

Virial Theorem

chmy564-19
Wed 16jan19

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]

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

Rudolf Clausius (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 r^n , then: $\langle T \rangle = \frac{1}{2} n \langle V \rangle$.

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

For Coulomb and gravitational, energy, $n = -1$, therefore

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle \quad , \text{i.e.,}$$

$-\langle V \rangle / \langle T \rangle = 2$ for all **atoms and molecules**, the **motions of the planets**, etc.

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 $-\langle V \rangle / \langle T \rangle = 2$ 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** ← **Obeys virial theorem**

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

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

```
-----  
Center   Atomic      Forces (Hartrees/Bohr)  
Number   Number      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
```

H -Atom Orbitals and Nodal Properties

<http://www.orbitals.com/orb/orbtable.htm>

[David Manthey's Grand Orbital Table](#)

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

<http://www.falstad.com/qmatom/>

Levine: pp102, 107-110

Chem 514

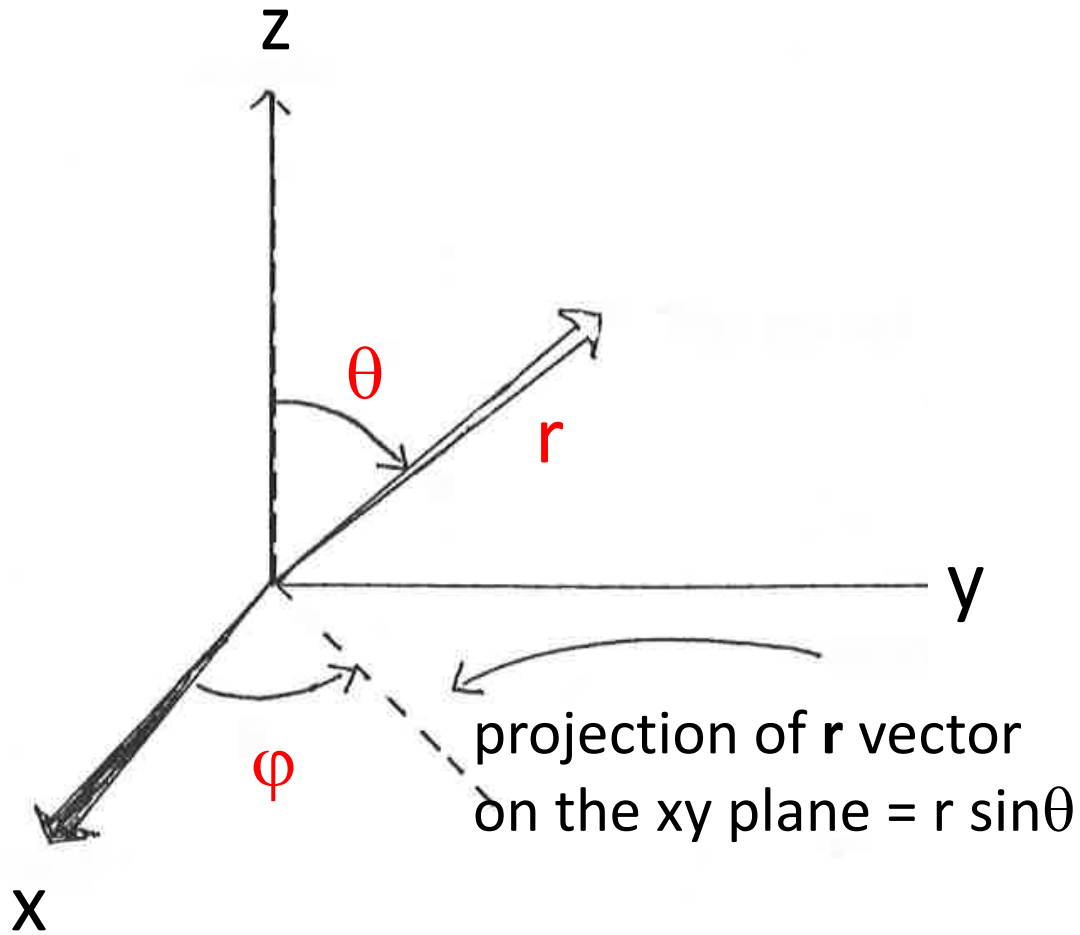
Handout #7

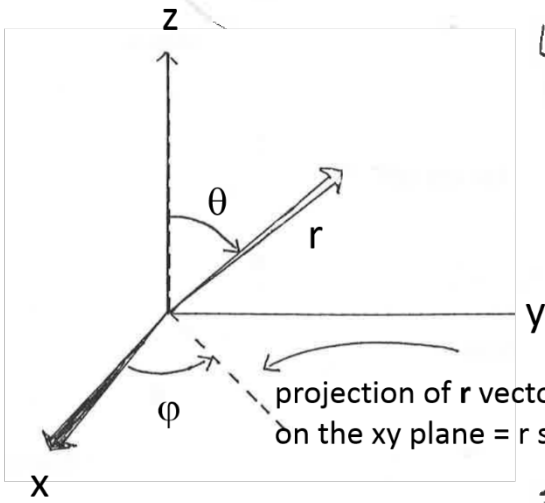
October, 1985

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).





$$\psi_{nlm} = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$$

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

$$= \left(L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) e^{-\frac{Zr}{na_0}} \right) P_l^{lm}(\cos \theta) e^{im\phi}$$

$$= \left(L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) e^{-\frac{Zr}{na_0}} \right) \cdot Y_{l,m}(\theta, \phi)$$

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

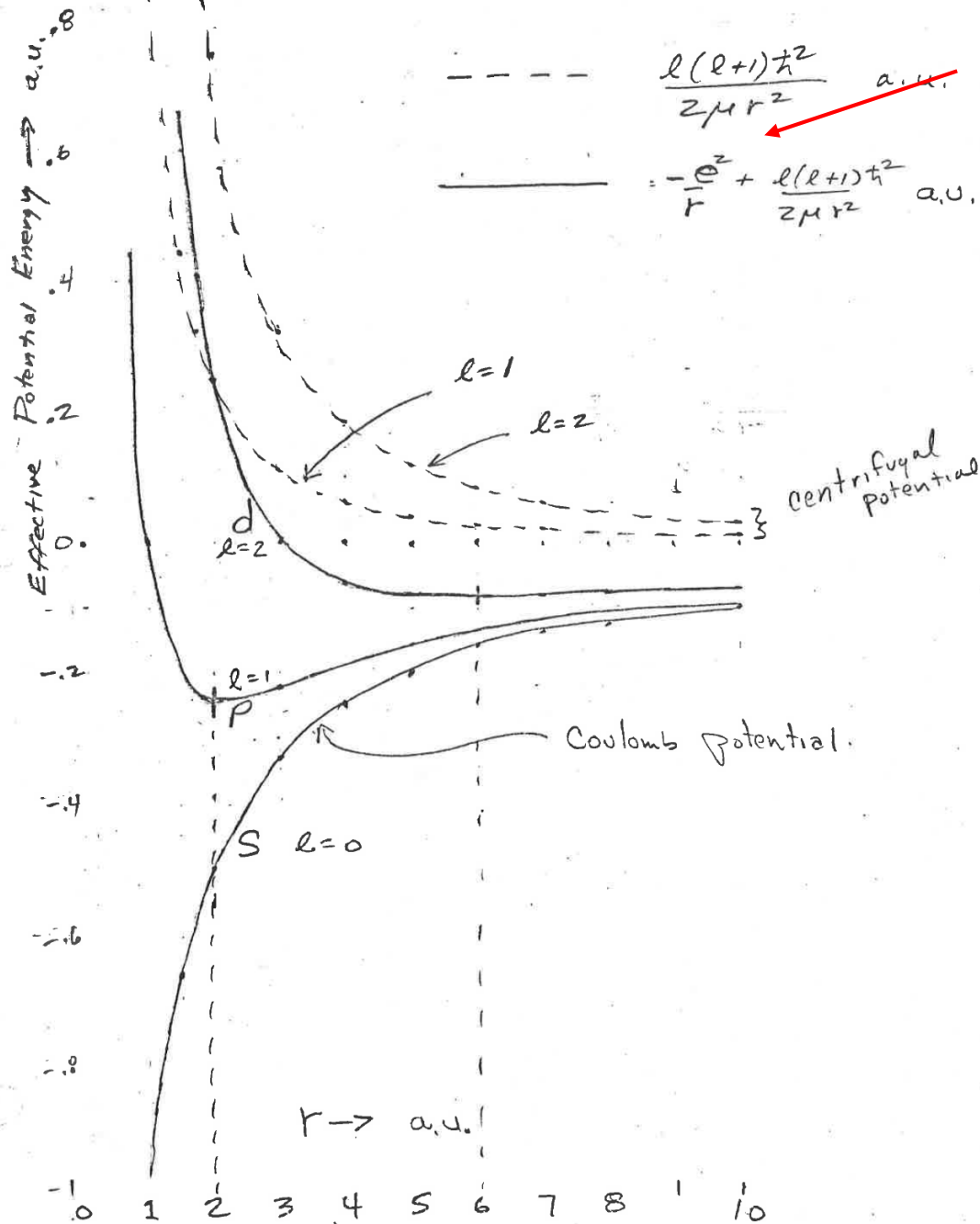
The P_l^{lm} are the famous associated Legendre polynomials

each has powers of $\cos \theta$ 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.

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

The $R_{nl}(r)$ describes the Radial Motion (in and out). The L_{n+l}^{2l+1} 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.

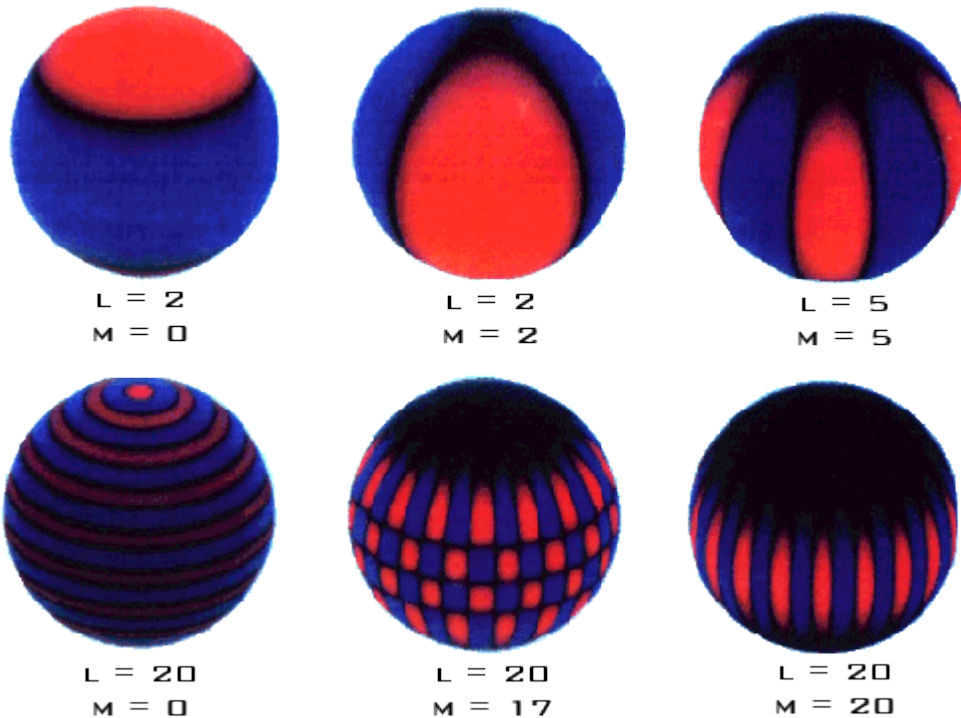
Effective Potential Energy (includes pseudo potential)



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

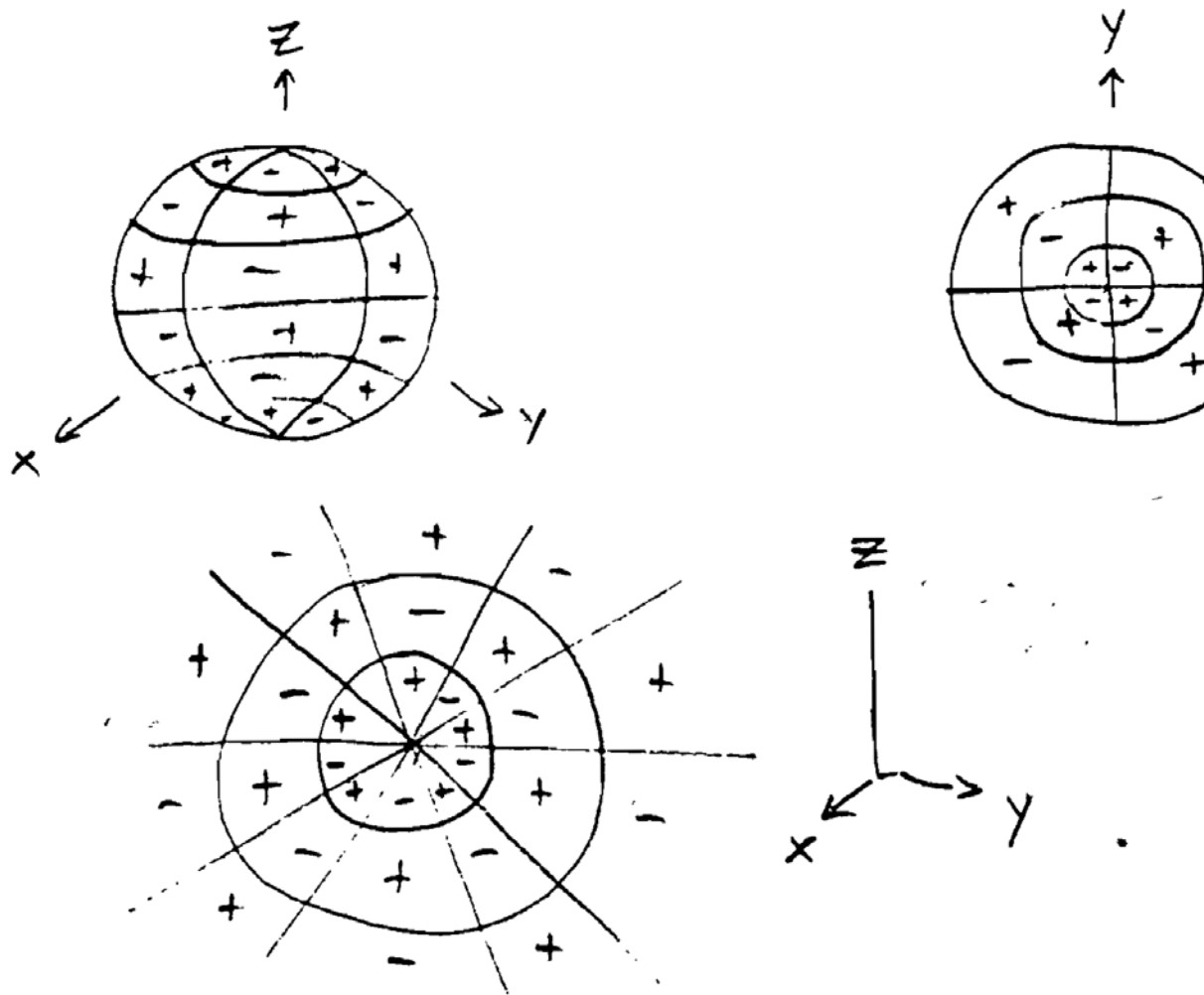
<http://bison.ph.bham.ac.uk/index.php?page=bison,background>

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.



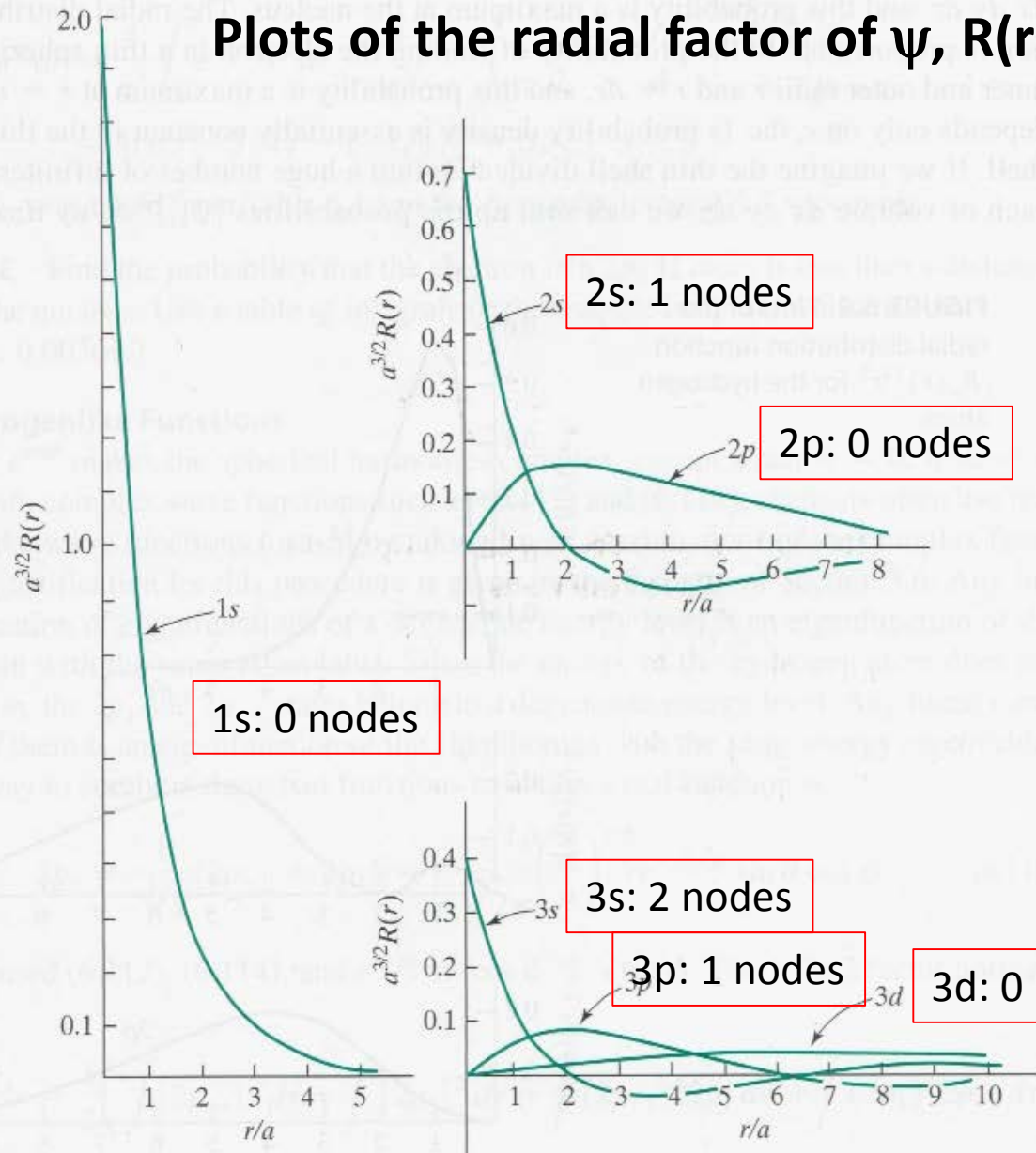
These nodes depend on the l , and m quantum numbers of $Y_{lm}(\theta, \phi)$

0 1 2 3 4 5 6 7 8 9 10
s p d f g h i j k l m



Plots of the radial factor of ψ , $R(r)$

FIGURE 6.8 Graphs of the radial factor $R_{nl}(r)$ in the hydrogen-atom ($Z = 1$) wave functions. The same scale is used in all graphs. (In some texts, these functions are not properly drawn to scale.)



possible values of θ and ϕ , keeping r fixed. This amounts to integrating (6.115) over θ and ϕ . Hence the probability of finding the electron between r and $r + dr$ is

$$[R_n(r)]^2 r^2 dr \int_0^{2\pi} \int_0^\pi |Y_l^m(\theta, \phi)|^2 \sin \theta d\theta d\phi = [R_n(r)]^2 r^2 dr \quad (6.116)$$

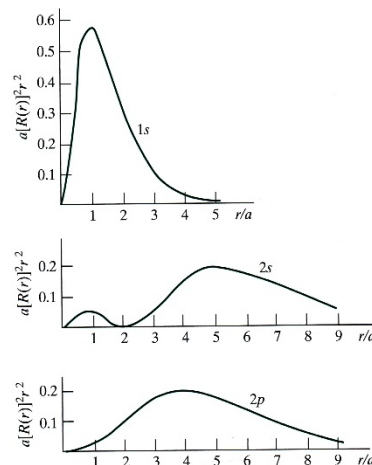
since the spherical harmonics are normalized:

$$\int_0^{2\pi} \int_0^\pi |Y_l^m(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1 \quad (6.117)$$

as can be seen from (5.72) and (5.80). The function $R^2(r)r^2$, which determines the probability of finding the electron at a distance r from the nucleus, is called the **radial distribution function**; see Fig. 6.9.

For the $1s$ ground state of H, the probability density $|\psi|^2$ is from Eq. (6.104) equal to $e^{-2r/a}$ times a constant, and so $|\psi_{1s}|^2$ is a maximum at $r = 0$ (see Fig. 6.14). However, the radial distribution function $[R_{1s}(r)]^2 r^2$ is zero at the origin and is a maximum at $r = a$ (Fig. 6.9). These two facts are not contradictory. The probability density $|\psi|^2$ is proportional to the probability of finding the electron in an infinitesimal box of volume $dx dy dz$, and this probability is a maximum at the nucleus. The radial distribution function is proportional to the probability of finding the electron in a thin spherical shell of inner and outer radii r and $r + dr$, and this probability is a maximum at $r = a$. Since ψ_{1s} depends only on r , the $1s$ probability density is essentially constant in the thin spherical shell. If we imagine the thin shell divided up into a huge number of infinitesimal boxes each of volume $dx dy dz$, we can sum up the probabilities $|\psi_{1s}|^2 dx dy dz$ of being in

FIGURE 6.9 Plots of the radial distribution function $[R_n(r)]^2 r^2$ for the hydrogen atom.



Complex H Wavefunctions

$$2s = \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a} \right)^{3/2} \left(1 - \frac{Zr}{2a} \right) e^{-Zr/2a}$$

$$2p_{-1} = \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta e^{-i\phi}$$

$$2p_{-1} = 2p_x - i2p_y$$

$$2p_1 = 2p_x + i2p_y$$

Eigenfunctions of L_z operator

$$L_z |2p_{-1}\rangle = -1 |2p_{-1}\rangle \quad m = -1$$

$$L_z |2p_1\rangle = +1 |2p_1\rangle \quad m = +1$$

TABLE 6.2 Real Hydrogenlike Wave Functions

$$1s = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$

$$2s = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{3/2} \left(2 - \frac{Zr}{a} \right) e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \cos \theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \cos \phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \sin \phi$$

$$3s = \frac{1}{81(3\pi)^{1/2}} \left(\frac{Z}{a} \right)^{3/2} \left(27 - 18 \frac{Zr}{a} + 2 \frac{Z^2 r^2}{a^2} \right) e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \cos \theta$$

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \cos \phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \sin \phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \cos \phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \sin \phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}} \left(\frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \sin 2\phi$$

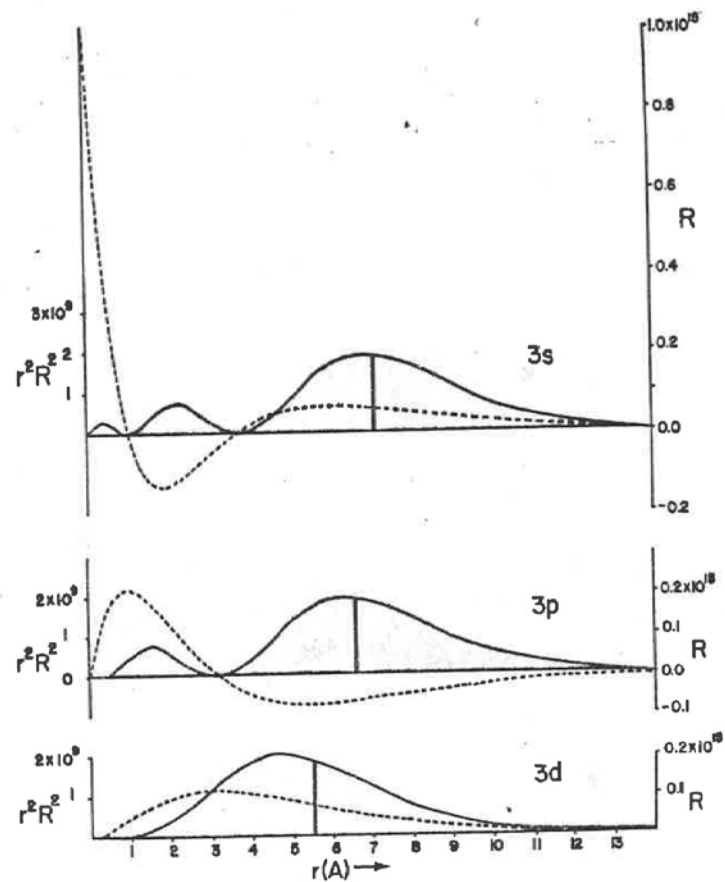
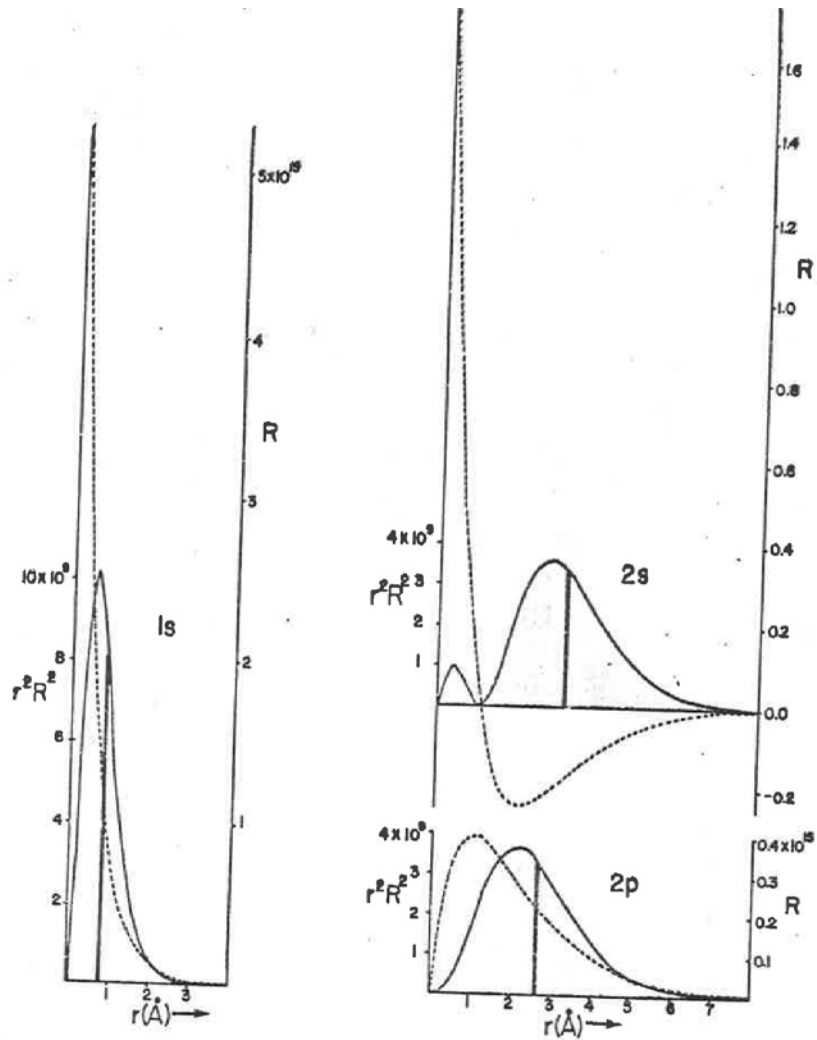
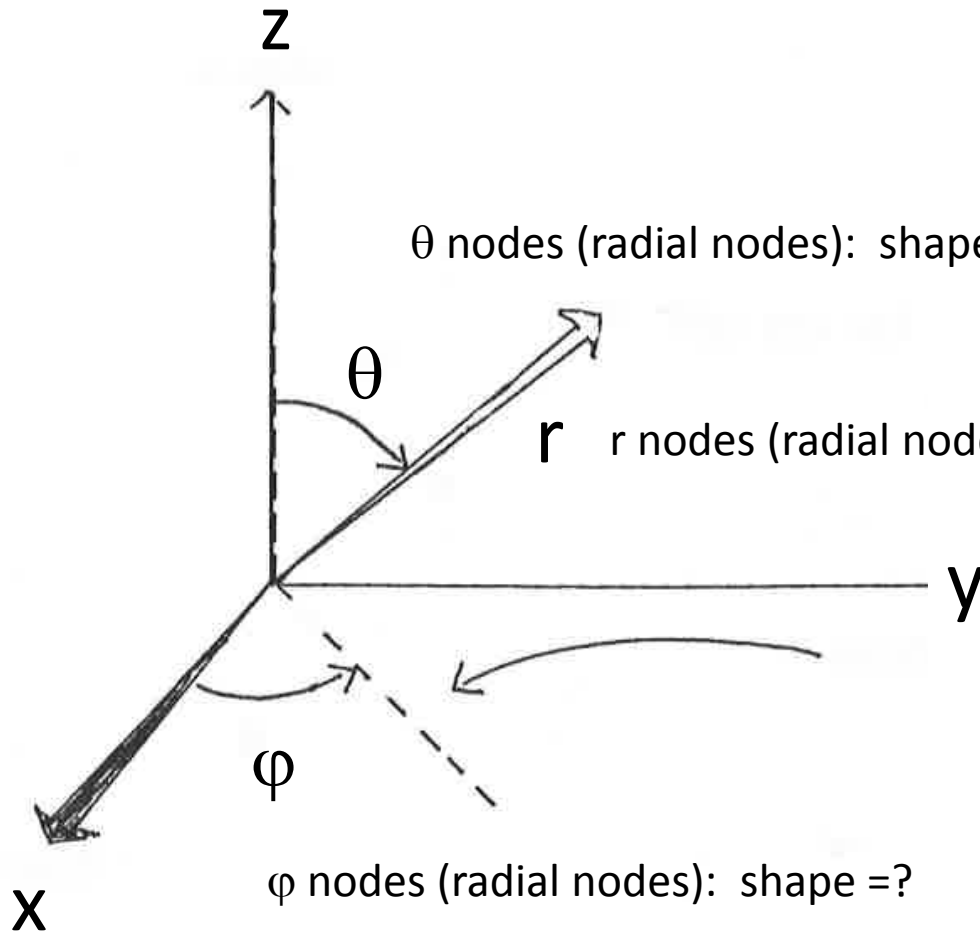


Fig. 4-2. Graphs of radial wave functions, $R_{nl}(r)$ (dashed lines), and distribution functions, $r^2 R_{nl}^2(r)$ (solid lines), for the hydrogen atom. Units of R are $\text{m}^{-3/2}$ and units of $r^2 R^2$ are m^{-1} . Vertical lines mark the average value of r for an electron in each orbital.

Shapes of nodes



θ nodes (radial nodes): shape =?

cones on z axis
(includes the xy plane,
a cone with $\theta = 90$)

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

$$\frac{\partial^2 \Phi}{\partial \varphi^2} = -a \Phi$$

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

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

Integer values come from requirement that

$$\Phi(\varphi) = \Phi(\varphi + 2\pi)$$

The significance is found from noting that

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

$$\frac{L_z^2}{2\mu (r \sin \theta)^2} = \frac{(P_{ang})_z^2}{2\mu} \quad \begin{array}{l} \text{Angular} \\ \text{= Kinetic energy} \end{array}$$

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

Examine the Schrodinger Equation and note that

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

so

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

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**

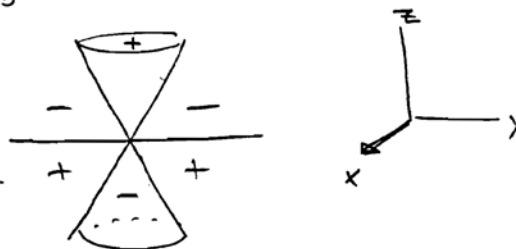
They are the associated Legendre polynomials and have the form:

$$P_l^{m_l}(\cos\theta) = (c_1 \cos^{\ell-|m_l|}\theta + c_2 \cos^{\ell-|m_l|-2}\theta + \dots) \sin^{|m_l|}\theta$$

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 $\theta = 90^\circ$ case, which is a flattened cone (the xy plane). Thus, for 4f, $m = 0$,

$$P_4^{0} = P_3^0 \propto \frac{5}{3} \cos^3\theta - \cos\theta$$

there are 3 conical nodes



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

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

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

4. **The R Equation and Functions**

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

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

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

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

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

5. The Energy

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

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

$$\frac{\hbar^2}{2\mu a_0^2} = \frac{e^2}{2a_0}$$

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

Since $\Psi = R(r) \Theta(\theta) \Phi(\phi)$

the nodal surfaces

correspond to

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

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

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

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

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.

<u>n</u>	<u>l</u>	<u>m</u>	<u>name</u>	<u>r nodes</u>	<u>Θ nodes</u>	<u>Φ nodes</u>	<u>Total</u>
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 P _{x,y}	0	0	1	1
3	0	0	3s	2	0	0	2
3	1	0	3pz	1	1	0	2
3	1	1	3p _{x,y}	1	0	1	2
3	2	0	3d _{z²}	0	2	0	2
3	2	1	3d _{xz,yz}	0	1	1	2
3	2	2	3d _{xy,x²-y²}	0	0	2	2

The obvious relationships hold true for all cases:

$$\text{total nodes} = n-1$$

$$\text{number of } \phi \text{ nodes} = m$$

$$\text{total angular nodes} = l$$

$$\text{number of } \ominus \text{ nodes} = l - |m|$$

$$\text{number of } r \text{ nodes} = n - l - 1$$

Thus, a 4f orbital with $m = 2$ has 3 nodes total. But $l = 3$ so there

2 ϕ nodes and 1 \ominus node and there are no spherical (r) nodes *This orbital*

looks like :

\hat{z}
↑

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 cross-section 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

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 crosssection 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	

