Virial Theorem

chmy564-17
Mon 23jan17

Levine pp 416-426 and
https://en.wikipedia.org/wiki/Virial_theorem

From Wikipedia, the free encyclopedia In mechanics, the **virial theorem** provides a general equation that relates the average over time of the total kinetic energy, of a stable system consisting of *N* particles, bound by potential forces, with that of the total potential energy where angle brackets represent the average over time of the enclosed quantity. Mathematically, the theorem states

$$\langle T \rangle = -\frac{1}{2} \sum_{k=1}^{N} \langle \vec{F}_k \cdot \vec{r}_k \rangle$$

where $\mathbf{F}_k$ represents the force on the *k*th particle, which is located at position $\mathbf{r}_k$. The word **virial** for the right-hand side of the equation derives from *vis*, the Latin word for "force" or "energy", and was given its technical definition by Rudolf Clausius in 1870.[1]

Rudolf Claussius (Wikipedia)

1850, first stated the basic ideas of the **Second Law of Thermodynamics**.

In 1865 he introduced the concept of **entropy**.

In 1870 he introduced the **virial theorem** which applied to heat.

The **virial theorem** applies to ALL stable systems, classical and quantum.

For example, Fritz Zwicky in ~1930 was the first to use the virial theorem to deduce the existence of unseen matter, which is now called **dark matter** – still a major mystery in astrophysics.

Major bottom line:

When the potential energy, **V**, due to interaction of any two particles is proportional to $\mathbf{r^n}$, then: $\langle \mathbf{T} \rangle = \frac{1}{2}\, n \langle \mathbf{V} \rangle$.

For Coulomb energy, n = -1, therefore

$\langle \mathbf{T} \rangle = -\frac{1}{2} \langle \mathbf{V} \rangle$ for all **atoms and molecules**, the **motions of the planets**, etc.

For a harmonic oscillator, $V=1/2\, kx^2$, n= 2 so that
$\langle \mathbf{T} \rangle = \langle \mathbf{V} \rangle$, again in either classical or quantum mechanics.

Our Main Interest:

In **Quantum Chemistry,** obeying of the **virial theorem** is checked at each iteration of ab initio SCF energy computations at each geometry of an optimization to ensure that (<T> = -1/2 <V>, as seen in a piece of typical output from Gaussian 09:

Initial guess from the checkpoint file: "9H-2ap.chk"

B after Tr= 0.000000 0.000000 0.000000

Rot= 1.000000 0.000000 0.000000 0.000150 Ang= 0.02 deg.

Keep R1 ints in memory in canonical form, NReq=13642697.

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

SCF Done: E(RHF) = -461.898845425 A.U. after 10 cycles

NFock= 10 Conv=0.66D-08 **-V/T= 2.0019**

Calling FoFJK, ICntrl= 2127 FMM=F ISym2X=0 I1Cent= 0 IOpClX= 0 NMat=1 NMatS=1 NMatT=0.

***** Axes restored to original set *****

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	7	-0.000241441	-0.000077968	0.000305746
2	6	0.000214225	0.000060731	-0.000156949
3	1	-0.000040286	-0.000008538	-0.000006346
4	7	-0.000167728	-0.000065086	0.000348129

Spherical Harmonics: Curvature, Kinetic Energy, and Orbital Nodes in Spherical systems

http://www.falstad.com/qmatom/
David Manthey's Grand Orbital Table

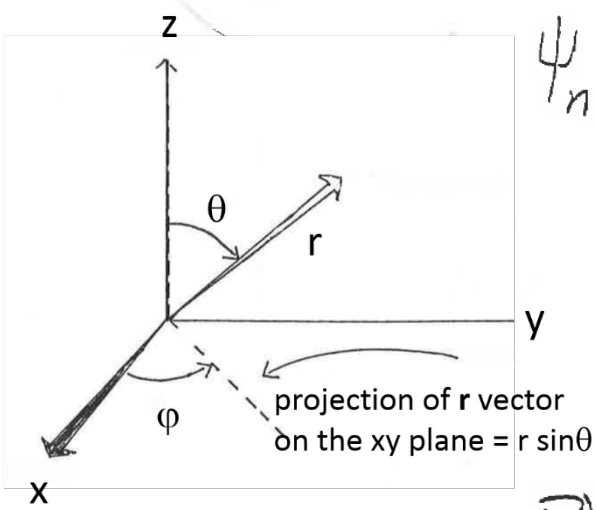
Levine: pp102, 107-110

Chem 514 Handout #7 October, 1985

More on Atomic Orbitals

1. Nature of the solutions

We won't be concerned with the details of "solving" the Schrodinger Equation for the H atom in this course, but, it's not too hard to show that one may break it down into 3 separate equations, each depending on only one of the 3 variables r, Θ , and ϕ. Whenever this happens, one finds that the well behaved solutions (the orbitals) are products of 3 functions, each depending on only r, Θ or ϕ and each orbital is characterized by 3 integer quantum numbers, n, l, and m, (3 because space is 3-dimensional).



$$\psi_{n\ell m} = R_{n\ell}(r)\,\Theta_{\ell m}(\theta)\,\Phi_m(\phi)$$

$$= \left(L^{2\ell+1}_{n+\ell}\left(\frac{2Zr}{n a_0}\right) e^{-\frac{Zr}{n a_0}}\right) P^{|m|}_{\ell}(\cos\theta)\, e^{im\phi}$$

$$= \left(L^{2\ell+1}_{n+\ell}(\rho)\, e^{-\frac{\rho}{2}}\right) \cdot Y_{\ell,m}(\theta,\phi)$$

Why does $R_{nl}(r)$ depend l, the total angular momentum quantum number?

The $P^{|m|}_{\ell}$ are the famous associated Legendre polynomials each has powers of cos θ in it. The product of the two angular parts is the same for every spherical problem, not just for quantum mechanics of atoms. Thus it's given a special name and symbol.

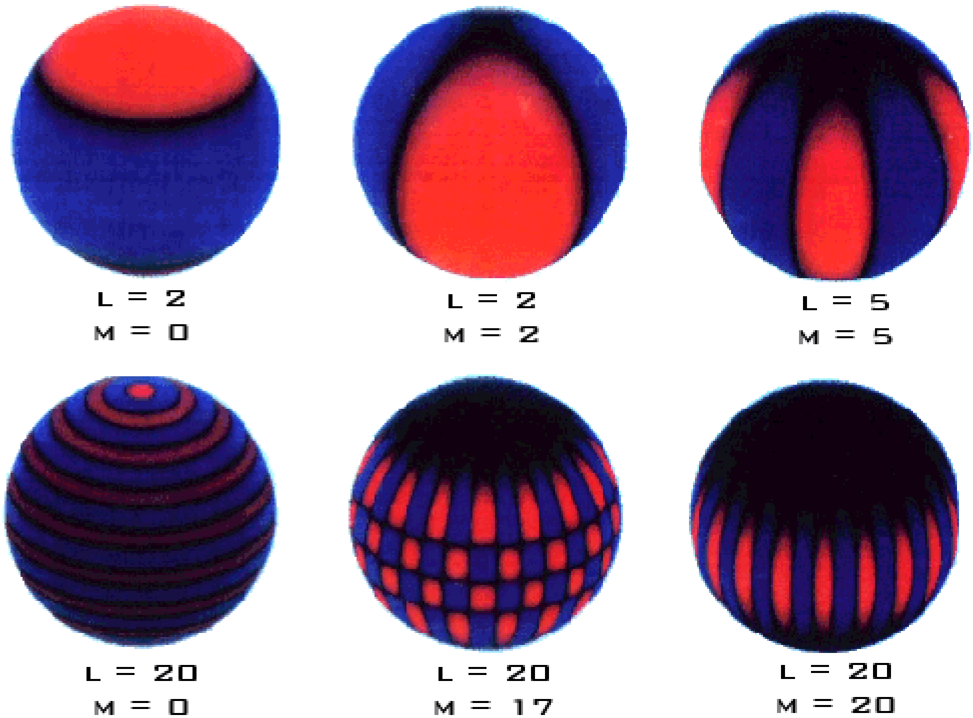
$$Y_{\ell m}(\theta,\phi) = \text{SPHERICAL HARMONICS}$$

$R_{nl}(r)$ is the product of a polynomial (which provides NODES, and and and exponential, which has no nodes.

The $R_{nl}(r)$ describes the Radial Motion (in and out). The $L^{2\ell+1}_{n+\ell}$ are the famous associated Laguerre Polynomials. All these equations and solutions were known and solved by mathematicians in the 1800's or earlier. This should serve to make the distinction between theory and mathematics. The same math appears in many different theories. What Schroedinger did was discover how to map physical reality onto existing mathematics.

http://bison.ph.bham.ac.uk/index.php?page=bison,background

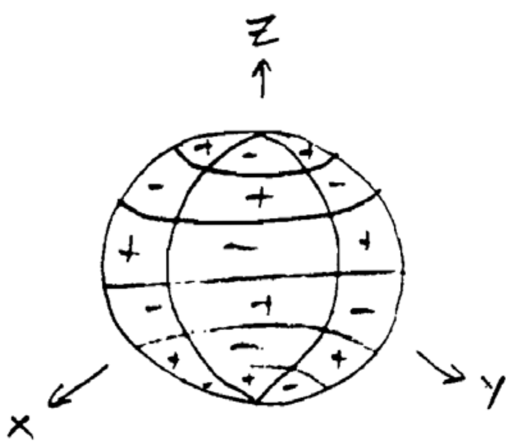
The Sun is a sphere.   Below are calculations of the nodal patterns of seismic waves in the Sun, published by an Astrophysics group at the University of Birmingham in England.

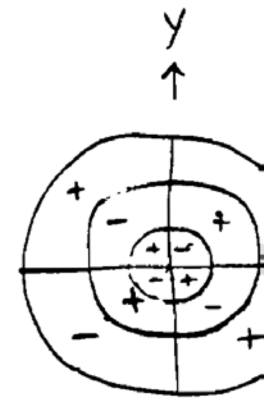


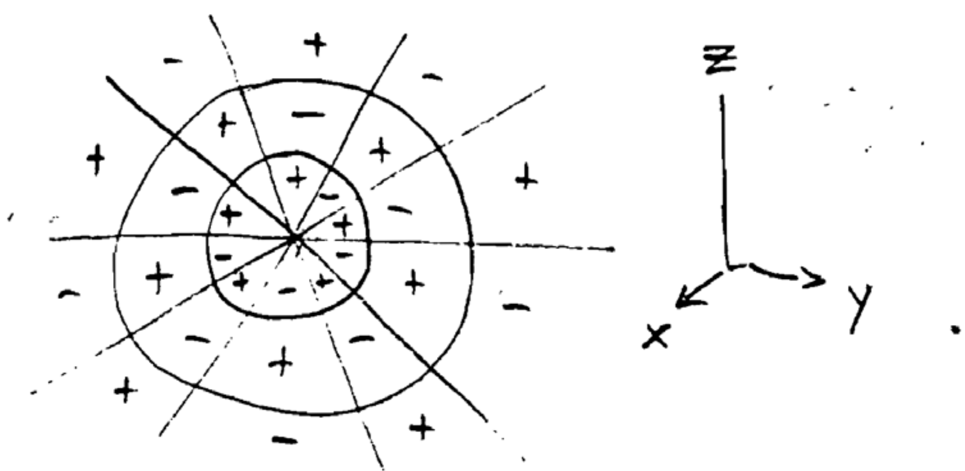
These nodes depend on the l, and m quantum numbers of $\mathbf{Y_{lm}(\theta,\varphi)}$

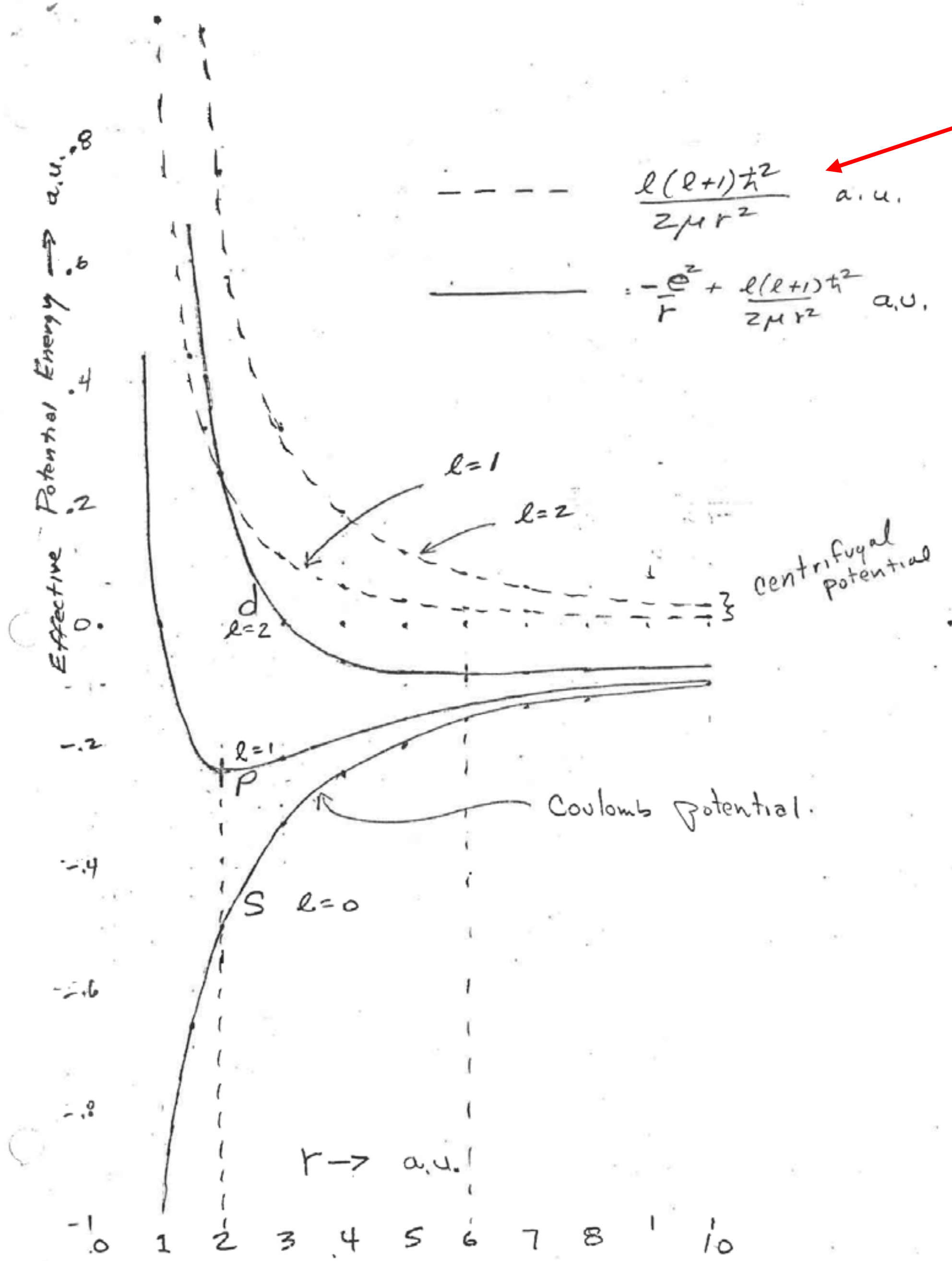
EXAMPLE: n=10, l=7, m=2 , i.e., a 10j orbital.

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

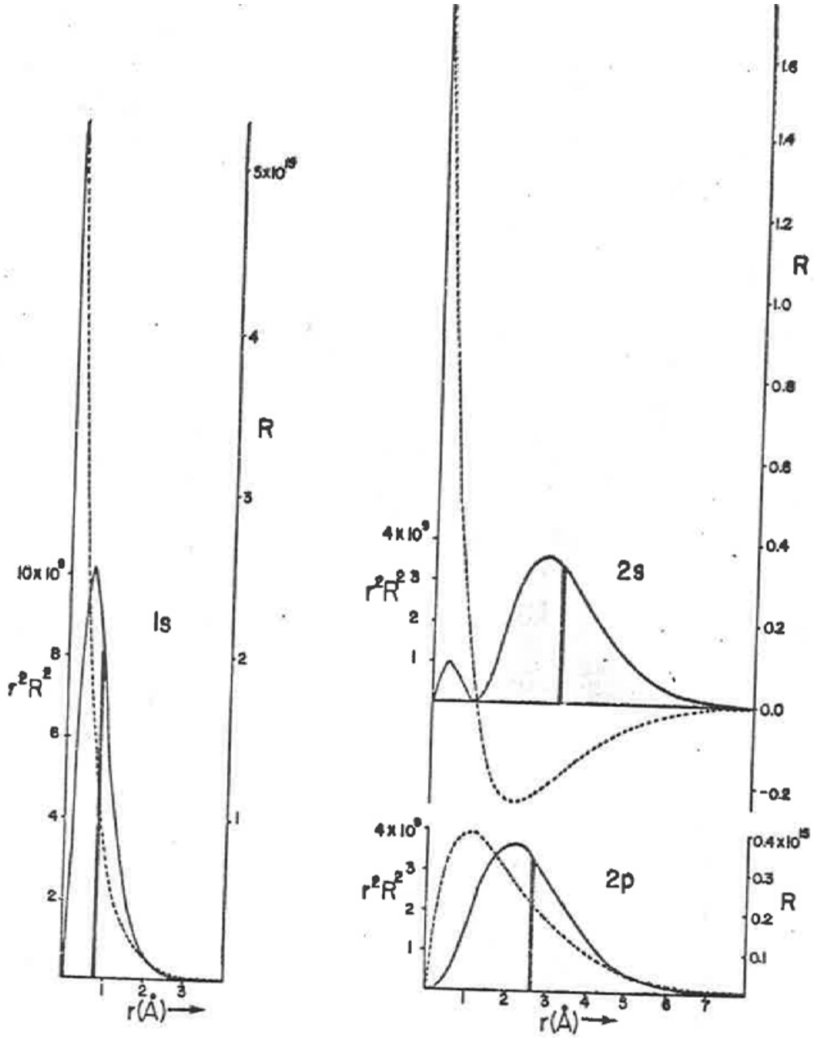








Angular kinetic energy (a "pseudo potential"). Its derivative gives "centrifugal force".



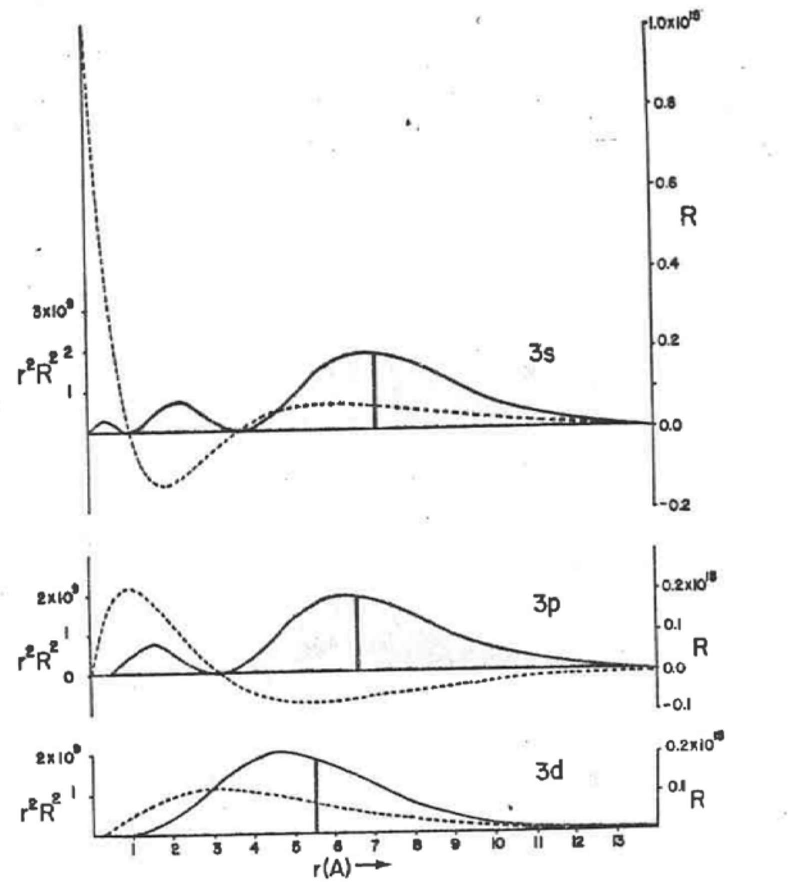
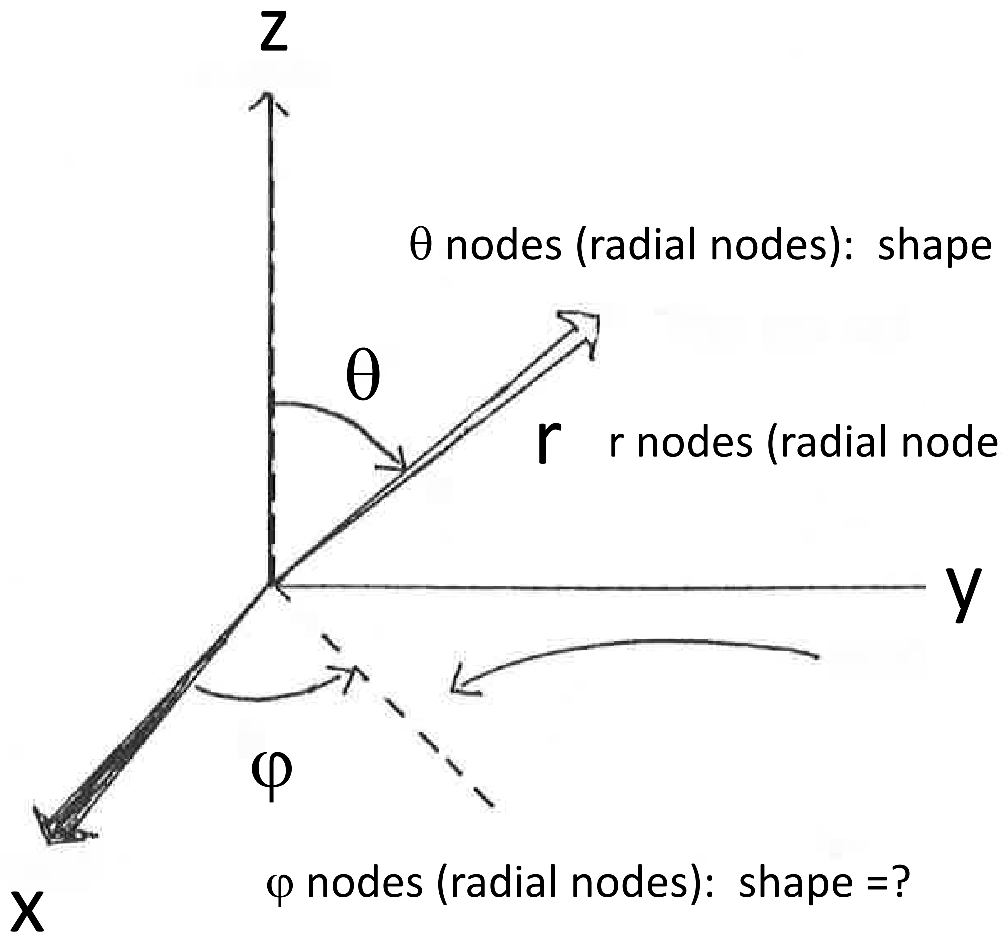


Fig. 4-2. Graphs of radial wave functions, $R_{n\ell}(r)$ (dashed lines), and distribution functions, $r^2R^2_{n\ell}(r)$ (solid lines), for the hydrogen atom. Units of R are $m^{-3/2}$ and units of r^2R^2 are m^{-1}. Vertical lines mark the average value of r for an electron in each orbital.

Shapes of nodes



θ nodes (radial nodes): shape =? **cones** on z axis (includes the xy plane, a cone with θ =90)

r nodes (radial nodes): shape =? **spherical**

φ nodes (radial nodes): shape =? **planes** CONTAINING z axis i.e., perpendicular to xy plane

2. The Φ Equation

Its fairly easy to show that $\frac{\partial^2}{\partial\varphi^2}\Phi = -a\Phi$

and that $\Phi = N e^{-im\varphi}$

$m = 0, \pm 1, \pm 2, \ldots\ldots$

Integer values come from requirement that $\Phi(\varphi) = \Phi(\varphi + 2\pi)$

The significance is found from noting that

$$L_z = (P_{ang})_z \, r\sin\theta$$

$$\frac{L_z^2}{2\mu (r\sin\theta)^2} = \frac{(P_{ang})_z^2}{2\mu}$$ = Angular Kinetic energy

due to motion around the z axis, i.e., that in xy plane.

Examine the Schroedinger Equation and note that

$$\mathcal{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial \varphi^2}$$

so

$$\mathcal{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

Note the parallel to linear momentum.

Thus $$\mathcal{L}_z \, \Phi_m = m\hbar \, \Phi_m$$

and Φ_m are eigenfunctions of $\mathcal{L}_z$ with eigenvalues $m\hbar$.

3. The Θ Functions

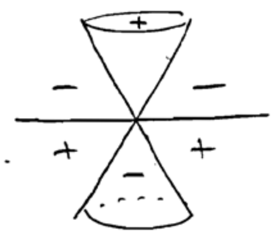
They are the associated Legendre polynomials and have the form:

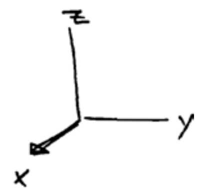
$$P_\ell^{|m|}(\cos\theta) = \left(c_1 \cos^{\ell-|m|}\theta + c_2 \cos^{\ell-|m|-2}\theta + \ldots\right)\sin^{|m|}\theta$$

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 $\Theta = 90°$ case, which is a flattened cone (the xy plane). Thus, for 4f, m = o ,

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

there are 3 conical nodes





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

ℓ = # 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

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

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

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

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

5. The Energy $$E_n = -\frac{Z^2e^2}{2n^2a_0} = -\frac{(Ze)(e)}{2\left(\frac{n^2a_0}{Z}\right)} = \frac{1}{2}\langle V_N\rangle = \frac{1}{2}\left\langle -\frac{Ze^2}{r}\right\rangle$$

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

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

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

$$r = \text{const.} = \text{sphere}$$

$$\theta = \text{const.} = \text{cone} \quad (\text{about } z)$$

$$\phi = \text{const.} = \text{planes} \perp \text{to } xy$$

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.

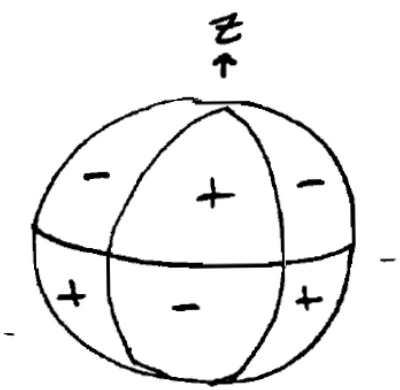
n	ℓ	m	name	r nodes	θ nodes	φ nodes	Total
1	0	0	1s	0	0	0	0
2	0	0	2s	1	0	0	1
2	1	0	2pz	0	1	0	1
2	1	1	2 Px,y	0	0	1	1
3	0	0	3s	2	0	0	2
3	1	0	3pz	1	1	0	2
3	1	1	3px,y	1	0	1	2
3	2	0	$3d_{z^2}$	0	2	0	2
3	2	1	$3d_{xz,yz}$	0	1	1	2
3	2	2	$3d_{xy,x^2-y^2}$	0	0	2	2

What are the formulas for the number of each type of node and thetotal number of nodes?

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	=	$\ell - \lvert m \rvert$
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 :



special note on DRAWING ATOMIC ORBITALS

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

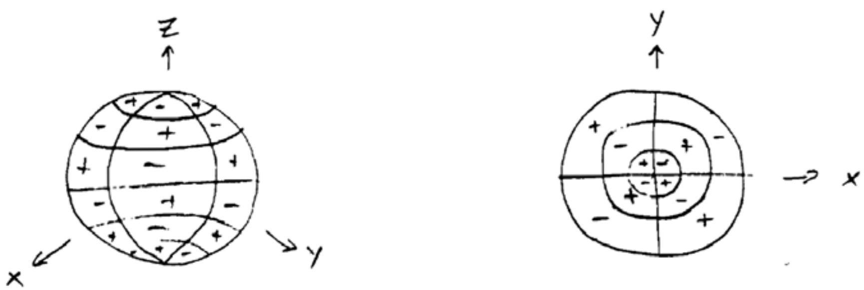
(1)First make two perspective drawings of the orbital values on a spherical shell at a distance beyond the last r node. One of these should be looking down the z axis, the other from the side so as to show all of the planar nodes. These two will show the number of conical and planar nodes but will not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