General Chemistry I
Tutorial 04

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Outline

Quiz 4.1

The wave function for the H 3s orbital is:

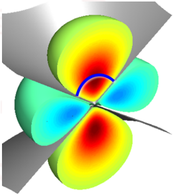
$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} a_0^{-3/2} \left(27 - 18\sigma + 2\sigma^2\right) \exp(-\sigma/3)$$

where r is the distance between the electron and the nucleus, and $a_0 = 0.53\mathring{A}$ is Bohr radius. Find the values of r (in Å) for which nodes exist for the H 3s orbital.

The nodal planes of the $3d_{z^2}$ orbital are two cones. According to the angle part:

$$Y_{d_{z^2}} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

Find out the cone angle (in degrees) of the nodal planes.



Three Quantum Numbers

Wave function / Orbital in 3 dimension depends on 3 quantum numbers: n, l and m. Or to say, each array (n, l, m) determines a specific quantum state. **Principle quantum number**(n): indexes the individual energy levels.

$$E = E_n = -\frac{Z^2}{n^2} Ry$$

Angular momentum quantum number(l): can take any integral value from 0 to n-1. It determines angular momentum of orbitals.

$$L = \sqrt{l(l+1)\hbar^2} \approx l\hbar$$

Magnetic quantum number(m): can take any integral value from -l to l.
It determines projection of angular momentum on z axis. $M_z = m\hbar$
(Usually, we let z direction be the direction of external magnetic field.)
Allowed orbitals for n=2:

$$(l = 0,\ m = 0),\ (l = 1,\ m = -1),(l = 1,\ m = 0),(l = 1,\ m = 1)$$

For every value of n, the number of allowed combination of l and m is given by:

$$= 1 + 3 + 5 + ... + (2n - 1) = n^2$$

Mathematical Foundation of Wave Functions

For each quantum state (n,l,m), corresponding wave function is given by:

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

where wave function is divided into 2 parts: radial part $R_{nl}(r)$ and angular part $Y_{lm}(\theta,\phi)$.

Probability:

$$\mathrm{d}p = \psi_{nlm}^2 \mathrm{d}V = R_{nl}^2(r)Y_{lm}^2(\theta,\phi)\mathrm{d}V$$

In a spherical coordinate:

$$\mathrm{d}V = r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

Thus,

$$\mathrm{d}p = R_{nl}^2(r)r^2Y_{lm}^2(\theta,\phi)\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

Wave Functions and Shape of Orbitals

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n\ell}(r)$
$\ell = 0\left\{ Y_s = \left(\frac{1}{4\pi}\right)^{1/2} \right.$	$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-\sigma)$
	$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)\exp(-\sigma/2)$
	$R_{3s} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)\exp(-\sigma/3)$
$\ell = 1$: $Y_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$	$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma\exp(-\sigma/2)$
$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)\exp(-\sigma/3)$
$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$\ell = 2$: $Y_{d_{z^2}} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2\exp(-\sigma/3)$
$Y_{d_{xz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$	
$Y_{d_{yz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$	
$Y_{d_{xy}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$	
$Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$	

Wave Functions and Shape of Orbitals

- s orbitals:

$$Y_s = \left(\frac{1}{4\pi}\right)^{1/2}$$

Angular part Y_{lm} is a constant(no angular node, l=0), thus $psi_{nlm}(r, \theta, \phi)$ is independent of θ and ϕ, which makes it spherically shaped.

- p orbitals:

$$Y_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

$$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

There's always an angular node for p orbital(l=1) and thus p orbitals appears like a dumbbell.

Wave Functions and Shape of Orbitals

- d orbitals:

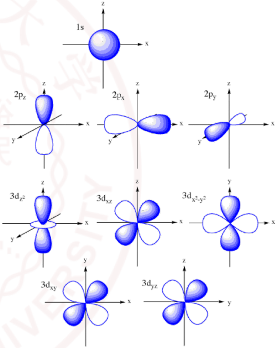
$$Y_{d_{xz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta \cos\theta \cos\phi$$

$$Y_{d_{yz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta \cos\theta \sin\phi$$

$$Y_{d_{xy}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$$

$$Y_{d_{z^2}} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \cos 2\phi$$



Radial probability density

Radial probability density $r^2 R_{n0}^2(r)$: the probability density of finding the electron at any point in space at a distance r from the nucleus, after integrating over all angles θ and ϕ.

In other words, $r^2 R_{n0}^2(r) dr$ gives the probability of finding electron in a shell of thickness $\mathrm{d}r$ at distance r from nuclei.