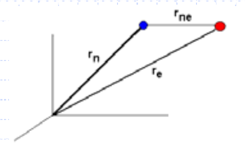
Physical Chemistry

Lecture 16

The Hydrogen Atom, a Central-Force Problem

The hydrogen atom

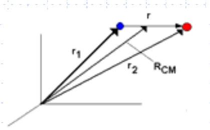
- Consists of two particles, a positively charged nucleus and a negatively charged electron
- Hamiltonian has three terms
  - Nuclear kinetic energy
  - Electronic kinetic energy
  - Nuclear-electron Coulombic potential energy



$$H = T_n + T_e + V_{ne} = \frac{p_n^2}{2m_n} + \frac{p_e^2}{2m_e} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}_{ne}|}$$

Center of mass

- Hamiltonian as a function of nuclear and electronic co-ordinates is complex
- Define
  - Center of mass, $\mathbf{R}_{CM}$
  - Relative position, $\mathbf{r}$
  - Total mass, M
  - Reduced mass, μ



$$\mathbf{R}_{CM} = \frac{m_1}{M}\mathbf{r}_1 + \frac{m_2}{M}\mathbf{r}_2$$

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

$$M = m_1 + m_2$$

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

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

Simplification of the hydrogen-atom problem

- By substitution, the hydrogen-atom Hamiltonian becomes

$$H = \frac{1}{2M}P_{CM}^2 + \frac{1}{2\mu}p^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = H_{CM} + H_{rel}$$

- Decompose into two problems

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

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

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

$$H\Psi = E\Psi$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\Psi = E\Psi$$

- The dependence of ∇^2 on angular variables simplifies the problem
  - Eigenfunctions of L^2 are well known

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) - \frac{1}{2\mu r^2}L^2\Psi - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\Psi = E\Psi$$

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

The radial equation

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

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

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

$$r = \sigma a_0 \qquad a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2}$$

- 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	$L_{n\ell}(x)$
1	0	1
2	0	2 - x
2	1	1
3	0	$3 - 2x + 2x^2/9$
3	1	$4 - 2x/3$
3	2	1

- Energies of the state depend only on n

$$E_n = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2} \qquad g_n = n^2$$

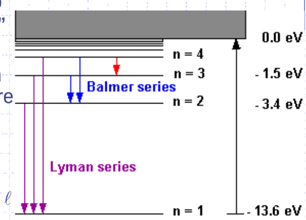
Energies

- Can give energies in "macroscopic units"
  - Joules
  - Ergs
- Often convenient to use "atomic units"
  - Hartree
  - Rydberg
  - Electron volt

1 *hartree* ≡ 27.2114 *electron volts*
1 *rydberg* ≡ 13.606 *electron volts* ≡ 0.5 *hartree*
1 *electron volt* ≡ 96.4853 *kilojoules / mole*

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

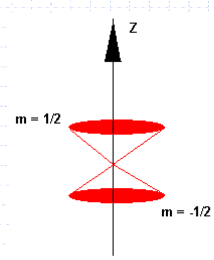
- The spatial part is incomplete
- One incorporates spin as a separate co-ordinate
- Wave function is a product

$$\Psi_{n,l,m,I,m_I}(r,\theta,\phi) = A\,R_{nl}(r/a_0)Y_{lm}(\theta,\phi)\psi_{spin,S,m_s}$$

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

Electron spin

- S = ½
- Two states
  - m = ½ or α
  - m = - ½ or β
- Eigenstates of the spin angular momentum operators
  - $S^2\,\alpha = ½(½+1)\hbar^2\,\alpha$
  - $S^2\,\beta = ½(½+1)\hbar^2\,\beta$
  - $S_z\,\alpha = (\hbar/2)\,\alpha$
  - $S_z\,\beta = -(\hbar/2)\,\beta$



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
  - $g_n = n^2$