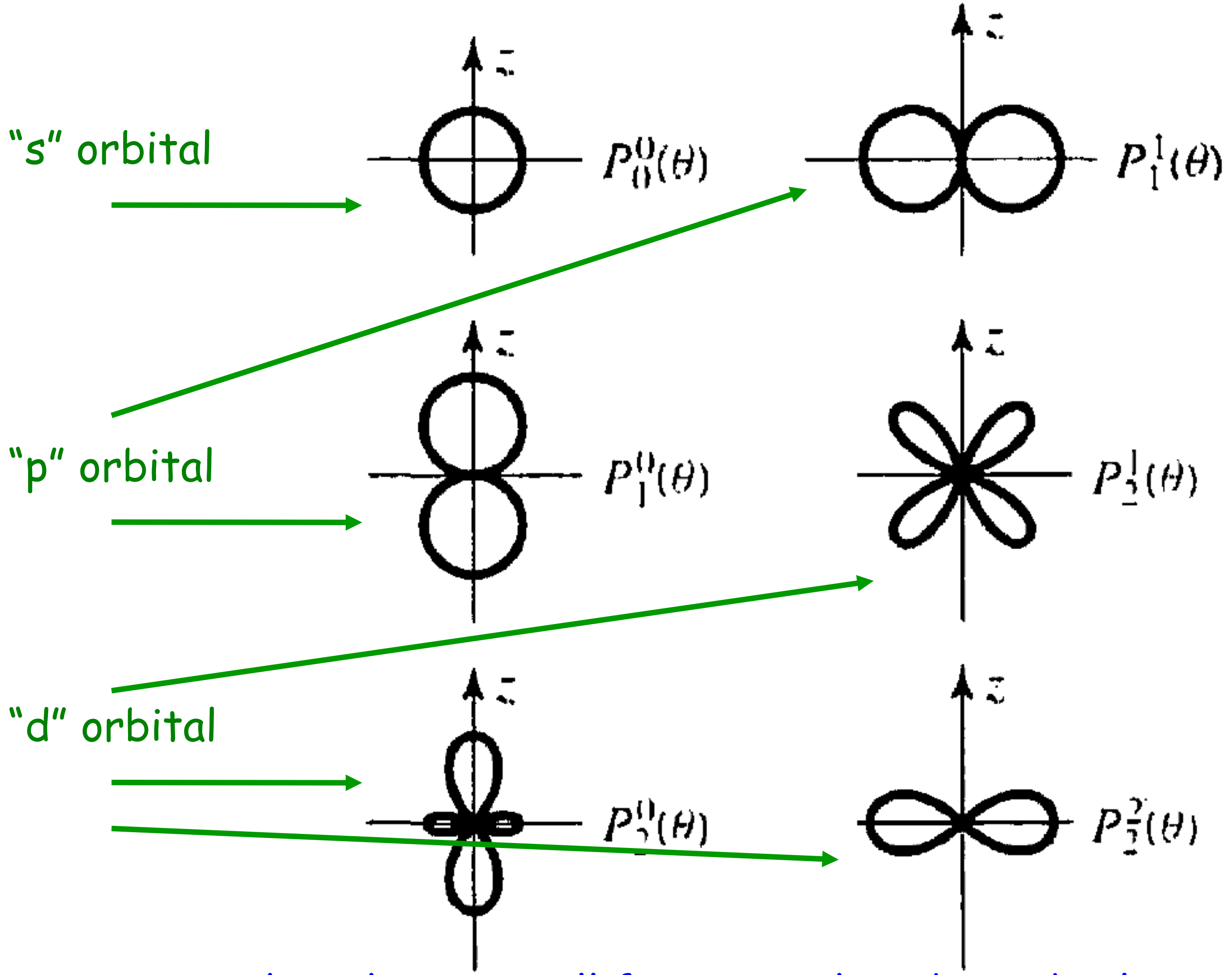
If you graph these functions, the "orbitals" that you have seen many times before since high school start appearing!



However, note that these are all functions that depend only on θ, not on ϕ. Thus, they are invariant under z axis rotations. Not the full orbitals yet.

The final "touch" to get the usual orbitals requires putting all together:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

where $\Theta(\theta) = A P_l^m(\cos\theta)$ and $\Phi(\phi) = e^{im\phi}$

with the "quantization" condition:

$$l = 0,\ 1,\ 2, \dots;\quad m = -l,\ -l+1,\ \dots,\ -1,\ 0,\ 1,\ \dots,\ l-1,\ l$$

We also need to normalize using $d^3\mathbf{r} = r^2 \sin\theta\, dr\, d\theta\, d\phi$

$$\int |\psi|^2 r^2 \sin\theta\, dr\, d\theta\, d\phi = \underbrace{\int |R|^2 r^2\, dr}_{=1} \underbrace{\int |Y|^2 \sin\theta\, d\theta\, d\phi}_{=1} = 1$$

=1 (usually Y's are normalized in tables)

For the angular component this means:

$$\int_0^{2\pi}\int_0^{\pi} |Y|^2 \sin\theta \, d\theta \, d\phi = 1$$

Remember!

By this procedure the famous **spherical harmonics** arise containing the orbitals that you know from other classes:

1"s", l=0	$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
pz	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
3"p", l=1 px, py	$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1)e^{\pm i\phi}$
	$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
five "d", l=2	$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

seven "f", l=3

Note: I am considering a graphing task to gain some extra points, details to follow

In a compact form, we finally arrive to:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} \, e^{im\phi} \, P_l^m(\cos\theta)$$

with $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$

and the orthonormality condition

$$\int_0^{2\pi} \int_0^{\pi} [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin\theta \, d\theta \, d\phi = \delta_{ll'} \delta_{mm'}$$

"l" is the azimuthal quantum number (or angular momentum)
"m" is the magnetic quantum number (or z-axis projection of the angular momentum)

4.1.3: The Radial Equation

For the angular component we are DONE. But the radial portion depends on $V(r)$, changing from problem to problem.

Reminder:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R$$

Before proceeding, another redefinition!

$$u(r) = r\,R(r)$$

$$dR/dr = d[u(r)/r]/dr = (1/r)(du/dr) - u(r)/r^2$$

$$d/dr[\,r^2 dR/dr] = r\, d^2u(r)/dr^2$$

It is indeed a simplification! (check formula)

The new radial equation becomes … (make sure you **do the math** to prove that this is correct; you have to multiply all by $-\hbar^2/2mr$)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Mathematically identical to the 1D old problem (if r->x, u->ψ) with an effective potential that includes a centrifugal term:

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

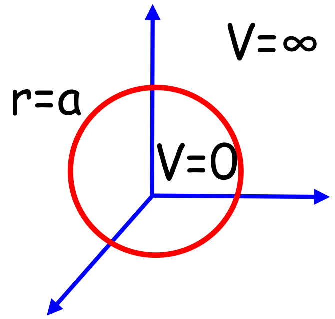
Normalization becomes

$$\int_0^\infty |u|^2\, dr = 1$$

[because $u(r) = r\, R(r)$]

Example 4.1: infinite spherical well

$$V(r) = \begin{cases} 0, & \text{if } r \le a \\ \infty, & \text{if } r > a \end{cases}$$



(Note: in *HW7* you will solve the infinite cubic well)

Steps very similar to 1D. Same "*k*" etc., but with a centrifugal component

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2\right]u \qquad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

Difference between 1D and 3D equations

If l=0, then it is the exact **same** Sch. Eq. of the 1D infinite square well! We know the general solution:

$$\frac{d^2u}{dr^2} = -k^2u \;\Rightarrow\; u(r) = A\sin(kr) + B\cos(kr)$$

But the boundary conditions are different. The condition u(r=a)=0 is as before. But u(r=0) is a bit different.

The true function we need is R(r) = u(r)/r. Thus, we must choose *B*=0 to avoid a divergence at r=0
A nonzero "A" is ok because when r→ 0, sin(kr)/kr = 1.

Then, at "the end of the day" it is all the same as in 1D:
sin(ka)=0 → *ka*=Nπ, with
N=1,2,3, … →

$$E_{N0} = \frac{N^2\pi^2\hbar^2}{2ma^2}$$

Now we have to place all together!

In general: $$\psi_{Nlm}(r,\theta,\phi) = R_{Nl}(r)Y_l^m(\theta,\phi)$$

$$R_{Nl}(r) = u_{Nl}(r)/r$$

For l=0: $Y_0^0(\theta,\phi) = 1/\sqrt{4\pi}$

for l=0, $u_{Nl=0}(r) = A\sin(kr)$ with normalization $A = \sqrt{2/a}$

Then, the final answer for arbitrary N, l=0, m=0 is:

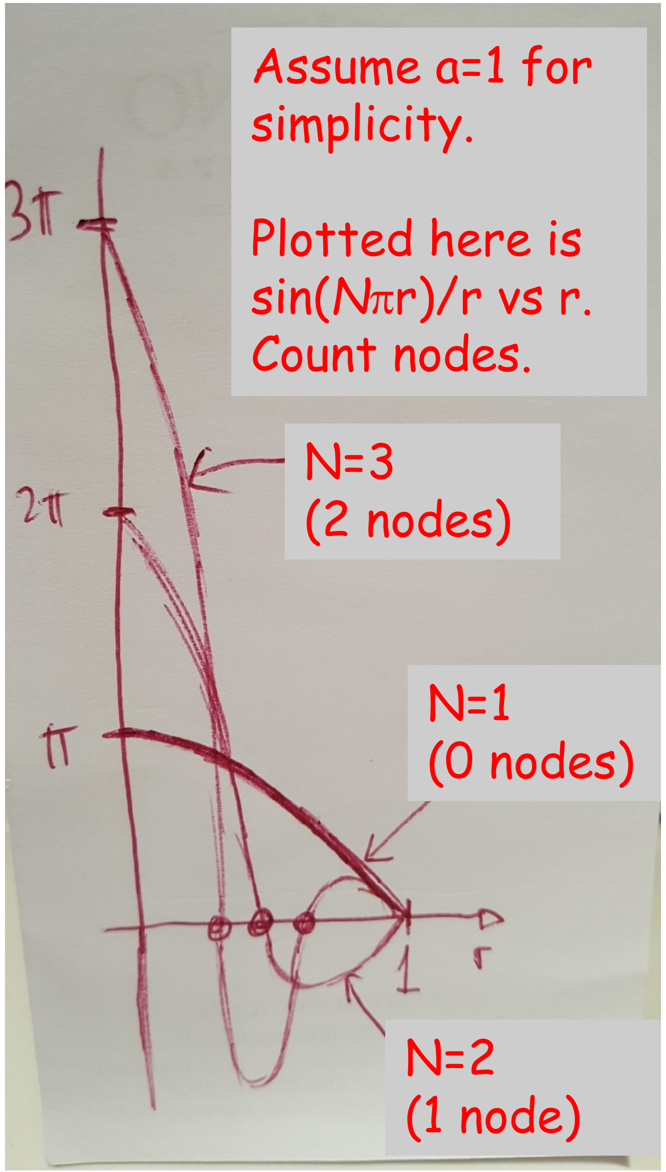
$$\psi_{N00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(N\pi r/a)}{r}$$

Common error: forgetting this r.

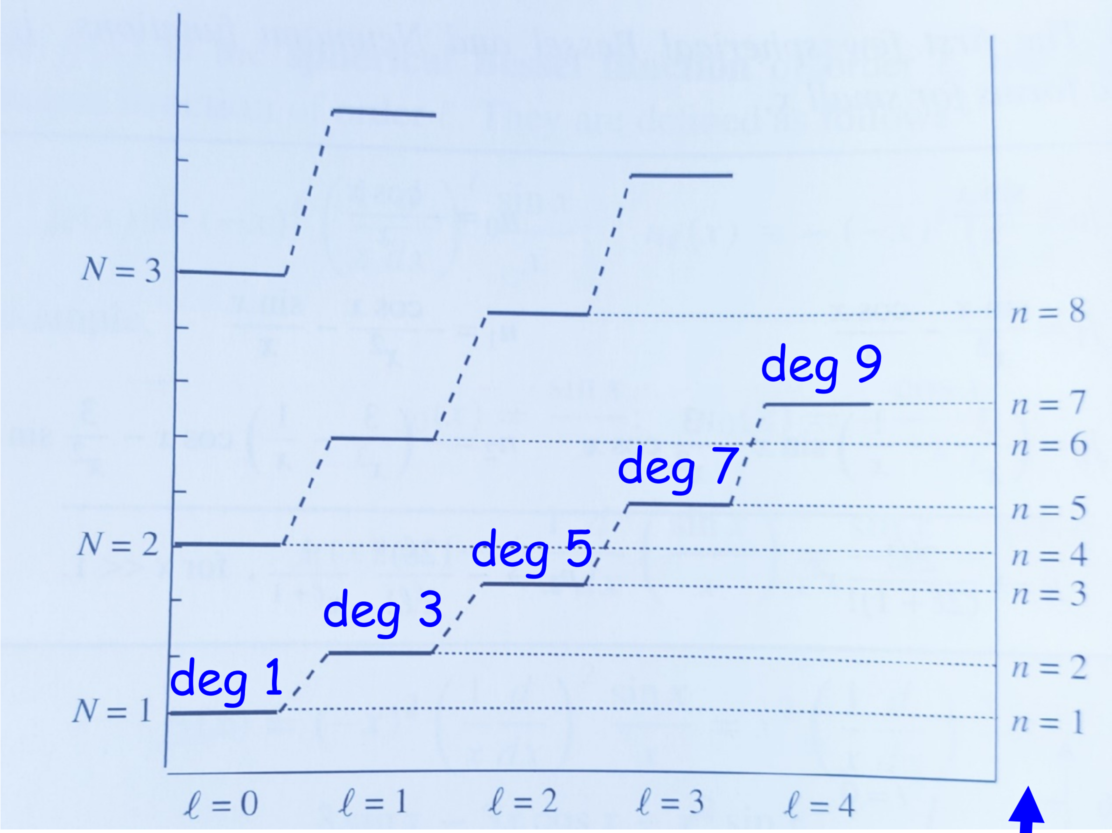
$$\psi_{N00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(N\pi r/a)}{r}$$

These l=0 wave functions have no angular dependence i.e. they are spheres (the spherical harmonic is a constant). Only r dependence for l=0.

But they have nodes in the r axis [for index *N*, there are *N-1* nodes (i.e. spherical surfaces where the wave function vanishes; kind of "onions" made of positive and negative spheres)].



We have to start thinking in terms of multiple "quantum numbers" and the labels become complicated.



For the "spherical well" we have to use the labels *N* and *l*. For each *l* (such as 0,1,2,…), then *N*=1,2,3, … labels solutions from the bottom up

We can also count with a single index "n", but doing so is not illuminating.

Here each level has a degeneracy 2*l*+1 due to m