

$$H|nlm\rangle = \frac{-c}{n^2}|nlm\rangle \quad c = 13.6 \text{ eV}$$

Hydrogen

$$L^2|nlm\rangle = l(l+1)\hbar^2|nlm\rangle$$

$$L_z|nlm\rangle = m\hbar|nlm\rangle$$

$$|nlm\rangle \doteq \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

Time Evol

$$|\psi(t)\rangle \doteq \psi_{nlm}(r, \theta, \phi, t)$$

$$= R_{nl}(r) Y_l^m(\theta, \phi) e^{-iE_n t/\hbar}$$

$$E_n = -\frac{c}{n^2}$$

Superposition

$$|\Psi(t)\rangle = \sum_{n, l, m} C_{nlm} R_{nl}(r) Y_l^m(\theta, \phi) e^{-iE_n t/\hbar}$$

$$\langle nlm | \Psi(t) \rangle = C_{nlm}$$

Example: 1s 2p ($m=0$)

$$\Psi(t) \rightarrow P(t) \propto \cos\left(\frac{E_2 - E_1}{\hbar} t\right)$$

Oscillatory dipole

Example: 2s 2p ($m=0$)

$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}} |200\rangle + \frac{1}{\sqrt{2}} |210\rangle$$

$$\Psi(r, \theta, \phi, t) = \frac{1}{\sqrt{2}} \psi_{200} e^{-iE_2 t/\hbar} + \frac{1}{\sqrt{2}} \psi_{210} e^{-iE_2 t/\hbar}$$

$$= \frac{1}{\sqrt{2}} \left(\psi_{200}(r, \theta, \phi) + \psi_{210}(r, \theta, \phi) \right) e^{-iE_2 t/\hbar}$$

$$\psi(r, \theta, \phi, t) = \frac{1}{\sqrt{2}} (\psi_{200} + \psi_{210}) e^{-iE_2 t/\hbar}$$

$$P(r, \theta, \phi, t) = |\psi|^2$$

$$= \frac{1}{2} (\psi_{200}^* + \psi_{210}^*) (\psi_{200} + \psi_{210}) \\ \times \underbrace{(e^{+iE_2 t/\hbar}) (e^{-iE_2 t/\hbar})}_{=1}$$

$$P(r, \theta, \phi, t) = P(r, \theta, \phi)$$

model fixed dipole

Superposition States (normalized)

→ E degenerate
n same l, m diff ✓

$$\frac{1}{\sqrt{2}} |200\rangle + \frac{1}{\sqrt{2}} |211\rangle$$

→ L^2 degeneracy?

l same n, m diff ✓

$$\frac{1}{\sqrt{2}} |210\rangle + \frac{1}{\sqrt{2}} |31,-1\rangle$$

$$l < n$$

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

→ L_z degeneracy?

m same n, l diff ✓

$$\frac{1}{\sqrt{2}} |210\rangle + \frac{1}{\sqrt{2}} |320\rangle$$

$$\langle H \rangle = \frac{-c}{9} = \frac{-c}{n^2} \langle L_z \rangle = 0$$

$$L^2 = 6\hbar^2 \text{ or } 2\hbar^2$$

$$(l = 2 \text{ or } 1)$$

$$\frac{1}{\sqrt{2}} (|320\rangle + |310\rangle)$$

$$\frac{1}{\sqrt{2}} (|321\rangle + |31-1\rangle)$$

$$\langle L_z \rangle = 2P_{l_z} (\text{e-value})$$

$$c/a \quad c/4 \quad n=3, 2$$

$$\langle L^2 \rangle = 2\hbar^2 \quad l=1$$

$$m = 1, 0$$