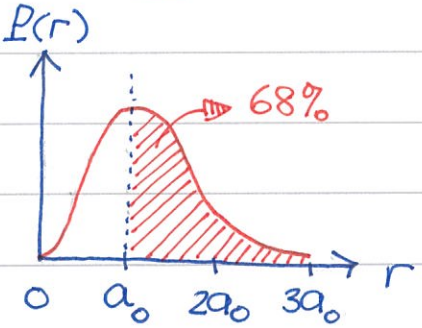
$$\phi_{100}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

a_0 is the Bohr radius.

The above wave function is very simple without (θ, φ) dependence. We are often curious about the probability density at radius r which requires an extra surface factor $4\pi r^2$.

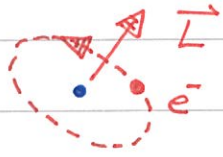
$$P(r) = 4\pi r^2 |\phi|^2 = \frac{4r^2}{a_0^3} e^{-2r/a_0}$$

one can check that $\int_0^\infty P(r)\,dr = 1$ ☺



Plot the radial probability density $P(r)$. Its maximum occurs at $r = a_0$. But, by simple integration, the probability to find the electron outside the Bohr's radius a_0 is 68% ▽

The above results should convince you to give up the so-called "stable orbits" in Bohr's model. In addition, the ground state in Bohr's model carries non-zero angular momentum. ← WRONG !!!

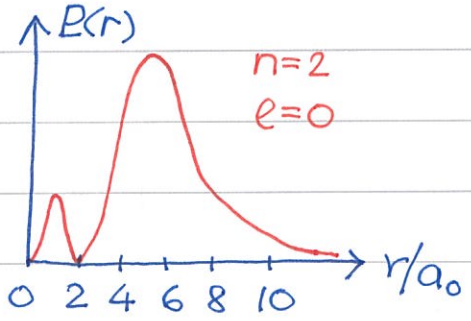
Bohr's model  $L=\hbar$

 $\vec{L}=0$!

Higher energy states. Let us march forward to $n=2$ states. There are 4 stationary states with $n=2$ — one for $\ell=0$ and three for $\ell=1$. The $n=2$, $\ell=0$ state is

$$\phi_{200}(r,\theta,\varphi)=\frac{1}{4\sqrt{2\pi a_0^3}}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}$$

← It has a node @ $r=2a_0$



Plot the radial probability density $P(r)=4\pi r^2|\phi|^2$. One node @ $r=2a_0$ and two peaks. But, the peak locations are not predicted by the Bohr's model anymore (it would be $4a_0$ in this case).

The $n=2$, $\ell=1$ states carry angular dependence ...

$$\phi_{210}(r,\theta,\varphi)=\frac{1}{4\sqrt{2\pi a_0^3}}\frac{r}{a_0}e^{-r/a_0}\cos\theta$$

$$\phi_{211}(r,\theta,\varphi)=\frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0}e^{-r/a_0}\sin\theta\, e^{i\varphi}$$

$$\phi_{21\bar{1}}(r,\theta,\varphi)=\frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0}e^{-r/a_0}\sin\theta\, e^{-i\varphi}$$

Q: The potential energy does not depends on (θ,φ). Why do they depend on (θ,φ)?

Try to find the node !! For ϕ_{210}, the node occurs at $\theta=\frac{\pi}{2}$. For ϕ_{211} and $\phi_{21\bar{1}}$, the node happens at $\theta=0$ ($\theta=\pi$).

→ All $n=2$ stationary states have $n-1=1$ node.

⓫ The missing quantum number — spin. In order to explain the magic numbers 2, 6, 10, ..., we need to introduce another quantum number;

$$m_s = \pm \frac{1}{2}\hbar$$

arisen from $|\vec{S}| = \sqrt{S(S+1)}\,\hbar$ where $S = \frac{1}{2}$ for electrons !!!

The spin was introduced to explain the structure of the periodic table first. Interestingly enough, spin also gives rise to magnetic dipole moment — very much like rotating charged object;

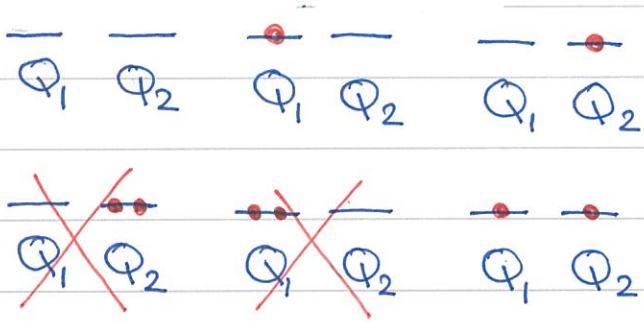
$$\vec{\mu} = -g\mu_B(\vec{S}/\hbar) \quad \text{where } g \approx 2$$

Because an electron is a point, it is meaningless to talk about its spinning motion. Dirac tried to solve the puzzle by combining quantum mechanics and special relativity.

$$\Psi = (\Psi_{e\uparrow}, \Psi_{e\downarrow}, \Psi_{p\uparrow}, \Psi_{p\downarrow}).$$

He found that one needs at least 4 components to describe the electron : spin-up electron, spin-down electron, spin-up positron and spin-down positron. The origin of spin arises from relativity and cannot be described by the Schrödinger equation ⊙⊙!

⓬ Pauli exclusion principle. Electrons carry $S = \frac{1}{2}$ and thus are fermions. According to Pauli exclusion principle, no two fermions can stay in the same stationary state. Consider two stationary states Φ_1, Φ_2. They can at most accommodate 2 electrons. This gives us a simple rule to understand the periodic table.



It is convenient to use letter codes for ℓ,

ℓ=	0	1	2	3	4	5
code	s	p	d	f	g	h

Let us try to fill up $n=2$ stationary states ☺

		1S	2S	2P				
2	Li	↑↓	↑				$1s^2 2s^1$	metals
	Be	↑↓	↑↓				$1s^2 2s^2$	metals
6	B	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$	
	C	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$	
	N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$	
	O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$	
	F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$	
	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$	

The magic number for transition metals arises from 3d states $(2S+1)\times(2\ell+1) = 2\times 5 = 10$ states. Can you figure out other magic numbers in the periodic table? Try it ☺

清大東院
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