

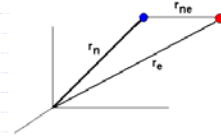
Physical Chemistry

Lecture 16

The Hydrogen Atom, a Central-Force Problem

The hydrogen atom

- Consists of two particles, a positively charged nucleus and a negatively charged electron



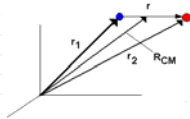
- Hamiltonian has three terms

- Nuclear kinetic energy
- Electronic kinetic energy
- Nuclear-electron Coulombic potential energy

$$H = T_n + T_e + V_{ne} = \frac{p_n^2}{2m_n} + \frac{p_e^2}{2m_e} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|r_{ne}|}$$

Center of mass

- Hamiltonian as a function of nuclear and electronic coordinates is complex



- Define
 - Center of mass, R_{CM}
 - Relative position, r
 - Total mass, M
 - Reduced mass, μ

$$R_{CM} = \frac{m_1}{M} r_1 + \frac{m_2}{M} r_2$$

$$r = r_2 - r_1$$

$$M = m_1 + m_2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{p_{CM}^2}{2M} + \frac{p^2}{2\mu}$$

Simplification of the hydrogen-atom problem

- By substitution, the hydrogen-atom Hamiltonian becomes

$$H = \frac{1}{2M} p_{CM}^2 + \frac{1}{2\mu} p^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = H_{CM} + H_{rel}$$

- Decompose into two problems

$$H_{CM} \Psi_{CM} = E_{CM} \Psi_{CM} \quad H_{rel} \Psi_{rel} = E_{rel} \Psi_{rel}$$

$$\Psi = \Psi_{CM} \Psi_{rel} \quad E = E_{CM} + E_{rel}$$

Center-of-mass problem

- A particle of mass, M , moving in no potential
- Like the particle-in-a-box problem
- Energies and wave functions known from that model
- Translational **degrees of freedom** of the hydrogen atom

The relative problem

- Consider relative motion of nucleus and electron, with only Coulombic interaction

$$H\Psi = E\Psi \quad -\frac{\hbar^2}{2\mu} \nabla^2 \Psi - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \Psi = E\Psi$$
- The dependence of ∇^2 on angular variables simplifies the problem
 - Eigenfunctions of L^2 are well known

$$\Psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$$

The radial equation

- Use of the spherical harmonic functions gives an equation for the radial part

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} \right) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} R - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} R = ER$$

- This can be put into dimensionless form by defining the radial distance in bohrs

$$r = \sigma a_0 \quad a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2}$$

- The dimensionless equation is related to **Laguerre's differential equation**

$$R_{n\ell}(\sigma) = A \sigma^\ell L_{n-\ell}(\sigma) \exp(-\sigma/n)$$

Hydrogenic energies and eigenfunctions

- Products of spherical harmonic functions with functions related to Laguerre polynomials

$$\Psi_{n\ell m}(r, \theta, \phi) = A_{n\ell m} [r/a_0]^\ell L_{n-\ell}(r/a_0) \exp(-r/na_0) Y_{\ell m}(\theta, \phi)$$

- Laguerre polynomials

n	ℓ	L _ℓ (x)
1	0	1
2	0	2 - x
2	1	x
3	0	3 - 3x + 2x ² /2
3	1	4 - 2x/3
3	2	x ²

- Energies of the state depend only on n

$$E_n = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_0} \frac{1}{n^2} \quad g_n = n^2$$

Energies

- Can give energies in "macroscopic units"

- Joules
- Ergs

- Often convenient to use "atomic units"

- Hartree
- Rydberg
- Electron volt

$$\begin{aligned} 1 \text{ hartree} &= 27.2114 \text{ electron volts} \\ 1 \text{ rydberg} &= 13.606 \text{ electron volts} \\ &= 0.5 \text{ hartree} \\ 1 \text{ electron volt} &= 96.4853 \text{ kilojoules / mole} \end{aligned}$$

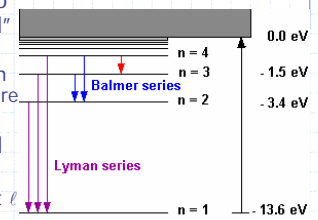
Hydrogen-atom energy levels

- Defined relative to the "vacuum level"

- Energy level in which the electron and the nucleus are just pulled apart

- States are labeled by n and ℓ

- States of different ℓ given by letters
 - s (ℓ = 0)
 - p (ℓ = 1)
 - d (ℓ = 2)



Addition of spin

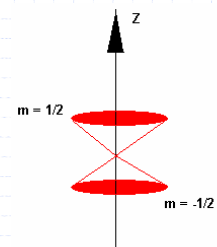
- The spatial part is incomplete
- One incorporates spin as a separate coordinate
- Wave function is a product

$$\Psi_{n,\ell,m,\ell,m_\ell}(r, \theta, \phi) = A R_{n\ell}(r/a_0) Y_{\ell m}(\theta, \phi) \psi_{\text{spin}, S, m_s}$$

- Energy is unchanged by addition of spin variables
- Increases degeneracy

Electron spin

- $S = \hbar/2$
- Two states
 - $m = \hbar/2$ or α
 - $m = -\hbar/2$ or β
- Eigenstates of the spin angular momentum operators
 - $S^2 \alpha = \hbar^2/4 \alpha$
 - $S^2 \beta = \hbar^2/4 \beta$
 - $S_z \alpha = (\hbar/2) \alpha$
 - $S_z \beta = -(\hbar/2) \beta$



Summary

- ◆ Central-force (hydrogen-atom) problem separates
 - Center of mass movement (translation)
 - Relative motion
 - Angular part is constant-angular-momentum problem
 - Radial part is related to Laguerre's equation
- ◆ Energy depends on principal quantum number, n , as predicted by Rydberg
- ◆ Degeneracy
 - States with same n but different angular momentum quantum numbers, ℓ and m , have same energy
 - $g_n = n^2$