Lecture 2

Representing Atomic Orbitals

with the Help of Wavefunctions

'If you cannot understand the arrangements of electrons in atoms, or represent electrons properly, you will never understand chemical reactions or the periodic relationship underlying the chemistry of the elements.'

Draper 2002

You need wave mechanics



Representations of Orbitals

For an atomic system containing one electron (e.g. H, He⁺ etc.) The wavefunction Ψ is a solution of the Schrödinger equation.

It describes the behaviour of an electron in a region of space called an atomic orbital $(\varphi - \text{phi})$.

Each wavefunction has two parts, the radial part which changes with distance from the nucleus and an angular part whose changes correspond to different shapes.

 $\psi_{xyz} = \varphi_{radial}(\mathbf{r}) \ \varphi_{angular}(\phi, \theta)$

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

Orbitals have

- SIZE determined by $R_{nl}(r)$ = radial part of the wavefunction
- SHAPE determined by $Y_{lm}(\phi, \theta)$ = angular part of the wavefunction(spherical harmonics)
- ENERGY determined by the Schrodinger equation. (Calculated exactly for one-electron systems, and by trial and error manipulations for more complex systems).

Polar Coordinates

- To describe the wavefunction of atomic orbitals we must describe it in three dimensional space
- For an atom it is more appropriate to use spherical polar coordinates:



Location of point P

Cartesian = x, y, z

 \rightarrow r, ϕ , θ

d.bu.edu/applets/SPCExp/SPCExp.html

Wavefunctions for the 1s atomic orbital of H

The mathematical wavefunctions for hydrogen-like orbitals

$$R_{nl}(r) \qquad Y_{lm}(\phi,\theta)$$

$$2\left(\frac{Z}{a_0}\right)^{3/2} e^{(-\rho r/2)} \qquad \left(\frac{1}{4\pi}\right)^{1/2} \qquad \rho = \left(\frac{2Z}{na_0}\right)$$

For hydrogen this simplifies further as Z=1 and $a_0=1$ (in atomic units) and $\rho = 2$. Hence

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

 $\overline{2\sqrt{\pi}}$

 $2e^{(-r)}$

15

1*s*

Normalisation

Constants are such that

$$\int \varphi^2 \partial \tau = 1$$

that is the probability of the electron in an orbital must be 1 when all space is considered

angular component is constant \rightarrow Spherical

Graphical representation of a Radial Wavefunction

• R(r) of the 1s orbital of H

$$\mathbf{R}(\mathbf{r}) = 2e^{(-r)}$$

It decays exponentially with r It has a maximum at r = 0

R(r) has no physical meaning.

 $R(r)^2$ does. It represents the probability density of the electron at a point in space

 $R(r)^2$ is a maximum at r = 0



Radial distribution functions (RDF)

- Relating the probability of an electron at a point in space to the probability of an electron in a spherical shell at a radius r (an orbit-lke picture)
- This is called the Radial Distibution Function (RDF) as in generated by multiplying the probability of an electron at a point which has radius r by the volume of a sphere at a radius of r
- Consider a sphere volume as we move at a small slice is 4pr² dr



Wave functions of ns orbitals

2s(r)

 $\frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \rho r) e^{(-\rho r/2)}$

$$\rho = \left(\frac{2Z}{na_0}\right)$$

 $\frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} (6 - 6\rho r + (\rho r)^2) e^{(-\rho r/2)}$

3s(r)



so for H 2s, Z=1, n=2, $\rho=1$

for H 3s Z=1, n=3, $\rho=2/3$

 $\frac{1}{2\sqrt{2}}(2-r)e^{(-r/2)}$

 $\frac{1}{9\sqrt{3}} \left| 6 - 4r + \left(\frac{2}{3}r\right)^2 \right| e^{(-r/3)}$

Wave functions of Hydrogen ns orbitals

For H 2s(r) =

$$\frac{1}{2\sqrt{2}}(2-r)e^{(-r/2)}$$

exponential decreases more slowly than 1s and it changes sign

For H 3s(r) =

$$\frac{1}{9\sqrt{3}} \left[6 - 4r + \left(\frac{2}{3}r\right)^2 \right] e^{(-r/3)}$$

3s changes sign twice with two nodes (r = 1.9, 7.1 a.u.)

$$R(r) = 0 \rightarrow RADIAL NODE$$

2s at (2-r) = 0 (i.e. r = 2 a.u.)

Note: $e^{(-r/n)}$ \rightarrow the larger n the more diffuse the orbital



Can wavefunctions be negative ?

- The sign of a wave function is not important
 - for considering electron density which is related to the square of the wave function and has to be positive
- It is important when two wavefunctions interact (see later)
- It does not matter that the 2*s* is represented as positive and negative in books you can see that the electron density $R(r)^2$ is the same



Radial Nodes

- The point at which R(r) = 0 (not including the origin) is called a radial node
- Number of radial node = n l 1

1s = 1 - 0 - 1 = 0 2s = 2 - 0 - 1 = 1 3s = 3 - 0 - 1 = 2 3p = 3 - 1 - 1 = 13d = 3 - 2 - 1 = 0

- In general the more nodes contained within e.g. a set of s orbitals the higher the energy of the orbital like a wave that crosses the x axis many times
- Why are there radial nodes ?
 - Pauli exclusion principle dictates that no two electrons can have the same set of quantum numbers
 - Actually no two electron can overlap (i.e occupy same space)
 - Overlap integral = $\int \varphi_A^* \varphi_B \partial \tau = 0$ (analogous to normalisation) atomic orbitals are said to be Orthogonal
 - Satisfied for AO's with same l by having change(s) in the wave function sign
 - Satisfied for AO's with different *l* because the angular component ensures no overlap

RDF's of ns orbitals

- 1s 1 peak. 2s - 2 peaks 3s - 3 peaks
 - Maximum at $r = a_0$ Maximum at $r \approx 5 a_0$
 - Maximum at $r \approx 13 a0$
- Bohr Model \rightarrow radius of a_0
- Bohr Model \rightarrow radius of 4 a₀
- Bohr Model \rightarrow radius of 9 a₀

These maximum correspond to the distance from the nucleus at which the electron has the highest probability of being found i.e. the optimum size of a sphere of very small thickness in which to find an electron in a 1s, 2s or 3s oribtial.



Representing atomic orbitals

- How do the radial wavefunctions and the RDF reflect experimental observations of electron density ?
- In 2D we can use dot diagrams to look at the whole wave function
 - s orbitals have spherical symmetry
 - The electron density is zero radial nodes
 - The most probable point for locating an electron is the nucleus
 - The most probable shell at radius r for locating an electron increases from 1s to 2s to 3s oribitals.



Boundary Surfaces

- Represent the wave function/atomic orbital in 3D
 - Draw a 3D surface at a given value of φ
 - Define the surfac such that it encloses a space in which the electron spends most of its time
 - The surface now depicts outer shape and size of the orbital
 - The inner structure of the wave function is hidden beneath the surface





p orbitals - wavefunctions

- There are three p orbitals for each value of $n (p_x, p_y, p_z)$
- The radial function is the same for all *np* orbitals
- The angular terms are different \rightarrow different shapes (orientations)
 - Although $2p_x$, $3p_x$, $4p_x$ have the same shape

p orbitals – radial functions

• Radial wave function for hydrogen p orbitals (Z=1) for 2p $n = 2 \rightarrow \rho = 1$ for 3p $n = 3 \rightarrow \rho = 2/3$

$$R(2p) = \frac{1}{2\sqrt{6}} r e^{(-r/2)}$$

$$R(3p) = \frac{1}{9\sqrt{6}} \left(4 - \frac{2r}{3}\right) \frac{2r}{3} e^{(-2r/3)}$$

- Equation for no. of radial nodes = $n l 1 \rightarrow 2p = 0$, 3p = 1- Ensures 2p and 3p orthogonal 0.2
- All *p* orbitals are multiplied by r $\rightarrow R(r) = 0$ at r = 0

Required to match the angular function \rightarrow angular node



p orbitals – angular functions boundary surfaces

- All p orbitals have the same shape
- Angular function give rise to direction
- Can represent *p* orbital as dot diagrams or boundary surfaces

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

- 1 angular nodal plane p_x (yz plane), p_y (xz plane) p_z (xy plane)
 - Ensures that *p* orbitals are orthogonal to *s* orbitals



p orbitals – RDF's

- Radial distribution function show probability at a given radius
- 2p function no nodes, maximum at $r = 4 a_0$ (same as n = 2 for Bohr model)
- 3p function two peaks, maximum at $r \approx 12 a_0$



Introduction to Molecular Orbital Theory 6 lecture Course Dr. S. Draper

Tutorial Sheet 1

- 1. What is the relationship between the possible angular momentum quantum numbers to the principal quantum number?
- 2. How many atomic orbitals are there in a shell of principal quantum number *n* ?
- 3. Draw sketches to represent the following for 3s, 3p and 3d orbitals.
 - (i) the radial wave function
 - (ii) the radial distribution
 - (iii) the angular wave function
- 4. Penetration and shielding are terms used when discussing atomic orbitals
 - (i) Explain what the terms penetration and shielding mean.
 - (ii) How do these concepts help to explain the structure of the periodic table ?
- 5. Draw the *d* atomic orbitals as enclosed surfaces, showing the sign of the original wavefunction on each lobe. Label these orbitals.