Consider now the excited states, starting with n=2:

$$E_2 = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV}$$

Because $n = j_{max} + l + 1$, then n=2 allows for $l=0$, $j_{max}= 1$ or $l=1$ ($m=-1,0,+1$), $j_{max}= 0$. This will be the 2s and three 2p's orbitals. Degeneracy 4 (in general, degeneracy is n^2).

(1) If $l=0$, $j_{max}= 1$, use $c_1 = [2(j + l +1 - n) / (j+1)(j+2l+2)]\, c_0$ with $n=2$, $j=0$ and $l=0$, and you get $c_1 = - c_0$ so the polynomial becomes $v(\rho)=c_0(1-\rho)$ with c_0 again used to normalize.

$$\boxed{R_{20}(r) = \frac{c_0}{2a}\left(1 - \frac{r}{2a}\right) e^{-r/2a}}$$

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

The factors 2 arise from $\rho = (1/an)\, r$.

(2) If $l=1$, $j_{max}= 0$, you get $c_1 = 0$ so the polynomial is only c_0 as it happens in the ground state.

Use the general formula $R_{nl}(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho)$ with $l=1$ and $n=2$.

$$\boxed{R_{21}(r) = \frac{c_0}{4a^2} r e^{-r/2a}}$$

The front factor comes from $\rho^2/r = (r/2a)^2/r$.

The spherical harmonics are:

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

In general, the polynomials $\nu(\rho)$ are called **associated Laguerre polynomials**

$$v(\rho) = L^{2l+1}_{n-l-1}(2\rho)$$

and there are tables with these polynomials.

Putting all together, for arbitrary *(n,l,m)* the normalized wave functions are:

$$\boxed{\psi_{nlm} = \underbrace{\sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L^{2l+1}_{n-l-1}(2r/na)\right]}_{R_{nl}(r)} Y^m_l(\theta, \phi)}$$

$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$

$$R_{40} = \frac{1}{4}a^{-3/2}\left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right)\exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}}a^{-3/2}\left(1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right)\frac{r}{a}\exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}}a^{-3/2}\left(1 - \frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2\exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}}a^{-3/2}\left(\frac{r}{a}\right)^3\exp(-r/4a)$$

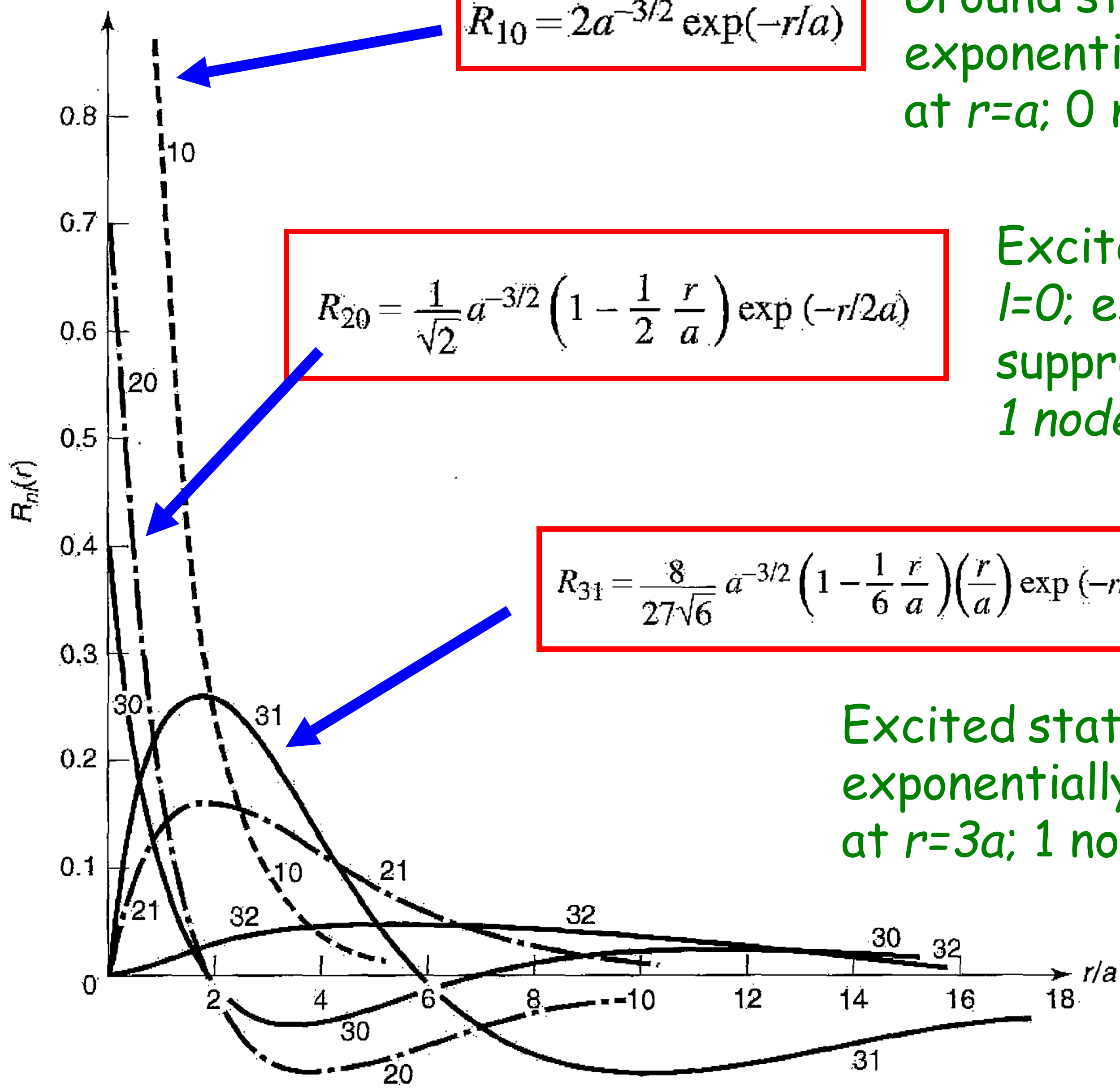
Only l=0 are nonzero at the center r=0, like in the spherical well.

3 nodes

2 nodes

1 nodes

0 nodes



$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

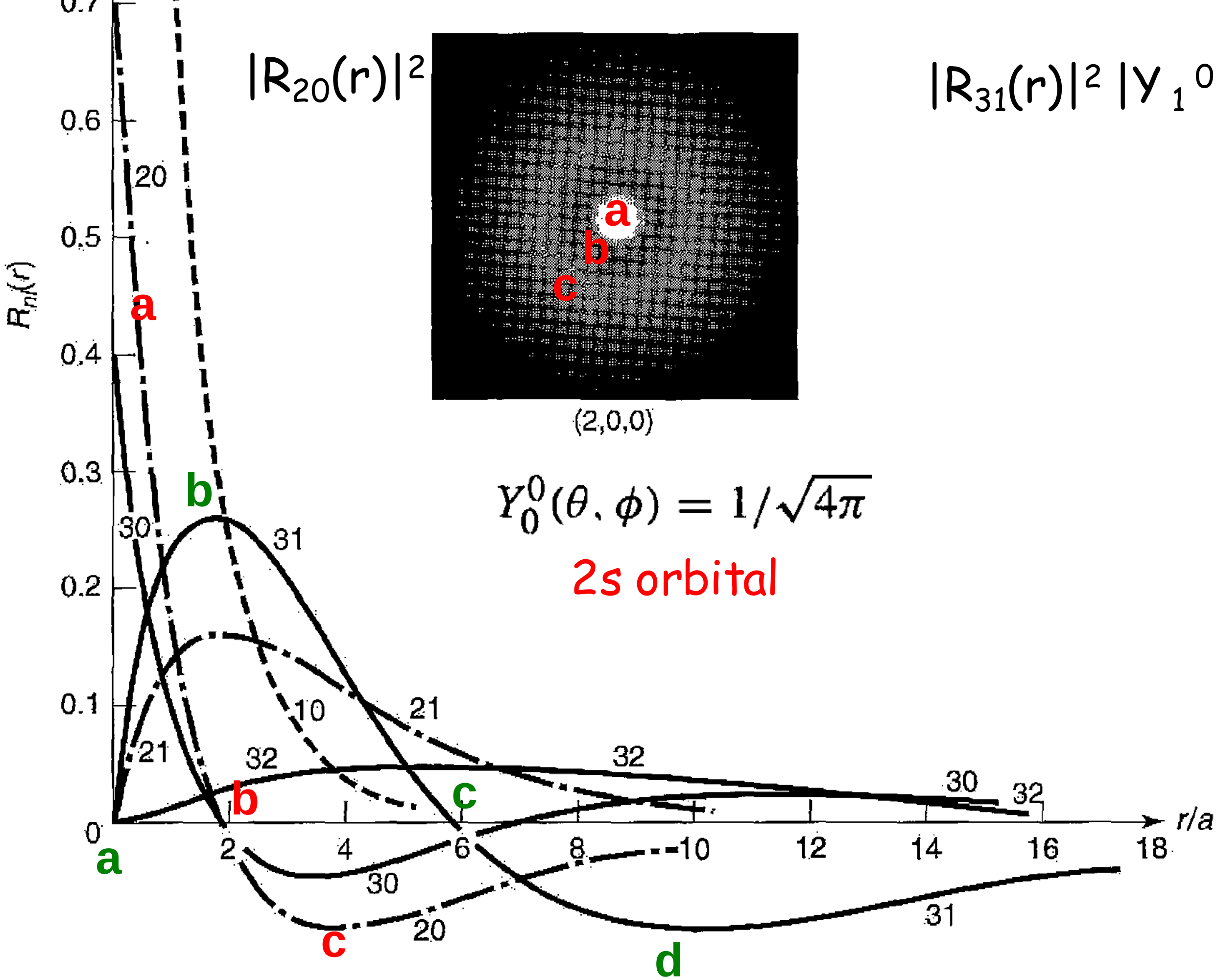
Ground state $n=1$ $l=0$; exponentially suppressed at $r=a$; 0 node

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1-\frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

Excited state $n=2$ $l=0$; exponentially suppressed at $r=2a$; 1 node.

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1-\frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

Excited state $n=3$ $l=1$; exponentially suppressed at $r=3a$; 1 node.



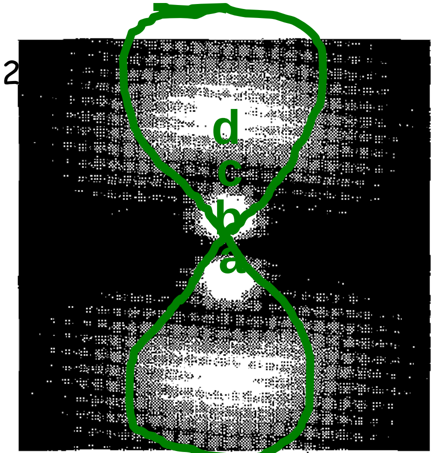
$|R_{20}(r)|^2$

(2,0,0)

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

2s orbital

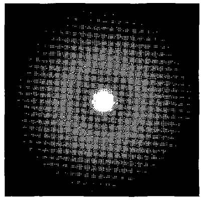
$|R_{31}(r)|^2 \ |Y_1^{\,0}|^2$



(3,1,0)

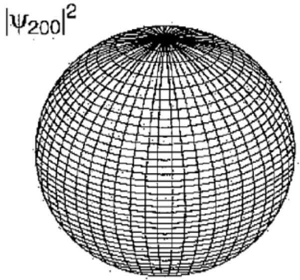
$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$3p_z$ orbital

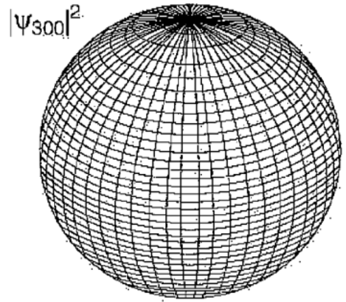


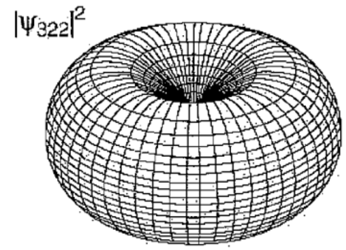
(2,0,0)

2s orbital

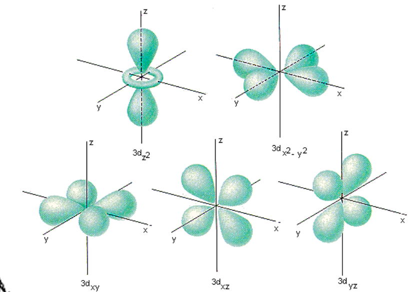


3s orbital

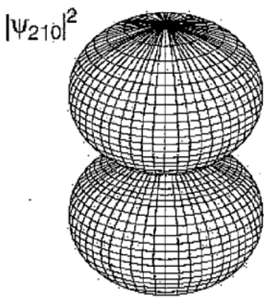




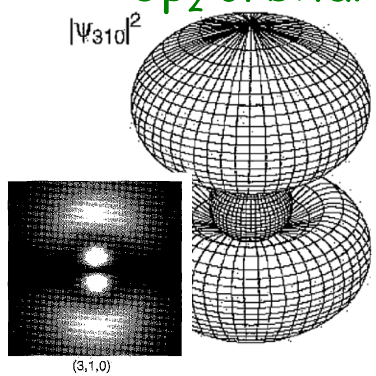
linear combination of canonical 3d orbitals: x2-y2, 3z2-r2, xy,yz,zx

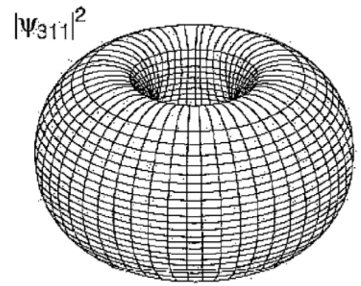


$2p_z$ orbital



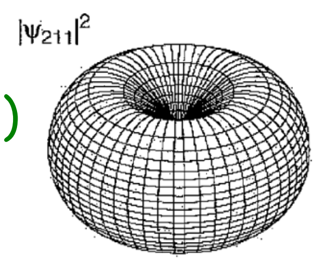
$3p_z$ orbital

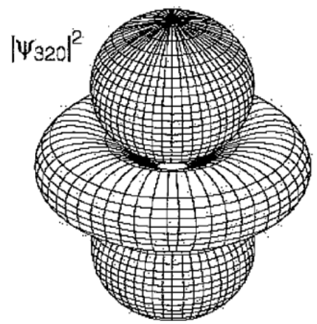




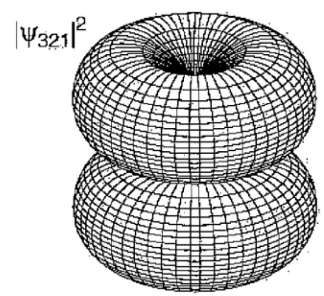
$3(p_x+ip_y)$ orbital

$2(p_x+ip_y)$ orbital





$3d_{3z2-r2}$ orbital



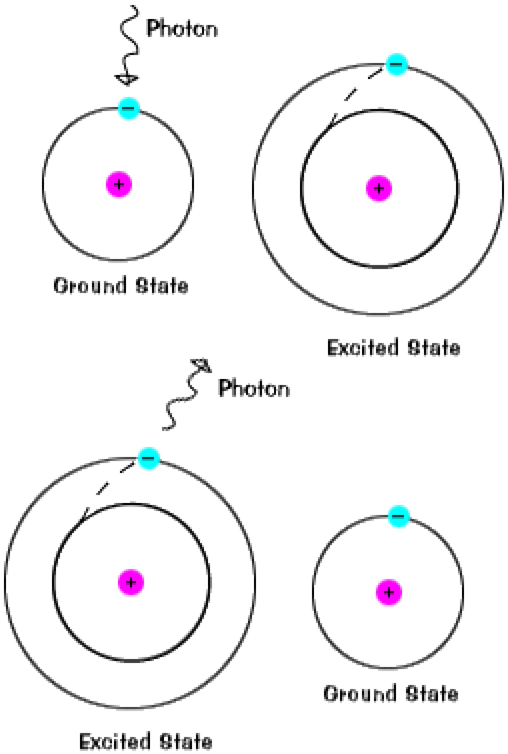
linear combination of canonical 3d orbitals

And as usual, the wave functions are orthonormal:

$$\boxed{\int \psi_{nlm}^{*}\,\psi_{n'l'm'}\,r^2 \sin\theta\, dr\, d\theta\, d\phi = \delta_{nn'}\,\delta_{ll'}\,\delta_{mm'}}$$

$$\underbrace{\delta_{nn'}}_{\text{Because of radial equation.}}\;\underbrace{\delta_{ll'}\,\delta_{mm'}}_{\text{Because of spherical harmonics.}}$$

4.2.2: The Spectrum of Hydrogen



Emission of photons:

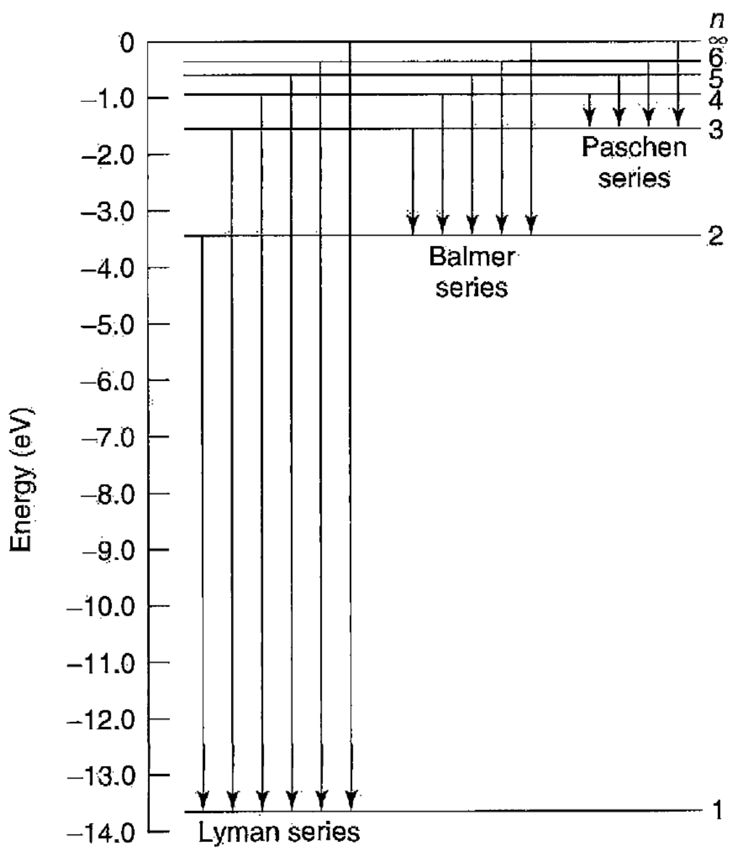
$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

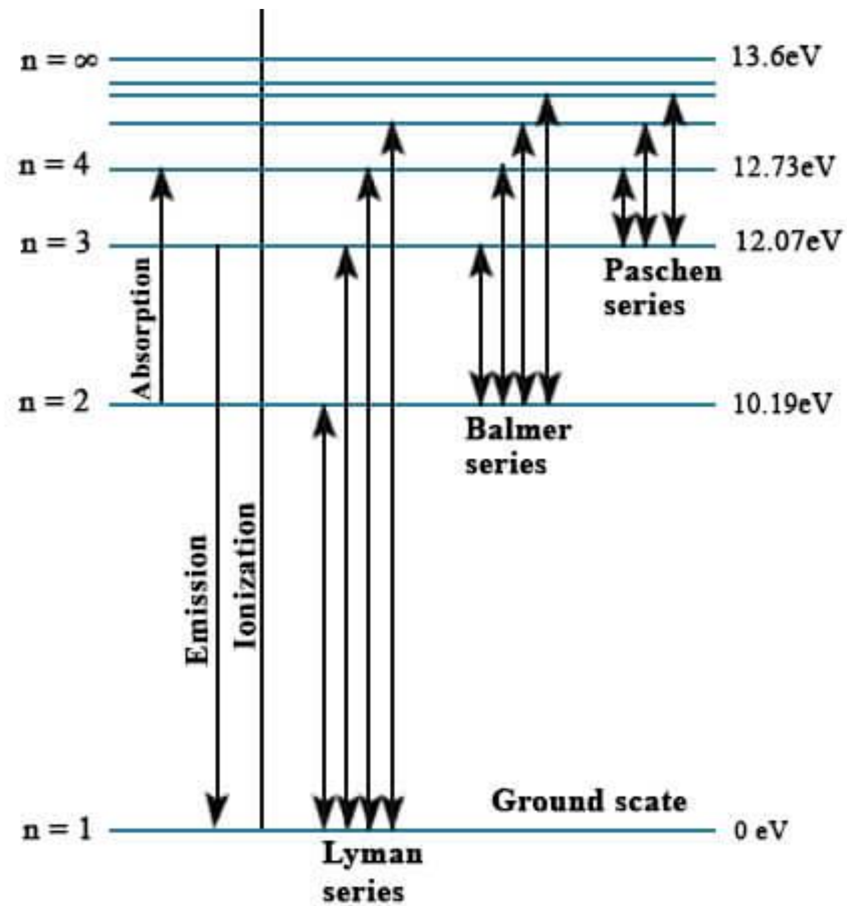
$$E_\gamma = h\nu \qquad \lambda = c/\nu.$$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$R \equiv \frac{m}{4\pi c\hbar^3} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

R= Rydberg constant; formula found before Sch Eq just empirically.


n
0
−1.0
−2.0
−3.0
−4.0
−5.0
−6.0
−7.0
−8.0
−9.0
−10.0
−11.0
−12.0
−13.0
−14.0
Energy (eV)
∞
6
5
4
3
2
1
Paschen series
Balmer series
Lyman series


n = ∞
n = 4
n = 3
n = 2
n = 1
13.6eV
12.73eV
12.07eV
10.19eV
0 eV
Absorption
Emission
Ionization
Paschen series
Balmer series
Lyman series
Ground scate

Bohr Model for Hydrogen Atom

(measurement in nanometers)