Effective potential

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

the term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ is called the repulsive centrifugal barrier its effect is to reduce the effective of the potential well.

r

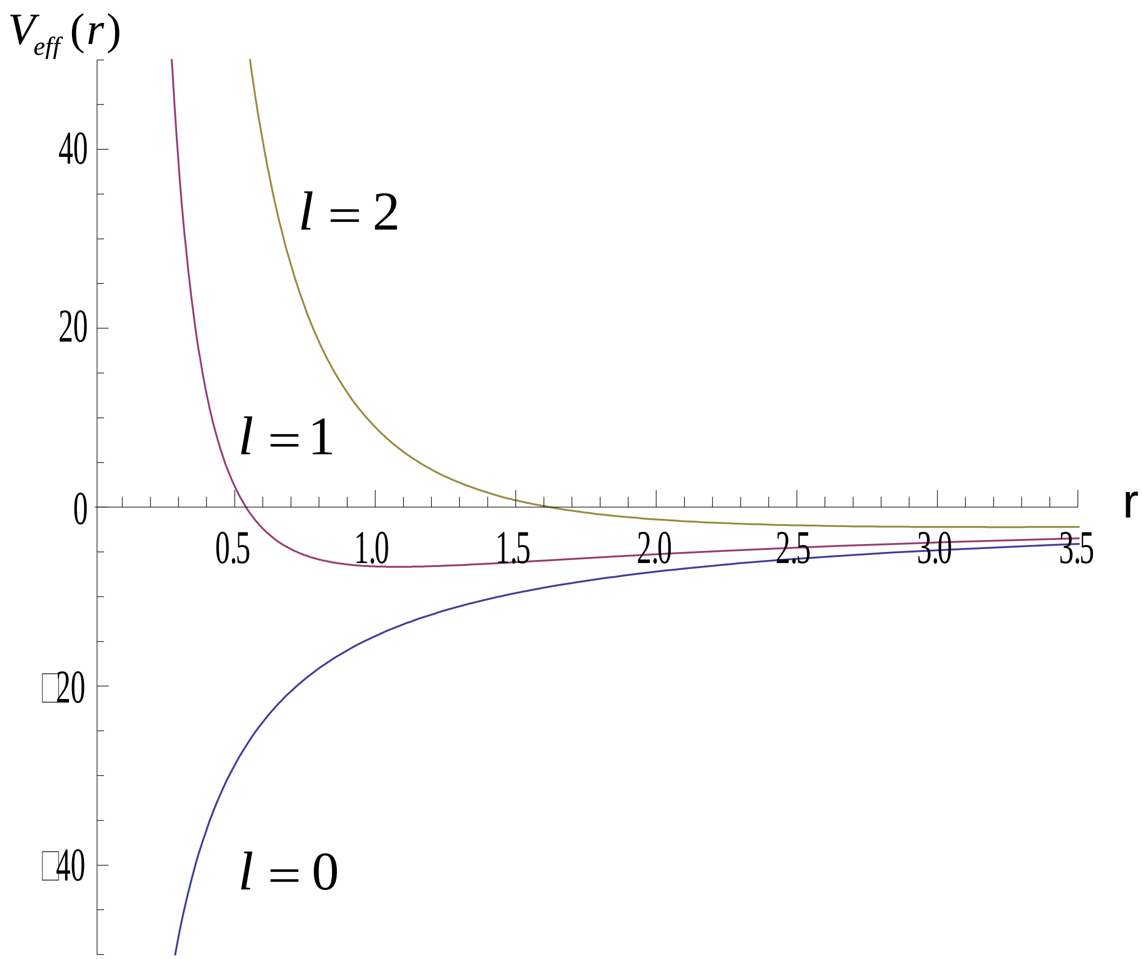
Effective potential for hydrogen atom

$$V_{eff}(r) = -\frac{e^2}{(4\pi\varepsilon_0)r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \approx -\frac{1.44(ev.nm)}{r} + \frac{l(l+1)(197.3)^2.(ev.nm)^2}{2(0.5\times 10^6 ev)r^2}$$

$$\approx -\frac{14.4(ev.A^o)}{r} + \frac{l(l+1)(197.3)^2.(10.ev.A^o)^2}{2(0.5\times 10^6 ev)r^2} \approx -\frac{14.4}{r} + \frac{l(l+1)3.89}{r^2}$$

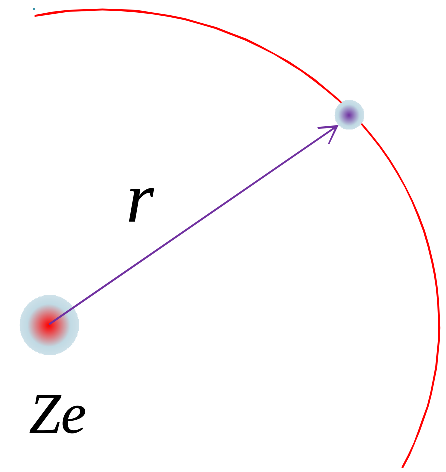
the unit of distance is A^0

the unit of energy is eV



The Hydrogenic Atom

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r}$$



The interaction potential depends
Only on the relative coordinate of
The two particles (electron and nucleus).
We will separate the motion of the centre-of-mass
(as you will see in the H.W), thus working
In the centre-of-mass system
(where the total momentum of the atom is zero)
The Hamiltonian of the atom reduces to that
describing the relative motion of the two particle.

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}+V(r)\right]R_{El}(r)=ER_{El}(r)$$

$$\mu=\frac{mM}{m+M}$$

$m =$ Electrom mass

$M =$ Nucleus mass

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}+\frac{2\mu}{\hbar^2}\frac{Ze^2}{(4\pi\varepsilon_0)r}+\frac{2\mu}{\hbar^2}E\right]R_{El}(r)=0$$

$$\rho=\eta r$$

$$r=\frac{\rho}{\eta}$$

$$dr=\frac{d\rho}{\eta}$$

$$\eta=\sqrt{-\frac{8\mu E}{\hbar^2}}\,,\ \lambda=\frac{\mathrm{Ze}^2}{(4\pi\varepsilon_0)\hbar}\sqrt{-\frac{\mu}{2E}}$$

$$\left[\eta^2 \frac{d^2}{d\rho^2} + \eta^2 \frac{2}{\rho}\frac{d}{d\rho} - \eta^2 \frac{l(l+1)}{\rho^2} + \frac{2\mu}{\hbar^2}\frac{Ze^2}{(4\pi\varepsilon_0)\rho}\eta + \frac{2\mu}{\hbar^2}E\right] R_{El}(\rho) = 0$$

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{1}{\rho}\underbrace{\frac{2\mu}{\hbar^2}\frac{Ze^2}{(4\pi\varepsilon_0)\eta}}_{\lambda} + \underbrace{\frac{2\mu}{\hbar^2\eta^2}E}_{-\frac{1}{4}}\right] R_{El}(\rho) = 0$$

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right] R_{El}(\rho) = 0$$

$$\left[\frac{d^2}{d\rho^2}+\frac{2}{\rho}\frac{d}{d\rho}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}-\frac{1}{4}\right]R_{El}(\rho)=0$$

$$\rho\rightarrow\infty\ ,\qquad \left[\frac{d^2}{d\rho^2}-\frac{1}{4}\right]R_{El}(\rho)=0$$

This makes us to expect that

$$\boxed{R_{El}(\rho)=F(\rho)e^{-\rho/2}}$$

$$\frac{dR_{El}}{d\rho}=\frac{d}{d\rho}\left(F(\rho)e^{-\rho/2}\right)=F'e^{-\rho/2}-\frac{1}{2}Fe^{-\rho/2}$$

$$\frac{d^2R_{El}}{d\rho^2}=\frac{d^2}{d\rho^2}\left(F(\rho)e^{-\rho/2}\right)=F''e^{-\rho/2}-F'e^{-\rho/2}+\frac{1}{4}Fe^{-\rho/2}$$

$$F''(\rho)+\left(\frac{2}{\rho}-1\right)F'(\rho)+\left(\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right)F(\rho)=0$$

$$F(\rho)=\rho^l L(\rho)$$

$$F'=l\rho^{l-1}L+\rho^l L'$$

$$F''=\rho^l L''+2l\rho^{l-1}L'+l(l+1)\rho^{l-2}L$$

$$\rho L''+(2l+2-\rho)L'+\left[\lambda-1-\frac{l(l+1)}{\rho}+\frac{l(l-1)}{\rho}+\frac{2l}{\rho}-l\right]L=0$$

$$\rho L''(\rho)+(2(l+1)-\rho)L'(\rho)+(\lambda-l-1)L(\rho)=0$$

$$\rho L''(\rho) + (2l + 2 - \rho)L'(\rho) + (\lambda - l - 1)L(\rho) = 0$$

$$x \frac{d^2 L_m^k(x)}{dx^2} + (1 + k - x)\frac{dL_m^k(x)}{dx} + mL_m^k(x) = 0$$

Differential equation of associate Laguerre polonomial

Identical if

$$m = \lambda - l - 1 = n - l - 1$$

$$k = 2l + 1$$

$$\lambda = n$$

λ must be integer because m is integer

$n \equiv$ principle quantum number

$n = 1, 2, 3, \cdots$

orbital q.n $\quad l \le n - 1$

magnetic q.n $\quad -l \le m \le l$

$$L_m^k(x) \equiv \text{associate Laguerre polonomial}$$

So the solution of the above eq. is $L_{n-l-1}^{2l+1}(\rho)$

$$R_{El}(\rho) = A\rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho)$$

$$\rho = \eta r = \left(\frac{2Z}{a_\mu n}\right) \cdot r$$

$$R_{El}(r) = A\left(\frac{2Z}{a_\mu n}\right)^l r^l \exp[-\frac{Z}{a_\mu n} r] L_{n-l-1}^{2l+1}(\frac{2Z}{a_\mu n} r)$$

Determination the normalization constant

$$\int |\psi(r,\theta,\phi)|^2 dV = 1$$

$$\int |Y_{lm}(\theta,\phi)|^2 d\Omega \cdot \int |R_{El}(r)|^2 r^2 dr = 1$$

$$\int |R_{El}(r)|^2 r^2 dr = 1$$

$$|A|^2 \left(\frac{a_\mu n}{2Z}\right)^3 \int_0^\infty \rho^{2l} e^{-\rho} \left(L_{n-l-1}^{2l+1}\right)^2 \rho^2 d\rho = 1$$

$$\int_0^\infty \rho^{2l} e^{-\rho} \left(L_{n-l-1}^{2l+1}\right)^2 \rho^2 d\rho = \frac{2n[(n+l)!]^3}{(n-l-1)!}$$

$$A = \sqrt{\left(\frac{2Z}{a_\mu n}\right)^3 \cdot \frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

$$R_{nl}(r)=\sqrt{\left(\frac{2Z}{a_\mu n}\right)^3\cdot\frac{(n-l-1)!}{2n[(n+l)!]^3}}\left(\frac{2Z}{a_\mu n}\right)^l r^l \exp[-\frac{Z}{a_\mu n}r]L_{n-l-1}^{2l+1}(\frac{2Z}{a_\mu n}r)$$

$$\psi_{nlm}(r,\theta,\phi)=R_{nl}(r)Y_{lm}(\theta,\phi)$$

Represent a bound state wave function.

A bound state: is one in which the probability that the electron will escape from the attraction of the proton is zero.

Principle Q.n $n=1,2,3,\cdots$

Orbital Q.n $l=0,1,2,\cdots,n-1$

Magnetic Q.n $m=-l,\cdots,l$

value of l	0	1	2	3	4
code letter	s	p	d	f	g

Calculating associate Laguerre polonomial

$$L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x)$$

$$L_j(x) = e^x \frac{d^j}{dx^j}\left(e^{-x} x^j\right)$$

$$L_0^1(x) = 1$$

$$L_1^1(x) = -2x + 4$$

$$L_0^3(x) = 6$$

$$L_0(x) = 1$$

$$L_1(x) = -x + 1$$

$$L_2(x) = x^2 - 4x + 2$$

$$L_3(x) = -x^3 + 9x^2 - 18x + 6$$

The normalized radial wave functions for Hydrogen like atom (HLA)

$$R_{10}^{HLA}(r) = 2\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu}$$

Complete ground state wave function for Hydrogen like atom(HLA)

$$\psi_{100}^{HLA}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-\left(\frac{Z}{a_\mu}\right)r}$$

The first few normalized radial wave functions for H-atom (Z=1)

$$R_{10}(r) = 2a_{\mu}^{-3/2} e^{-r/a_{\mu}}$$

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

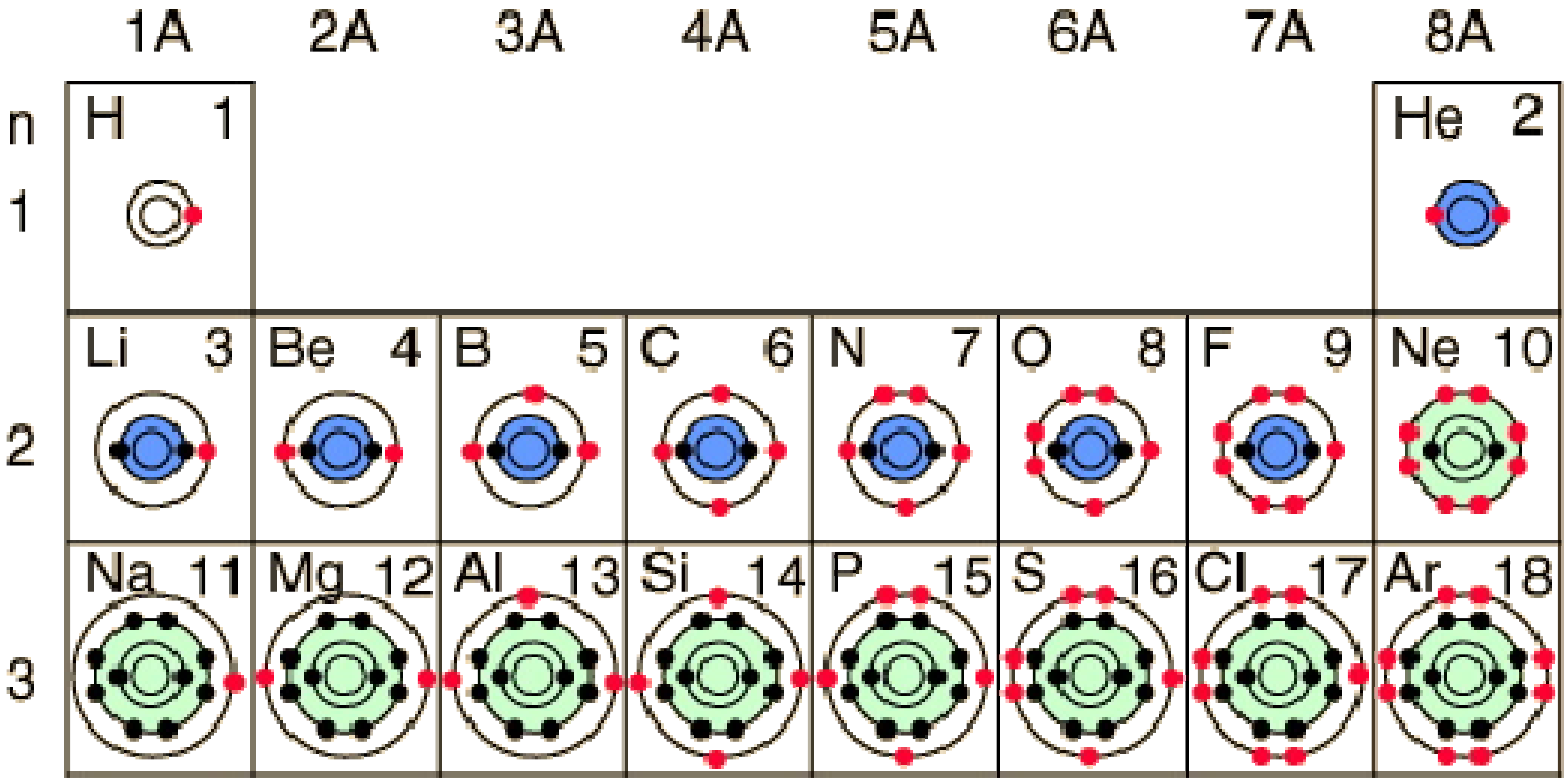
Few complete wave functions for H-atom

Ground state wave function
For the H-atom

$$\psi_{100}(r,\theta,\phi) = R_{10}(r) Y_{00}(\theta,\phi) = \boxed{\frac{1}{\sqrt{\pi a_{\mu}^{3}}} e^{\frac{-r}{a_{\mu}}}}$$

$$\psi_{200}(r,\theta,\phi) = R_{20}(r) Y_{00}(\theta,\phi) = \frac{1}{\sqrt{8\pi a_{\mu}^{3}}} \left(1 - \frac{r}{2a_{\mu}}\right) e^{\frac{-r}{2a_{\mu}}}$$

shell	n	l	m	Spectroscopic-notation	Wave-functions
		quantum numbers			
K	1	0	0	1s	ψ_{100}
L	2	0	0	2s	ψ_{200}
	2	1	0	$2p_{0}$	ψ_{210}
	2	1	± 1	$2p_{\pm 1}$	ψ_{201}, ψ_{20-1}
M	3	0	0	3s	ψ_{300}
	3	1	0	$3p_{0}$	ψ_{310}
	3	1	± 1	$3p_{\pm 1}$	ψ_{311}, ψ_{31-1}
	3	2	0	$3d_{0}$	ψ_{320}
	3	2	± 1	$3d_{\pm 1}$	ψ_{321}, ψ_{31-1}
	3	2	± 2	$3d_{\pm 2}$	ψ_{322}, ψ_{32-2}


1A
2A
3A
4A
5A
6A
7A
8A
n
1
2
3
H 1
He 2
Li 3
Be 4
B 5
C 6
N 7
O 8
F 9
Ne 10
Na 11
Mg 12
Al 13
Si 14
P 15
S 16
Cl 17
Ar 18

Probability density

The radial distribution function

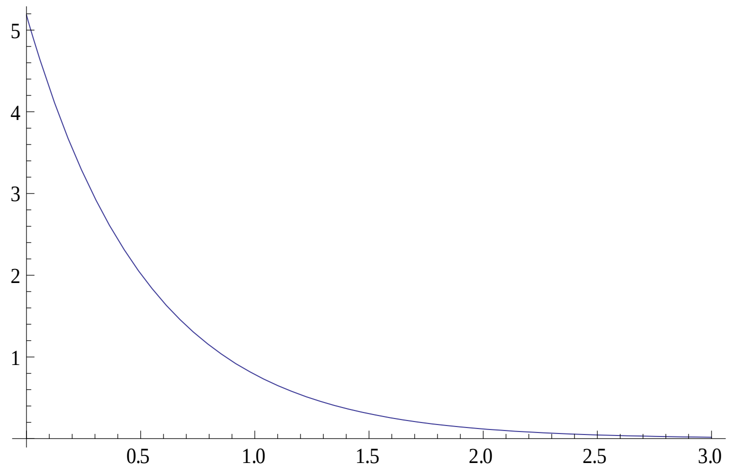
$$D_{nl}(r) = r^2 \left| R_{nl}(r) \right|^2$$

Gives the probability per unit length that the electron is to be found at a distance r from the nucleus.

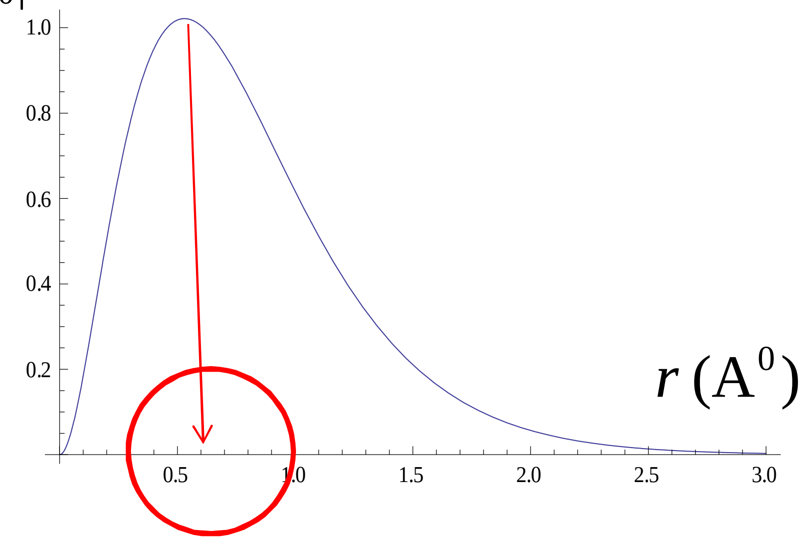
$$\int \left|\psi(r,\theta,\phi)\right|^2 dV = \int \left|Y_{lm}(\theta,\phi)\right|^2 d\Omega \cdot \int \left|R_{nl}(r)\right|^2 r^2 dr =$$

$$\int \underbrace{\left|R_{nl}(r)\right|^2 r^2}\, dr = \int_0^\infty D_{nl}(r)dr$$

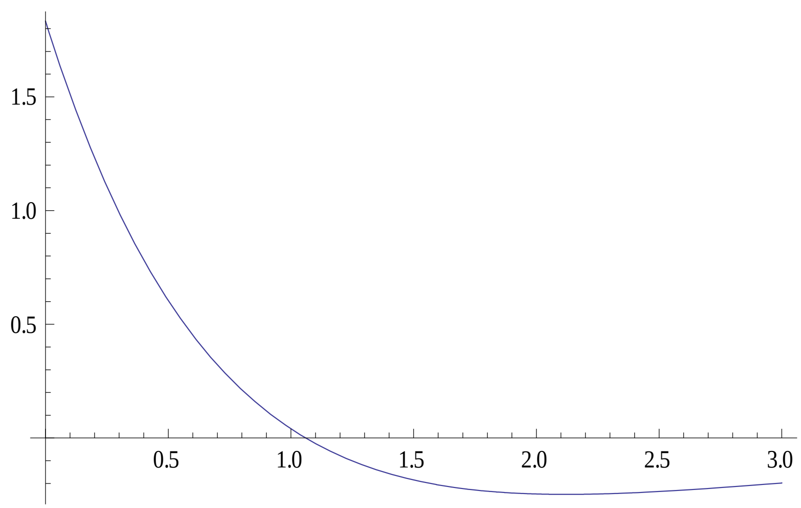
R_{10}



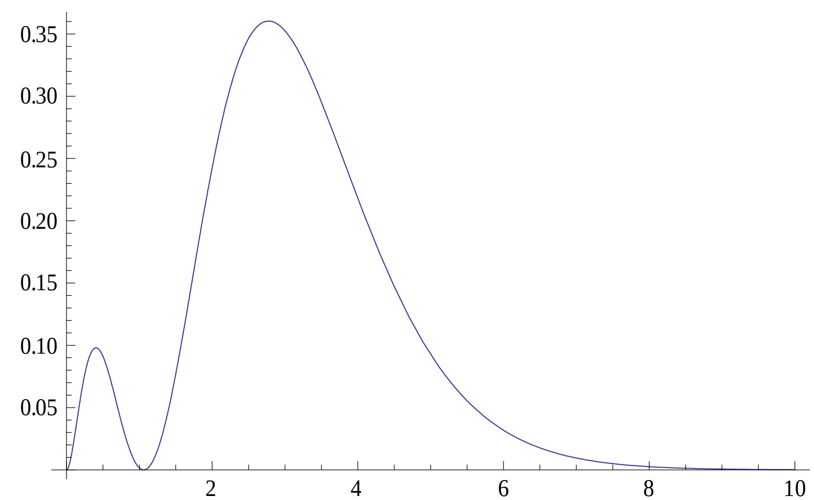
$r^2|R_{10}|^2$



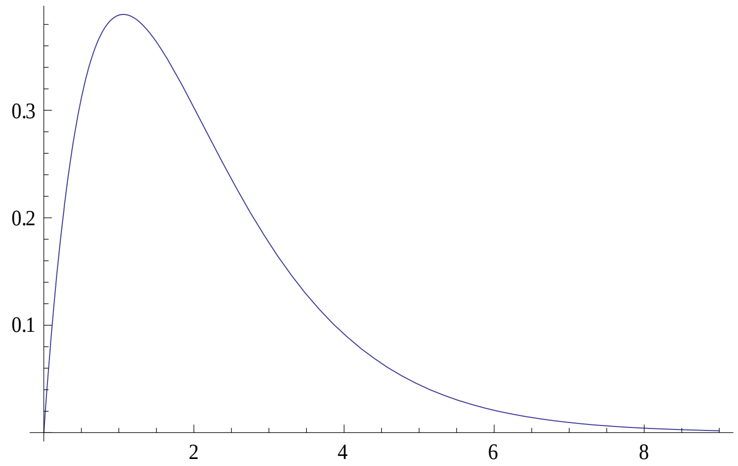
R_{20}



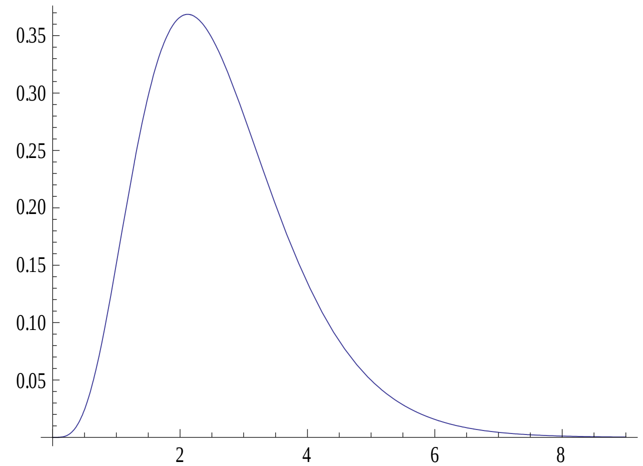
$r^2|R_{20}|^2$



$R_{21}(r)$

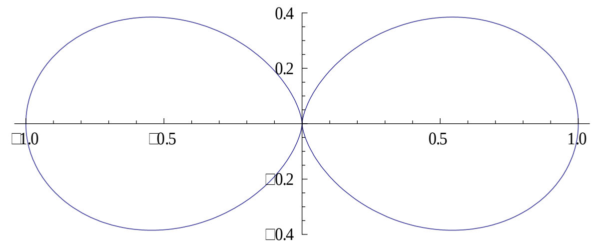


$r^2|R_{21}|^2$

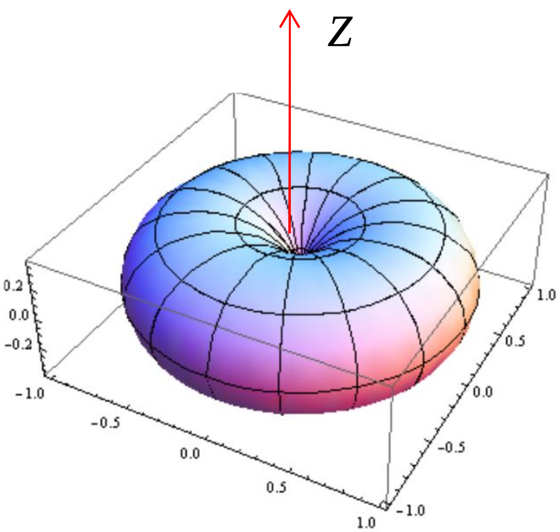


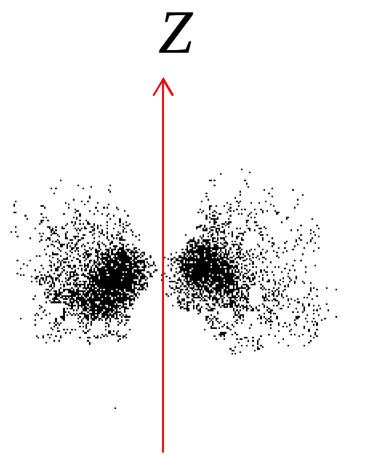
Electron Cloud

An **electron cloud picture for any state** represents the product of the appropriate radial and angular probability densities as a cloud of varying density.

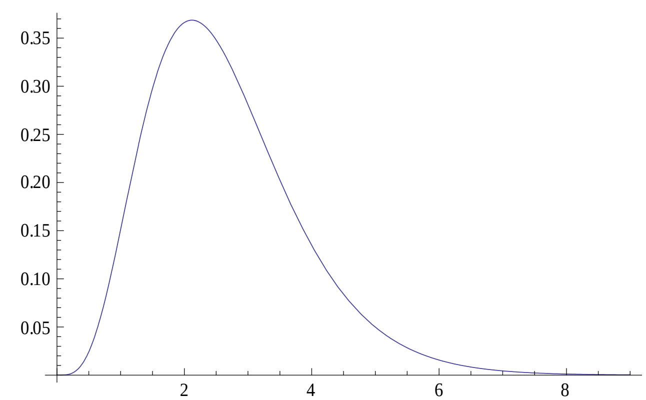


$|Y_{11}|^2$

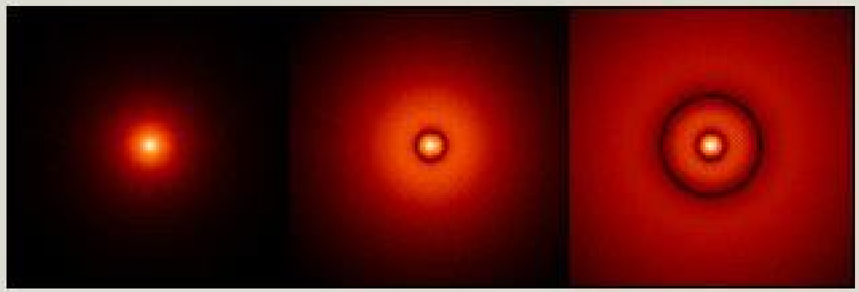




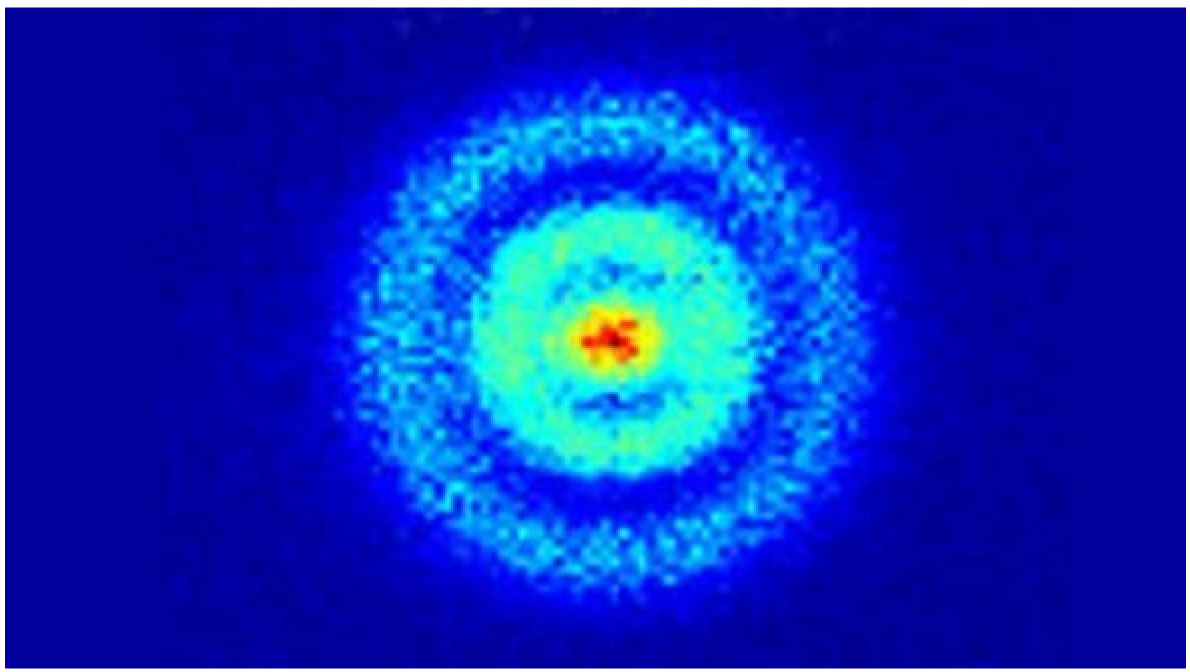
$r^2|R_{21}|^2$



Electron cloud for the *n = 2, l = 1, ml = ±1 states. (only* a section in the *(x, y) plane is* shown.)



Probability density of the electron for the ground and two excited states of Hydrogen. Brighter regions are regions where the electron is more likely to be found.



Eigenvalues

$$n = \lambda = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar}\sqrt{-\frac{\mu}{2E}}$$

$$n^2 = \left(\frac{Ze^2}{(4\pi\varepsilon_0)\hbar}\right)^2\left(-\frac{\mu}{2E}\right)$$

$$E = -\left(\frac{Ze^2}{(4\pi\varepsilon_0)\hbar}\right)^2\left(\frac{\mu}{2}\right)\left(\frac{1}{n^2}\right)$$

$$E_n = -\frac{1}{2}\mu c^2\frac{(\alpha Z)^2}{n^2}$$

$$\alpha = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} \cong \frac{1}{137}$$

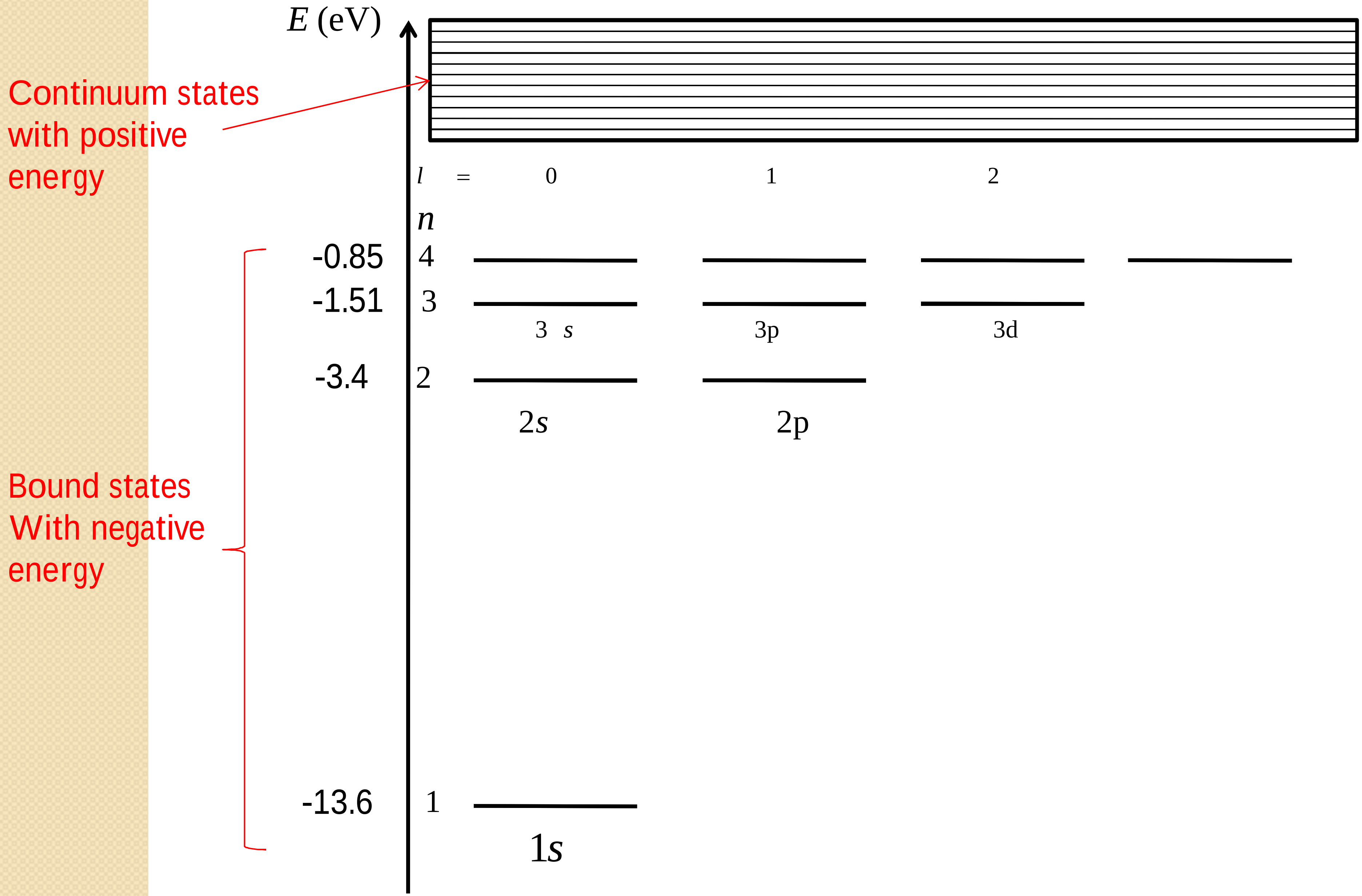
Fine structure constant

$$E_n = -\frac{\hbar^2}{2\mu a_\mu^2}\cdot\frac{Z^2}{n^2} = -13.6\frac{Z^2}{n^2}$$

Bohr radius

$$a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2} = 0.529\ \mathrm{A}^0$$

$$a_\mu = \frac{m}{\mu}a_0$$


E (eV)
Continuum states with positive energy
l = 0 1 2
n
-0.85 4
-1.51 3
3 s
3p
3d
-3.4 2
2s
2p
Bound states With negative energy
-13.6 1
1s

Degeneracy

The energy level depend only on the principle quantum number.
For a given n we have n-1 values for L and for a given L we have 2L+1
M Values, so the total degeneracy of the bound-state energy level is
Given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = 2\left(\frac{n(n-1)}{2}\right) + n = n^2$$

The degeneracy with respect to the Quantum number m is present for any
Central potential (spherically symmetric) while the degeneracy with respect
To L is characteristic of the Coulomb potential.

The probability of measuring E_i

$$P\left(E = E_i\right) = \left|\left\langle \psi_{ilm} \middle| \Psi \right\rangle\right|^2 = \left|\int \psi_{ilm}^{*} \Psi dv\right|^2$$

H-atom binding energy

The ground state (that is, the state of lowest energy) is the state n=1.
For this state

$$E_1 = -13.6\,\mathrm{eV}$$

So, the binding energy (the amount of energy you would have to impart to The electron in order to ionize the atom) of the H-atom is 13.6 eV.

H-atom spectrum

$$\Delta E = E_m - E_n = -\frac{13.6}{m^2} - \left(-\frac{13.6}{n^2}\right) = 13.6\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{ eV}$$

please notice that $m > n,\ n \equiv \text{final energy level } (n_f)$

$$f = \frac{\Delta E}{h} = \frac{c}{\lambda}$$

$$\Rightarrow \frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{13.6 \text{ eV}}{1239.8 \text{ eV.nm}}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$\frac{1}{\lambda} = 0.0109695\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{ nm}^{-1}$$

$$\frac{1}{\lambda} = 1.09695 10^7\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{ m}^{-1}$$

$$\lambda = 91.162\left(\frac{n^2 m^2}{m^2 - n^2}\right) \text{ nm}$$

Compare what we have obtain with the Rydberg Formula for the spectrun of Hydrogen.

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \text{ m}^{-1}$$

$$R = 1.097\,10^7 \text{ m}^{-1}$$

R is known as the Rydberg constant. The above formula was discovered Empirically in the nineteenth century.

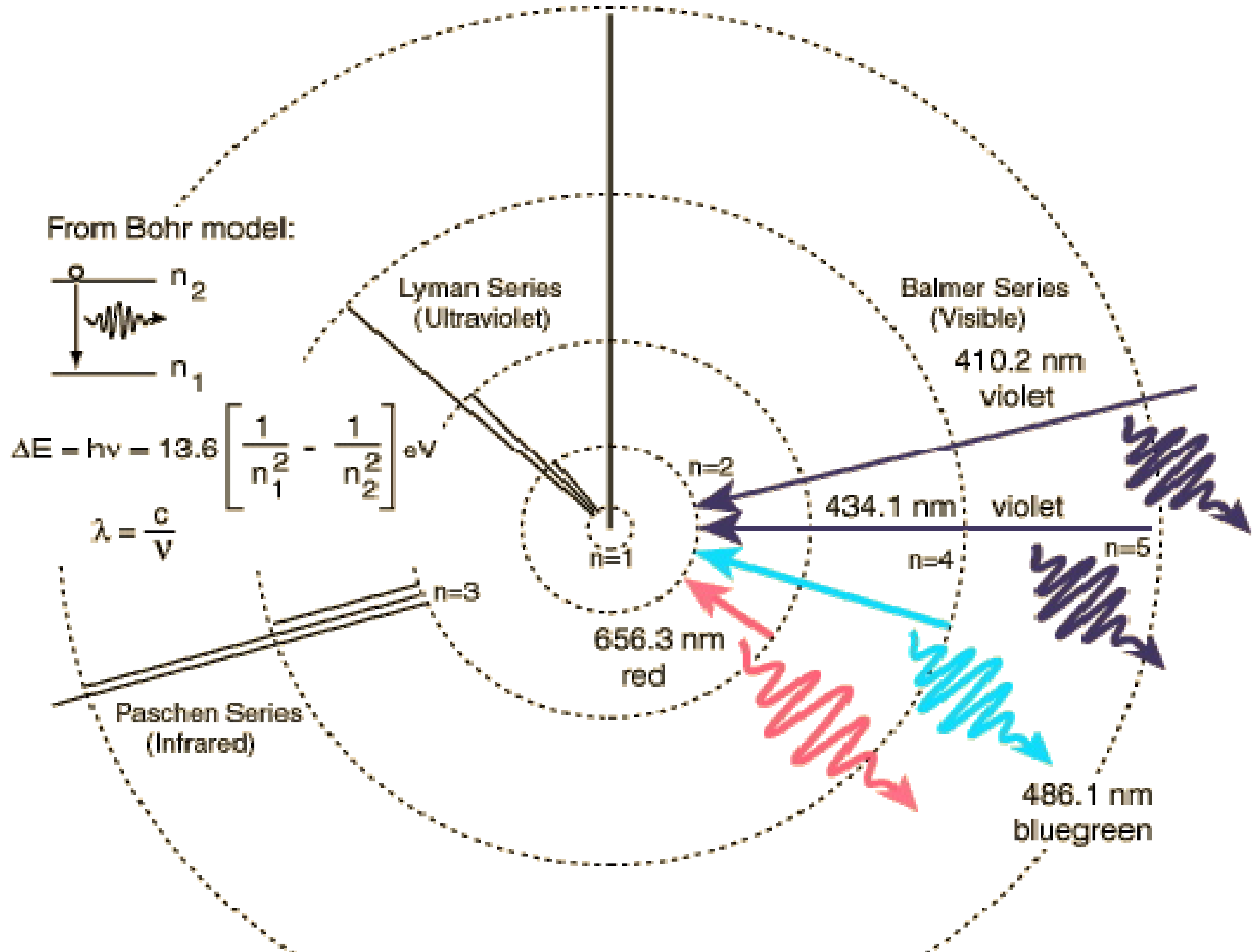
As you see they coincide !

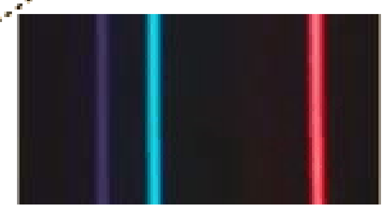
Transitions to the ground state (n=1) lie in the ultraviolet; they known to Spectroscopists as the Lyman series.

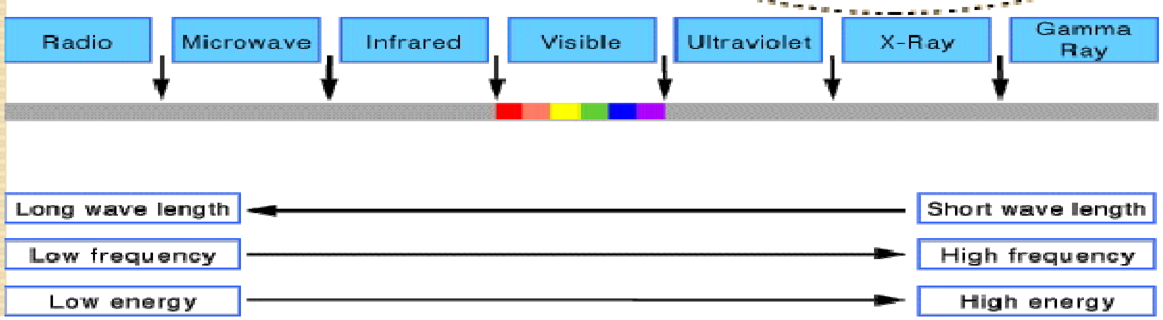
Transitions to the first excited state (n=2) fall in the visible region; they Constitute the Balmer series. Transitions to n=3 are in the infrared, and Known as Paschen series.

$$\lambda = 91.162\left(\frac{n^2 m^2}{m^2 - n^2}\right) \quad \text{nm}$$

n	m	λ (nm)
1	2	121.6
1	3	102.6
1	4	97.2
2	3	656.4
2	4	486.2
2	5	434.1


From Bohr model:
n_2
n_1
$\Delta E = h\nu = 13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] eV$
$\lambda = \frac{c}{\nu}$
Lyman Series
(Ultraviolet)
Balmer Series
(Visible)
410.2 nm
violet
434.1 nm violet
n=2
n=1
n=3
n=4
n=5
656.3 nm
red
486.1 nm
bluegreen
Paschen Series
(Infrared)




Radio
Microwave
Infrared
Visible
Ultraviolet
X-Ray
Gamma Ray
Long wave length
Short wave length
Low frequency
High frequency
Low energy
High energy