Quantum Physics 1

Class 21

- We have found the angular solutions to the Schrodinger equation for any spherically symmetric potential.
- Now let's find the radial solutions for two cases.

The *r* part of the 3D TISE

$$-r^2\frac{\hbar^2}{2m}\frac{\partial^2(rR)}{\partial r^2}+r^2(V-E)(rR)=-l(l+1)$$

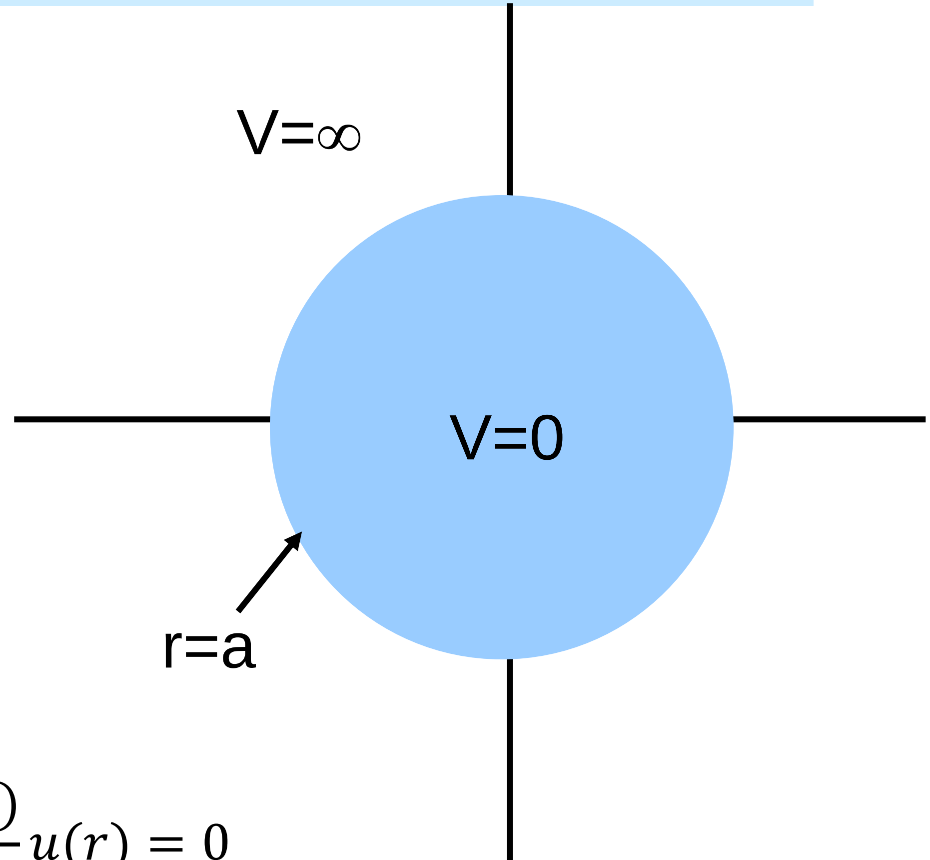
The R equation can be simplified by letting $u(r) = rR$.

$$-\frac{\partial^2(u(r))}{\partial r^2}+\frac{l(l+1)}{r^2}u(r)+\frac{2m}{\hbar^2}(V-E)u(r)=0$$

R must finite, continuous, and smooth,

so u(r) must be continuous and smooth and go to zero at r=0.

Spherical infinite square well (SISW)



$$V = \begin{cases} 0 & r < a \\ \infty & r \geq a \end{cases}$$

inside

$$\frac{\partial^2(u(r))}{\partial r^2} + \frac{2m}{\hbar^2}(E)u(r) - \frac{l(l+1)}{r^2}u(r) = 0$$

outside

$$u(r) = 0$$

SISW: solution for *l*=0

$$\frac{\partial^2(u(r))}{\partial r^2} + k^2 u(r) = 0$$

$$u(r) = A\sin k\,r + B\cos k\,r$$

$= A\sin k\,r$ because u must $= 0$ at r=0

Boundary condition at a gives: $k_n = \dfrac{n\pi}{a}$

$$R(r) = \frac{u(r)}{r} = \frac{A\sin\frac{n\pi r}{a}}{r};$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2ma^2} = \frac{2\hbar^2 n^2 \pi^2}{md^2}$$

SISW: *any l*

$$\frac{\partial^2(u(r))}{\partial r^2} - \frac{l(l+1)}{r^2}u(r) + k^2 u(r) = 0$$

Let's try to simplify by looking at
asymptotic behavior at r $\rightarrow 0$

$$\frac{\partial^2(u(r))}{\partial r^2} - \frac{l(l+1)}{r^2}u(r) = 0$$

Try a guess of $u(r) = r^n$

$n(n-1)r^{n-2} - l(l+1)r^{n-2} = 0$

which will be true if $n = -l$ or $n = (l+1)$

The negative n solution is unphysical,
so $n = (l+1)$ it is.

SISW: any l solutions

Factoring out the asymptotic behavior and assuming a series solution:

$$u(r) = \sum_{\beta=0}^{\infty} a_\beta r^{\beta+l+1}$$

$$\frac{\partial^2(u(r))}{\partial r^2} - \frac{l(l+1)}{r^2} u(r) + k^2 u(r) = 0$$

$$\sum_{\beta=2}^{\infty} a_\beta r^{\beta+l-2} (\beta + l + 1)(\beta + l) - l(l+1) \sum_{\beta=0}^{\infty} a_\beta r^{\beta+l-2}$$

$$+ k^2 \sum_{\beta=0}^{\infty} a_\beta r^{\beta+l} = 0$$

matching up orders of r^β:

$$a_{\beta+2}(\beta + l + 3)(\beta + l + 2) - l(l+1) a_{\beta+2} + k^2 a_\beta = 0$$

$$((\beta + 2) + (l + 1))((\beta + 2) + l) - l(l+1)$$

$$= [(\beta + 2) + (2l + 1)](\beta + 2)$$

$$a_{\beta+2} = \frac{k^2}{(2l + \beta + 3)(\beta + 2)} a_\beta$$

SISW: any *l* solutions

So now we have: $R_l(r) = r^l \sum_{\beta=0}^{\infty} a_\beta r^\beta$ with $a_{\beta+2} = \frac{k^2}{(2l+\beta+3)(\beta+2)} a_\beta$

which forms two possible series in β.
The even series starts with a_0.

Letting $2b = \beta$ we now have: $R_l(r) = r^l \sum_{b=0}^{\infty} a_{2b} r^{2b}$

with $a_{2(b+1)} = \frac{k^2}{4\left(l + b + \frac{3}{2}\right)(b+1)} a_{2b}$

which can be recognized as the series for
spherical Bessel functions: $j_l(z)$

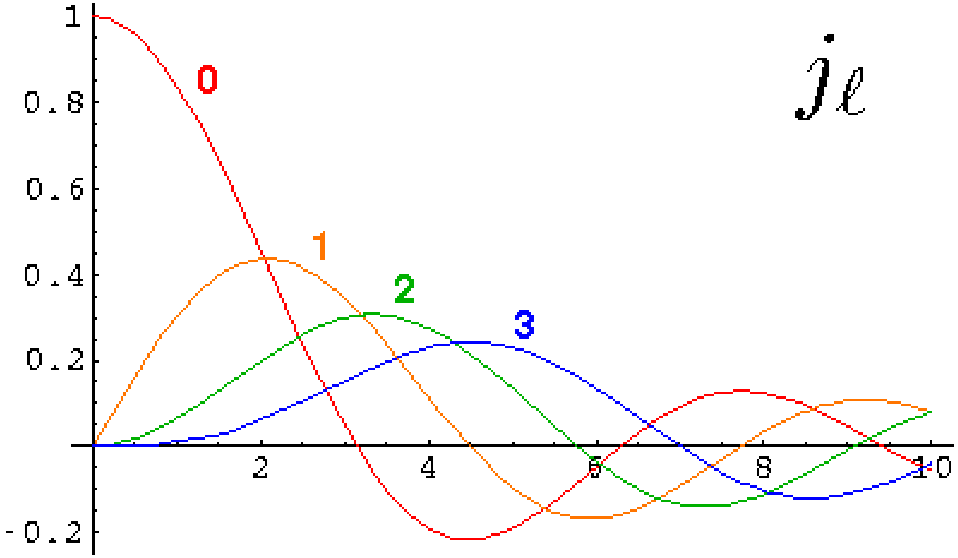
SISW: any l solutions

$$u(r) = \sum_{n=0}^{\infty} a_n r^{\frac{n}{2}+l}$$

$$R_l(r) = N j_l(r)$$

$$j_l(z) \equiv \sqrt{\frac{\pi}{2z}} J_{l+1/2}(z)$$

The other independent solution leads to terms that blow up at r=0 and is therefore unphysical.



$J_{l+1/2}(z)$ is the regular Bessel function of half order.

Spherical Bessel functions

The series for spherical Bessel functions looks complicated but it simplifies to well known functions:

$$j_0(z) = \frac{\sin z}{z}$$

$$j_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z}$$

$$j_2(z) = \left(\frac{3}{z^3} - \frac{1}{z}\right)\sin z - \frac{3}{z^2}\cos z$$

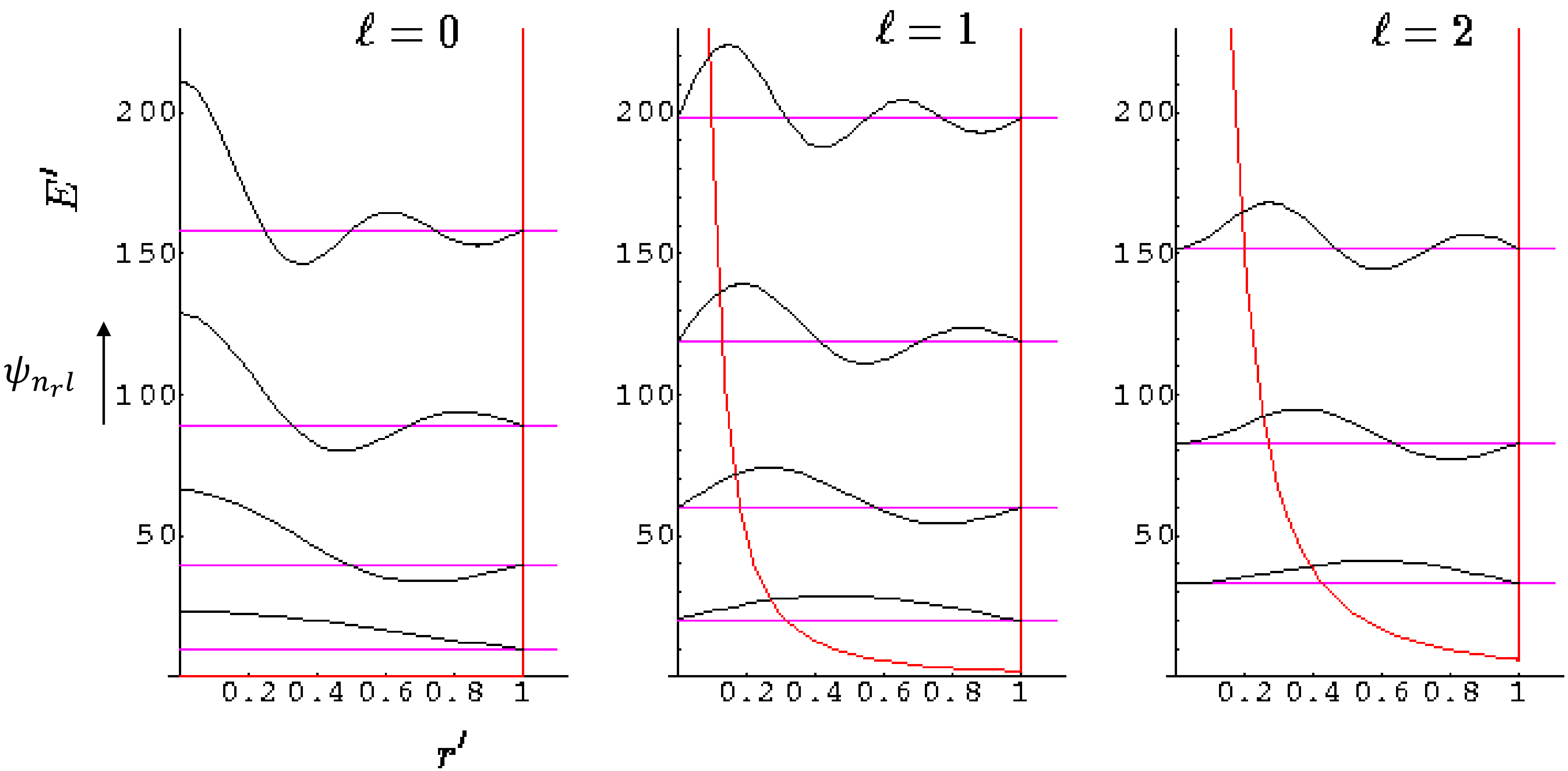
SISW: general solution

Solutions to the infinite well require that
$j_l(ka) = 0$
so for each l we have many possible solutions for k which we will label n_r.

$$\psi_{n_r l m_l}(r, \theta, \varphi) = \frac{\sqrt{2}}{\left|j_{l+1}\left(k_{n_r} a\right)\right|} j_l\left(k_{n_r} r\right) Y_{lm}(\theta, \varphi)$$

where the k_{n_r} are the zeroes of $j_l(k_{n_r} a)$

SISW: solutions



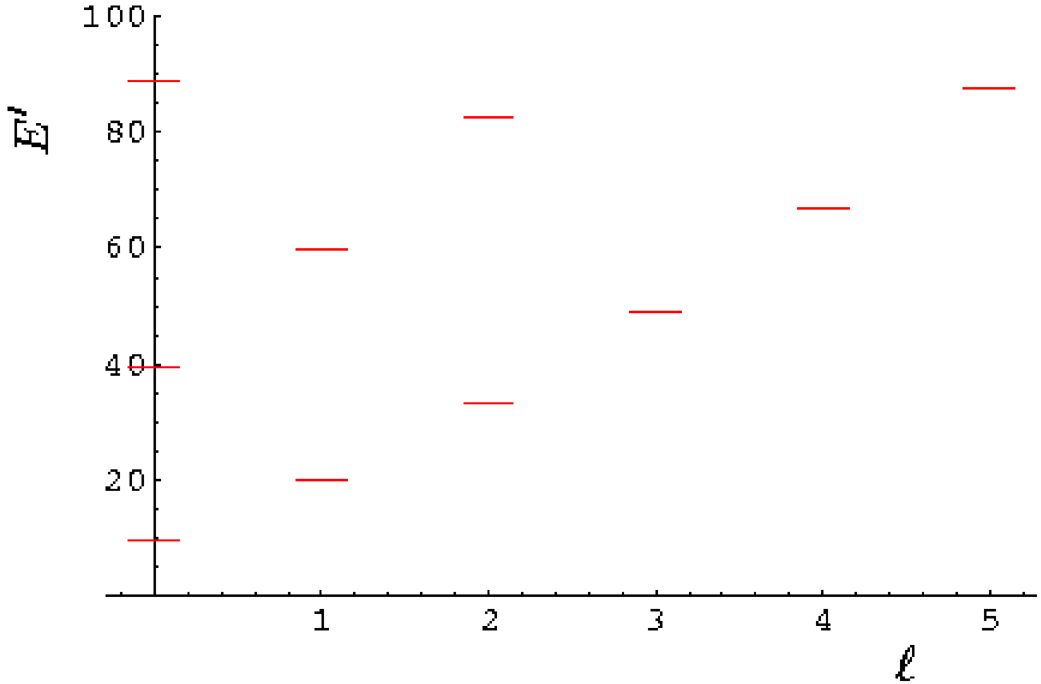
The red line above is the effective potential due to the non-zero angular momentum term.

SISW: solutions

l	n_r	$k_{n_r}a$
0	0	π
1	0	4.5
2	0	5.8
0	1	2π
3	0	7
1	1	7.7

- Here is a table of roots of spherical Bessel functions.
- Note that the $l=0$ solutions are multiples of π, as you expect for the sine function.

SISW: Energy levels



E' is in units of $\dfrac{\hbar^2}{2ma^2}$

The radial equation for the Coulomb potential

$$-\frac{\partial^2(u(r))}{\partial r^2}+\frac{l(l+1)}{r^2}u(r)+\frac{2m}{\hbar^2}(-\frac{e^2}{4\pi\varepsilon_0 r})u(r)=Eu(r)$$

Let $\rho=\frac{r}{a_0}$ where $a_0 = 4\pi\varepsilon_0\frac{\hbar^2}{me^2}$

Let $\varepsilon=\frac{E}{E_R}$ where $E_R=\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2}$

and so: $-\frac{\partial^2(u(\rho))}{\partial\rho^2}+\frac{l(l+1)}{\rho^2}u(\rho)+\frac{2}{\rho}u(\rho)=\varepsilon u(\rho)$

l=0 + Coulomb potential

Let's look at forms of the radial equation for $l = 0$ in the large r limit:

$$\rho \to \infty \quad \frac{d^2u}{d\rho^2} + \varepsilon u = 0 \quad \Rightarrow u \propto e^{-\sqrt{\varepsilon}\rho}$$

Remember that ε is negative because these are bound states and the potential is negative.

We now search for solutions to the full equation using the polynomial expansion approach.

The lowest order polynomial with the right behavior as $\rho \to 0$ is $u(\rho) = re^{-\sqrt{\varepsilon}\rho}$.

(Think about the number of roots for a polynomial.)

l=0 Coulomb solutions

Substituting back into the original diff eq

$$-\frac{\partial^2\left(\rho e^{-\sqrt{\epsilon_1}\,\rho}\right)}{\partial\rho^2}+\frac{2}{\rho}\rho e^{-\sqrt{\epsilon_1}\,\rho}=\varepsilon\rho e^{-\sqrt{\epsilon_1}\,\rho}$$

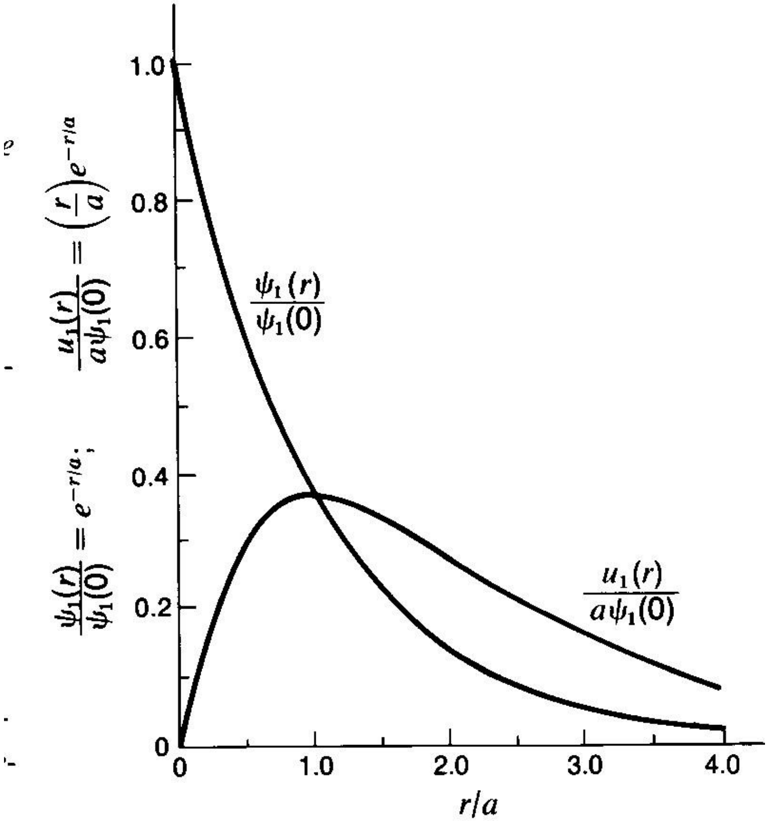
Taking derivatives, dividing out $e^{-\sqrt{\epsilon_1}\,\rho}$.

$$-(-\sqrt{\varepsilon_1}-\varepsilon_1\rho)-1=\varepsilon_1\rho$$

$$\Rightarrow \quad \varepsilon_1=-1$$

$$E_1=\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2}$$

$= -13.6eV$ (Rydberg)



Higher order l=0 Coulomb solutions

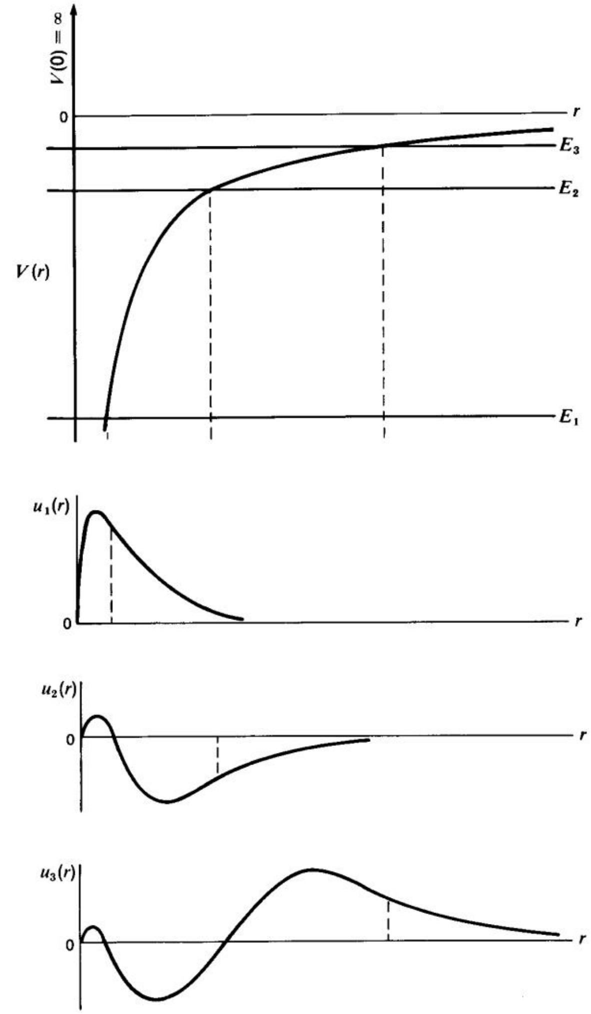
We look for solution of increasing polynomial order in similar manner and can find:

$$u_2 \propto [2\rho - \rho^2]e^{-\sqrt{\epsilon_2}\rho}$$
$$with\,\epsilon_2 = \frac{\epsilon_1}{4}$$

$$u_3 \propto [27\rho - 18\rho^2 + 2\rho^3]e^{-\sqrt{\epsilon_3}\rho}$$
$$with\,\epsilon_3 = \frac{\epsilon_1}{9}$$

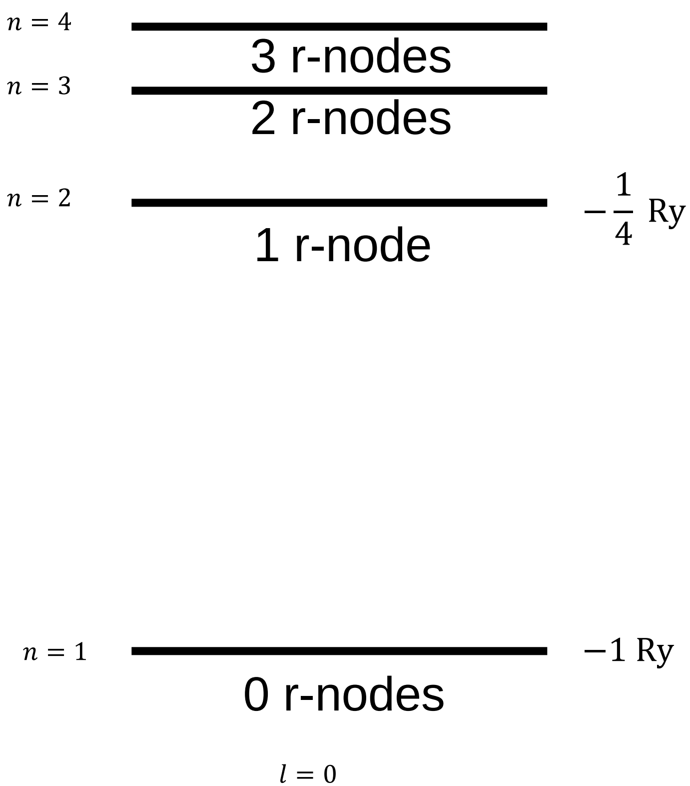
and we find that the energies are:

$$E_n = \frac{E_1}{n^2}$$

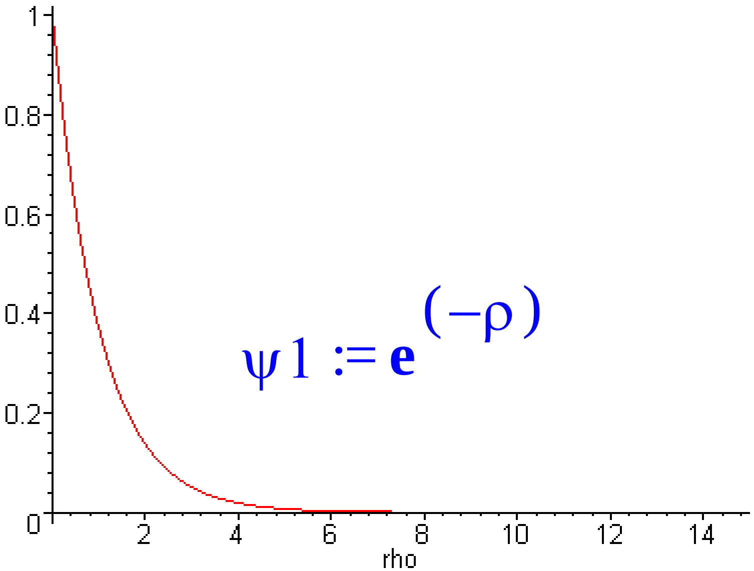


Energy levels for solutions so far (1)

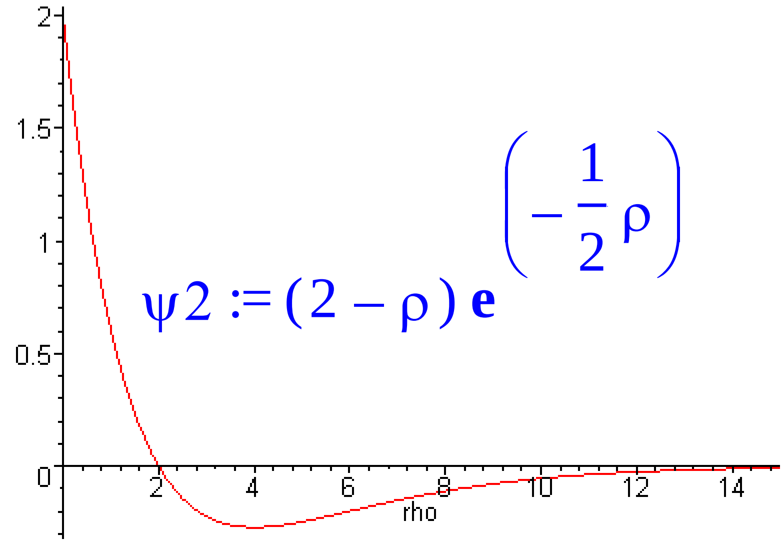
$$E_n = \frac{-1}{n^2}$$



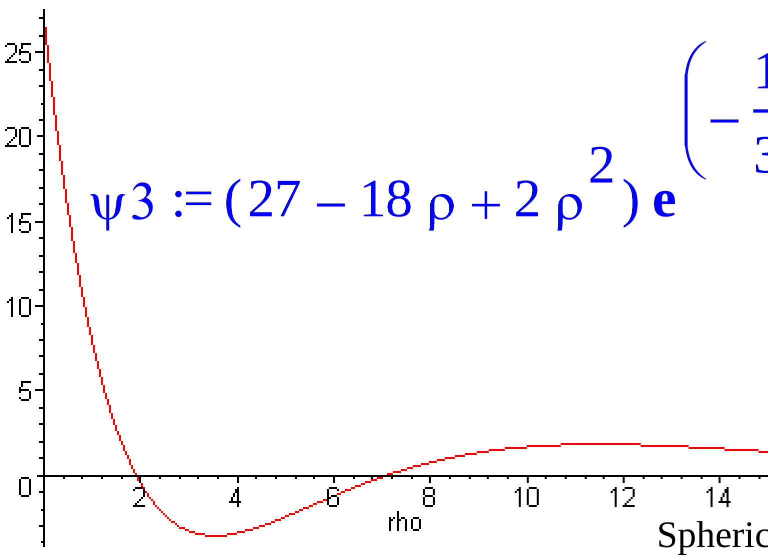
The l=0 wavefunctions



$$\psi 1 := \mathbf{e}^{(-\rho)}$$



$$\psi 2 := (2 - \rho)\, \mathbf{e}^{\left(-\frac{1}{2}\rho\right)}$$



$$\psi 3 := (27 - 18\,\rho + 2\,\rho^2)\, \mathbf{e}^{\left(-\frac{1}{3}\rho\right)}$$

3 D viewer (Falstad)

Probability of finding electron at r: radial probability

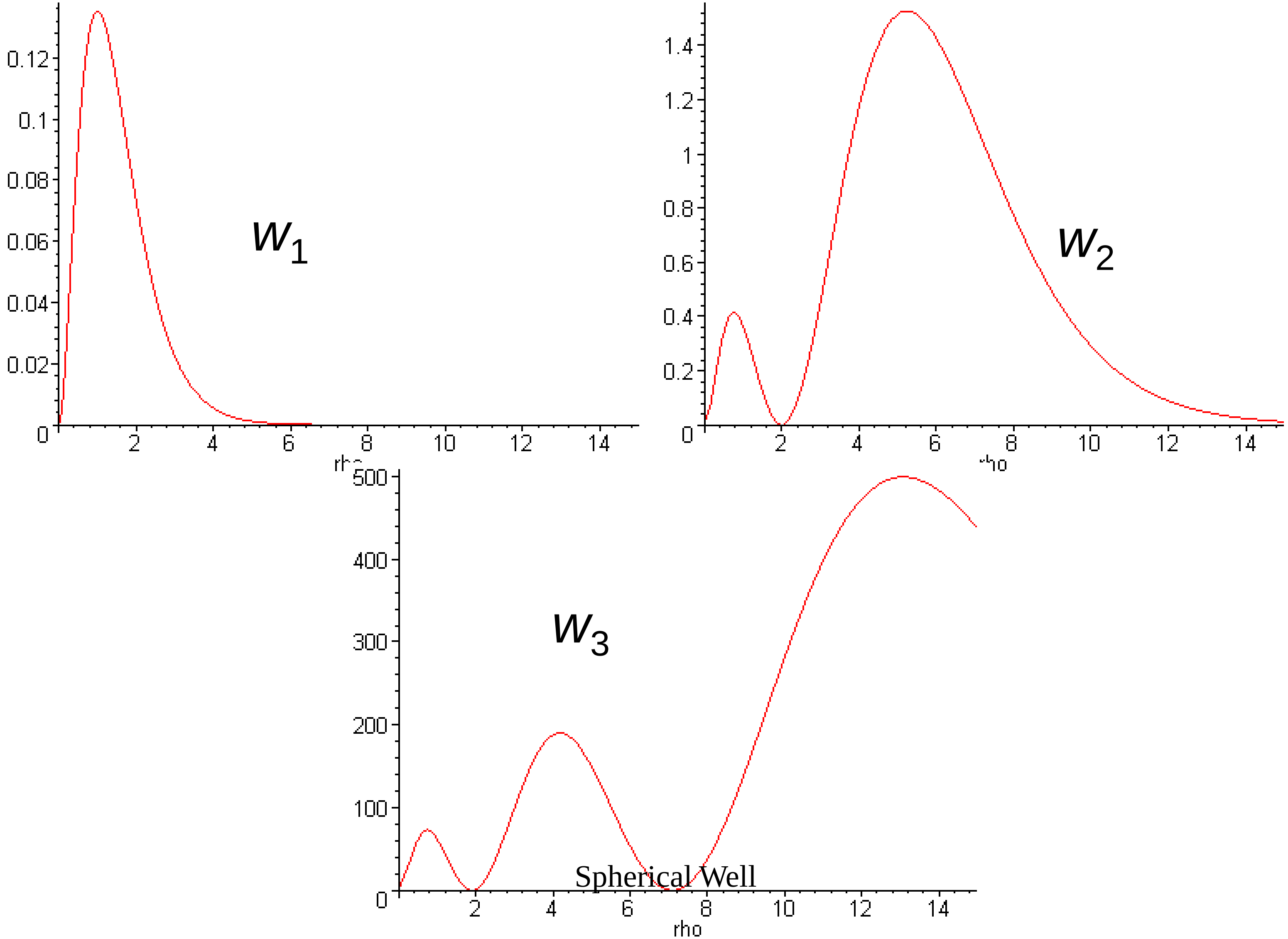
$\Psi^*\Psi$ is the probability of finding the electron in a particular position. If we want the probability of finding the electron at a distance between r and r+dr from the nucleus, then we have to integrate $\Psi^*\Psi$ around the sphere.

$$w(\rho) = \int_0^{2\pi}\int_0^{\pi} r^2 \sin\theta\, R^2(\rho)\, Y^*_{lm}(\theta,\varphi) Y_{lm}(\theta,\varphi) d\theta d\varphi$$

For l=0, $w(\rho) = 4\pi r^2 R^2 = 4\pi u^2$

Radial Probability Density$\equiv \Psi^*\Psi 4\pi r^2$

Radial probability density for l=0 solutions



Information from the radial probability density – most likely distance

At what distance is the electron most likely to be found?

For the $n = 1, l = 0$ state:

$$\frac{d(\rho^2 R^2)}{d\rho} = \frac{du^2}{d\rho} = 2\frac{du}{d\rho} = 2\frac{d(\rho e^{-\rho})}{d\rho}$$

$$= 2(e^{-\rho} - \rho e^{-\rho}) = 0$$

$\rho = 1$!!!

$r = a_0 = 0.5$ Angstroms

Asymptotic Radial solutions for *l*>0

$$-\frac{\partial^2(u(\rho))}{\partial\rho^2}+\left(\frac{l(l+1)}{\rho^2}-\frac{2}{\rho}\right)u(\rho)=\varepsilon u(\rho)$$

For large ρ: $\dfrac{d^2u}{d\rho^2}\approx-\varepsilon u \quad \Rightarrow \quad u\propto e^{-\sqrt{\varepsilon}\rho}$

For small ρ: $\dfrac{d^2u}{d\rho^2}\simeq\dfrac{l(l+1)}{\rho^2}u \quad \Rightarrow \quad u\propto\rho^{l+1}$ or ρ^{-l}

∴ Guess solutions of the form: $u\propto\rho^{l+1}e^{-\sqrt{\varepsilon}\rho}$
Note that this guessed solution corresponds to a radial solution with no nodes.

If we plug this guess back into the full equation, we get

$$\varepsilon=-\frac{1}{(l+1)^2}.$$

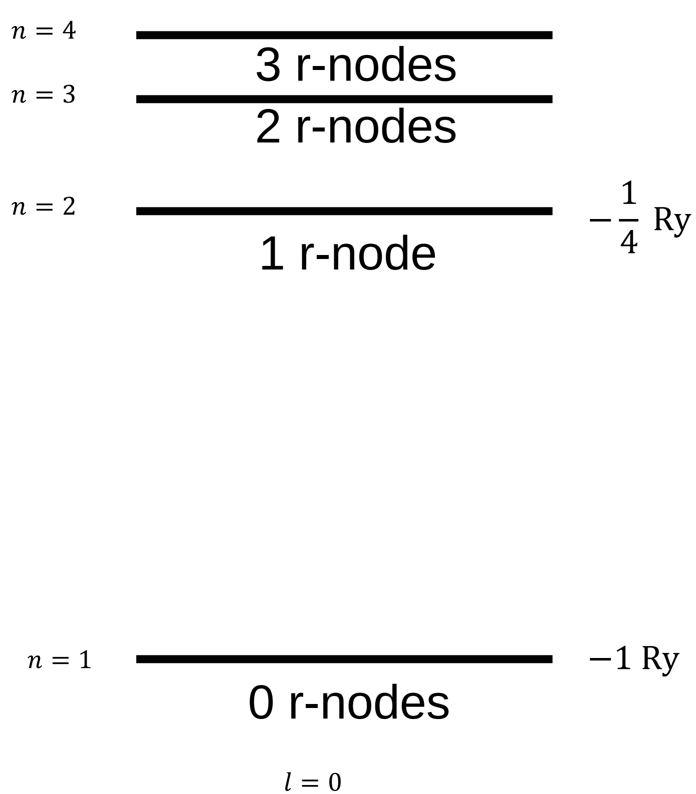
The energy solution we have found corresponds to the l=0 solution for $n=l+1$.

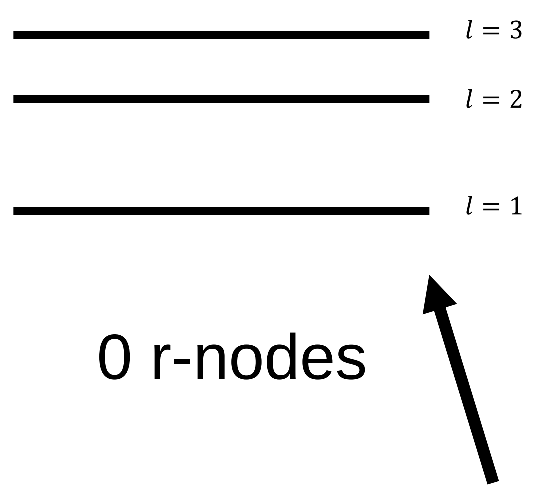
A pattern in the solutions

n	l=0	l=1 one θ node	l=2
1	$e^{-\rho}$ no r nodes	no sol'n	no sol'n
2	$(1-\frac{\rho}{2})e^{-\rho/2}$ one r node	$\rho e^{-\rho/2}\cos\theta$ no r nodes	no sol'n
3	$(27-18\rho$ $+2\rho^2)e^{-\rho/3}$ two r nodes		$\rho^2 e^{-\rho/3} Y_{2m}$ no r nodes

Energy levels for solutions so far

$$E_n = \frac{-1}{n^2}$$





Because the energies line up,
these states are labeled
by the corresponding n number.

What about solutions with more r-nodes?

Let's look at a solution with one r–node:

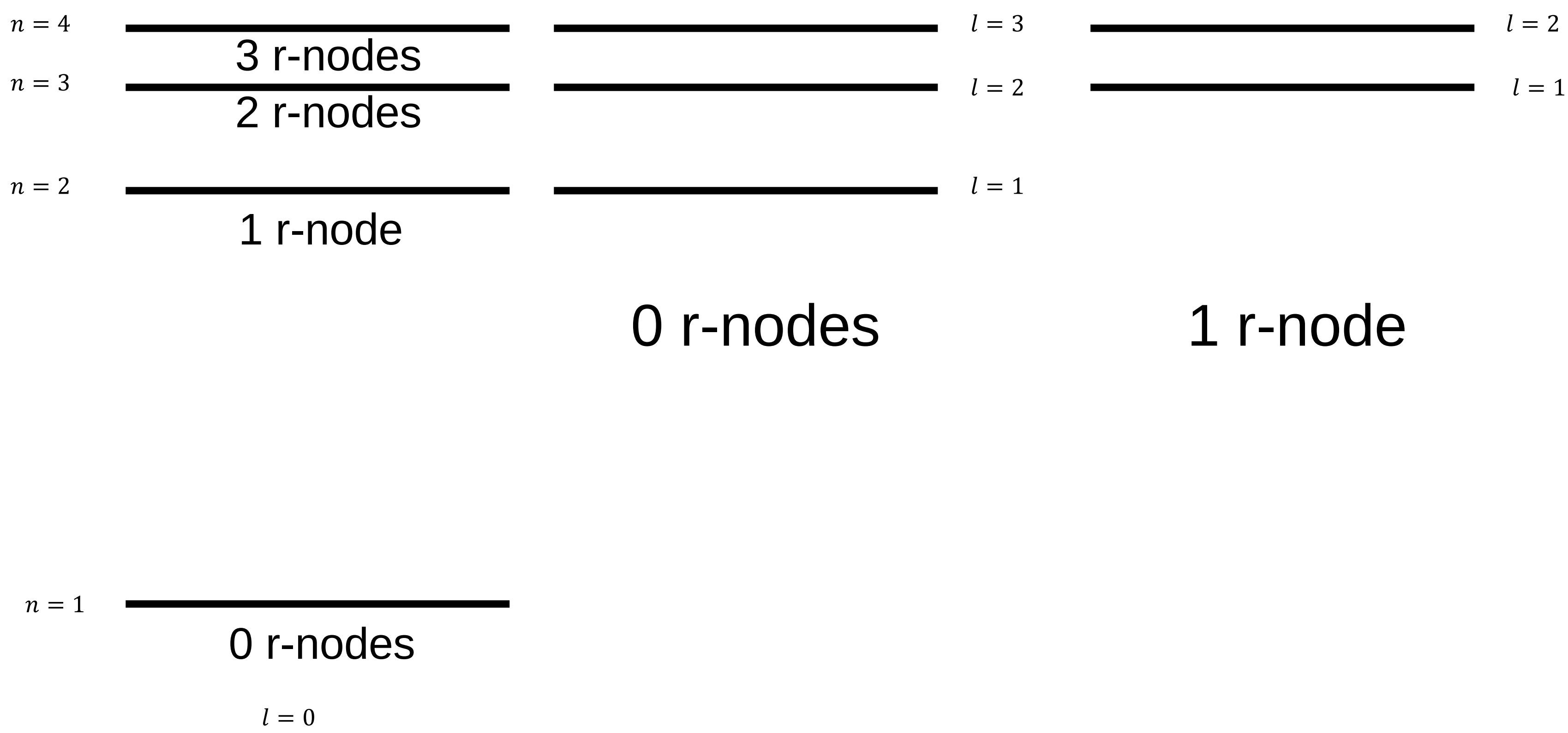
Guess: $u(\rho) = (c_0 - c_1\rho)\rho^{l+1}e^{-\rho\sqrt{\varepsilon}}$

We find that this can be a solution if: $\varepsilon = -\dfrac{1}{(l+2)^2}$.

This is the same energy as our nodeless solution with $n = l + 2$.

Energy levels for solutions so far

$$E_n = \frac{-1}{n^2}$$



A table of the radial wavefunctions

n	l=0	l=1	l=2
1	$e^{-\rho}$	No sol'n	No sol'n
2	$(1-\frac{\rho}{2})e^{-\rho/2}$	$\rho e^{-\rho/2}$	No sol'n
3	$(27-18\rho+2\rho^2)e^{-\rho/3}$	$\rho(6-\rho)e^{-\rho/3}$	$\rho^2 e^{-\rho/3}$

Atomic energy structure

This should begin to look familiar.

- The energy levels correspond to the energies of the Bohr model.
- For n=1 energy level, only l=0 is found.
- For the n=2 energy level, only l=0 and l=1 solutions are found.
- For the n=3 level, only l=0,1,2 are found.
- In chemistry, we designate the l=0 case as *s*, l=1 as p, l=2 as *d*, and l=3 as *f*.
- Note the m_l does not affect the energy of a state because it does not appear in the radial equation.

A big summary of energy levels and quantum numbers

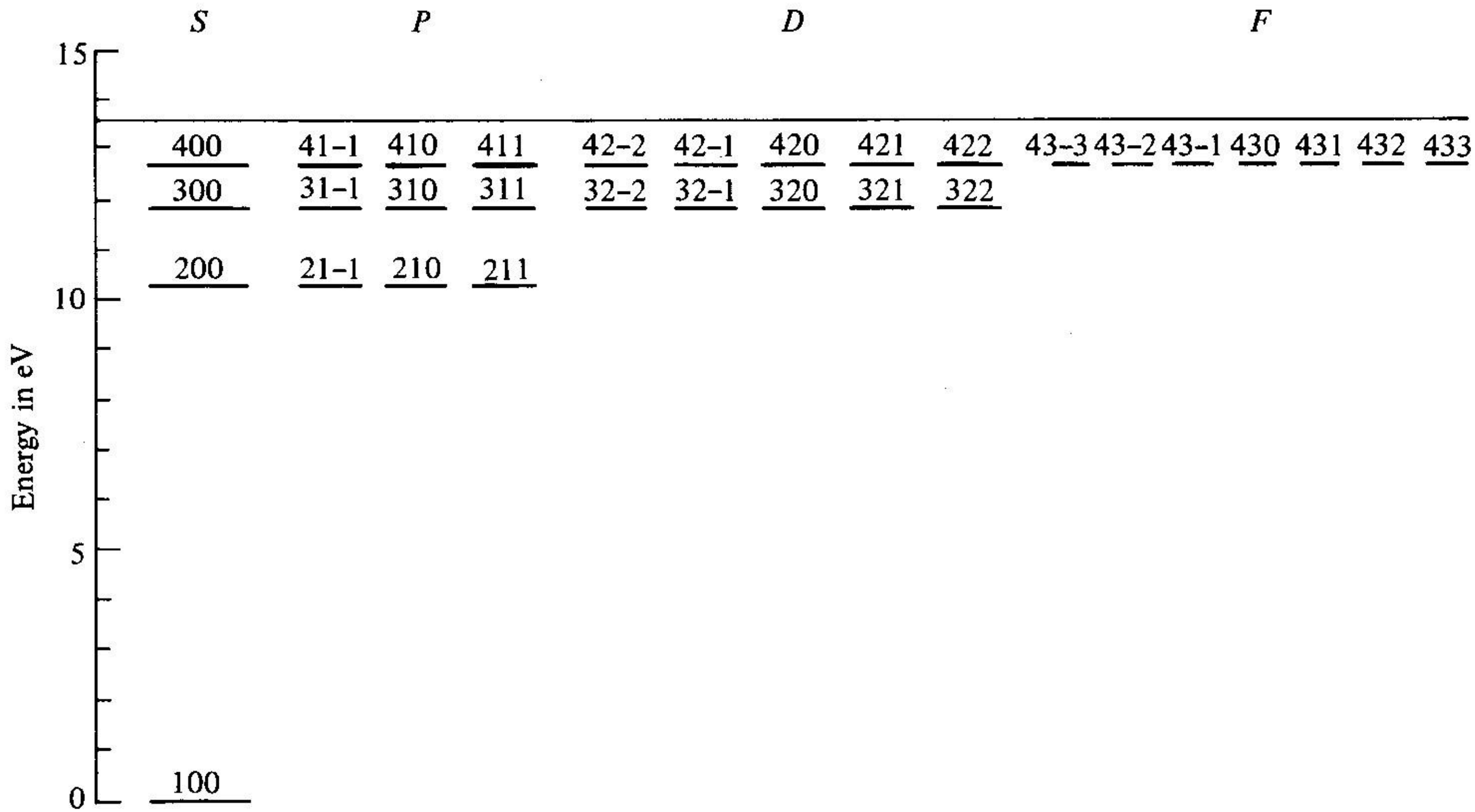


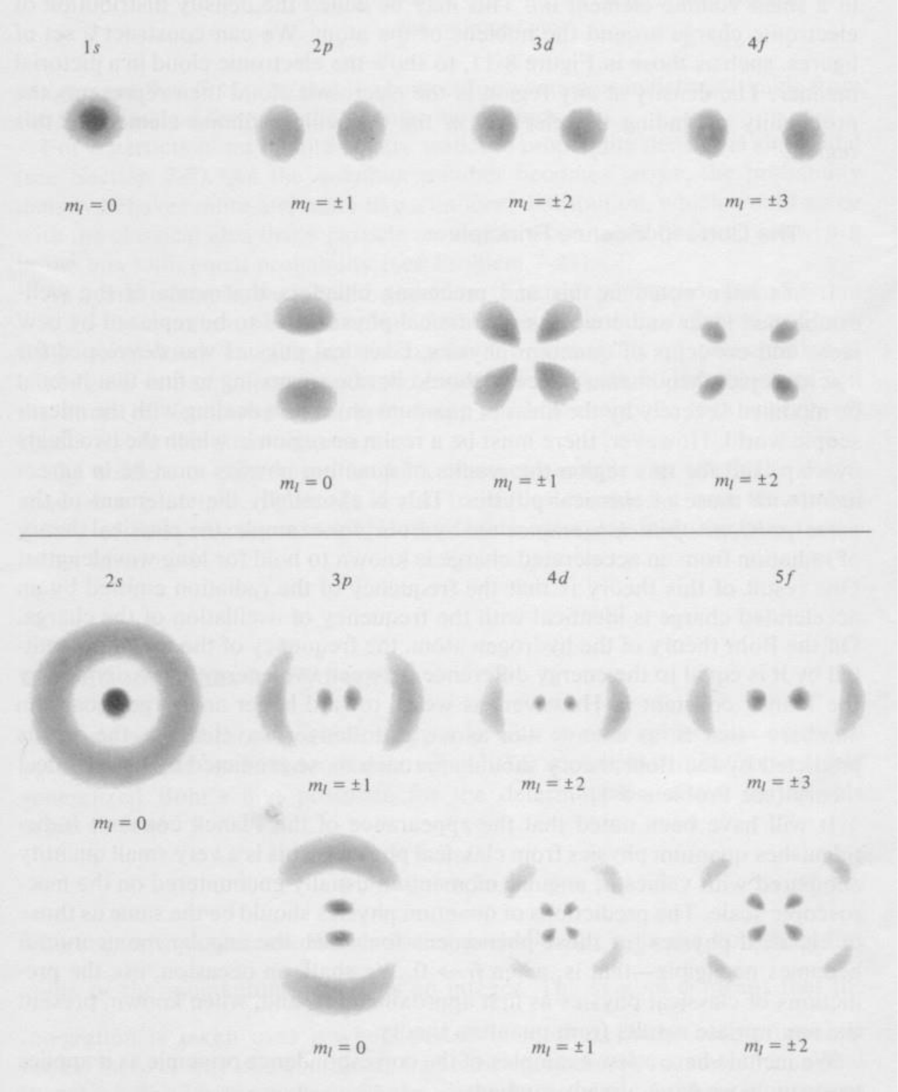
Figure 8-9 Energy-level diagram for hydrogen showing degenerate substates. Each state is denoted by the values of n, l, m_l.

(from Semat 1972)

TABLE 7.1 Some Hydrogen Atom Wave Functions from Krane, Modern Physics

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{(2a_0)^{3/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	±1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\mp\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	0	0	$\frac{2}{(3a_0)^{3/2}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	±1	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\mp\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	0	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
3	2	±1	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\mp\sqrt{\frac{15}{4}} \sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	±2	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$

A big summary of pictures of wavefunctions



(from Semat 1972)

What we observe: emission from transitions between states

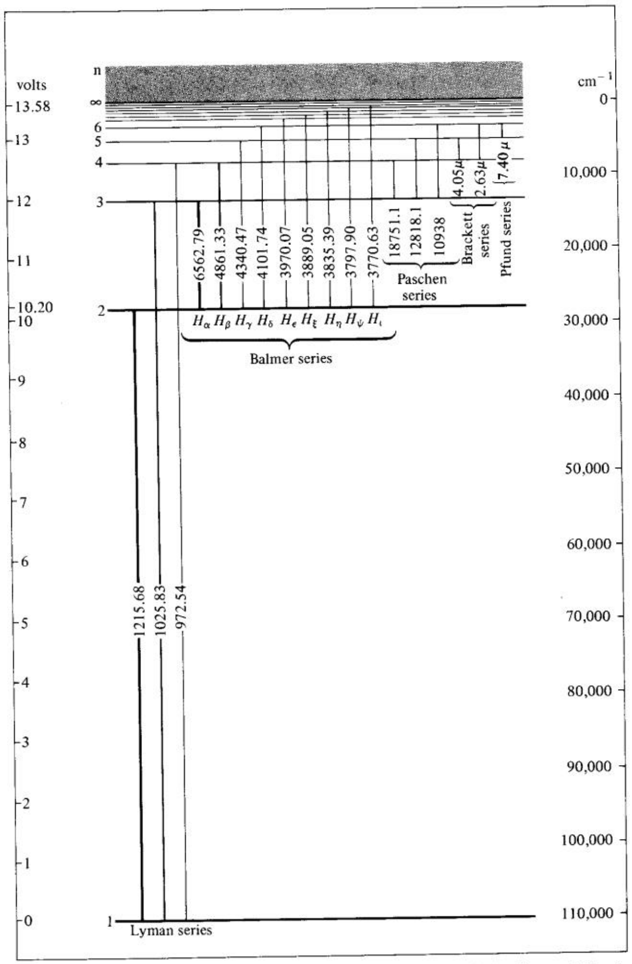


Figure 8-5 Energy-level diagram for hydrogen. Wavelengths of the lines of the Lyman, Balmer, and Paschen series are in angstroms.

$$E_{photon} = 1Ry \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Solution of the Schrodinger Equation for a Coulomb potential explains everything you were told about the H atom in your chemistry courses!!

- The Rydberg energy – 13.6 eV
- The Bohr radius – a_0~0.53 angstroms
- Energy levels: $E = E_{Rydberg}/n^2$
- Observed spectral lines:

$$\Delta E = E_{Rydberg}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

- Number of states at each energy level.
- s, p, d, f orbitals corresponding to l=1, 2, 3, 4