

Chemistry 332

Introduction to Molecular Spectroscopy and Statistical Thermodynamics

General Description: Chemistry 332 introduces the basic applications of quantum theory to atomic and molecular structure. Approximate methods for solving Schrödinger's are discussed, emphasizing energy levels, spin and their relation to selection rules and rotational, vibrational and electronic spectroscopy. In the second part of the course, quantum and statistical theory are combined to introduce statistical thermodynamics. Applications to systems of chemical interest are presented, including the molecular interpretation of thermodynamic quantities, such as the internal energy, entropy, heat capacity and equilibrium constants for chemical reactions.

Instructor: Derek Leaist (dleaist@stfx.ca), Office PSC 3072, Lab PSC 3020

Lectures: Mon. 11:15 am, Tues. 1:15 pm, Thurs. noon (NT 412)

Tutorials: selected Fridays, 2:15 to 5:00 pm (AX 23A)

Textbook: *None required.* Many textbooks covering the course material are available at reasonable prices (or free). Copies of the course notes and supplementary reading material will be provided.

Problem Sets: About eight problem sets will be assigned to cover the course material. They are important in order to understand the material, and should be completed and handed in. Portions of the assignments will be taken up in the tutorial sessions together with other problems of interest.

Chemistry 332 Course Outline

- 1. Hydrogen-Like Atoms:** Wave functions, probability densities, orbital angular momentum, and electron spin. Spectra of hydrogen-like atoms. Magnetic effects.
- 2. Multi-Electron Atoms:** The quantum mechanical treatment of the helium atom. The variational theorem and approximate methods for solving Schrödinger's equation. Hartree-Fock self-consistent field method. Pauli exclusion principle and the Aufbau construction of the periodic table of elements. Ionization energy and electron affinity. Introduction to atomic spectroscopy. Term symbols.
- 3. H_2^+ and H_2 Molecules and Chemical Bonding:** Quantum mechanics of bonding in the hydrogen molecule ion and the hydrogen molecule. The Born-Oppenheimer approximation.
- 4. Molecular Structure:** Molecular orbital description and electronic configuration of diatomic molecules. Electronic structure of polyatomic molecules. Dipole moments and intermolecular forces.
- 5. Rotational and Vibrational Spectroscopy.** Spectra of diatomic molecules. Introduction to the rotational and vibration of polyatomic molecules. Raman and Fourier transform spectroscopy.
- 6. Electronic Spectroscopy of Molecules.** Molecular energy levels and selection rules. Electronic absorption spectra of diatomic molecules. The Franck-Condon principle. Measurement of dissociation energies. Introduction to the electronic spectra of polyatomic molecules. Fluorescence and phosphorescence. Lasers.
- 7. Introduction to Statistical Mechanics:** Brief review of classical thermodynamic energy and entropy. The Boltzmann distribution over accessible energy levels. Partition functions and the molecular interpretation of the energy and entropy.
- 8. Applications of Statistical Thermodynamics:** Translational, rotational, vibrational and electronic contributions to the thermodynamic properties of ideal gases. Equilibrium constants for ideal gas reactions. Fluctuations in thermodynamic quantities.

Chemistry 332 Course Schedule (2022)

Classes: Thursday January 6th to Tuesday April 5th (NT 412)

Tutorials: Fridays, 2:15 to 5:00 pm (AX 23A)

26 January

02 February

09 March

16 March

30 March

Term Tests: **Wednesday 09 February, 2:15 to 5:00 pm, AX 23A**
Wednesday 23 March, 2:15 to 5:00 pm, AX 23A

Final Exam: April exam period (date TBA)

Chemistry 332 Marking

Final Exam (date TBA) 45 %

Midterm Tests (two, 20% each) 40 %

Problem Sets (about eight) 15 %

100 %

Chemistry 332 Study Material

See: Chem 332 Moodle pages

Moodle backup:

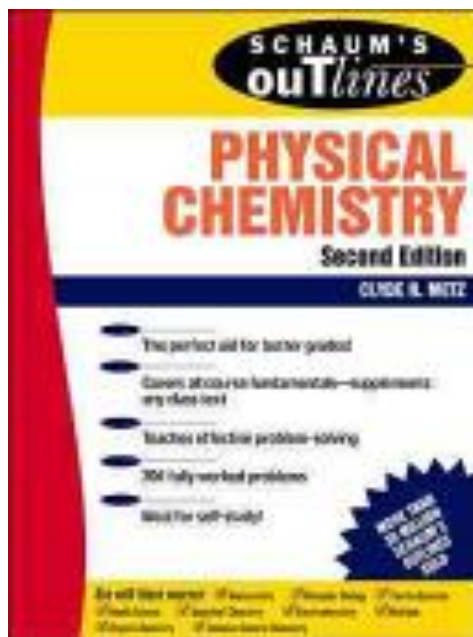
<https://people.stfx.ca/dleaist/Chem232/>

- PowerPoint course notes
- tutorial questions (with answers)
- equation sheets
- sample problem assignments (with answers)
- sample term tests (with answers)
- list of topics and terminology for each section
- pdf copies of supplementary reading from:

T. Engel, P. Reid. *Physical Chemistry*, Pearson.

R. J. Silbey, R. A. Alberty. M. G. Bawendi.
Physical Chemistry, 4th Ed., Wiley.

for concise summaries and worked problems:



Schaum's Outline of Physical Chemistry

2nd edition (\$25 Amazon.ca)

Clyde A. Metz

Chapters on quantum mechanics and spectroscopy, also thermodynamics, electrochemistry, kinetics, and transport properties.

Part 1. The Electronic Structure of Atoms

The wave function of an atom contains all the information about the properties of the atom. The wave functions for the hydrogen atom and other one-electron atoms (such as He^+ and Li^{2+}) can be calculated **exactly** by solving Schrödinger's equation. Approximate methods must be used to calculate the wave functions for atoms containing two or more electrons. These numerical calculations can be very accurate, but require complicated computer calculations.

So we start with (brief review from Chem 331):

Hydrogen-Like Atoms

What are they? He^+ ($Z = 2$), Li^{2+} ($Z = 3$), Be^{3+} ($Z = 4$), *etc.* Ions with *one nucleus and one electron* (two bound particles), atomic number $Z > 1$.

Also a few rare, but interesting, “exotics”, such as muonium (more on that in the tutorial!).

Why are they important? Schrödinger's equation can be solved **exactly** for hydrogen-like atoms, using the reduced mass concept to simplify the two-body problem to an effective one-body problem. This greatly expands the number of chemical systems that can be treated analytically by quantum mechanical principles. (For molecules and multi-electron atoms, cumbersome and less accurate numerical methods must be used to solve Schrödinger's equation.)

For hydrogen-like atoms, the **electrostatic potential energy** and the **reduced mass** in Schrödinger's equation for the hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

are changed to (notice the factor of Z)

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

m_e is the electron mass and m_N is the nucleus mass.

Schrodinger Equation for Hydrogen-Like Atoms

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

with Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The Laplacian operator ∇^2 can be separated into radial and angle-dependent terms

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \frac{\hat{L}^2}{\hbar^2}$$

The angle-dependent terms can be represented by the operator \hat{L}^2 for the square of the angular momentum.

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= \hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Partial separation of variables leads to solutions of Schrödinger's equation of the form

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

$R_{n\ell}(r)$ is called the hydrogen-like radial wave function and $Y_{\ell m}(\theta, \phi)$ are spherical harmonics. As for the hydrogen atom,

principal quantum number	$n = 1, 2, 3, 4, \dots$	
orbital angular momentum quantum number	$\ell = 0, 1, 2, \dots, n - 1$	$(\ell < n)$
magnetic quantum number	$m = 0, \pm 1, \pm 2, \dots, \pm \ell$	

A Few Solutions to Schrödinger's Equation for Hydrogen-Like Atoms:

(the **Bohr radius** is $a_0 = \epsilon_0 \hbar^2 / \pi m e^2$)

$$n = 1, \ell = 0, m = 0 \quad \psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0)$$

$$n = 2, \ell = 0, m = 0 \quad \psi_{200} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \exp(-Zr/2a_0)$$

$$n = 2, \ell = 1, m = 0 \quad \psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} \cos \theta \exp(-Zr/2a_0)$$

$$n = 2, \ell = 1, m = \pm 1 \quad \psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} \sin \theta \exp(-Zr/2a_0) \exp(\pm i\phi)$$

Okay, but how can a chemist or physicist use these wave functions?

1. Energies of Hydrogen-Like Atoms

For an isolated hydrogen atom (no externally applied magnetic fields or other fields), the energy depends only on the principal quantum number n . The same result obtained for hydrogen-like atoms:

$$E_n = -\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2} \quad (\text{no externally applied fields})$$

Why is the energy negative and proportional to Z^2 ?

The energy equation can be simplified by lumping the constants together to form a single parameter. If the energy is expressed in cm^{-1} , the unit favored by spectroscopists, this factor \mathfrak{R} called the **Rydberg constant**.

Photon energies $h\nu$ are inversely proportional to wavelengths

$$h\nu = hc/\lambda$$

so energies are converted from units of Joules to wavenumbers by dividing by hc (and don't forget to convert from m^{-1} to cm^{-1} !)

$$\tilde{E}_n = \frac{E_n}{hc} = -\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^3 c n^2}$$

Using energies \tilde{E}_n in wavenumbers defined by

$$\tilde{E}_n = -\frac{\mathfrak{R}Z^2}{n^2}$$

the Rydberg constant (in wavenumbers) is

$$\mathfrak{R} = \frac{\mu e^4}{8\varepsilon_0^2 ch^3}$$

The Rydberg constant depends on fundamental physical constants and the mass of the nucleus.

For the hydrogen atom, $\mathfrak{R}_H = 1.096\,775\,856 \times 10^5 \text{ cm}^{-1}$

For the deuterium atom, $\mathfrak{R}_D = 1.097\,074\,275 \times 10^5 \text{ cm}^{-1}$

In the limit $m_e/m_N \rightarrow \infty$, $\mathfrak{R}_\infty = 1.097\,373\,153 \times 10^5 \text{ cm}^{-1}$

Notice the extraordinary precision of Rydberg constants. This is possible because frequencies can be measured very precisely and accurately.

2. Ionization Energies: $A^{Z-1} \rightarrow A^Z + e^-$

The ionization energy of a hydrogen-like atom is defined as the energy required to take the atom from its ground state ($n_i = 1$) to the dissociated state $n_f = \infty$ where the electron and nucleus are infinitely far apart. In wavenumbers:

$$\tilde{E}_{\text{IONIZATION}} = \tilde{E}_f - \tilde{E}_i = -\frac{\mathfrak{R}Z^2}{\infty^2} - \left(-\frac{\mathfrak{R}Z^2}{1^2} \right) = \mathfrak{R}Z^2$$

$$\begin{aligned} \text{For the hydrogen atom } (Z = 1) \quad \tilde{E}_{\text{IONIZATION}} &= \mathfrak{R}_H = 10967.75\,856 \text{ cm}^{-1} \\ &= 2.178722 \times 10^{-19} \text{ J} \\ &= 13.605698 \text{ eV} \end{aligned}$$

For hydrogen-like atoms, ignoring small changes in the reduced mass, the ionization energies are

$$\tilde{E}_{\text{IONIZATION}} \approx Z^2 \mathfrak{R}_H = 13.606 Z^2 \text{ eV}$$

$$13.606 \times 2^2 = 54.424 \text{ eV for He}^+, \quad 13.606 \times 3^2 = 122.45 \text{ eV for Li}^{++}, \text{ etc.}$$

3. Electronic Spectra of Hydrogen-Like Atoms

The **selection rules** for transitions between atomic energy levels are

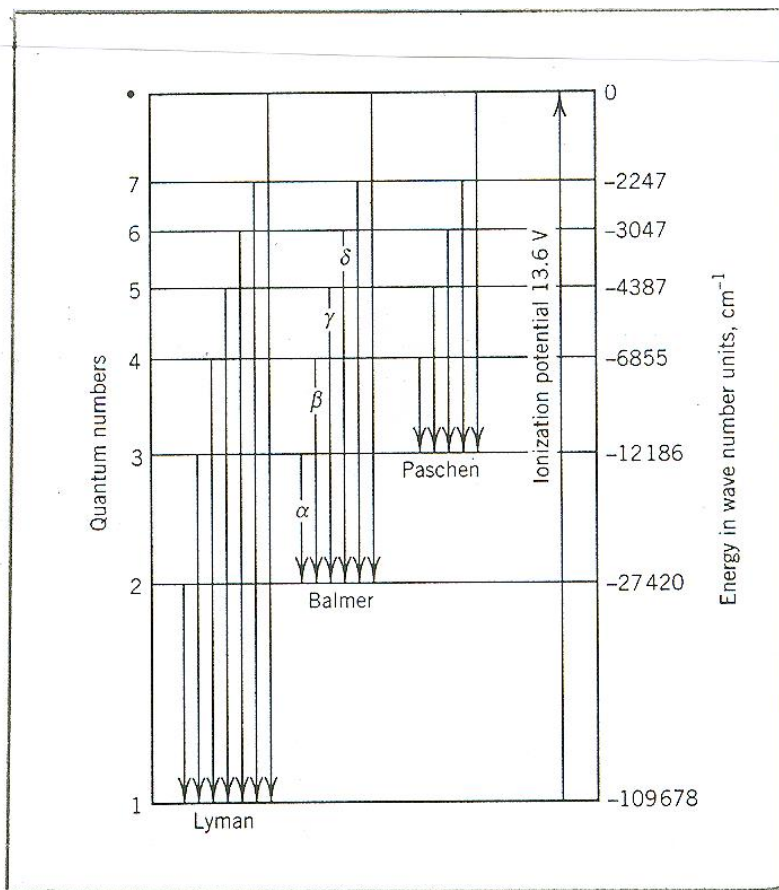
$$\Delta n \text{ unrestricted} \qquad \Delta \ell = \pm 1 \qquad \Delta m = \pm 1, 0$$

Transitions from any initial n_i value to any final n_f are therefore “allowed”.

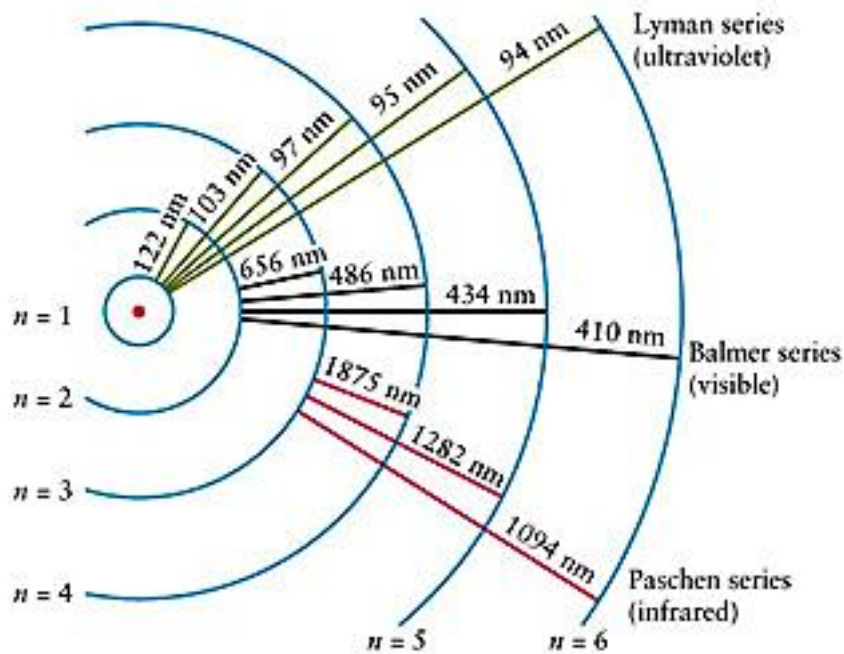
For emission spectra: $n_f < n_i$ **For absorption spectra,** $n_f > n_i$

The photon energy $\Delta E = h\nu = E_f - E_i$ in wavenumbers is

$$\tilde{E}_f - \tilde{E}_i = \mathfrak{R}Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$



Hydrogen Atom Spectra
(in Wavenumbers)



Electronic Transitions for Hydrogen Atoms (in nm)

4. Electron Density – Important for Atomic Structure

For a hydrogen-like atom, the probability of finding the electron in the volume element $d\tau = dx dy dz$ is $(\psi_{nlm})^* \psi_{nlm} d\tau$. (Recall that the asterisk denotes the complex conjugate of ψ_{nlm} , where all values of i in ψ_{nlm} are converted to $-i$.)

Transforming to more-convenient spherical r, θ, ϕ coordinates with $d\tau = r^2 \sin\theta dr d\theta d\phi$ gives

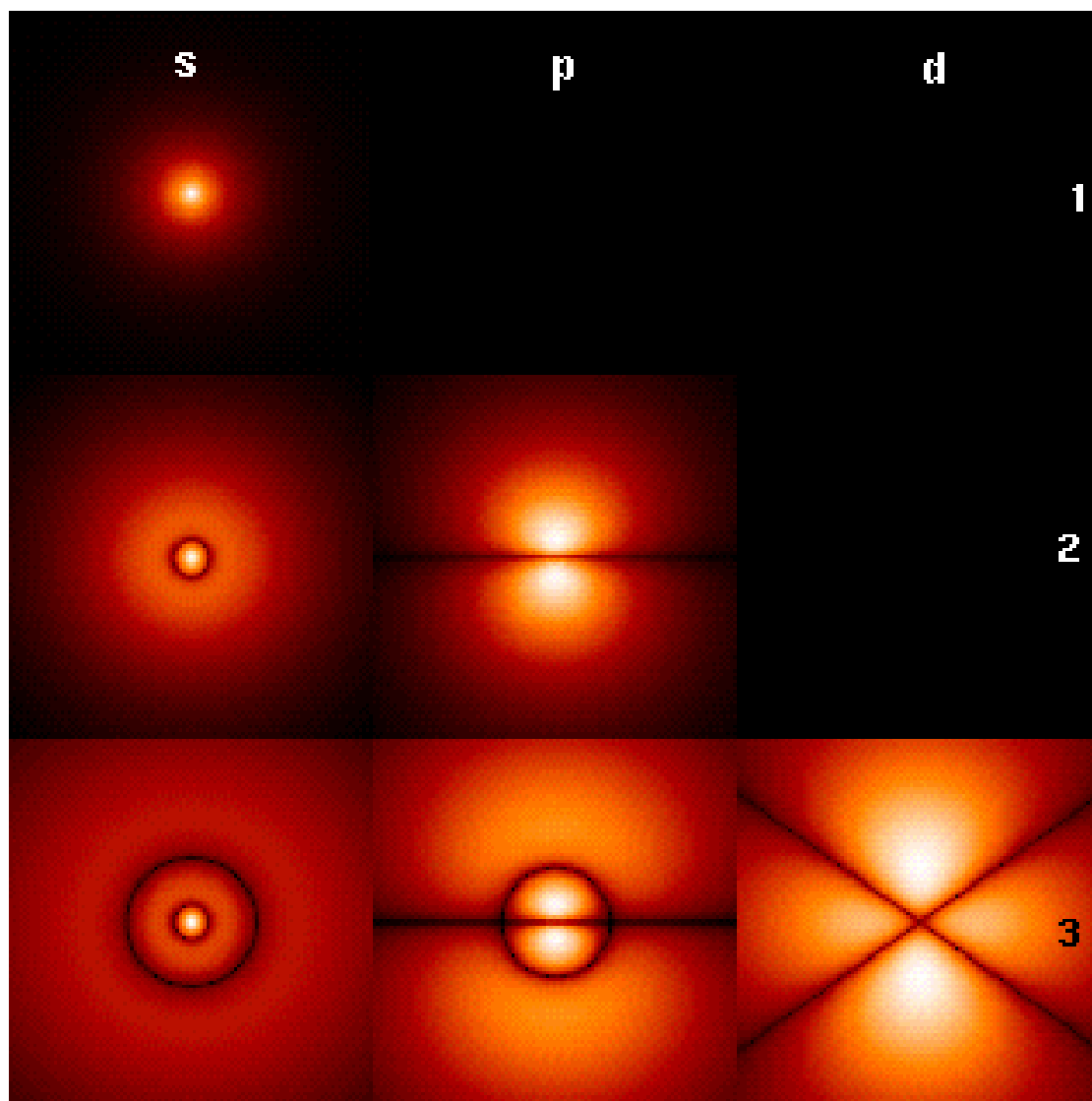
$$\text{electron density} = r^2 \sin\theta \psi_{nlm}(r, \theta, \phi)^* \psi_{nlm}(r, \theta, \phi)$$

Finding the maximum value of the electron density gives the most probable locations of the electron. The locations of zero electron density are called nodes. Nodes are required to make the wave functions orthogonal:

$$\int (\psi_{n'l'm'})^* \psi_{n'l'm'} d\tau = 0 \quad \text{if } n \neq n' \quad \text{or} \quad l \neq l' \quad \text{or} \quad m \neq m'$$

Electron Densities for $n = 1, 2, 3$ and $\ell = 0$ (s), 1 (p), 2(d)

(graphical display)



Stereo plots of probability electron probability densities

See:

D. T. Cromer, Stereo plots of hydrogen-like electron densities, *Journal of Chemical Education*, 45, 626–631 (1968)

Online Views of Hydrogen Orbitals

www.falstad.com/qmatom

- shows real wave functions (used by chemists)
- also complex wave functions
- phase information can be color coded
- views can be rotated in three dimensions
- radial probability distribution can be plotted
- time evolution also simulated