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

\[ H = T_n + T_e + V_{ne} = \frac{p_n^2}{2m_n} + \frac{p_e^2}{2m_e} - \frac{\epsilon^2}{4\pi\epsilon_0 r_{ne}} \]

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, \( \mu \)

\[ R_{CM} = \frac{M}{m_n}r_n + \frac{m_e}{m_n}r_e \]

\[ r = r_n - r_e \]

\[ M = m_n + m_e \]

\[ \mu = \frac{m_n m_e}{m_n + m_e} \]

\[ \frac{p_n^2}{2m_n} + \frac{p_e^2}{2m_e} = \frac{p^2}{2\mu} \]

Simplification of the hydrogen-atom problem

- By substitution, the hydrogen-atom Hamiltonian becomes

\[ H = \frac{1}{2M}p_{CM}^2 + \frac{1}{2\mu}p^2 - \frac{\epsilon^2}{4\pi\epsilon_0 r} \]

\[ H_{CM} + H_{rel} \]

- Decompose into two problems

\[ H_{CM}\psi_{CM} = E_{CM}\psi_{CM} \]

\[ H_{rel}\psi_{rel} = E_{rel}\psi_{rel} \]

\[ \psi = \psi_{CM}\psi_{rel} \]

\[ E = E_{CM} + E_{rel} \]

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

\[ \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\epsilon^2}{4\pi\epsilon_0 r} \]

\[ E_{rel} = \frac{\epsilon^2}{4\pi\epsilon_0 r} \]

- The dependence of \( L^2 \) on angular variables simplifies the problem
- Eigenfunctions of \( L^2 \) are well known
The radial equation

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

\[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{\ell (\ell + 1)}{r^2} \right) \psi_n^\ell(\theta, \phi) - \frac{1}{2} \frac{e^2}{\alpha^2 r} \psi_n^\ell(\theta, \phi) = -ER \]

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

\[ r = \frac{\alpha}{\alpha} \quad a_0 = \frac{1}{\alpha} \quad E = \frac{\hbar^2}{2m \alpha^2} \]

The dimensionless equation is related to Laguerre's differential equation

\[ R_n^\ell(r) = A r^\frac{\ell}{2} L_n^\ell(\frac{1}{2}r/a_0) \exp\left(-\frac{r}{2a_0}\right) \]

Hydrogenic energies and eigenfunctions

Products of spherical harmonic functions with functions related to Laguerre polynomials

\[ \psi_{n\ell m}(r, \theta, \phi) = A_n^\ell \left[ r \right] L_n^\ell(r/a_0) \exp\left(-\frac{r}{a_0}\right) Y_{nm}(\theta, \phi) \]

Laguerre polynomials

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Energies of the state depend only on \( n \)

\[ E_n = \frac{\hbar^2}{2ma_0^2} \frac{1}{n^2} \]

Energies

Can give energies in “macroscopic units”
- Joules
- Ergs

Often convenient to use “atomic units”
- Hartree
- Rydberg
- Electron volt

1. Hartree \( \approx 27.2114 \) electron volts
1. Rydberg \( \approx 13.606 \) electron volts
1. Electron volt \( \approx 96.4853 \) 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 \( \ell \)
- States of different \( \ell \) given by letters
  - s (\( \ell = 0 \))
  - p (\( \ell = 1 \))
  - d (\( \ell = 2 \))

Addition of spin

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

\[ \Psi_{n\ell m s}(r, \theta, \phi) = A R_n^\ell(r/a_0) Y_{nm}(\theta, \phi) \psi_{s\ell m n} \]

Energy is unchanged by addition of spin variables
- Increases degeneracy

Electron spin

- \( S = \frac{1}{2} \)
- Two states
  - \( m = \frac{1}{2} \) or \( \alpha \)
  - \( m = - \frac{1}{2} \) or \( \beta \)
- Eigenstates of the spin angular momentum operators
  - \( S^2 \alpha = \frac{1}{2} \) or \( 1 \)
  - \( S^2 \beta = \frac{1}{2} \) or \( 0 \)
  - \( S_3 \alpha = (1/2) \alpha \)
  - \( S_3 \beta = -(1/2) \beta \)
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, $\ell$ and $m$, have same energy
  - $g_n = n^2$