Chapter 7: Atomic Physics - *Physics of the atom.*

Quantum Mechanics

$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi$ *Schrodinger Eq.*

$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(r) \;\Rightarrow\; H_{3D} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$

$\vec{p} = \frac{\hbar}{i}\vec{\nabla}$ $\quad r \to r,$ *and* $E \to i\hbar\frac{\partial}{\partial t}$ *are operators*

Generalized solutions are of the form

$\Psi(\vec{r},t) = \sum_n \psi_n(\vec{r})e^{-i\frac{E_n}{\hbar}t}$ *we must find the eigenvalues* E_n *and eigenfunctions* ψ_n

$H\psi_n = E_n\psi_n$ *eigenvalue equation*

Once we have Ψ we can measure property of the system A by calculating the expectation value, $<A> = \oint \Psi^* A \Psi \, dV$ *where* $\Psi^*\Psi = PDF$

3D Rigid Rotator Problem (tumbling)

$H = \frac{1}{2}I\omega^2 = \frac{1}{2}\frac{L^2}{I}$ *with* $L = I\omega$ *angular momentum* $(L = \vec{r}\, x \frac{\hbar}{i}\vec{\nabla})$

$H\psi_n = E\psi_n$

$\frac{1}{2I}L^2\psi_n = E_n\psi_n \quad L^2(\theta,\varphi) = -\hbar^2\left(\frac{\hbar}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$

Spherical Harmonics

$\psi_n = Y_{lm}(\theta,\varphi)$ *well known solution to the Laplace Equation*

$Y_0^0 = \frac{1}{2}\sqrt{\frac{1}{\pi}}, \quad Y_1^0 = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, \quad Y_1^{\pm 1} = \frac{\mp}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\varphi}$

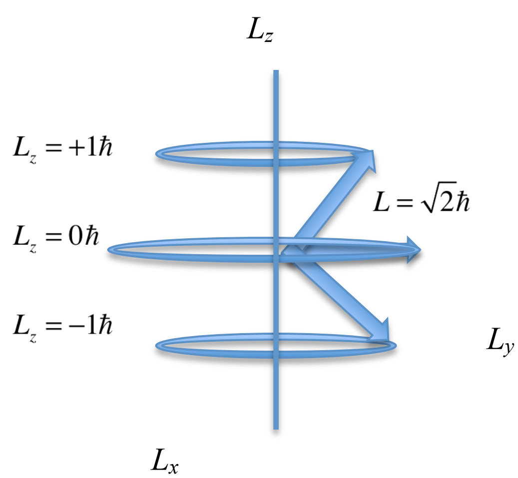
$L^2 Y_{lm} = \overbrace{\ell(\ell+1)\hbar^2}^{eigenvalue} Y_{lm}$ *or* $<L^2> = \ell(\ell+1)\hbar^2$

$E_\ell = \frac{1}{2I} < L^2 > = \frac{1}{2I}\ell(\ell+1)\hbar^2 \qquad l = 0,1,2,3,...$

Conservation of Angular Momentum

(For systems that conserve angular momentum

or have rotational symmetry)



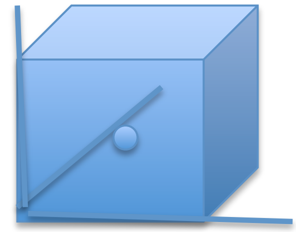
$<L^2> = \ell(\ell+1)\hbar^2 \qquad \ell = 0,1,2,3..$

$<L_z> = m\hbar^2 \qquad m = -\ell ....+\ell$

$<L_x> =$ *not constant (precessing)*

$<L_y> =$ *not constant (precessing)*

3D Particle in a Box *(V=0 inside box, V=∞ outside box)*



$$H\Psi = E\Psi \qquad \textit{Energy eigenvalue equation}$$

$$\frac{-\hbar^2}{2m}\nabla^2\Psi = E\Psi \quad \textit{with } \vec{p} = \hbar\vec{k} \quad \vec{k} \equiv \textit{wave number}$$

$$\textit{let } \Psi = \psi_x\, \psi_y\, \psi_z$$

$$\frac{-\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\Psi = (E_{nx} + E_{ny} + E_{nz})\Psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi_x = E_{nx}\psi_x \qquad \psi_x = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$E_{nx} = \frac{(\hbar k_x)^2}{2m} \quad k_x = \frac{n\pi}{L} \quad n = 1,2,..$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dy^2}\psi_y = E_{ny}\psi_y \qquad \psi_y = \sqrt{\frac{2}{L}}\sin\left(\frac{m\pi y}{L}\right)$$

$$E_{ny} = \frac{(\hbar k_y)^2}{2m} \quad k_y = \frac{m\pi}{L} \quad m = 1,2,..$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dz^2}\psi_z = E_{nz}\psi_z \qquad \psi_z = \sqrt{\frac{2}{L}}\sin\left(\frac{\ell\pi z}{L}\right)$$

$$E_{nz} = \frac{(\hbar k_z)^2}{2m} \quad k_z = \frac{\ell\pi}{L} \quad \ell = 1,2,..$$

$$E_{nm\ell} = \frac{\hbar^2\,\pi^2}{2mL^2}(n^2 + m^2 + \ell^2)$$

$$\Psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi y}{L}\right)\sin\left(\frac{\ell\pi z}{L}\right)$$

Question: What is the degeneracy of the ground state in the 3D particle in a box?

$E_{100} = E_{010} = E_{001} = \dfrac{\hbar^2\,\pi^2}{2mL^2}$ degeneracy=3

Question: What is the average L_x for the particle in a box ($L = r \times p$)?

$$< L_x > = < yp_z - zp_y > = < yp_z > - < zp_y >$$

$$< yp_z > = \int \Psi^*(yp_z)\Psi dV = \int_0^L \psi_x^*\psi_x dx \int_0^L \psi_y^* y\psi_y dy \int_0^L \psi_z^* p_z\psi_z dz$$

$$= \{1\}\ \{\neq 0\}\ \{0\} = 0$$

$$< zp_y > = 0$$

$$< L_x > = 0 \quad < L_y > = 0 \quad < L_z > = 0 \quad \textit{or } < \vec{L} > ! \textit{ no torques}$$

Question: What is the energy of an electron trapped in $L=a_0$ (Boht radius) box?

$$E_{100} = \frac{\hbar^2\,\pi^2}{2ma_0^{\,2}} = \frac{\hbar^2\,(3.14159)^2}{2(5.11\,MeV/c^2)(5.29x10^{-11}m)^2}$$

Hydrogen Atom $V(r) = -k\frac{Ze^2}{r}$

$H = \frac{\vec{p}^2}{2\mu} + V(r)$ $\mu = \frac{m_e m_p}{m_e + m_p}$ *reduced mass*

$p^2 = \frac{p_r^{\ 2}}{2\mu} + \frac{p_\Omega^{\ 2}}{2\mu} = \frac{p_r^{\ 2}}{2\mu} + \frac{L^2}{2\mu r^2}$ *radial and angular momenta*

$H = \frac{p_r^{\ 2}}{2\mu} + \frac{L^2}{2\mu r^2} + V(r)$

$H|\psi> = E|\psi>$ *Solve eigenvalue equation* $|\psi>_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$

$[\frac{p_r^{\ 2}}{2\mu} - k\frac{Ze^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}]|\psi> = E_n|\psi>$ *where* $|\psi>_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$

$\psi_{n\ell m} = R_{n\ell}(r) Y_\ell^m(\theta,\varphi)$

$\int |R_{n\ell}(r) Y_\ell^m(\theta,\varphi)|^2 dV = 1$

$n = 1,2,3,4$

$\ell = 0,1,2,3,..(n-1)$

$m = -\ell ......+\ell$

$E_n = -\frac{1}{2}\frac{kZe^2}{r_n} = -\frac{Z^2}{n^2} 13.6\,eV$

$r_n = \frac{n^2\hbar^2}{\mu k Z e^2} = n^2\frac{a_0}{Z}$

$a_0 = \frac{\hbar^2}{\mu k e^2}$ *Bohr radius*

$R_{n\ell}(r)$ *Laguerre Polynomials*

$R_{10}(r) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$

$R_{20}(r) = \frac{1}{\sqrt{2a_0^3}}(1 - \frac{r}{2a_0})\, e^{-r/2a_0}$

$R_{21}(r) = \frac{1}{2\sqrt{6a_0^3}}\frac{r}{a_0}\, e^{-r/2a_0}$

$Y_\ell^m(\theta,\varphi)$ *Spherical Harmonic*

$Y_0^0 = \frac{1}{2}\sqrt{\frac{1}{\pi}}$

$Y_1^0 = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$

$Y_1^{\pm 1} = \frac{\mp}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\varphi}$

Questions:

1) What is r_1 for H? Hydrogen Z=1, n=1 $r_1 = a_0$

2) What is r_1 for positronium (e+ e-) atom? $\mu = \frac{m_e m_e}{m_e + m_e} = \frac{1}{2} m_e$ $r_1 \to 2r_1 = 2a_0$

3) What is the ground state energy of positronium? E_1=-13.6/2 eV = 6.8 eV

4) The Laguerre Polynomials are an Orthonormal Set of eigenfunctions (like i,j,k unit vectors).

Can we show that $\int_0^\infty R_{10}R_{10}r^2 dr = 1$ *and* $\int_0^\infty R_{10}R_{20}r^2 dr = 0$

$$I = \frac{4}{a_0^3}\int_0^\infty e^{-2r/a_0} r^2 dr = \frac{4}{a_0^3}\frac{e^{-2r/a_0}}{(2/a_0)}(r^2 + \frac{2r}{(2/a_0)} + \frac{2}{(2/a_0)^2})\Big|_0^\infty$$

$$I = \frac{2}{a_0^2} e^{-2r/a_0}(r^2 + a_0 r + \frac{a_0^{\ 2}}{2})\Big|_0^\infty = \frac{2}{a_0^2}(0 - \frac{a_0^{\ 2}}{2}) = -1$$

$$\int x^2 e^{-ax} = -\frac{e^{-ax}}{a}(x^2 + \frac{2x}{a} + \frac{2}{a^2}) \text{ where } a = 2/a_0$$