Lecture 30: The Hydrogen Atom

Phy851 Fall 2009

Example 2: Hydrogen Atom

- The Hamiltonian for a system consisting of an electron and a proton is:

$$H = \frac{P_e^2}{2m_e} + \frac{P_p^2}{2m_p} - \frac{e^2}{4\pi\varepsilon_0 \left|\vec{R}_e - \vec{R}_p\right|}$$

- In COM and relative coordinates, the Hamiltonian is separable:

$$H = H_{CM} + H_r$$

$$H_{CM} = \frac{P_{CM}^2}{2M} \qquad H_r = \frac{P^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0 R}$$

- The energy eigenvalue equations are:

$$H_{CM}^{(C)}\left|E_{CM}\right\rangle^{(C)} = E_{CM}\left|E_{CM}\right\rangle^{(C)}$$

$$H_r^{(R)}\left|E_r\right\rangle^{(R)} = E_r\left|E_r\right\rangle^{(R)}$$

$$H\left|E_{CM}\right\rangle^{(C)} \otimes \left|E_r\right\rangle^{(R)} = \left(E_{CM} + E_r\right)\left|E_{CM}\right\rangle^{(C)} \otimes \left|E_r\right\rangle^{(R)}$$

Central Potential Ansatz

- For a spherically symmetric potential, we can choose to form simultaneous eigenstates of H_r, L^2, and L_z:

$$\left|E_r\right\rangle^{(R)} = \left|n,\ell,m\right\rangle^{(R)}$$

$$H_r\left|n,\ell,m\right\rangle^{(R)} = E_n\left|n,\ell,m\right\rangle^{(R)}$$

$$L^2\left|n,\ell,m\right\rangle^{(R)} = \hbar^2\ell(\ell+1)\left|n,\ell,m\right\rangle^{(R)}$$

$$L_z\left|n,\ell,m\right\rangle^{(R)} = \hbar m\left|n,\ell,m\right\rangle^{(R)}$$

- Separate the radial and angular degrees of freedom:

$$\left|n,\ell,m\right\rangle^{(R)} = \left|n,\ell\right\rangle^{(r)} \otimes \left|\ell,m\right\rangle^{(\Omega)}$$

$$\left\langle r\middle|n,\ell\right\rangle^{(r)} = r^{-1}R_{n,\ell}(r)$$

$$\left\langle \theta,\phi\middle|\ell,m\right\rangle^{(\Omega)} = Y_\ell^m(\theta,\phi)$$

- The Radial wave equation is then:

$$E_n R_{n,\ell}(r) = \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)R_{n,\ell}(r)$$

Natural Units

$$E_n R_{n,\ell}(r) = \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \right) R_{n,\ell}(r)$$

- Introduce dimensionless units:

$$r = \lambda\rho$$

$$R_{n,\ell}(\lambda\rho) = u(\rho)$$

$$E_n = -\frac{\hbar^2}{2\mu\lambda^2}\varepsilon_n$$

- The radial equation becomes:

$$u'' + \left(\frac{2\mu\lambda e^2}{4\pi\varepsilon_0\hbar^2}\frac{1}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \varepsilon_n \right) u = 0$$

Consult the Sacred Text

$$u'' + \left(\frac{2\mu\lambda e^2}{4\pi\varepsilon_0 \hbar^2} \frac{1}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \varepsilon_n \right) u = 0$$

- From p.781, Handbook of Mathematical Functions:
  - IF

$$u'' + \left(\frac{2n_r + \alpha + 1}{2\rho} + \frac{1-\alpha^2}{4\rho^2} - \frac{1}{4} \right) u = 0$$

$$n_r = 0,1,2,3,\ldots,\infty$$

  - THEN

$$u(\rho) = C\, e^{-\frac{\rho}{2}} \rho^{\frac{\alpha+1}{2}} \underbrace{L_{n_r}^{(\alpha)}(\rho)}_{\text{Generalized Laguerre Polynomial}}$$

  - We just need:

$$\frac{2n_r + \alpha + 1}{2} = \frac{2\mu\lambda e^2}{4\pi\varepsilon_0 \hbar^2}$$

$$\frac{1-\alpha^2}{4} = -\ell(\ell+1)$$

$$\frac{1}{4} = \varepsilon_n$$

Sort Out the Details

$$\frac{2n_r+\alpha+1}{2}=\frac{2\mu\lambda e^2}{4\pi\varepsilon_0\hbar^2} \qquad \frac{1-\alpha^2}{4}=-\ell(\ell+1) \qquad \frac{1}{4}=\varepsilon_n$$

- Solve for ε_n:

$$\varepsilon_n=\frac{1}{4}$$

- Solve for α:

$$\alpha^2=4\ell^2+4\ell+1$$

$$\alpha=2\ell+1$$

- Solve for λ:

$$\lambda=\frac{4\pi\varepsilon_0\hbar^2}{2\mu\, e^2}\left(n_r+\ell+1\right)$$

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu\, e^2}$$

$$\lambda=\frac{a_0}{2}\left(n_r+\ell+1\right)$$

To get a_0:

$$E_1=-\frac{e^2}{4\pi\varepsilon_0 a_0}$$

$$-\frac{\hbar^2}{2\mu a_0^2}=-\frac{e^2}{4\pi\varepsilon_0 a_0}$$

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

'Bohr Radius'

$a_0=5.29\times10^{-11}$ m

$\sim 10^{-10}$ m

Original Units

- The energy levels are given by:

$$E_n = -\frac{\hbar^2}{2\mu\lambda^2}\varepsilon_n \qquad \lambda = \frac{a_0}{2}\left(n_r + \ell + 1\right) \qquad \varepsilon_n = \frac{1}{4}$$

$$E_n = -\frac{\hbar^2}{2\mu\, a_0^2}\frac{1}{\left(n_r + \ell + 1\right)^2}$$

- The principle quantum number is therefore:

$$n = n_r + \ell + 1$$

$$n_r = 0,1,2,\ldots,\infty$$

$$\ell = 0,1,2,\ldots,\infty$$

$$E_n = -\frac{\hbar^2}{2\mu\, a_0^2}\frac{1}{n^2}$$

$$n = 1,2,3,\ldots\infty$$

$$E_1 = -\frac{\hbar^2}{2\mu a_0^2} = -13.6\ \text{eV} = 2.18\times 10^{-18}\ \text{J}$$

$$E_n = \frac{E_1}{n^2}$$

$$n_{r,\min} = 0 \qquad \ell_{\max} = n - n_{r,\min} - 1 = n - 1$$

- For a given n, the allowed ℓ values are:

$$\ell = 0,\ldots,n-1$$

Radial Wavefunction:

$$u(\rho) = C\, e^{-\frac{\rho}{2}} \rho^{\frac{\alpha+1}{2}} L_{n_r}^{(\alpha)}(\rho)$$

$$\alpha = 2\ell + 1 \quad \longrightarrow \quad \frac{\alpha+1}{2} = \ell + 1$$

$$\lambda = \frac{a_0}{2} n, \quad \lambda\rho = r \quad \longrightarrow \quad \rho = \frac{2r}{n a_0}$$

$$R_{n,\ell}(\lambda\rho) = u(\rho) \quad \longrightarrow \quad R_{n,\ell}(r) = u\left(\frac{2r}{n\, a_0}\right)$$

$$R_{n,\ell}(r) = C\, e^{-\frac{r}{n a_0}} \left(\frac{2r}{n\, a_0}\right)^{\ell+1} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{n\, a_0}\right)$$

$$\psi_{n,\ell,m}(r,\theta,\phi) = \sqrt{\frac{8(n-\ell-1)!}{2n(a_0 n)^3 (n+\ell)!}}\, e^{-r/a_0 n} \left(\frac{2r}{a_0 n}\right)^{\ell} L_{n-\ell-1}^{(2\ell+1)}\left(\frac{2r}{a_0 n}\right) Y_\ell^m(\theta,\phi)$$

Degeneracy of the nth level:

- We have:

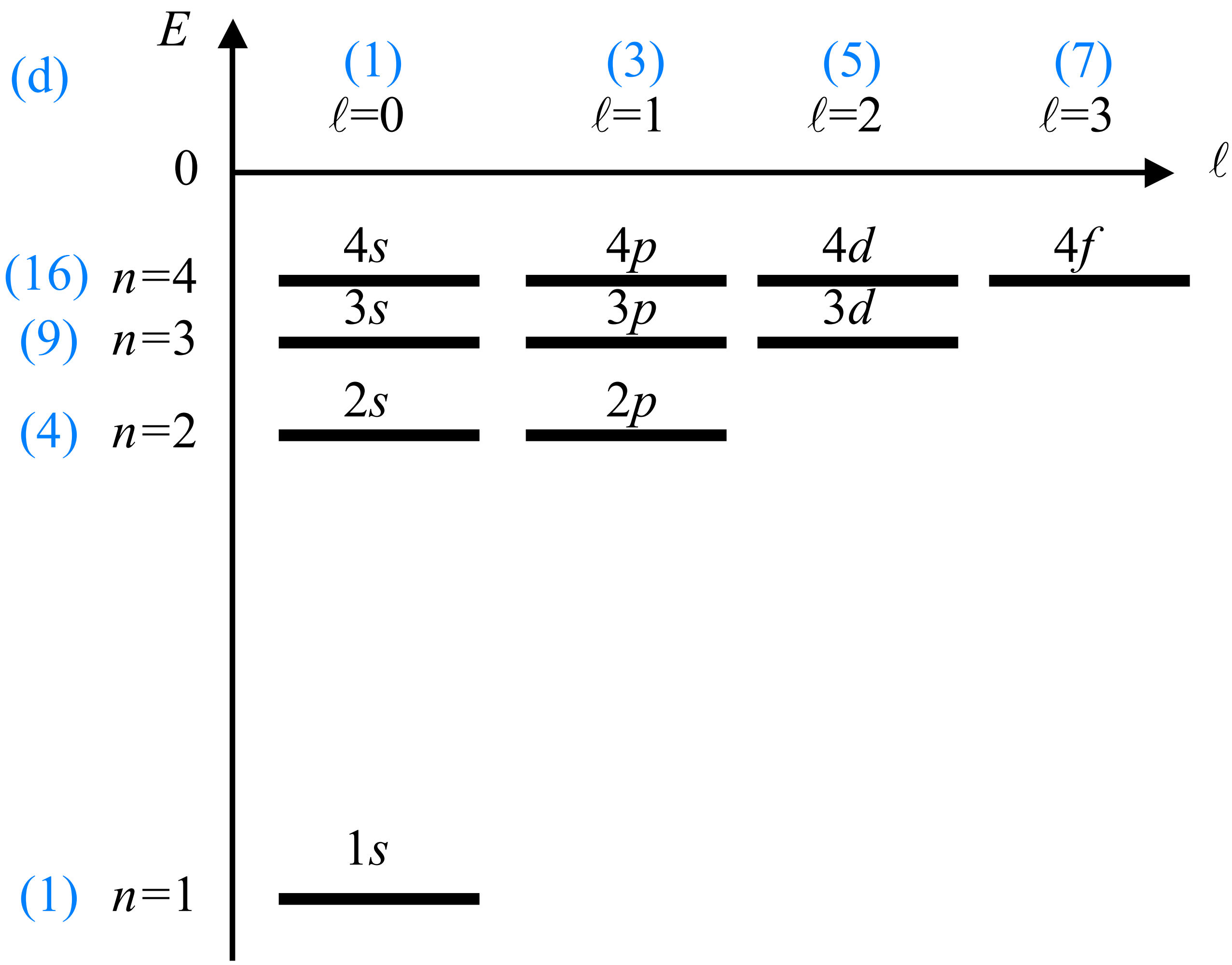
$$n = 1,2,3,\ldots$$
$$\ell = 0,1,\ldots,n-1$$
$$m = -\ell,-\ell+1,\ldots,\ell$$

$$d_n = \sum_{\ell=1}^{n-1}(2\ell+1) \quad + 1$$
$$= 2\sum_{\ell=1}^{n-1}\ell + (n-1) \quad +1$$
$$= 2\frac{1}{2}n(n-1) + (n-1) \quad +1$$
$$= n^2$$

$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$

$$d_n = n^2$$

Energy Level Diagram



- By taking spin into account (two spin states per orbital), and using the Pauli principle, the degeneracies of these levels explain much of the structure of the periodic table:
  - 2, 8, 18, 32,….

Hydrogen Spectrum

- We know that a hydrogen atom absorbs and emits light only at specific frequencies
- This is due to the presence of quantum resonances

- There is a resonance associated with each transition between two energy levels
  - Resonance frequencies:

$$\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar}$$