

Lecture #11: H atom II

Orbital \vec{L} $\vec{L} = \vec{r} \times \hat{p}$ $\hat{p} = \frac{\hbar}{i} \vec{\nabla}$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{s} \frac{\partial}{\partial \theta} \left(s \frac{\partial}{\partial \theta} \right) + \frac{1}{s^2} \frac{\partial^2}{\partial \phi^2} \right] \quad s = r \sin \theta$$

and $\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$

We can find simultaneous eigenstates of these operators because they commute

$$[\hat{L}_z, \hat{L}^2] = [\hat{L}_z \hat{L}^2 - \hat{L}^2 \hat{L}_z] \quad \text{commutator}$$

$$[\hat{L}_z, \hat{L}^2] Y(\theta, \phi) = 0$$

easy to see because ϕ only appears as $\frac{\partial}{\partial \phi}$.

Separation of variables let $Y(\theta, \phi) = P(\theta) F(\phi)$

$$\hat{L}_z F(\phi) = m \hbar F \quad \text{eigenvalue equation}$$

$$\frac{\partial F}{\partial \phi} = i m F \quad m \text{ dimensionless}$$

$$F(\phi) = e^{i m \phi}$$

Continuity of wave function $F(\phi) = F(\phi + 2\pi)$

so $m = 0, \pm 1, \pm 2, \dots$ integer

$$\frac{d^2 F}{d\psi^2} = -m^2 F \quad \text{so}$$

$$\hat{L}^2(PF) = \lambda \hbar^2 PF \quad \text{eigenvalue equation}$$

$$-\hbar^2 \left[\frac{F}{s} \frac{d}{d\theta} \left(s \frac{dF}{d\theta} \right) + \frac{P}{s^2} (-m^2) F \right] = \lambda \hbar^2 PF$$

$$\frac{1}{Ps} \frac{d}{d\theta} \left(s \frac{dF}{d\theta} \right) - \frac{m^2 F}{s^2} = -\lambda$$

$$-\left[\frac{1}{s} \frac{d}{d\theta} \left(s \frac{dF}{d\theta} \right) - \frac{m^2 F}{s^2} \right] = -\lambda P \quad \text{eigenvalue equation for } P(\theta)$$

Associated

Solutions are Legendre Polynomials $P_m(\theta)$.

$$\lambda = l(l+1) \quad \text{and} \quad |m| \leq l$$

$$-l \leq m \leq l \quad 2l+1 \text{ values of } m$$

$$P_{00} = 1$$

$$P_{10} = 2 \cos \theta$$

$$P_{11} = \sin \theta$$

$$P_{20} = 4(3\cos^2 \theta - 1)$$

Spherical harmonics are

$$Y_{lm}(\theta, \phi) = (-1)^m C_{lm} P_m(\theta) e^{im\phi}$$

normalized so that $\int d\Omega Y_{lm}^* Y_{lm} = 1$

$$\int d\Omega = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad \text{all solid angle}$$

To summarize,

$$\hat{L}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \phi)$$

$$\hat{L}_z Y_{\ell m}(\theta, \phi) = \hbar m Y_{\ell m}(\theta, \phi)$$

$$-|m| \leq \ell \quad \ell = 0, 1, 2, \dots; \quad (2\ell+1) \text{ m values}$$

Spherical harmonics are also orthogonal

$$\int d\Omega Y_{\ell m}^* Y_{\ell' m'} = \delta_{\ell\ell'} \delta_{mm'}$$

Energy, Quantum number

$$\psi = R(r) Y_{\ell m}(\theta, \phi)$$

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} (rR) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} R - \frac{\alpha \hbar c}{r} R = E R$$

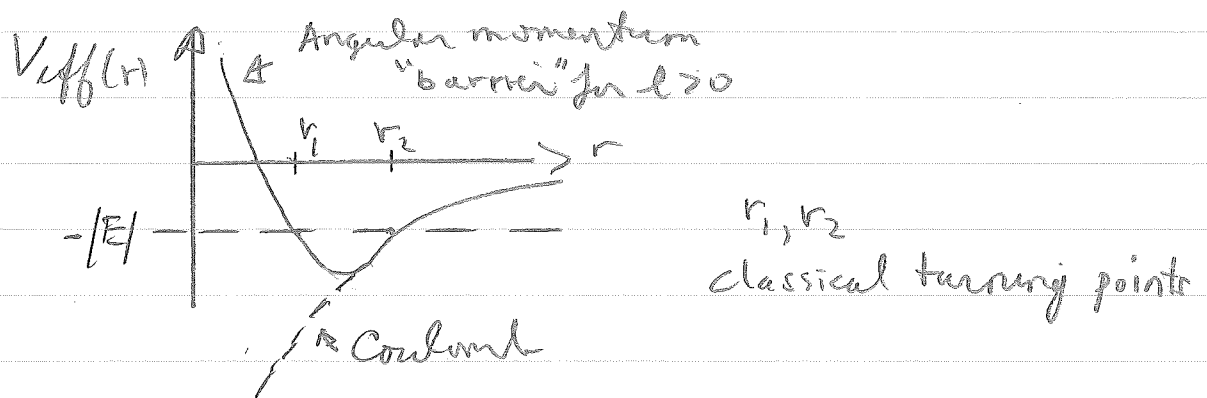
expect eigenvalue to depend on ℓ .

$$\underline{\text{let}} \quad u(r) = rR \quad \frac{d^2 u}{dr^2} \equiv u''$$

$$-\frac{\hbar^2}{2m} u'' + \left[\frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{\alpha \hbar c}{r} \right] u = E u$$

$V_{\text{eff}}(r)$

effective potential



for $r \rightarrow \infty$,

$$-\frac{\hbar^2}{2m} u'' + \frac{\hbar^2 l(l+1)}{2mr^2} u \approx 0$$

$$u'' = \frac{l(l+1)}{r^2} u$$

$$\text{so } u \rightarrow (\text{const}) r^{l+1} \quad \text{as } r \rightarrow \infty \quad \text{and } R \rightarrow \text{const } r^{-l} \quad \text{as } r \rightarrow 0$$

Angular momentum "barrier" pushes wave function away from $r = 0$.

Solutions $R_{nl}(r)$

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

Principle quantum number

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

Orbital quantum number

$$|m| \leq l$$

Magnetic quantum number

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

$R_{n\ell}$ normalized as

$$\int_0^{\infty} r^2 dr |R_{n\ell}|^2 = 1$$

Some explicit examples: $a_0 = \frac{\hbar}{\alpha m c}$

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

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

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

Energy eigenvalues

$$E_n = -\frac{1}{2} m c^2 \alpha^2 \left(\frac{1}{n^2} \right)$$

independent of l

$$= (-13.6 \text{ eV}) \frac{1}{n^2}$$

Remarks

- ① E independent of m consequence of spherical symmetry of potential
- ② E independent of l consequence of $\frac{1}{r}$ potential (classically, closed elliptic orbits)

only other potential with this dynamical symmetry is harmonic

- ③ energy level "shell" degeneracy

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

