

Lecture 7

N principal quantum number: 1,2,3 up to ∞

Ψ in general is a function of r, θ, ϕ and t denoted as $\Psi(r, \theta, \phi, t)$. We will look at wave functions which are called stationary waves, i.e. Ψ which are not dependent on t . This means we will not look at a wave function when a chemical reaction is happening, it will be before and after. In those cases we are looking at Ψ when the atom is stable and sitting idle. The Ψ we will look at will be $\Psi(r, \theta, \phi)$ also known as time-independent QM. When we go and solve Schrodinger equation for $\Psi(r, \theta, \phi)$, two more quantum number drop out in the differential equation.

We get a new quantum no l , called the angular momentum quantum number because it dictates how much angular momentum the electron has. It also has allowed values. They are 0, 1, 2, ..., $(n-1)$. Why should it be smaller than n . Classically thinking l would denote the angular momentum. The total energy is dictated by n which is both KE and PE. So it has to be smaller than n .

The third quantum number which drops out is m , called the magnetic quantum number, since it dictates how an atom moves in a magnetic field. But more precisely what m is the z -component of the angular momentum l . The allowed values of m are $m=0, +1, +2, \dots, +l$. The largest value is l . Since it is z component it also has direction, so m can be $-1, -2, \dots, -l$.

For $n=1, l=0, m=0$called 100 state and if we have an electron in the 100 state we are going to describe the electron by a wave function ψ_{100} .

For $n=2, l=0, m=0$: the wave function is ψ_{200} . The other wave functions possible for $n=2$ are ψ_{210}, ψ_{211} and ψ_{21-1} . All these five states have the same energy i.e. $-R_H/4$. They are what we call degenerate.

The other way of representing the wave function is a orbital...the orbital is actually the wave-function. If $l=0$, we call it s . For $l=1$, we call it p . If $l=2$, we call it d . So all ψ_{210}, ψ_{211} and ψ_{21-1} would be called $2p$.

When $l=1, m=0$, we call it p_z . When $m=1$, it is p_x and when $m=-1$ it is p_y . This is not fully correct because the Schrodinger equation solution of ψ_{211} and ψ_{21-1} are complex wave functions. For us to think about p_x and p_y wave function, we take a linear combination. p_x is $\psi_{211} + \psi_{21-1}$ while p_y is $\psi_{211} - \psi_{21-1}$ - this gives you real functions.

For $n=1$, only one state. In $n=2$, four degenerate states. For $n=3$, 9 states.

For $l=2, m=-2$ is $3d_{xy}$, $m=-1$ is d_{yz} , $m=0$ is d_{z^2} , $m=1$ is d_{xz} , $m=2$ $d_{x^2-y^2}$.

For $m= -2, -1, +1$ and $+2$, those wave functions when we solve Schrodinger's equation are complex wave functions. Again we take linear combination make them real. For $m=0$ the d_{z^2} is a real function.

Shapes of the wave functions

What do these wave functions actually look like:

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

TABLE 2.1 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

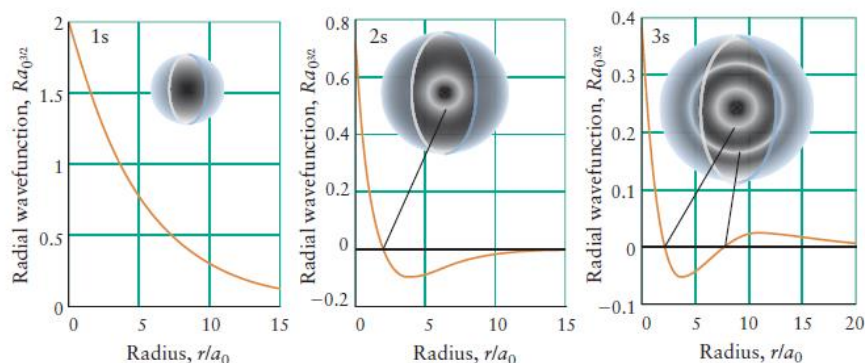
(a) Radial wavefunctions			(b) Angular wavefunctions		
n	l	$R_{nl}(r)$	l	" m_l " [†]	$Y_{lm_l}(\theta, \phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	1	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2}\right) e^{-Zr/3a_0}$	1	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
3	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi$
3	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$	2	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \sin \phi$
			2	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \cos \phi$
			2	$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi$
			2	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$

*Note: In each case, $a_0 = e_0 h^2 / \pi m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

[†]In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l .

The angular part of s wave function is not angle dependent.

Let us look at the radial part.....first let us observe the s orbital:

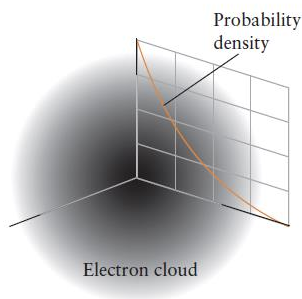


For 1s, the exponential drop is the result of the function having e^{-r/a_0} . The wave function at all values of r has a positive value. What about 2s wave function: the plot is shown above. We start at a large positive value and we get to a value of r where ψ becomes 0, that is a radial node. This radial node occurs at $r=2a_0$. The wavefunction gets more and more negative, starts increasing again and then approaches 0. At the radial node the wave function changes sign, the amplitude of the wave function becomes positive to negative. Sign of amplitude important because in a chemical reaction when two atoms come together and two electrons that are represented by are overlapping....if we bring them together.....they need to have the same sign of the amplitude for constructive interference- chemical bonding. Ψ_{300} has two nodes: at $1.9 a_0$ and $7.1 a_0$.

What does the wave function actually mean and how does it actually represent the electron....this was a very puzzling question....how does this represent where the particles are....the answer to this question is that there is no answer to this question. Wave function is just a mathematical function...a wave function is a wave function- you can not draw a correct analogy to the classical world. However, Max Born said that if I take the wave function and I square it, if I interpret that as a probability density then I can interpret all the predictions made in the Schrodinger equation within that framework.

$$[\Psi_{n\ell m}(r, \theta, \phi)]^2 = \text{probability density i.e. probability/unit volume}$$

That really works. The interpretation agrees with our observations and hence we believe it to be correct. But it is just an assumption. It is just an interpretation....there is no derivation for it....it just works.



For 1s, probability of finding an electron per unit volume at some at some value of r , θ and ψ . It doesn't matter what θ and ψ is in this case as it is spherically symmetric. The 2s probability density is a maximum at the nucleus. It decays uniformly in all directions and it decays so much that at some point you have no probability density. It then increases again since it has changed sign.

We have talked about probability density but not probability yet. To determine probability, we are going to look at the radial probability distribution function. RPD is probability of finding an electron in a spherical shell. The spherical shell will be some distance away from the nucleus. The spherical radius r and a thickness dr . Then the RPD is the probability of an electron at a distance r with a thickness dr i.e. from a distance r to $r+dr$.

If we have to calculate probability (RPD), then we take the probability density (ψ^2) and then we can multiply by the unit volume that is $4\pi r^2 dr$. The result will be a probability.

