Hamiltonian: Spherical Polar Coordinates

$$x \quad = \quad r \quad \sin \quad \theta \quad \cos \quad \phi$$

$$y \quad = \quad r \quad \sin \quad \theta \quad \sin \quad \phi$$

$$z \quad = \quad r \quad \cos \quad \theta$$
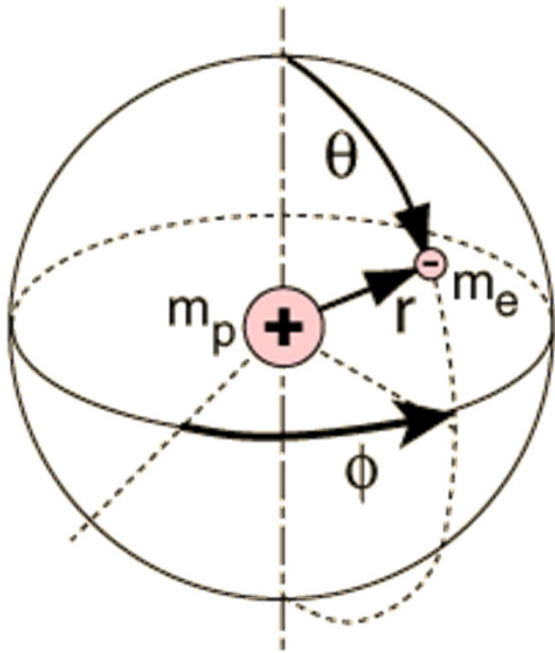
Solve this PDE →need to separate variables r, θ, φ: **POSSIBLE**

A **Completely Solvable** problem!!

(kind of rare, in QM!)

- Wave-particle duality of light (interference expt.; photoelectric G P.E. effect)

- Wave-particle duality exp. for electron (negatively charged particles $\Rightarrow$ the Hitachi interference experiment
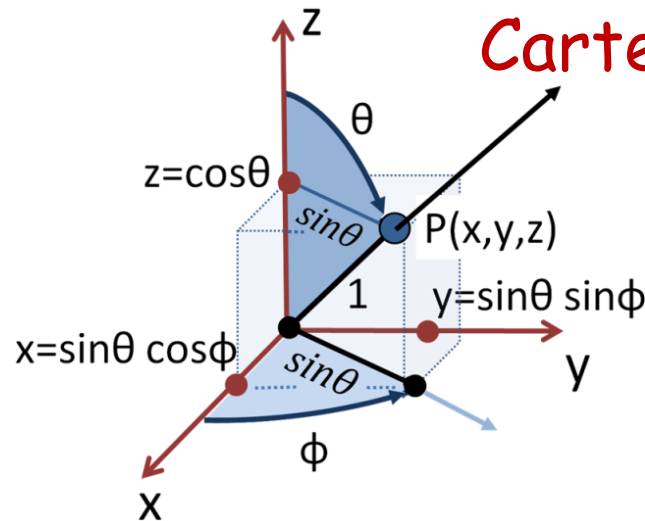
- Matter Waves: de Broglie $\Rightarrow$ $\lambda = \frac{h}{P}$

- Heisenberg's uncertainty principle $\Rightarrow$ $\Delta p_x \cdot \Delta x \geqslant \frac{h}{4\pi}$

- Schrödinger's Equation $\Rightarrow$ $\hat{H} \psi = E \psi$ (for H-atom)

  Energy $\nearrow$

  operator

  wave-function

  Binding energy of e^- in H-atom

  ψ can $\searrow$

  Cartesian Coordinates

  to

  polar spherical coordinates

  nucleus x $\bullet (x,y,z)$

Spherical Polar Coordinates

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$z = \cos\theta$

$x = \sin\theta \cos\phi$

$y = \sin\theta \sin\phi$

P(x,y,z)

Conversion from Cartesian coordinates ?

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$

- 'r' ranges from 0 to ∞

- the co-latitude θ ranges from 0 (north pole) to Π (south pole)

- the azimuth φ ranges from 0 to 2Π
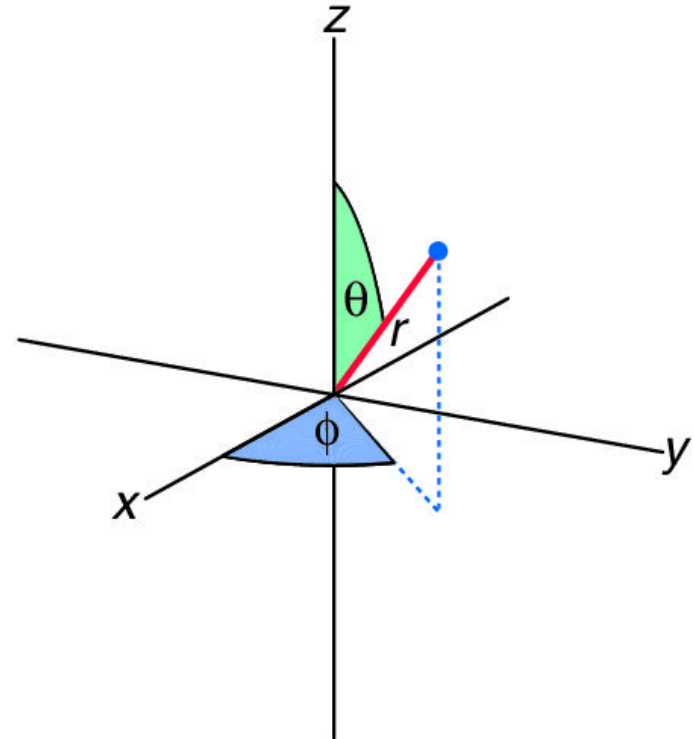
What we learnt from solving SE?

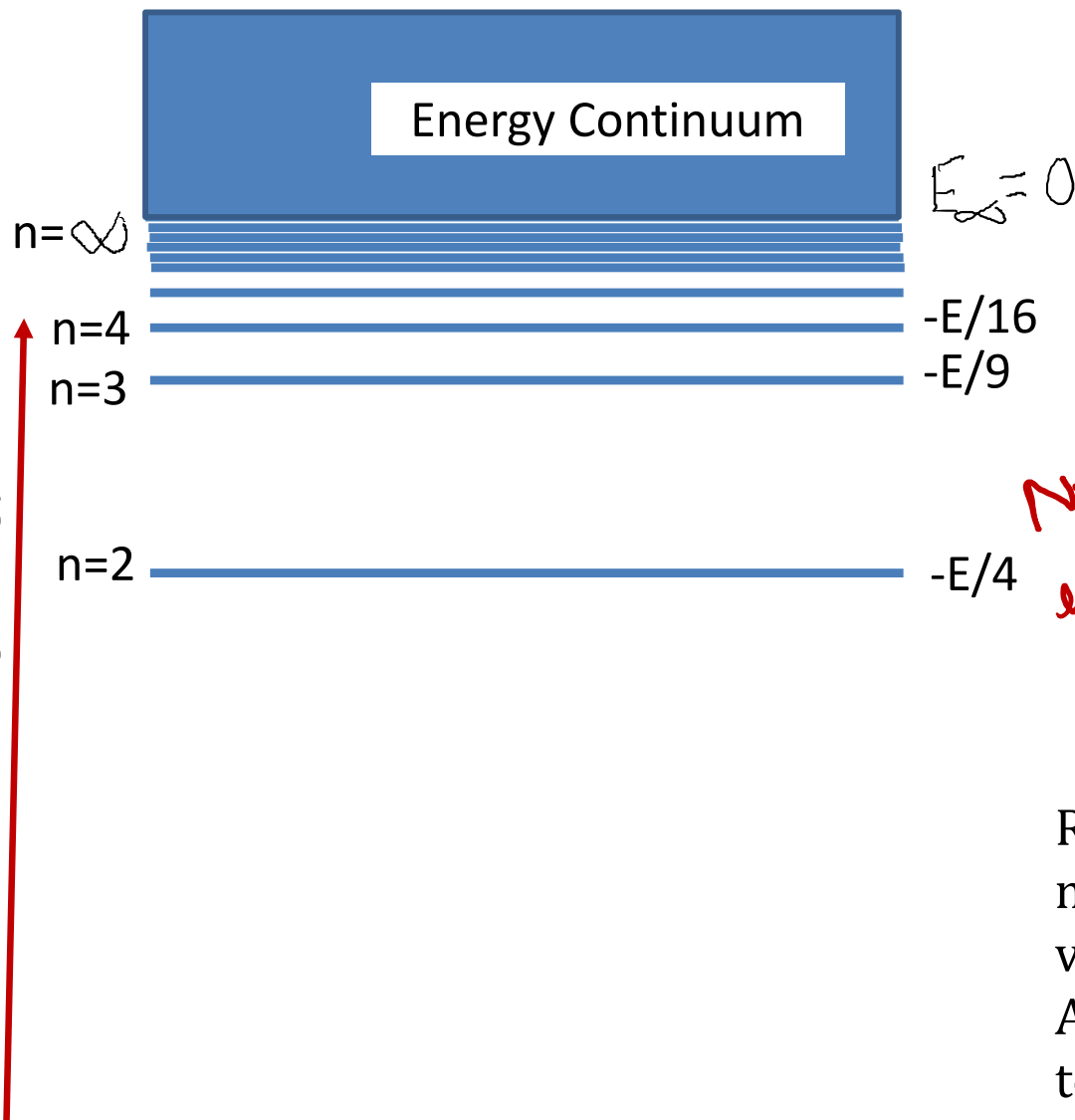Formulate a correct Hamiltonian
(total energy) Operator H

Solve $H\Psi=E\Psi$ (2nd order PDE)
by separation of variable and
intelligent trial/guess solutions

**Probability and
Average Values**

Energies of states
Corresponding to
Quantum Numbers

Quantum Numbers
that specify the
"state" of the system

Energy Continuum

$n=\infty$

$n=4$ $-E/16$

$n=3$ $-E/9$

$n=2$ $-E/4$

$n=1$ $-E = R_h$

Increasing Energy

$E_\infty = 0$

Handwritten notes:

$n=1 ; E = -R_h$

$n=2 ; E = -\dfrac{R_h}{4}$

$n=3 ; E = -\dfrac{R_h}{9}$

$E = -\dfrac{1}{n^2}\boxed{\dfrac{me^4}{8\varepsilon_0^2 h^2}}$

$\Downarrow$

R_h

$E = -\dfrac{R_h}{n^2}$

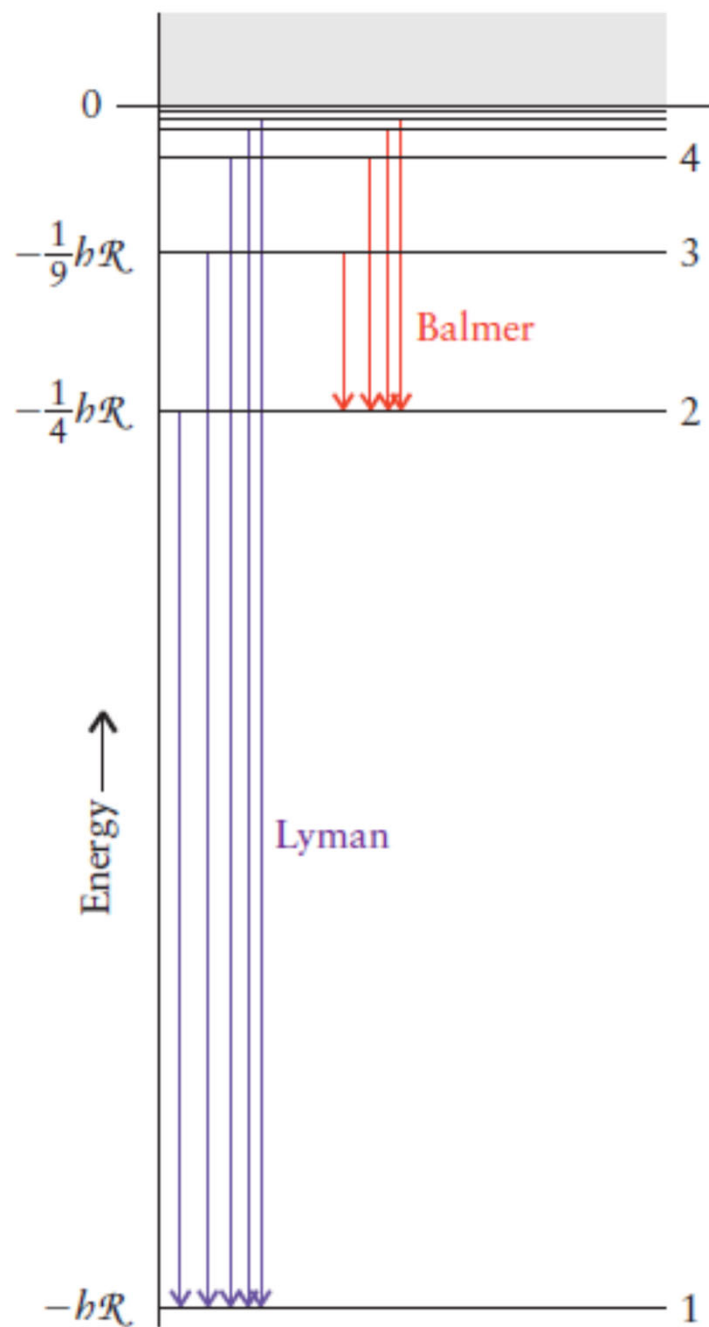Not possible for electron to be bond by energy $-R_h$ or $-\dfrac{R_h}{2}$ or $-\dfrac{R_h}{3}$

R_h is Rydberg Constant = 2.17987×10^{-18} J

n= principal quantum numbers; allowed values 1,2,3,....∞

Allowed energies are often written in terms of n

For energies of H-like atoms such as He^+:

$$E = -\dfrac{Z^2 R_h}{n^2}$$

$$n_j = \otimes = -\frac{R_h}{n_1^2}$$

$$n_2 = -\frac{R_h}{n_2^2}$$

$$\Delta E = -R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Ψ (r, θ, φ, t)

- Ψ in general is a function of r, θ, φ and t denoted as Ψ (r, θ, φ, t)

- We will look at wave functions which are called stationary waves, i.e. Ψ which are not dependent on t- in those cases we are looking a Ψ when the atom is stable and sitting idle

- The Ψ we will look at will be Ψ (r, θ, φ) also known as time-independent QM

- When we go and solve Schrodinger equation for Ψ (r, θ, φ), two more quantum number drop out in the differential equation.

l: The angular Quantum Number

- We get a new quantum no l, called the angular momentum quantum number because

- It dictates how much angular momentum the electron has

- It also has allowed values- 0, 1, 2, ..., (n-1)

- Classically thinking l would denote the angular momentum

m: Magnetic Quantum Number

- The third quantum number which drops out is m, called the magnetic quantum number

- It dictates how an atom moves/behaves in a magnetic field

- More precisely what m is the z-component of the angular momentum

- Allowed values of m are m=0, ±1, ±2, …., ±l

Ψ_{nlm} = Orbitals

- For n=1, l=0, m=0, the elctron is called to be in 100 state and the wave function corresponding to this electron is ψ_{100} $\longrightarrow$ $n=2$ $l=0,1$ $m=0,\pm1$

- The other wave functions possible for n=2 are ψ_{200}, ψ_{210}, ψ_{211} and ψ_{21-1} ψ_{2s}

- All these four states have the same energy i.e. $-R_H/4$

- The other way of representing the wave function is a orbital...the orbital is actually the wave-function

- If l=0, s; l=1, p; l=2, d

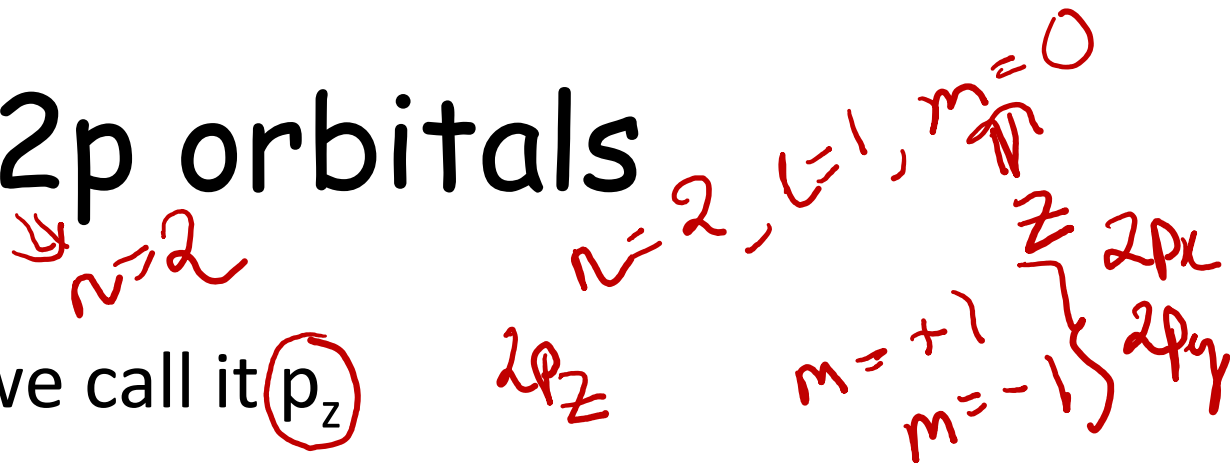- So all ψ_{210}, ψ_{211} and ψ_{21-1} would be called 2p. $2p$

The 2p orbitals

- When l=1, m=0, we call it p_z

- When m=1, it is p_x and when m=-1 it is p_y

- Not fully correct because the Schrodinger equation solution of ψ_{211} and ψ_{21-1} are complex wave functions

- For us to think about p_x and p_y wave function, we take a linear combination. P_x is $\psi_{211} + \psi_{21-1}$ while p_y is $\psi_{211} - \psi_{21-1}$

d orbitals

- For n=1, only one state

- In n=2, four degenerate states

- For n=3, 9 degenerate states

- For l=2, m=-2 is $3d_{xy}$, m=-1 is d_{yz}, m=0 is d_{z2}, m=1 is d_{xz}, m=2 d_{x2-y2}

- For m=0 the d_{z2} is a real function

- For m= -2, -1, +1 and +1, those wave functions when we solve Schrodinger's equation are complex wave functions. Again we take linear combination make them real