

Hydrogen Atom

S.E. IN SPHERICAL COORDINATES

Laplacian operator in spherical coordinates

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

T.I.S.E. in 3D:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = E \psi(r)$$

Thus:

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] \right] + V \psi = E \psi$$

Like what we have done for the orbital angular momentum we look for solutions which are separable in products:

$$\psi(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m}(\theta, \varphi)$$

S.E. IN SPHERICAL COORDINATES

$$\psi(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m}(\theta, \varphi)$$

By inserting this product into the S.E.:

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] \right] + V R Y = E R Y$$

Dividing by YR and multiplying by $\frac{2mr^2}{\hbar^2}$ we have:

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{r^2} \left[\frac{R}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] \right] + V R Y = (E R Y - V R Y) \frac{2m r^2}{\hbar^2}$$

$$-\left[\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] \right] + (V - E) \frac{2m}{\hbar^2 r^2} = 0$$

S.E. IN SPHERICAL COORDINATES

By separating parts depending on r and angles:

$$\left[\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - (V(r) - E) \frac{2m}{\hbar^2 r^2} \right] + \frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] = 0$$

Eih! Look at the second part... We may notice that the second part of this S.E. is identical to the square of the ang. Momentum

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

And we know that:

$$L^2 Y_{l,m}(\theta, \varphi) = l(l+1) \hbar^2 Y_{l,m}(\theta, \varphi)$$

Thus, it is clear that:

$$\frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] = -l(l+1)$$

Angular Equation

the angular part is identical to the eigenvectors equation of L^2 :

$$\frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] = -l(l+1)$$

In fact, again:

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

And its eigenvectors equation is:

$$L^2 Y_{l,m}(\theta, \varphi) = l(l+1) \hbar^2 Y_{l,m}(\theta, \varphi)$$

We know very well its eigenvectors; they are the spherical harmonics!

$$Y_{l,m}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{l,m}(\cos \theta) e^{im\varphi}$$

$P_{l,m}$ are the associated Legendre Polynomials

S.E. IN SPHERICAL COORDINATES

By separating parts depending on r and angles:

$$\left[\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - (V(r) - E) \frac{2m}{\hbar^2 r^2} \right] + \frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] = 0$$

Thus, it is clear that for the angular part:

$$\frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right] = -l(l+1)$$

And to satisfy the S.E. also the radial part:

$$\left[\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - (V(r) - E) \frac{2m}{\hbar^2 r^2} \right] = l(l+1)$$

Radial Equation

For the radial part:

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

By using $u(r) \equiv rR(r)$

Radial Equation

For the radial part:

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

By using $u(r) \equiv rR(r)$

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

V_{eff}
EFFECTIVE POTENTIAL

Centrifugal term:
it tends to throw
the particle outward

$$V_{\text{centr}} = \frac{L^2}{2m r^2}$$

Which is called the "radial equation".

$$R = \frac{u}{r}$$

$$\frac{dR}{dz} = \left[r \frac{du}{dz} - u \right] \frac{1}{r^2}$$

$$r^2 \frac{dR}{dz} = r \frac{du}{dz} - u$$

$$\frac{d}{dz} \left[r^2 \frac{dR}{dz} \right] = \frac{du}{dz} + r \frac{d^2 u}{dz^2} - \frac{du}{dz}$$

Radial Equation

For the radial part:

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

By using $u(r) \equiv rR(r)$

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

V_{eff}
EFFECTIVE POTENTIAL

Centrifugal term:
it tends to throw
the particle outward

It has the same form of the 1D S.E., but with the "effective potential", which contains an extra term: the centrifugal term.

Which is called the "radial equation".

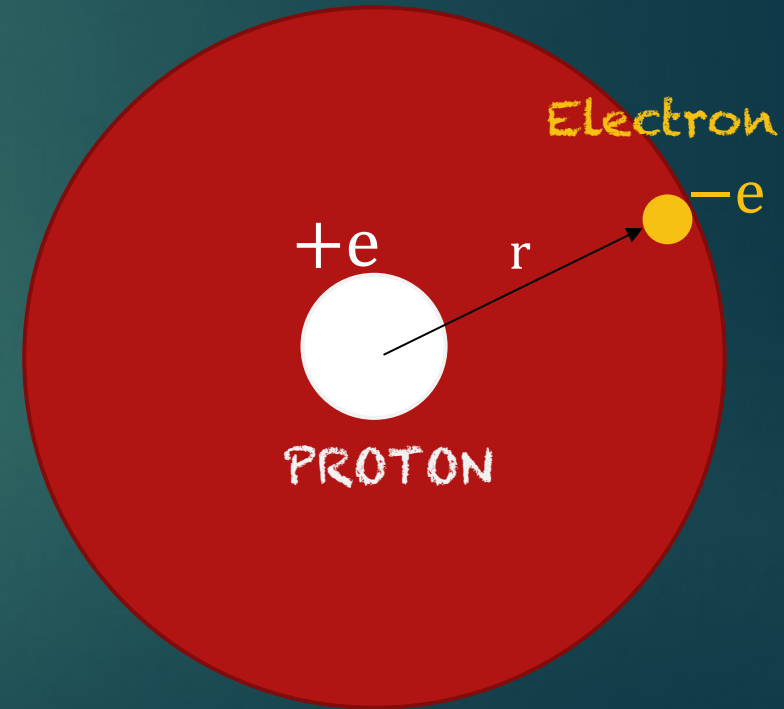
Hydrogen atom

The hydrogen atom consists of an electron, of charge $-e$ and mass m_e and a proton, of charge $+e$ and mass m_p , moving in the Coulomb potential. Thus, the potential energy is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad \text{vacuum permittivity is } \epsilon_0 = 8.854 \times 10^{-12} \text{ C/V m}$$

The radial equation will be:

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$



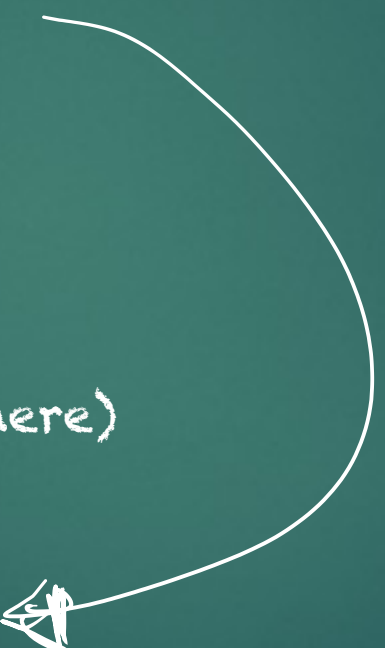
Hydrogen atom

The radial equation will be:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

In analogy with : $E = \frac{\hbar^2 k^2}{2m}$

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \quad (E \text{ is negative here})$$

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] u$$


Hydrogen atom

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] u \rightarrow$$

$$\frac{1}{\kappa^2} \left[r \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] r R$$

$$u = r R$$

$$\frac{du}{dz} = R + \frac{dR}{dz} z$$

$$\frac{du}{dz^2} = \frac{dR}{dz} + \frac{d^2 R}{dz^2} z + \frac{dR}{dz}$$

$$= \frac{d^2 R}{dz^2} z + 2 \frac{dR}{dz}$$

$$\frac{1}{\kappa^2} \frac{d^2 R}{dr^2} + \frac{2}{r\kappa^2} \frac{dR}{dr} - \left[1 - \gamma \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] R = 0$$

Hydrogen atom

$$\frac{1}{\kappa^2} \frac{d^2 R}{dr^2} + \frac{2}{r\kappa^2} \frac{dR}{dr} - \left[1 - \gamma \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] R = 0$$

$$\text{If } \kappa r = z \\ \frac{1}{\kappa} \frac{d}{dr} = \frac{d}{dz}$$

$$\frac{d^2 R}{dz^2} + \frac{2}{z} \frac{dR}{dz} - \left[1 - \frac{\gamma}{z} + \frac{l(l+1)}{z^2} \right] R = 0$$

Suppose that: $R(z) = \Omega(z) \frac{e^{-z}}{z}$

$$\left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} + \frac{\gamma}{z} - \frac{l(l+1)}{z^2} \right] \Omega = 0$$

Hydrogen atom

Suppose that: $R(z) = \Omega(z) \frac{e^{-z}}{z}$

$$\frac{dR}{dz} = \frac{e^{-z}}{z^2} \left[z \frac{d\Omega}{dz} - (z+1)\Omega \right]$$

$$\frac{d^2R}{dz^2} = \frac{e^{-z}}{z^3} \left[z^2 \frac{d^2\Omega}{dz^2} - 2z(z+1) \frac{d\Omega}{dz} + (z^2 + 2z + 2)\Omega \right]$$

\Rightarrow

$$\frac{d^2R}{dz^2} + \frac{2}{z} \frac{dR}{dz} = \frac{e^{-z}}{z^3} \left[z^2 \frac{d^2\Omega}{dz^2} + (-2z^2 - 2z) \frac{d\Omega}{dz} + (z^2 + 2z + 2)\Omega + 2z \frac{d\Omega}{dz} - (z+2)\Omega \right]$$

Hydrogen atom

$$\frac{d^2 R}{dz^2} + \frac{2}{z} \frac{dR}{dz} = \frac{e^{-z}}{z^3} \left[z^2 \frac{d^2 \Omega}{dz^2} + (-2z^2 - 2z) \frac{d\Omega}{dz} + (z^2 + 2z + 2) \Omega + 2z \frac{d\Omega}{dz} - (2z + 2) \Omega \right] =$$

$$= \frac{e^{-z}}{z^3} \left[z^2 \frac{d^2 \Omega}{dz^2} - 2z^2 \frac{d\Omega}{dz} + z^2 \Omega \right] =$$

$$= \frac{e^{-z}}{z} \left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} + 1 \right] \Omega$$

Hydrogen atom

$$\frac{d^2 R}{dz^2} + \frac{2}{z} \frac{dR}{dz} = \frac{e^{-z}}{z} \left[\frac{d^2}{dz^2} - z \frac{d}{dz} + 1 \right] \Omega$$

Thus:

$$\frac{d^2 R}{dz^2} + \frac{2}{z} \frac{dR}{dz} - \left[1 - \frac{\gamma}{z} + \frac{l(l+1)}{z^2} \right] R = 0$$

$$= \frac{d^2 \Omega}{dz^2} - 2 \frac{d\Omega}{dz} + \Omega - \left[1 - \frac{\gamma}{z} + \frac{l(l+1)}{z^2} \right] \Omega = \left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} + \frac{\gamma}{z} - \frac{l(l+1)}{z^2} \right] \Omega$$

$$R = \Omega \frac{e^{-z}}{z}$$

Hydrogen atom

$$\left[\frac{d^2}{dz^2} - 2 \frac{d}{dz} + \frac{\gamma}{z} - \frac{l(l+1)}{z^2} \right] \Omega = 0$$

If we look for solutions expressed as power series of z

$$\Omega(z) = \sum_j c_j z^j$$

And inserting that in the S.E. above:

$$\sum_j c_j [j(j-1)z^{j-2} - 2jz^{j-1} + \gamma z^{j-1} - l(l+1)z^{j-2}] = 0$$

Hydrogen atom

$$\sum_j c_j [j(j-1)z^{j-2} - 2jz^{j-1} + \gamma z^{j-1} - l(l+1)z^{j-2}] = 0$$

We can write:
$$\sum_j j c_j z^{j-1} = \sum_j (j-1) c_{j-1} z^{j-2}$$

Thus:

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \gamma]$$

But we should check that R is square integrable for $r \rightarrow 0$,

and thus $z \rightarrow 0 \Rightarrow R = \Omega(z) \frac{e^{-z}}{z}$ This is only possible if:
 $\Omega \rightarrow 0$

Hydrogen atom

$$c_j[j(j-1) - l(l+1)] = c_{j-1}[2(j-1) - \gamma]$$

But we should check that R is square integrable for $r \rightarrow 0$,

and thus $z \rightarrow 0 \Rightarrow R = \Omega(z) \frac{e^{-z}}{z}$

This is only possible if:

$$\Omega(z) = \sum_j c_j z^j \rightarrow 0$$

This means that when j is the minimum, $c_{j_{\min}-1} = 0$
and thus:

$$j(j-1) - l(l+1) = 0$$

$$\Rightarrow j^2 - j - l^2 - l = 0$$

$$j = \frac{1 \pm \sqrt{1 + 4l(l+1)}}{2} = \frac{1 \pm \sqrt{4l^2 + 4l}}{2} = \frac{1 \pm (2l+1)}{2}$$

$$j_{\min} = -l \quad \text{or} \\ j_{\min} = l+1$$

Hydrogen atom

$$c_j[j(j-1) - l(l+1)] = c_{j-1}[2(j-1) - \gamma]$$

But we should check that R is square integrable for $r \rightarrow 0$,

and thus $z \rightarrow 0 \Rightarrow R = \Omega(z) \frac{e^{-z}}{z}$

This is only possible if:

$$\Omega(z) = \sum_j c_j z^j \rightarrow 0$$

This means that when j is the minimum, $c_{j_{\min}-1} = 0$
and thus:

$$j(j-1) - l(l+1) = 0$$

$$\Rightarrow j^2 - j - l^2 - l = 0$$

$$j = \frac{1 \pm (2l+1)}{2}$$

$$j_{\min} = -l \quad \text{or} \\ j_{\min} = l+1$$

But if $j_{\min} = -l$

For $z \rightarrow 0$

$$\Omega(z) = c_{-l} z^{-l} = c_{-l} \frac{1}{z^l} \rightarrow \infty$$

Diverges!

Hydrogen atom

$$j = \frac{1 \pm (2l + 1)}{2}$$

~~$$j_{min} = -l$$~~

$$j_{min} = l + 1$$

But if $j_{min} = -l$

For $z \rightarrow 0$

$$\Omega(z) = c_{-l} z^{-l} = c_{-l} \frac{1}{z^l} \rightarrow \infty$$

Diverges!

Hydrogen atom

$$c_j[j(j-1) - l(l+1)] = c_{j-1}[2(j-1) - \gamma]$$

For large j :

$$c_j[j(j-1)] = c_{j-1}[2(j-1)]$$

\Downarrow

$$c_j = c_{j-1} \frac{2}{j}$$

\Downarrow

$$\Omega(z) = \sum_j \frac{(2z)^j}{j!}$$

since

$$\Omega(z) = \sum_j c_j z^j$$

Hydrogen atom

$$c_j[j(j-1) - l(l+1)] = c_{j-1}[2(j-1) - \gamma]$$

For large j :

$$c_j[j(j-1)] = c_{j-1}[2(j-1)]$$

\Downarrow

$$c_j = c_{j-1} \frac{2}{j}$$

\Downarrow

$$\Omega(z) = \sum_j \frac{(2z)^j}{j!}$$

Power series expansion of exp.

$$e^z = \sum_j \frac{z^j}{j!}$$

Thus, for large j :

$$\Omega \rightarrow e^{2z}$$

Hydrogen atom

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \gamma]$$

For large j : $c_j = c_{j-1} \frac{2}{j}$

$$\Rightarrow \Omega(z) = \sum_j \frac{(2z)^j}{j!} \Rightarrow \Omega \rightarrow e^{2z}$$

but $R \sim \Omega(z) \frac{e^{-z}}{z} \Rightarrow R \rightarrow \frac{e^z}{z}$ For z and $r \rightarrow \infty$ it diverges

This is again not possible to grant that

$$\int |\psi|^2 dV : \text{finite}$$

It means that we must have a maximum index in the series, blocking the expansion

Hydrogen atom

$$c_j[j(j-1) - l(l+1)] = c_{j-1}[2(j-1) - \gamma]$$

It means that we must have a maximum index in the series, blocking the expansion

In other words, we must have a j_{max} : $c_{j_{max}+1} = 0$

$$c_{j_{max}+1} = \frac{2(j_{max} + 1 - 1) - \gamma}{(j_{max} + 1)(j_{max} + 1 - 1) - l(l + 1)} c_{j_{max}} = 0$$

$$\begin{aligned} \implies 2j_{max} - \gamma &= 0 \\ \Downarrow \\ j_{max} &= \gamma/2 \end{aligned}$$

Hydrogen atom

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \delta]$$

Thus $j_{\min} = l+1$ and $j_{\max} = \frac{\delta}{2}$

Rewriting $\Omega = \sum_m c_m z^m$

We had: $E = -\frac{\hbar^2 k^2}{2m}$

$l < m \leq \frac{\delta}{2}$
M must be larger than l
smaller than $m = \delta/2$

actually: $m = \frac{m_e m_p}{m_e + m_p}$ so-called reduced mass

Hydrogen atom

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \gamma]$$

Thus $j_{\min} = l+1$ and $j_{\max} = \frac{\gamma}{2}$

Rewriting $\Omega = \sum_m c_m z^m$

$l < m \leq \frac{\gamma}{2}$
 M must be larger than l
smaller than $m = \gamma/2$

$\Downarrow \gamma \geq 2m$

$$\gamma = \frac{m e^2}{2\pi \epsilon_0 \hbar^2 k} \Rightarrow k = \frac{m e^2}{2\pi \epsilon_0 \hbar^2 \gamma} = \left(\frac{m e^2}{4\pi \epsilon_0 \hbar^2} \right) \frac{1}{M} = \frac{1}{a M}$$

Hydrogen atom

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \gamma]$$

Thus $j_{\min} = l+1$ and $j_{\max} = \frac{\gamma}{2}$

Rewriting $\Omega = \sum_n c_n z^n$

We had: $\bar{E} = -\frac{\hbar^2 k^2}{2m}$ $\gamma = \frac{m e^2}{2\pi \epsilon_0 \hbar^2 k} \Rightarrow k = \frac{m e^2}{2\pi \epsilon_0 \hbar^2 \gamma} = \left(\frac{m e^2}{4\pi \epsilon_0 \hbar^2} \right) \frac{1}{M} = \frac{1}{a_M}$

$$\Rightarrow a \equiv \frac{4\pi \epsilon_0 \hbar^2}{m e^2} = 0,529 \cdot 10^{-10} \text{ m} = 0,529 \text{ \AA}$$

Bohr
radius

Hydrogen atom

$$c_j [j(j-1) - l(l+1)] = c_{j-1} [2(j-1) - \delta]$$

Thus $j_{\min} = l+1$ and $j_{\max} = \frac{\delta}{2}$

Rewriting $\Omega = \sum_n c_n z^n$

We had: $\bar{E} = -\frac{\hbar^2 k^2}{2m}$ $k = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \delta} = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{M}$

$$\Rightarrow E = -\frac{me^4}{8\pi^2\epsilon_0^2 \hbar^2 \delta^2} = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{M^2} = E_1 \frac{1}{M^2}$$

Hydrogen atom

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{m e^2} = 0,529 \cdot 10^{-10} \text{ m} = 0,529 \text{ \AA}$$

Bohr
radius

$$E = - \frac{m e^4}{8\pi^2 \epsilon_0^2 \hbar^2} = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = E_1 \frac{1}{n^2}$$

$$E_1 = - \frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \approx -13,6 \text{ eV}$$

↓

Ground state of Hydrogen

Hydrogen atom

$$E_1 = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a} = -13.6$$

$$a = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

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

For $n=2$ $E_2 = \frac{E_1}{4} = -3.4 \text{ eV}$

$$|m| \leq l < n$$

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

$$l = 0, 1, 2, 3 \dots n-1$$

s p d f

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

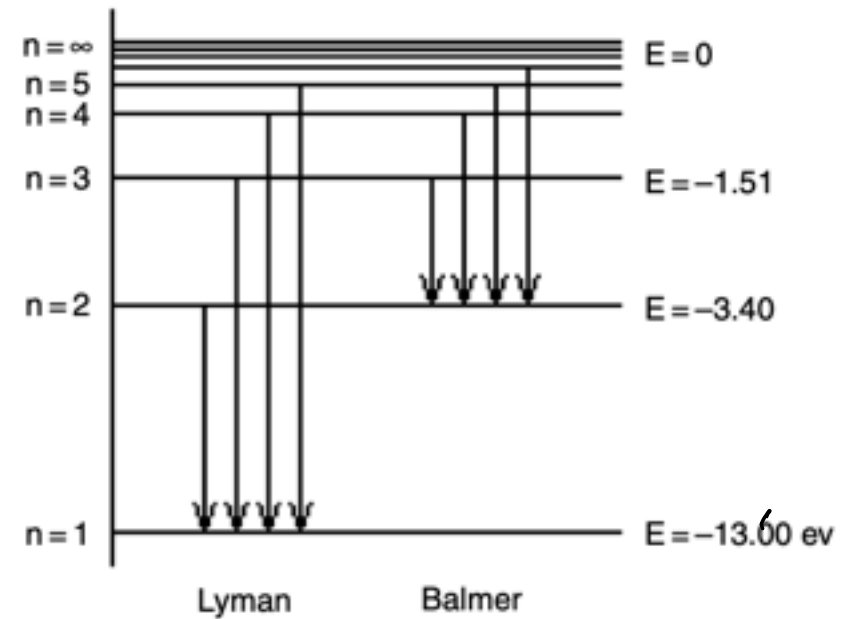


Figure 7.7 ► Energy levels of atomic hydrogen.

Hydrogen atom

An electron in a state of a hydrogen atom, characterized by the quantum numbers n , l , and m , should, in principle, remain in that state forever.

In practice, if the state is slightly perturbed (e.g., via interaction with a photon, atomic collisions, etc.) then the electron can make a transition to another stationary state with different quantum numbers.

The change in energy for the electron is:

$$\Delta E = E_0 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

If $\Delta E > 0$ there is emission of photon with $\nu = -\Delta E/h$

If $\Delta E < 0$ there is an absorption of a photon with $\nu = \Delta E/h$

Hydrogen atom

$$\Delta E = h\nu = E_0 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

But we know that wavelength and frequency are related each other:

$$\frac{1}{\lambda} = \frac{\nu}{c}$$

Then, the possible wavelengths of the photons emitted by a hydrogen atom are:

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

With:

$$R = \frac{-E_0}{hc} = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^3 c} = 1.097 \times 10^7 \text{ m}^{-1}$$

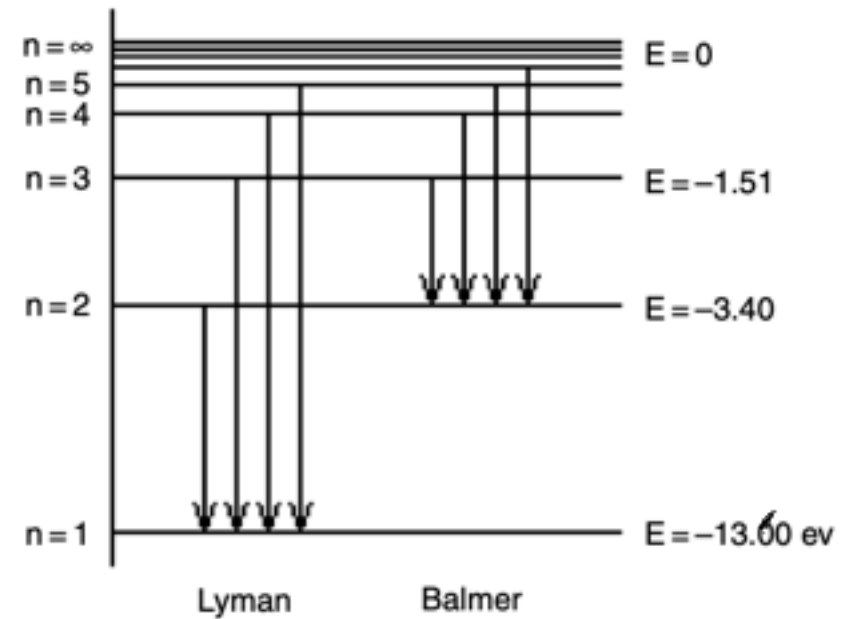


Figure 7.7 ► Energy levels of atomic hydrogen.

Hydrogen atom

With:

$$R = \frac{-E_0}{hc} = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^3 c} = 1.097 \times 10^7 \text{ m}^{-1}$$

R is called the Rydberg constant.

Its formula was discovered empirically in the nineteenth century by spectroscopists, and explained theoretically by Bohr.

Transitions to the ground-state ($n_f=1$) give rise to spectral lines in the ultraviolet band and are called the Lyman series.

Transitions to the first excited state ($n_f=2$) give rise to spectral lines in the visible band and they are called the Balmer series.

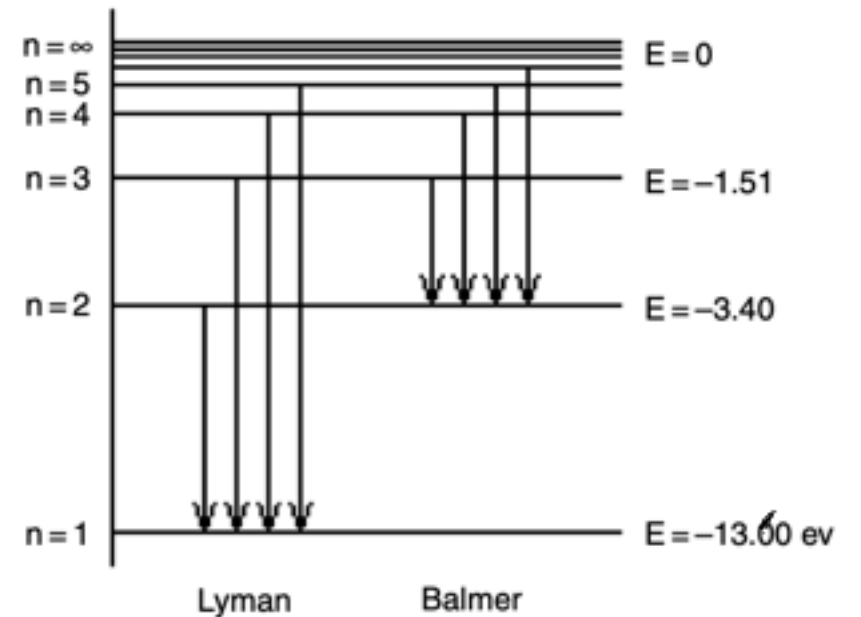


Figure 7.7 ► Energy levels of atomic hydrogen.

Hydrogen atom

It's clear that the wavefunction of hydrogen has 3 indexes (quantum number n, l, m):

$$\Psi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m}(\theta, \varphi)$$

$Y_{l,m}(\theta, \varphi)$ are the spherical harmonics, while $R_{n,l}(r)$ are the radial w.f.

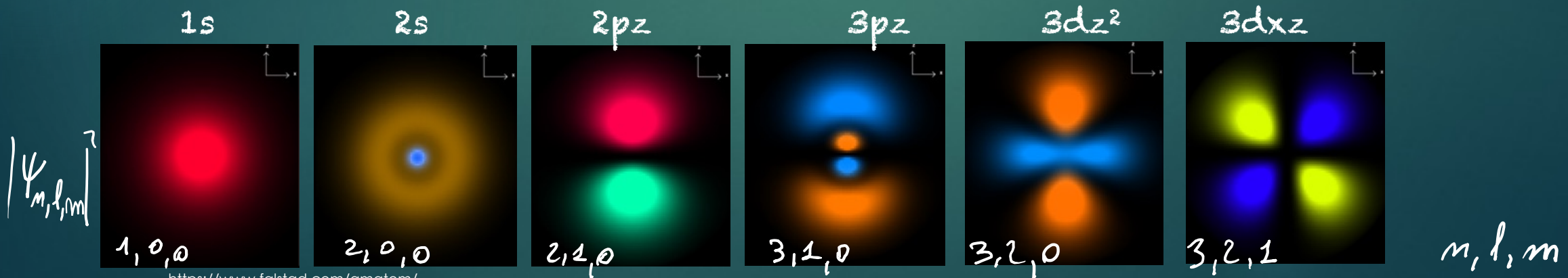
$$|m| \leq l < n$$

$$m = 1, 2, 3 \dots \quad l = 0, 1, 2, 3 \dots n-1 \quad m = 0, \pm 1, \pm 2 \dots \pm l$$

s p d f

Table 4.6: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$R_{10} = 2a^{-3/2} \exp(-r/a)$
$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{r}{2a}\right) \exp(-r/2a)$
$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$
$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2r}{3a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$
$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{r}{6a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$
$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$
$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3r}{4a} + \frac{3}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$
$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{r}{4a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp(-r/4a)$
$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{r}{12a}\right) \left(\frac{r}{a}\right)^2 \exp(-r/4a)$
$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$



Hydrogen atom

$$|m| \leq l < n$$

$$n = 1, 2, 3 \dots \quad l = 0, 1, 2, 3 \dots n-1 \quad m = 0, \pm 1, \pm 2 \dots \pm l$$

s p d f

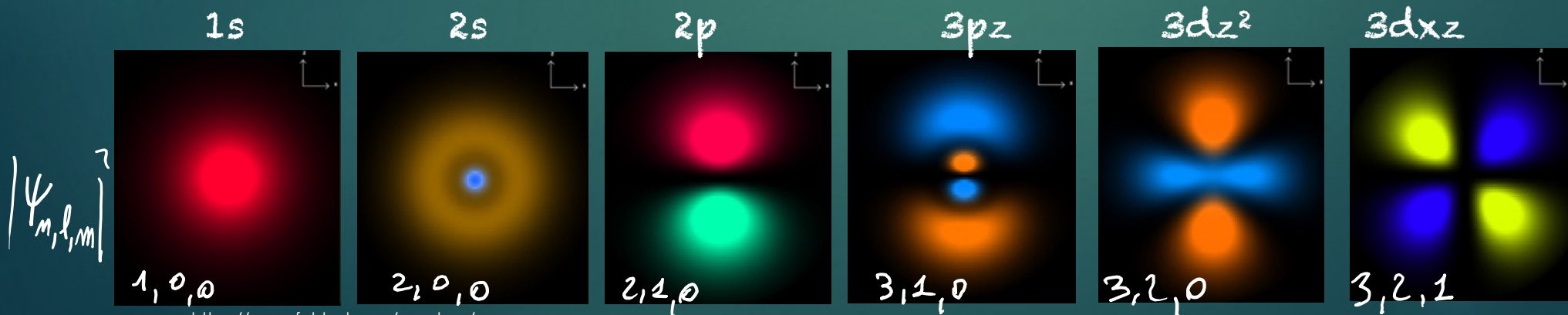
For $n=1$ $l=0$ $m=0$ $\psi_{100} \rightarrow E_1$

$n=2$ $l=0,1$ $m=0, \pm 1$ $\rightarrow \psi_{200}, \psi_{210}, \psi_{21\pm 1} \rightarrow 4\text{-fold degenerate } (n^2)$

$n=3$ $l=0,1,2$ $m=0, \pm 1, \pm 2$

$$\begin{aligned} &\psi_{3,0,0} \\ &\psi_{3,1,0} \\ &\psi_{3,1,\pm 1} \\ &\psi_{3,2,0} \\ &\psi_{3,2,\pm 1} \\ &\psi_{3,2,\pm 2} \end{aligned}$$

E_3
9-fold degenerate
(n^2)



$$|\psi_{n,l,m}|^2$$

n, l, m