CHEMISTRY 163A REVIEW TOPICS

The Chemistry 163A final will be based on quantitative (e.g., homework problems) and a conceptual understanding of the following topics.

I. Failures of Classical Mechanics and the Advent of Quantum Mechanics

   A. The Stern-Gerlach, Davisson-Germer, Rydberg, and Compton experiments with emphasis on the conflict between the observations and the predictions of classical mechanics.
   B. Wave-particle duality
   C. The important relationships involving energy, the frequency of electromagnetic radiation, linear momentum, the wavelength of a particle, etc.
   D. Correspondence principle

II. Fundamentals of Quantum Theory

   A. Bohr's treatment of hydrogen atom
   B. Mathematical foundation
      1. Operators
      2. Commutation
      3. Separation of variables technique
   C. Postulates of quantum mechanics
      1. Schrödinger time-dependent wave equation
      2. Probability density and physical interpretation of the wavefunction
      3. "Well-behaved" wavefunctions
      4. Expectation values
      5. Eigenvalues and measurement theory
      6. Derivation of time-independent Schrödinger equation
      7. Orthonormality of eigenfunctions
      8. Commutation, mutual eigenfunctions, and uncertainty principles

   D. Particle-in-a-box
      1. Importance of boundary conditions in determining the allowed energy levels (i.e., quantization)
      2. Orthonormality and expectation values using explicit wavefunctions
      3. Three-dimensional particle-in-a-box
         a. Extension of Schrödinger equation to three dimensions
         b. Separation of variables
         c. Degeneracy
         d. Model for translational motion (relative energy level spacing)
   E. Harmonic oscillator
      1. Separation of equations for center-of-mass and relative motion

2. Boundary conditions
3. $E_n = (n + 1/2)h\nu_0,\ \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$
4. Features of the harmonic oscillator wavefunctions
   a. Symmetry
   b. Shapes of low energy wavefunctions
   c. Extension beyond the classical turning point and tunneling
   d. Relation of the higher states to the Correspondence Principle
5. Model for vibrational motion
   a. What determines k, ν_0
   b. Relative energy level spacing

F. Rigid rotor
1. Model for rotational motion (relative energy level spacing)
2. $Y_{J,M_J}(\theta,\phi)$
3. $E_J = \frac{h^2}{8\pi^2 I} J(J+1)$
4. Degeneracy of 2J + 1 values of M_J for each J

III. Quantum Mechanics of One-Electron Atoms

A. Integration in spherical coordinates

B. Mathematical origin of the n, ℓ, m_ℓ and m_s numbers

C. Physical interpretations of the n, ℓ, m_ℓ and m_s numbers

D. $E_n = -\frac{1}{n^2}\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0} = \frac{-Z^2}{2n^2}$ in a.u.

$\hat{\ell}^2\psi_{n\ell m} = \ell(\ell+1)\hbar^2\psi_{n\ell m} \quad \hat{\ell}_z\psi_{n\ell m} = m\hbar\psi_{n\ell m}$

E. Relationship of n and ℓ to radial and angular nodes of hydrogen-like orbital

F. Real and complex Φ functions

G. Nodal properties and shapes of orbitals

H. Pauli spin functions $\alpha(\sigma)$, $\beta(\sigma)$

IV. Many-Electron Atoms

A. The $1/r_{12}$ term prevents exact solution

B. Variation theorem

C. Independent electron approximation
1. Screening and effective nuclear charge
2. $E = -Z_f^2/2n^2$
3. How penetration determines Z_f for s vs. p orbitals

D. Pauli exclusion principle; Slater determinants

E. Singlet and triplet 1s2s excited states of helium

1. Hund's rule $E_{singlet} > E_{triplet}$
2. Singlet and triplet spin wavefunctions and vector model of spin coupling

F. Aufbau principle and periodic table (atomic radii, I.P.'s, etc.)

V. Bonding in Molecules

A. Born-Oppenheimer approximation

B. Hydrogen molecules

1. What makes H_2 more stable than two H atoms?
2. Molecular orbital
   a. Bonding-antibonding m.o.'s
   b. Constructing many-electron wavefunctions from a configuration of m.o.'s

C. Homonuclear diatomics

1. Molecular orbitals
2. Classification and symmetry
3. Rationale for energy ordering
4. Configuration and molecular properties
   a. Stability
   b. Vibrational frequency
   c. Bond distance
   d. Paramagnetism

D. Heteronuclear diatomics

1. Which a.o.'s interact
2. Unequal a.o. contribution to m.o.'s

VI. Spectroscopy

A Spectral regions and relevant to molecular-electronic spectra

B. Probability of a transition

C *General* spects of:

1. Rotational spectroscopy
2. Vibrational spectroscopy
3. Rotation-vibration spectra
4. Electronic spectra
5. Electronic-vibration spectra
6. Raman spectroscopy

D. Spectroscopic vocabulary

1. Non-radiative transition (radiationless decay)
2. Fluorescence
3. Phosphorescence
4. Chemiluminescence