Chemistry 557 (1997) **Handout #8**

3. The Θ Functions

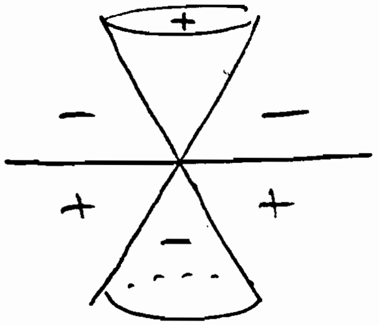
They are the associated Legendre polynomials and have the form:

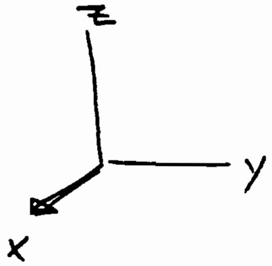
$$P_\ell^{|m|}(\cos\theta) = \left(c_1 \cos^{\ell-|m|}\theta + c_2 \cos^{\ell-|m|-2}\theta + \dots\right)\sin^{|m|}\theta$$

when these functions change sign the node is a cone, in general. The cones are about the z axis and come in pairs except the Θ = 90° case, which is a flattened cone (the xy plane). Thus, for 4f, $m = 0$,

$$P_\ell^{|m|} = P_3^0 \propto \frac{5}{3}\cos^3\theta - \cos\theta$$

there are 3 conical nodes





We will see that ℓ , the total angular momentum quantum number has the very neat significance:

$$\boxed{\ell = \#\text{ of angular nodes}}$$

so # of Θ nodes = $\ell - |m|$, i.e., the largest power of cos Θ in the polynomial.

4. The R Equation and Functions

Looking at the Schrodinger Equation from Handout #6 we can see

$$(T_{\text{radial}} + V(r) + T_{\text{ang}})\,\Psi_{nlm} = E_n\,\Psi_{nlm}$$

Where $T_{ang} = \mathcal{L}^2(\theta,\phi)/2\mu r^2$.

After operating on Ψ_{nlm} by T_{ang} the equation becomes

$$T_{rad} - \frac{Ze^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$$

which displays the angular kinetic energy as the centrifugal "potential". The plot attached to Handout #7 shows how the coulomb potential and the centrifugal "potentials" combine to make the radial motion have quite different character, depending on what ℓ is, i.e. whether it is an s, p, d ..... etc. orbital. This can be seen in the other figure attached to #7. In the s orbital the electron can be thought of as behaving somewhat like a comet. Classically it is constantly diving <u>through</u> the nucleus. If you think about it, you can realize that the electron must spend very little time near the nucleus since its velocity must reach enormously high values there where the force is so high because $F \propto \frac{1}{r^2}$. On the other hand, after the electron "passes through" the nucleus it takes a relatively long time to slow down, <u>stop</u>, and turn around. This is a way of "understanding" why the 3s electron is, on the average, found farther away from the nucleus than the p, which is, in turn, farther than the d. The 3d, with its high angular momentum, has the purest orbiting motion and only zero point radial motion (no radial nodes).

It is rather spectacular that such dramatically different states should have exactly the same energy, but this accidental degeneracy, as it is called, is true for all one-electron atoms. However, as you know, the degeneracy is removed for many-electron atoms.

5. The Energy

$$E_n = -\frac{Z^2e^2}{2n^2a_0} = -\frac{(Ze)(e)}{2\left(\frac{n^2a_0}{Z}\right)} = \overset{\text{from Virial Theorem}}{\overset{\swarrow}{\frac{1}{2}\langle V_n\rangle}} = \frac{1}{2}\left\langle -\frac{Ze^2}{r}\right\rangle$$

which shows that $$\left\langle \frac{1}{r} \right\rangle = \frac{1}{\left(\frac{n^2a_0}{Z}\right)}$$

Thus, the size of an orbital $\propto \frac{n^2}{Z}$, which is sensible. But one may also find E from, $E = -\langle T \rangle = \frac{-\hbar^2 Z^2}{n^2 2\mu a_0^2}$ in agreement with the uncertainty principle. Comparing the two formulas shows that

$$\frac{\hbar^2}{2\mu a_0^2} = \frac{e^2}{2a_0} \quad \text{or} \quad \boxed{a_0 = \frac{\hbar^2}{\mu e^2}}$$

6. Nodes

Since $\psi = R(r)\,\Theta(\theta)\,\Phi(\phi)$ the nodal surfaces correspond to

r = const. = sphere

θ = const. = cone (about z)

ϕ = const. = planes ⊥ to xy

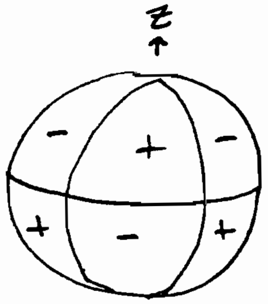
Let us now tabulate the first several orbitals and learn the formulas for number of each kind of node. Examine functions on p 23 of Murrell, et al.

n	ℓ	m	name	r nodes	θ nodes	ϕ nodes	Total
1	0	0	1s	0	0	0	0
2	0	0	2s	1	0	0	1
2	1	0	2pz	0	1	0	1
2	1	1	2 Px,y	0	0	1	1
3	0	0	3s	2	0	0	2
3	1	0	3pz	1	1	0	2
3	1	1	3px,y	1	0	1	2
3	2	0	$3d_{z^2}$	0	2	0	2
3	2	1	$3d_{xz,yz}$	0	1	1	2
3	2	2	$3d_{xy,x^2-y^2}$	0	0	2	2

The obvious relationships hold true for all cases:

total nodes = $n-1$
number of ϕ nodes = m
total angular nodes = ℓ
number of Θ nodes = $\ell-|m|$
number of r nodes = $n - \ell - 1$

Thus, a 4f orbital with $m = 2$ has 3 nodes total. But $\ell = 3$ so there 2 Φ nodes and 1 Θ node and there are no spherical$^{(r)}$ nodes This orbital looks like :



7. Overlap

We will briefly discuss the concept of overlap between neighboring atomic orbitals because it is a key criterion for bonding and may be employed effectivly for qualitative purposes with little knowledge of other bonding principles.

We are interested in whether the OVERLAP INTEGRAL = $\int \psi_A \psi_B \, dv = S_{AB} = 0$

or non-zero. When the overlap integral is large these orbitals ψ_A and ψ_B will be important in the bonding process.

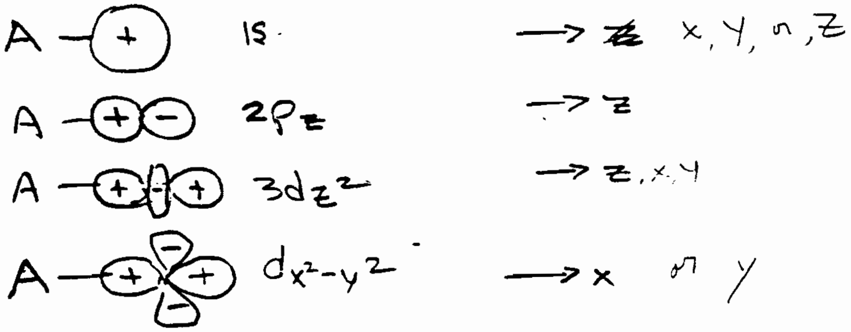
The first step is to determine the symmetry of each orbital with respect to the A-B bond, i.e., is it σ, π, or δ ? This can be rephrased into the question: If you look down the A-B bond axis does it look like s or p or d?

looks like s → σ

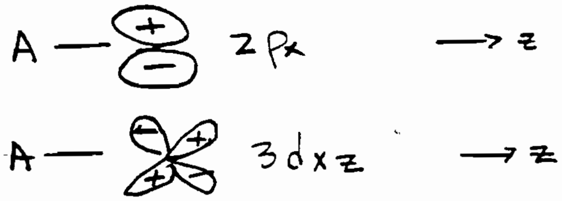
looks like p → π

looks like d → δ

Examples of σ :



Examples of π



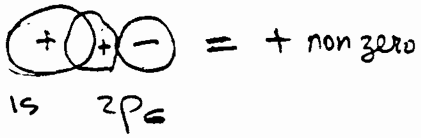
Example of δ

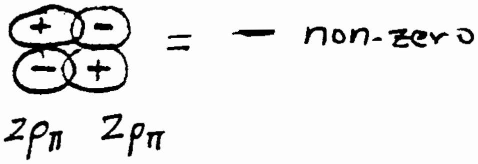
Rule: unless both orbitals, the one on A and the one on B, are of the same symmetry the overlap must be zero.

If both are σ we say they are involved in a σ bond. Likewise for π and δ. Note that all types, s, p, and d, can enter into σ bonds, only p and d can do π bonding and only two d orbitals can δ bond.

One may generally tell whether overlap is zero by visual inspection.

Thus





special note on DRAWING ATOMIC ORBITALS

The following procedure is suggested as the best way to display the nodal patterns of atomic orbitals.

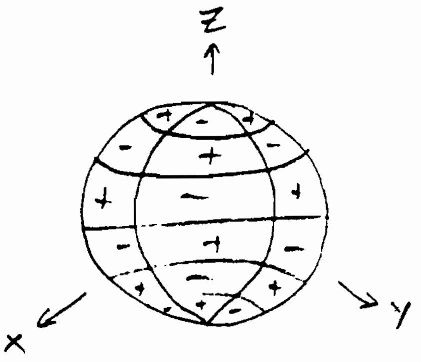
(1)First make two perspective drawings of the orbital values on a spherical shell at a distance beyond the last r node. One of these should be looking down the z axis, the other from the side so as to show all of the planar nodes. These two will show the number of conical and planar nodes but will not show the spherical(r) nodes.

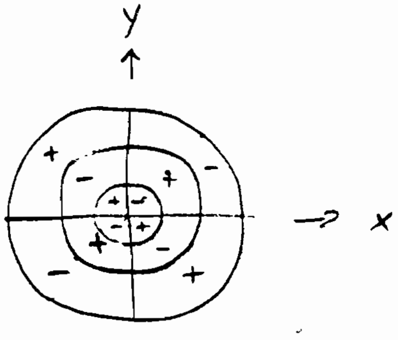
(2) Now draw a crossection through the center which cuts between two planar nodes. This will display the cones again and will also show the spherical nodes. The planes will not be seen on this view.

EXAMPLE:n=10,l=7,m=2 , i.e., a 10j orbital.

total nodes= 9 (n-1)
planes = 2
cones = 5
spheres = 2

(1)





(2)