Basics of Quantum Mechanics

CHEM 325 Physical Chemistry 2

Classical Physics

- Matter and Energy treated as separate Entities
  - Matter has mass and volume, motion governed by Newton's laws
  - Energy has no mass, and no volume; light described by Maxwell's equations
- Summarize System of Moving Particles by
  - Lagrangian: $L = K - V$
  - Hamiltonian: $H = K + V$

$$K = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \qquad p_i = mv_i$$

Classical Physics

- Reductionist View
  - Subdivide universe into smaller parts
- Size is Relative
  - Newton's laws apply to all
- Measurement Independent of Device
  - Precision depends on tool
  - Experiment itself does not affect result
- Failed miserably for Atomic Systems
  - Experiment showed size is absolute

Failure of Classical Physics

- Diffraction of Subatomic Particles
  - Davisson-Germer experiment
  - de Broglie relation $\lambda = h/p$
- Absorption and Emission of Light
  - Atomic line spectra vs. broad bands for molecular
  - Metallic luster
  - Compton effect
- Magnetism

Black-Body Radiation

- Emission of Light by hot Objects
  - Theoretical model of this is black body
- Laws Governing Black Bodies
  - Wien displacement law: $T \cdot \lambda_{max}$ = constant
  - Stefan-Boltzmann law: $\mathcal{E} = a \cdot T^4$
- Ultraviolet Catastrophe
  - Rayleigh-Jeans law: $d\mathcal{E} = \rho\, d\lambda$, $\rho = 8\pi kT/\lambda^4$
  - Relied on equipartition principle
- Planck Distribution $\rho = \dfrac{8\pi hc}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)}$
  - Assumed $E = n \cdot h \cdot \nu$

Heat Capacities

- Dulong and Petit's Law
  - Monatomic solid: $C_{V,m} = 3R \sim 25\ J \cdot K^{-1} \cdot mole^{-1}$
  - At low temperature significant deviation observed
- Einstein Formula: $C_{V,m} = 3Rf^2$

$$f = \frac{\Theta_E}{T}\left(\frac{e^{\Theta_E/2T}}{e^{\Theta_E/T} - 1}\right)$$

- Debye's Formula: $C_{V,m} = 3Rf$

$$f = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \qquad \Theta_D = \frac{h\nu_D}{k}$$

Photoelectric Effect

- Light-induced Electron Flow in Metals
  - Current = 0 below threshold frequency, no matter what light's intensity
  - KE of ejected electrons linearly dependent on frequency above threshold, but independent of intensity
  - Number of ejected electrons depends on intensity above threshold frequency
- Einstein's Treatment

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

Quantum Mechanics

- Size is Absolute
- All Measurements change System
  - Perfect precision is not always possible
- At most fundamental Level Matter and Energy are inseparable
  - Wave-particle duality
- Correspondence to Classical Physics
  - Newton's description modified
  - Limiting behavior of absolutely large things

Quantum-Mechanical Postulates and Principles

- Physical State of absolutely small Entities is described by a Wavefunction $\psi(x,y,z,t)$
  - Born's interpretation of ψ
  - Must be a single-valued, continuous function that is finite everywhere, goes to 0 at ∞ and has continuous first derivatives
  - Normalization
  - Dirac (bracket) notation

$$\langle\psi|\psi\rangle = \int \psi^*\psi d\tau = 1$$

Quantum-Mechanical Postulates and Principles

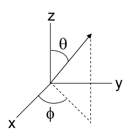
- Possible ψ are solutions to the appropriate Schrödinger Equation
  - Justification
  - Time-dependent form
  - Time-independent form (for conservative systems)

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$$

Quantum-Mechanical Postulates and Principles

- Operators are obtained from Classical Expressions by set Procedures

	Classical	Operator	Operation
Position	x	$\hat{x}$	multiplication
Linear momentum	p_x	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$
Angular momentum	L_z	$\hat{L}_z$	$-i\hbar\frac{\partial}{\partial \phi}$
Kinetic energy	E_K	$\hat{E}_K$	$\frac{-\hbar^2}{2m}\nabla^2$



Quantum-Mechanical Postulates and Principles

- Every dynamical Variable, corresponding to a physically observable Quantity, can be represented by a Hermitian linear Operator
  - Commutation of operators
  - Heisenberg uncertainty principle

$$\left(\Delta\hat{O}_1\right)\left(\Delta\hat{O}_2\right) \geq \frac{1}{2}\left|\left\langle \hat{O}_1, \hat{O}_2 \right\rangle\right|$$

$$\Delta\hat{O}_i = \left(\left\langle o_i^2 \right\rangle - \left\langle o_i \right\rangle^2\right)^{1/2}$$

Quantum-Mechanical Postulates and Principles

- For an Operator that corresponds to a physical Quantity, its Eigenvalues represent all possible Values of Quantity
- Expectation Value (Mean Value) for Measurements on a large Number of Particles is

$$\bar{F} = \langle F \rangle = \langle \psi | \hat{F} | \psi \rangle = \frac{\int_{-\infty}^{+\infty} \psi^* \hat{F} \psi d\tau}{\int_{-\infty}^{+\infty} \psi^* \psi d\tau}$$

Quantum-Mechanical Postulates and Principles

- Eigenfunctions of a Hermitian Operator corresponding to different Eigenvalues are orthogonal
  - Proof
  - Basis functions for the vector space
- Superposition Principle
  - Describe system as a linear combination of degenerate wavefunctions
  - Linear combination is also an eigenfunction

Perturbation Theory

- Method for arriving at Solutions to Real Systems
  - Start with a solvable problem
  - Add small perturbations until desired precision reached
- Versions
  - Time dependent-time independent
  - Degenerate vs. non-degenerate

Free Particle

- Zero Potential Energy
- Energy known
- Position is not known
  - Either dispersed uniformly through all space or periodic
  - Increasing number of states in superposition
  - Heisenberg
- Linear Momentum Vector's Magnitude known, but Direction is not well-defined
  - Superposition

Particle in a Box

- Infinite Potential Energy outside Box
- Energy is known and Quantized
  - Boundary conditions and quantum numbers
- Position somewhat known
  - Probability of finding particle, nodes
- If Potential is not Infinite
  - Particle can escape box
  - Tunneling
- Extension to multidimensional Boxes