Structure, Bonding and Spectroscopy **Chemistry BC 3253x**

Outline and Study Guide
(names and dates for historical interest; not to be memorized)

I. The Old Quantum Theory

A. Black body radiation
  background: electromagnetic radiation
  Experimental observations and the empirical Wein displacement law (1894)
  Rayleigh-Jeans theory (1900) and the ultraviolet catastrophe
  Solution: the Quantum hypothesis (Planck, 1900)
B. The photoelectric effect
  Experiment observing the effect (Hertz, 1887)
  Theory (Einstein, 1905)
  Refined experiments (Millikan, 1916)
  Modern experiments using the photoelectric effect.
C. The heat capacities of solids (Einstein, 1907)
D. The structure of the atom
  1. Early studies on subatomic particles
    a. Measurement of e/m (J.J. Thomson, 1897)
      Application to modern mass spectrometry
    b. Oil drop experiment (Millikan, 1909)
    c. particle scattering experiment (Geiger and Marsden, 1909)
    d. Planetary model (Rutherford, 1911)
  2. The spectrum of the hydrogen atom (Balmer 1885, Rydberg 1896)
  3. Bohr model of the one-electron atom (Bohr, 1913)
    assumptions:
      Quantized angular momentum ℓ
      The Correspondence Principle
    results:
      explanation of line spectra
      quantitative prediction of the Rydberg constant.

Readings: McQuarrie, Chapter 1

II. Elements of Modern Quantum Theory

A. Wave-particle duality for matter
  a. The deBroglie hypothesis (deBroglie, 1924): $\lambda = h/p$
  b. Electron diffraction (Davisson and Germer, G.P. Thomson, 1927)
B. Heisenberg uncertainty principle (Heisenberg, 1927):
  Representation of waves: Fourier series and Fourier transforms
    $\Delta x \, \Delta p_x \geq \hbar/2$ and $\Delta E \, \Delta t \geq \hbar/2$
C. Schrödinger equation (Schrödinger 1926): $\hat{H}\Psi = E\Psi$ or $\mathscr{H}\Psi = E\Psi$ or

$$\left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right\}\Psi(x) = E\,\Psi(x)$$

D. Some formal aspects of quantum mechanics
  1. Operators and observables. Eigenvalues and eigenfunctions
  2. Wave functions and probability densities. Normalization
    $\Psi(x)$ must be well behaved, continuous, and single valued.

E. Applications: two exact solutions of the Schrodinger equation
  1. The free particle: energies are not quantized
  2. The particle in a box [x = 0 to x = L] (some books use a instead of L)
    Boundary conditions → quantized energy levels
    Result: $\mathbf{E_n = n^2h^2/8mL^2}$ and $\Psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L)$
      Nodes and quantum numbers
    Application to spectra of conjugated molecules
    More dimensions: separation of variables; Symmetry and degeneracy

Readings: McQuarrie, Chapters 2 and 3

III. The Postulates of Quantum Mechanics

1. The state of a quantum mechanical system is fully specified by the function $\Psi(\mathbf{r}, t)$

   $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, d\tau$ is the probability that the system is in the volume element $d\tau$ at time t.
   r is a mutidimensional position vector for all particles in the system.
   Consequence: Ψ must be *square-integrable*.

2. For every classical observable there is a corresponding linear Hermitian quantum mechanical operator.
   Definition: an operator $\hat{A}$ is Hermitian if for well behaved functions f and g

   $$\int f^* \hat{A} g\, d\tau = \int g \hat{A}^* f^*\, d\tau$$

   Theorems:
   A. The eigenvalues of any Hermitian operator are real.
   B. The eigenfunctions of any Hermitian operator form a complete orthogonal set.

3. In any measurement of the observable associated with the operator ***A*** (or $\hat{A}$), the only values observed are the eigenvalues a of the equation

   $$\boldsymbol{A}\Psi = a\Psi$$

   where Ψ is the wavefunction for the system.

4. The expectation value for the variable a associated with operator **A** for a system in the state Ψ is given by

   $$\langle a \rangle = \int \Psi^* \hat{A} \Psi\, d\tau$$

5. The function $\Psi(r,t)$ which describes the complete spatial and temporal system is the solution to the time-dependent Schrodinger equation: $\boldsymbol{H}\Psi = i\hbar\, \partial\Psi/\partial t$

   If ***H*** is independent of t, then $\Psi_n(\mathbf{r}, t) = \psi_k(\mathbf{r}) \exp(-iE_n t/\hbar)$
   where $\psi_k(\mathbf{r})$ is a solution of the time-independent Schrodinger equation $\boldsymbol{H}\psi_k = E_k\psi_n$
   Operators and the Uncertainty principle:
   Theorem: Commuting Hermitian operators have simultaneous eigenfunctions.

Readings: McQuarrie, Chapter 4

IV. Two more exact solutions to the Schrodinger equation:

A. The Simple Harmonic Oscillator $V(x) = \frac{1}{2} k\Delta x^2$

1. SHO as an approximation to real molecular potentials V(r)
2. Method of solution
   - Reduced variables ε and ξ
   - Asymptotic solution: as $\xi^2 \rightarrow \infty$, $\Psi(\xi) \rightarrow \exp(-\xi^2/2)$
   - Differential equation for $H(\xi)$:
     - Series solution, recursion relation, finite polynomials
3. Results: $\mathbf{E_v = \hbar\omega (v+\frac{1}{2})}$ v = 0, 1, 2… and
   - $\Psi_v\{\xi) = (2^v v!\pi^{\frac{1}{2}})^{-\frac{1}{2}} H_v(\xi) \exp(-\xi^2/2)$ where $H_v(\xi)$ is Hermite polynomial
   - Zero point energy, nodes
   - Penetration of Ψ into nonclassical region
   - Application to infrared spectroscopy

Readings: McQuarrie, Chapter 5 [note that the order is quite different]

B. The Rigid Rotor

1. Spherical polar coordinates, determination of ∇^2 and $d\tau$
2. Separation of variables θ and φ
3. Results: $\mathbf{E = (\hbar^2/2\mu r^2)\, \ell(\ell+1)}$ $\ell = 0,1,2\ldots$, and $|m| \leq \ell$
   - $\Psi_{\ell m}(\theta,\varphi) = Y_{\ell m}(\theta,\varphi) = \Theta_{\ell .m}(\theta)\, \Phi_m(\varphi)$
     - $Y_{\ell m}(\theta,\varphi)$ = Spherical Harmonic
   - $\Theta_{\ell .m}(\theta) = N_{\ell .m}\, P_{\ell m}(\cos\theta)$
     - P= Associated Legendre Polynomial
   - $\Phi_m(\varphi) = (2\pi)^{-\frac{1}{2}} \exp(im\varphi)$
   - Shapes of the spherical harmonics: polar plots
   - Space Quantization of angular momenta
4. Rotational Spectroscopy: symbols (ℓ, m) often replaced by (J, m_J).
   - Pure rotational spectroscopy: microwave region
   - applications in astrophysics (radiofrequency telescopes).

Readings: McQuarrie, Chapter 6: 6.3-6.7

V. Atomic structure and atomic spectra

A. The Hydrogen Atom

1. Exact solution of the Schrödinger equation
   Separation of variables
   Angular equation same as rigid rotor: spherical harmonics
   Solution to the Radial equation R(r) [handout]
   Results: three quantum numbers (n, ℓ, m) n= 1, 2, 3...; $0 \le \ell < n$; $|m| \le \ell$
   $\mathbf{E_n = -\mu(ze^2/4\pi\varepsilon_0)^2 / 2\hbar^2 n^2}$ $= -z^2R/n^2$ (identical to Bohr result)
2. Interpretation of the results
   a. Orbitals and their properties.
      Representations of orbitals.
   b. Degeneracy of levels with same n but different ℓ, m
3. Orbital angular momentum. The effect of external magnetic fields.
4. Electron spin (Goudsmit and Uhlenbeck, 1926)
   a. The Stern-Gerlach experiment (1921).
   b. The effect of external magnetic fields.

B. Approximate Methods for many-electron systems

1. Time independent perturbation theory: first order energy correction
   $\Delta E = \int \Psi^0 \hat{H} \Psi^0 d\tau$ and $E^1 = E^0 + \Delta E$
   application to He: comparison with independent electron result.
   introduction of atomic units for QM calculations
2. Time dependent perturbation theory: electric dipole selection rules
   If $M_{if} \equiv \int \Psi_i * \hat{\mu} \Psi_f d\tau$ is zero, the transition $i \to f$ is forbidden
3. The Variation method
   a. Theorem: if Φ is an arbitrary normalized function, then $\varepsilon = \int \Phi * \hat{H} \Phi \, d\tau \ge E_0$
   b. Application: guess a function Φ with variable parameters
      Linear combinations of known functions $\to$ secular determinant
   c. Calculation of structure of many-electron atoms
      The self consistent field (SCF) model (Hartree and Fock, 1927-1930)

C. The structure and spectra of many-electron atoms

1. Spin and The Pauli Exclusion Principle
2. Spectra and energy levels
3. Atomic structure and periodic behavior
   Slater determinants
4. Term symbols and the vector model
5. Fine structure: the spin-orbit interaction

Readings: McQuarrie, chapters 6, 7, and 8

VI. Molecular quantum mechanics: the chemical bond

A. Types of interactions between atoms
- closed shell neutrals: Van der Waals forces
- closed shell ions: Ionic forces
- open shell atoms: covalent bonds

B. The Born-Oppenheimer approximation (1927)
- Separation of electron and nuclear motion

C. Valence bond (VB) theory for the H_2 molecule (Heitler and London, 1927)

D. Molecular orbital (MO) theory (Hund, Mullikan et al., 1930's)
1. One electron orbitals: H_2^+
2. Molecular Orbital (MO) theory for homonuclear diatomics
3. Heteronuclear bonds: polarity and electronegativity

E. Polyatomic molecules
1. Valence bond treatment of localized bonds
   - Hybrid atomic orbitals and molecular geometry
2. Semiempirical Huckel MO theory for delocalized systems
3. Transition metal complexes: Ligand field theory

F. Molecular electronic spectroscopy: the Franck Condon Principle

G. Modern computational methods: examples using PC Spartan
- basis sets, orbitals, density diagrams

Readings: McQuarrie, chapter 9