Emittance M: Total power emitted per unit area

$M = \sigma T^4$, (Stefan-Boltzmann law);

where, $\sigma = 5.67 \times 10^{-8}$ $Wm^{-2}K^{-4}$; (Stefan-Boltzmann constant)

Weins' displacement law:

$\lambda_{max} T = 2.9$ mm·K *OR* $\nu_{max}/T = \alpha k/h$ (where $\alpha \approx 2.821439\ldots$)

BBR: Failed attempts in explaining the trends

Why does the curve go through a maximum?

Attempts to explain BBR:

- Rayleigh and Jeans pictured the radiation energy in the cavity as a collection of oscillators. Using the classical physics and empirical observations, they derived the formula:

$$\rho(\lambda, T)\, d\lambda = \frac{8\pi k T}{\lambda^4}\, d\lambda$$

  Does well at long wavelength (low frequency), but fails miserably at short wavelengths (ultraviolet catastrophe)

- Wien, in his formulation guessed the qualitative trend at short wavelengths (high frequencies), but failed quantitatively at long wavelengths.

$$\rho(\lambda, T)\, d\lambda \quad \propto \quad \frac{e^{-\beta c/\lambda T}}{\lambda^5}\, d\lambda$$

BBR: Planck's quantum hypothesis explained it all

Assumption: Molecules of the black-body behave like simple harmonic oscillators and have characteristic vibrational frequency

Crucial assumption: The energy exchange between the walls of the black-body and the interior could only occur in integral multiples of a quantum of energy.

$$\Delta E = n h \nu; \quad n = 0, 1, 2, \ldots; \nu = c/\lambda$$

Using this, Planck derived radiation formula:

$$\rho(\lambda, T) d\lambda = \left(\frac{8 \pi h c}{\lambda^5}\right) \frac{d\lambda}{e^{hc/\lambda kT} - 1}; \text{ where, k is the Boltzmann constant.}$$

Planck found that with h=6.626 x 10^{-34}Js, the above expression gives perfect agreement with experiment

- Reduces to Rayleigh and Jeans law at larger wavelengths (lower frequencies)
- Reduces to Wein's formula at shorter wavelengths (higher frequencies)
- Differentiate in order to get Wein's displacement law
- Integrate in order to get Stefan-Boltzmann law

Einstein proposed particle nature of light and explained the photoelectric effect

- Einstein postulated that light may be considered as a collection of particles, each of energy $h\nu$

- Kinetic energy of emitted electrons is given by $K = h\nu - \varphi$, where the work function φ is the energy required to just overcome the binding energy of the electron, and with $\varphi = h\nu_0$, (ν_0 is threshold frequency) one obtains $K = h\nu - h\nu_0$
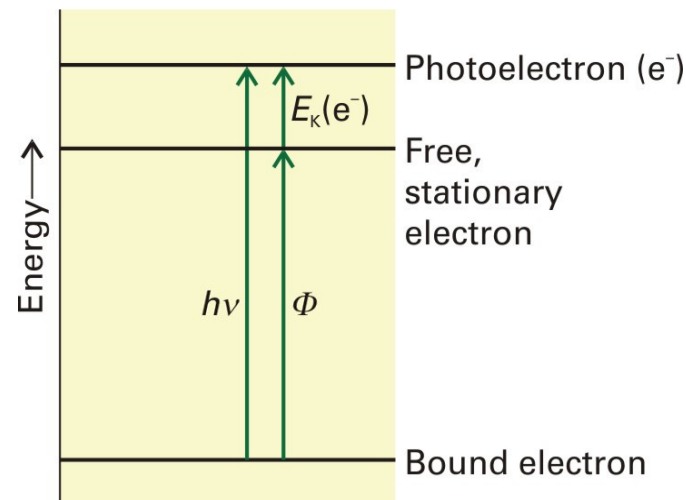
Intensity being proportional to the number of photons cannot bring about photoelectric effect if the frequency is less than the threshold frequency. Photoelectric current is proportional to number of photoelectrons, which is in turn proportional to intensity.
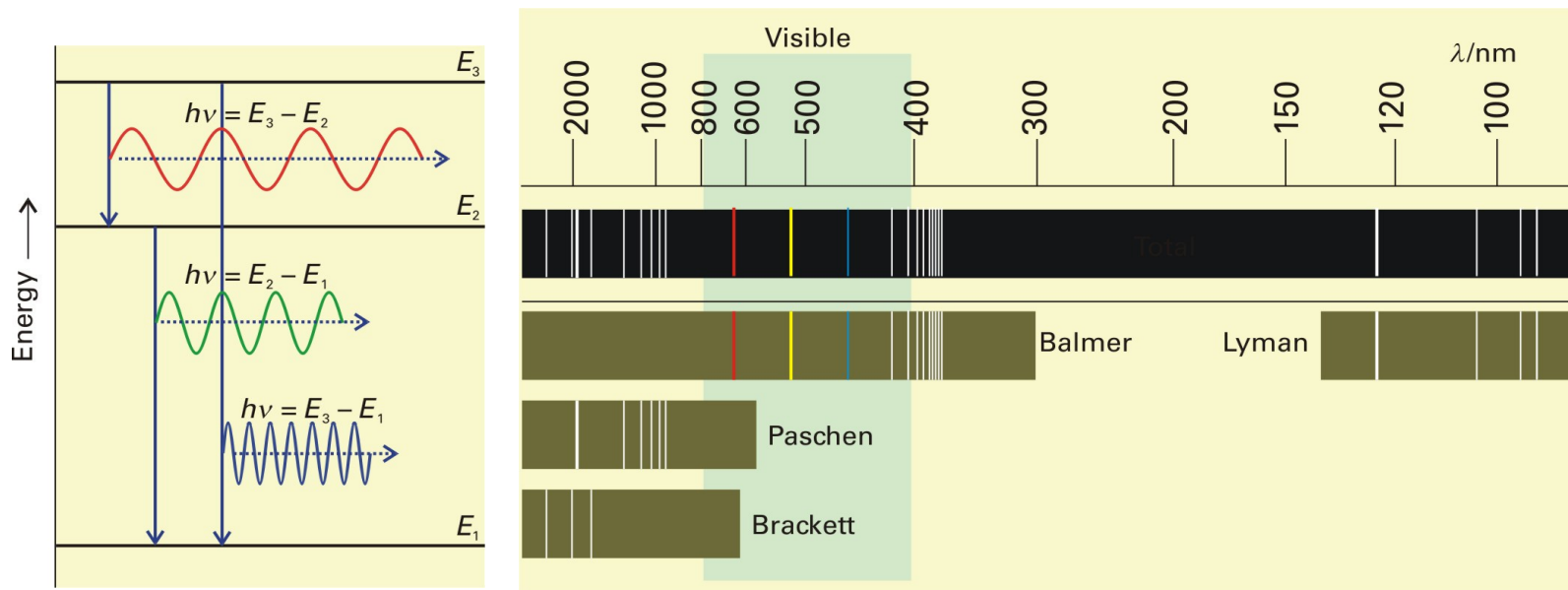
Emission spectrum of hydrogen atom – discrete lines observed

When the electron in the hydrogen atom undergoes a transition from energy level E_2 to E_1, the transition is accompanied by the emission of a photon of frequency $\nu = (E_2 - E_1)/h$, or in terms of the wave number

$$\tilde{\nu} = 1/\lambda = (E_2 - E_1)/hc = R(1/n_1^2 - 1/n_2^2)$$

Lyman, Balmer, Paschen, Brackett, Pfund series!

Bohr's model of hydrogen atom explained the line spectrum

- Electron (mass m and charge –e) moving in circular orbit of radius r about nucleus of charge Ze

$$mv^2/r = Ze^2/4\pi\varepsilon_0 r^2$$

- According to classical physics, electron must radiate energy, and fall into the nucleus

- Bohr postulated stable orbits with radius given by $mvr = nh/2\pi = n\hbar$, n=1,2,3,… - quantization of angular momentum

- Combining, one finds $r = (n^2/Z)a_0$, where

$a_0 = 4\pi\varepsilon_0\hbar^2/me^2$ is the Bohr radius

- Also the energy $E = p^2/2m - Ze^2/4\pi\varepsilon_0 r = -Ze^2/8\pi\varepsilon_0 r$

$E_n = -mZ^2e^4/32\pi^2\varepsilon_0^2\hbar^2 n^2 = -RhcZ^2/n^2$ where R is the Rydberg constant

de Broglie matter waves

- If light (radiation) can be viewed as a collection of particles, then can entities considered as particles also be seen as waves?

- For photons, using $pc = E = hc/\lambda$, one has for the momentum of a photon $p = h/\lambda$

- de Broglie postulated the existence of matter waves associated with particles, with a wave length given by $\lambda = h/p$, where p is the linear momentum

Heisenberg's Uncertainty Principle

It is impossible to specify simultaneously, with arbitrary precision, (a given Cartesian component of) the momentum and position of a particle

$$\Delta p_x \Delta x \geq \frac{\hbar}{2} \qquad \Delta p_y \Delta y \geq \frac{\hbar}{2} \qquad \Delta p_z \Delta z \geq \frac{\hbar}{2}$$

More generally, it is impossible to specify simultaneously, with an arbitrary precision, the canonically conjugate variables in quantum mechanics.
Canonically conjugate variables are the physically measurable quantities, which when multiplied have the dimensions as that of $\hbar$.
For example,
- Any (even non-cartesian) component of position and the conjugate momentum
- Angular position and angular momentum
- Energy and time

For energy time uncertainty measurement, the inequality is slightly different:

$$\Delta E \, \Delta t \geq \hbar$$

Wave function

Consider a particle moving along a positive *x*-direction.
The wave associated with the particle must be a well-behaved simple harmonic wave of the form:

$$\Psi(x,t) = A\,e^{i(\kappa x - \omega t)} \qquad (\kappa \text{ is propagation constant})$$

We have:

$$E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \hbar\omega \qquad\qquad p_x = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar\kappa$$

It follows,

$$\Psi(x,t) = A\,e^{\frac{i}{\hbar}(p_x \cdot x - E \cdot t)}$$

Wave function

We have obtained:

$$\Psi(x,t) = A\,e^{\frac{i}{\hbar}(p_x \cdot x - E \cdot t)}$$

We now study the spatial dependence of the function:

$$\frac{\partial \Psi}{\partial x} = A\,e^{\frac{i}{\hbar}(p_x \cdot x - E \cdot t)}\,\frac{i}{\hbar}\,p_x = \frac{i}{\hbar}\,p_x\,\Psi \qquad\qquad \hat{p}_x\,\Psi = \frac{\hbar}{i}\,\frac{\partial}{\partial x}\,\Psi$$

$$\hat{p}_x = \frac{\hbar}{i}\,\frac{\partial}{\partial x} \qquad \text{(Momentum Operator defined)}$$

Taking the second derivative wrt x, it follows

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2}\,\Psi \qquad\qquad p_x^2\,\Psi = -\hbar^2\,\frac{\partial^2}{\partial x^2}\,\Psi$$

Consequently, we have

$$\frac{p_x^2}{2m} = -\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2} \qquad \text{(K.E. Operator defined)}$$

Wave function

We have obtained:

$$\Psi(x,t) = A\, e^{\frac{i}{\hbar}(p_x \cdot x - E \cdot t)}$$

Next, we study the temporal dependence of the function:

$$\frac{\partial \Psi}{\partial t} = A\, e^{\frac{i}{\hbar}(p_x \cdot x - E \cdot t)} \frac{-i}{\hbar} E = \frac{1}{i\hbar} E\, \Psi \qquad\qquad \hat{E}\, \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \qquad \text{(Total energy operator*)}$$

Let *V(x)* be the potential energy operator.

It then follows:
$$-\frac{\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} + \hat{V}(x)\, \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\hat{H}\, \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad \text{(Time-dependent Schrödinger equation)}$$

The time dependent Schrödinger equation describes time evolution of the system

Variable separation

We have $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2 \Psi(x,t)}{\partial x^2}+\hat{V}(x)\Psi(x,t)=i\hbar\dfrac{\partial \Psi(x,t)}{\partial t}$

Suppose it is possible to express the wavefunction as $\Psi(x,t)=\psi(x)\phi(t)$

Then, by variable separation method, one can solve and obtain

$\hat{H}\psi=E\psi$, that is : $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}+\hat{V}(x)\psi=E\psi$

This is one dimensional time-independent Schrödinger equation.

The time-dependent part gives: $i\hbar\dfrac{d\phi}{dt}=E\phi \quad \Rightarrow \quad \phi(t)=e^{-iEt/\hbar}$

What will be the probability density in such a case?

$$|\Psi(x,t)|^2=\Psi(x,t)^*\Psi(x,t)$$
$$=\psi(x)^*\psi(x)\phi(t)^*\phi(t)=\psi(x)^*\psi(x)e^{iEt/\hbar}e^{-iEt/\hbar}=|\psi(x)|^2$$

The probability density (and hence, the probability) turns out to be time-independent! Such a state is said to be stationary.

Quantized energy levels and wavefunctions

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right); \qquad n = 1,2,3,\ldots$$

The subscript n in the wavefunction is to indicate that the wavefunction depends on the quantum number, n.
Why did we discard $n=0$?
What about $n=-1,-2,-3,\ldots$? Are they allowed? Which states do they represent?
(Find it out)

Homework: Normalize the wavefunction to show that constant, $A = \sqrt{\dfrac{2}{L}}$.

The normalized wavefunctions are thus, given by

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right); \qquad n = 1,2,3,\ldots$$

Energy of the system is quantized.

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{8\pi^2 m} = \frac{n^2 h^2}{8mL^2}; \qquad n = 1,2,3,\ldots$$

2D or rectangular box: [$V(x,y)=0$ for $0 \leq x \leq a$; $0 \leq y \leq b$ and $V(x,y)=\infty$ otherwise]

We have obtained:
$$-\frac{\hbar^2}{2m}\frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2}-E_x=\frac{\hbar^2}{2m}\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2}+E_y$$

The LHS is a function of x alone and RHS is a function of y alone, and x and y are independent variables. Therefore, each side would be equal to a constant. Since E_x and E_y are unknown constants, their values may be tuned such that each side in the above equation equals to zero, and we have:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2}-E_x=0 \qquad \Rightarrow \qquad \frac{d^2\psi_x}{dx^2}+\frac{2mE_x}{\hbar^2}\psi_x=0\,;0\leq x\leq a$$

$$\frac{\hbar^2}{2m}\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2}+E_y=0 \qquad \Rightarrow \qquad \frac{d^2\psi_y}{dy^2}+\frac{2mE_y}{\hbar^2}\psi_y=0\,;0\leq y\leq b$$

Thus, we obtain two 1D equations which can be solved by applying the boundary conditions to get:

$$\psi_{n_x,n_y}(x,y)=\psi_{x,n_x}(x)\psi_{y,n_y}(y)=\frac{2}{\sqrt{ab}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right) \qquad E_{n_x,n_y}=\frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right)$$

$$n_x=1,2,3,\ldots;\quad n_y=1,2,3,\ldots$$

PIB – 3D

3D box: [$V(x,y,z)=0$ for $0 \leq x \leq a$; $0 \leq y \leq b$; $0 \leq z \leq c$ and $V(x,y,z)=\infty$ otherwise]

The logic can be extended to 3D box or even multidimensional case.

For 3D, the kinetic energy operator is given by $-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}\right)\equiv -\dfrac{\hbar^2}{2m}\nabla^2$

The normalized wavefunction and energy are:

$$\psi_{n_x,n_y,n_z}(x,y,z)=\sqrt{\dfrac{8}{abc}}\sin\left(\dfrac{n_x\pi x}{a}\right)\sin\left(\dfrac{n_y\pi y}{b}\right)\sin\left(\dfrac{n_z\pi z}{c}\right)$$

$$n_x=1,2,3,\ldots;\quad n_y=1,2,3,\ldots;\quad n_z=1,2,3,\ldots$$

$$E_{n_x,n_y,n_z}=\dfrac{h^2}{8m}\left(\dfrac{n_x^2}{a^2}+\dfrac{n_y^2}{b^2}+\dfrac{n_z^2}{c^2}\right)$$

Special cases:
Square box (2D box with both the sides equal)
Cubic box (3D box with both the sides equal)
Cuboid box (3D box with two sides equal)

Energetic degeneracy – two or more energy levels having same energy

Homework – For Square and cubic boxes, find the energies of first ten levels and the degeneracy of each level.

Rotation: particle on a ring

Angular momentum: $|\vec{J}| = |\vec{r} \times \vec{p}| = I\omega$

$I = \mu r^2$ (Moment of intertia of the particle of mass μ moving in an orbit of radius r)

Consider the rotation in a plane orbit, say, in xy-plane, and centered at origin. The angular momentum vector would lie along the z-axis.

In polar coordinates, the operator form for z-component of the angular momentum is given by

$$\hat{J}_z = \frac{\hbar}{i} \frac{d}{d\phi}; \quad with \quad x = r\cos\phi; y = r\sin\phi$$

The kinetic energy corresponding to the rotational motion is $\dfrac{J_z^2}{2I}$

The rotational kinetic energy operator would, thus, be $\dfrac{\hat{J}_z^2}{2I} = -\dfrac{\hbar^2}{2I}\dfrac{d^2}{d\phi^2}$

Rotation: particle on a ring

We have *V(r)=0* at *r=r₀* and infinite otherwise.

Thus, for the orbit of fixed radius, *r=r₀*, the Schrödinger equation takes the form:

$$-\frac{\hbar^2}{2I}\frac{d^2\Phi(\phi)}{d\phi^2}=E\,\Phi(\phi)$$

The wavefunction, $\Phi(\phi)$ for rotation about the z-axis is a pure function of the azimuthal angle, ϕ.

The single-valuedness of the wavefunction requires that its values should repeat after each rotation, which results in the periodic boundary condition (also referred to as cyclic boundary condition):

$$\Phi(2\pi+\phi)=\Phi(\phi)$$

Particle on a ring

We have $\quad -\dfrac{\hbar^2}{2I}\dfrac{d^2\Phi(\phi)}{d\phi^2}=E\,\Phi(\phi) \quad\longrightarrow\quad \dfrac{d^2\Phi(\phi)}{d\phi^2}+\dfrac{2IE}{\hbar^2}\Phi(\phi)=0$

We substitute $\dfrac{2IE}{\hbar^2}=m^2$ and get $\quad \dfrac{d^2\Phi(\phi)}{d\phi^2}+m^2\,\Phi(\phi)=0$

The general solution is of the form $\quad \Phi(\phi)=Ae^{im\phi}$

Now we apply the periodic boundary condition and solve:

$\Phi(2\pi+\phi)=Ae^{im(2\pi+\phi)}=\Phi(\phi)=Ae^{im\phi}$
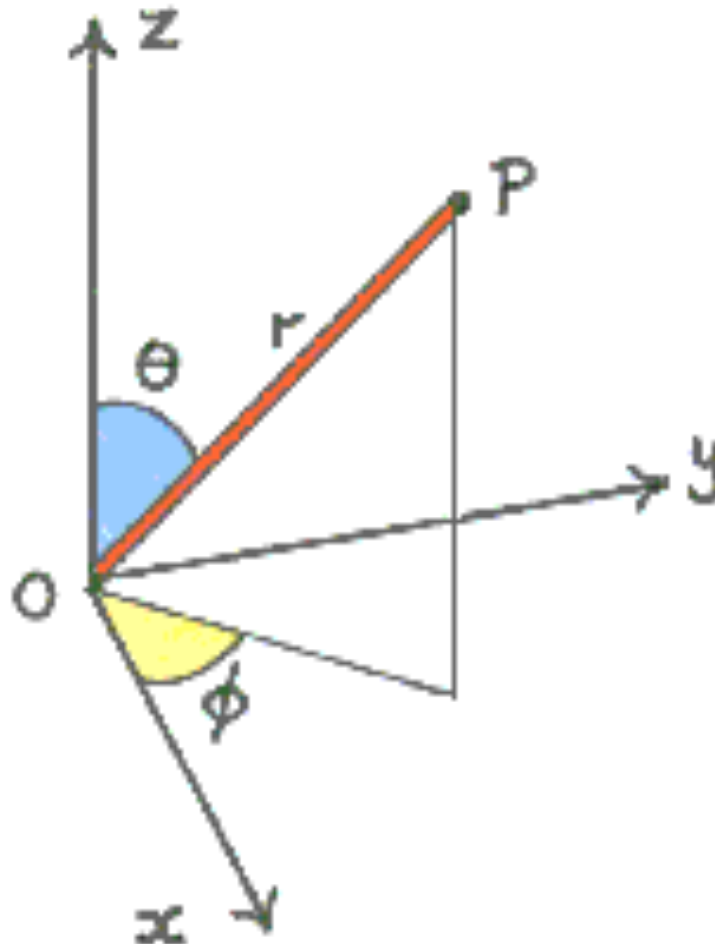
$Ae^{2\pi mi}e^{im\phi}=Ae^{im\phi}$

$e^{2\pi mi}=1 \qquad \Rightarrow \qquad m=0,\pm1,\pm2,\pm3,\ldots$

Homework: Normalize the wavefunction to evaluate the constant, A.

Rotation of sphere (revision)

Polar and azimuthal angles:

$$r = \left(x^2 + y^2 + z^2 \right)^{1/2}$$

$$\theta = \cos^{-1} \frac{z}{\left(x^2 + y^2 + z^2 \right)^{1/2}}$$

$$\phi = \tan^{-1} \frac{y}{x}$$

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

Rotation on a sphere – rigid rotor

Particle constrained to rotate on surface of sphere of radius R

Classically, $E = J^2/2mR^2$

Schrödinger equation involves the polar angle θ and the azimuthal angle φ as variables

On solving, and imposing the appropriate boundary conditions, obtain the 'spherical harmonics,' $Y_{l,m_l}(\theta,\varphi)$, characterized by two quantum numbers l and m_l.

The spherical harmonics are a product of two functions

$Y_{l,m_l}(\theta,\varphi) = \Theta_{l,m_l}(\theta)\Phi_{m_l}(\varphi)$; $m_l = -l, -l+1,..0,..l-1, l$

Energy $E_l = l(l + 1)\hbar^2/2I$ ← Depends on l, not on m_l

1D harmonic oscillator: characteristic features

- The wavefunctions are alternately even and odd functions corresponding to the even and odd values of v (vibrational quantum number).

- Number of nodes = v, no nodes for the ground state

- $E_v=(v+\frac{1}{2})h\upsilon$; Zero point energy $E_0= \frac{1}{2}\, h\upsilon$

- For ground state, probability density is maximum at mean position. As v increases, the probability density max gradually shifts towards the turning points – classical limit obtained as $v\rightarrow\infty$

Operator forms in spherical polar coordinates

K.E. Operator for radial motion: $$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

K.E. Operator for angular motion: $\mathscr{L}^2/2I$

Angular KE operator is expressed as:

$$-\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

This term arises from the square of the z-component of angular momentum

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

Schrödinger equation for hydrogenic atom

Potential energy is only due to the coulombic attraction between the electron and the nucleus

Spherical polar coordinate system is the most suitable for solving the Schrödinger equation for hydrogenic atom:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]-\frac{Ze^2}{4\pi\epsilon_0 r}\psi=E\psi$$

KE acting on ψ

PE acting on ψ

It can be proven that the quantity in the square bracket is $\nabla^2\psi$

$$\nabla^2\psi=\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}$$

Energy levels

Energy – Depends on principle quantum number, *n*.

Obtained as Hamiltonian eigenvalues:
$$\hat{H}\,\psi_{n,l,m_l}(r,\theta,\phi)=E_n\,\psi_{n,l,m_l}(r,\theta,\phi)$$

$$E_n=-\frac{\mu e^4 Z^2}{32\pi^2\varepsilon_0^2\hbar^2 n^2};\qquad n=1,2,3,\ldots$$

Note that energy doesn't depend on *l* and m_l.

Energy expression coincides with the Bohr model result.

The principle quantum number, *n*, imposes bound on the azimuthal quantum number, *l*, (l=0,1,2,...n–1), which in turn imposes restriction on the orbital magnetic quantum number, m_l, (m_l= -l, -l+1, ..., 0, ..., l–1, l).

The energy of a hydrogenic wavefunction depends only on the principle quantum number, and is independent of the azimuthal and the orbital magnetic quantum numbers.

Degeneracy with respect to
- energy (Hamiltonian eigenstates): *n² **
- Angular momentum: *2l + 1*
- Component of angular momentum – non-degenerate *

Magnitude of Angular momentum – orbital angular momentum quantum number (or azimuthal quantum number), *l*.

Hydrogenic orbitals are also eigenfunctions of $\mathcal{L}^2$ operator:

$$\mathcal{L}^2 \psi_{n,l,m_l} = l(l+1)\hbar^2 \psi_{n,l,m_l}$$

Thus, the magnitude of orbital angular momentum is

$$|\overline{\mathcal{L}}| = [l(l+1)]^{1/2}\hbar; \; l = 0,1,2,...., n-1; \text{ for given } n.$$

For given *l*, the orbitals are *(2l+1)*-fold degenerate *wrt* $\mathcal{L}^2$.

Hydrogenic orbitals-characteristics

The general form is $\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(r)Y_{l,m_l}(\theta, \varphi)$

Number of radial nodes is determined from the Radial function and equals to the degree of polynomial in *r*.

$$R_{n,l}(r) = N r^l \left(\sum_{j=0}^{n-l-1} (-1)^j a_j r^j \right) e^{-Zr/na_0}$$

Azimuthal quantum number equals to number of angular nodes

Principle quantum number

$Y_{l,m_l}(\theta, \varphi)$ are spherical harmonics: Polynomial of degree, "*l*" in $\cos\theta$ and/or $\sin\theta$ multiplied by $\Phi_{m_l}(\varphi)$