Phys 330 Spring 2020

Lecture #11: H atom II

Orbital $\vec{L}$

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

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

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

We can find simultaneous eigenstates of these operators because they <u>commute</u>

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

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

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

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

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

m dimensionless

$$\frac{\partial F}{\partial\phi} = imF$$

$$F(\phi) = e^{im\phi}$$

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

so $m = 0, \pm1, \pm2, \ldots$ integer

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

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

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

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

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

Solution are Associated Legendre Polynomials $P_{\ell m}(\theta)$.

$\lambda = \ell(\ell+1)$ and $|m| \leq \ell$

$-\ell \leq m \leq \ell$ $\quad 2\ell+1$ 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

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

normalized so that $\int d\Omega\, Y_{\ell m}^* Y_{\ell m} = 1$

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

To summarize,

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

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

$|m| \le \ell \qquad \ell = 0, 1, 2, \ldots; \; (2\ell+1)$ m values

Spherical harmonics are also orthogonal

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

Energy Quantum number

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

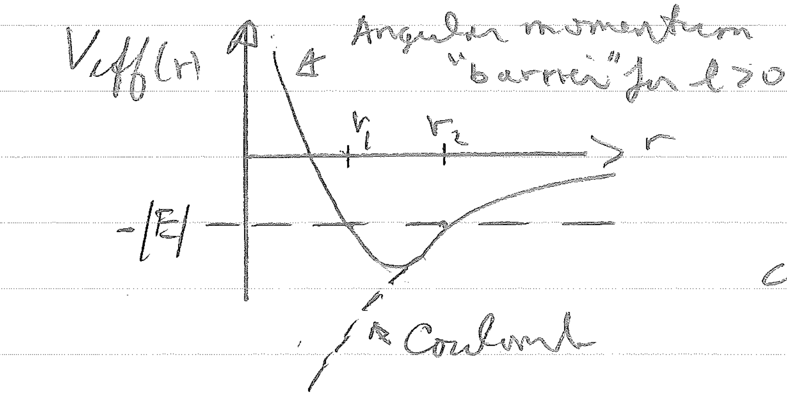
$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2}(rR) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} R - \frac{\alpha\hbar c}{r} R = E_\ell R$$

expect eigenvalue to depend on ℓ.

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

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

$V_{eff}(r)$ effective potential



r_1, r_2 classical turning points

for $r \to 0$,

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

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

so $\displaystyle u \xrightarrow[r\to 0]{} (\text{Const})\, r^{\ell+1}$ & $\displaystyle R \xrightarrow[r\to 0]{} \text{Const}\, r^{\ell}$

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

<u>Solutions $R_{n\ell}(r)$</u>

$n = 1, 2, 3, \ldots$ <u>Principle</u> quantum number

$\ell = 0, 1, \ldots,$ n-1 <u>Orbital</u> quantum number

$|m| \leq \ell$ <u>magnetic</u> Quantum number

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

$R_{n\ell}$ normalized as

$$\int_0^\infty r^2 dr \left[R_{n\ell}\right]^2 = 1$$

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 eigenvalue

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

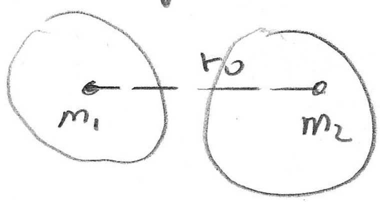
only other potential with this dynamical symmetry is harmonic

③ energy level "shell" degeneracy

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

Orbital angular momentum of diatomic molecules

diatomic molecules have very rigid bonds, so behave like rigid rotors



$r_0 \simeq 0.1\,nm$

Kinetic energy is

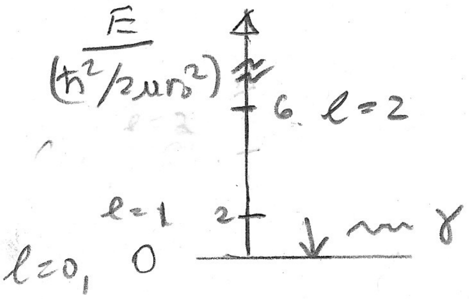
$$\frac{L^2}{2\mu r_0^2} \qquad \mu = \frac{m_1 m_2}{m_1+m_2} \quad \text{reduced mass}$$

$$|\vec{L}|^2 = L^2 = |\vec{r} \times (\mu \dot{\vec{r}})|^2$$

Q.M. wave function we know: $Y_{\ell m}(\theta,\phi)$

Quantized energy

$$\frac{\hat{L}^2}{2\mu r_0^2} Y_{\ell m} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2} Y_{\ell m} \qquad \ell = 0, 1, 2, \dots$$



transition emit microwave photon ($\sim$mm)

Typical energy

$$E = \frac{hc}{\lambda} = \frac{1240\ eV\cdot nm}{1\ mm} \simeq \frac{10^3\ eV\ 10^{-9}\ m}{10^{-3}\ m} = 10^{-3}\ eV$$

easily excited at room temperature

$$\langle KE \rangle_{300K} = \frac{1}{40}\ eV = 0.025\ eV$$