

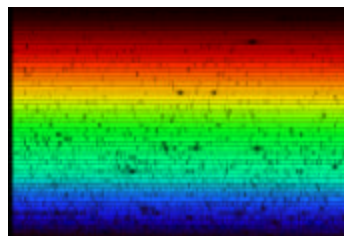
Chemistry 331

Lecture 6

Absorption spectra of atoms
The Schrödinger equation for hydrogen
The electronic structure of atoms

NC State University

The Solar Spectrum



- ⊛ There are gaps in the solar emission called Fraunhofer lines.
- ⊛ The gaps arise from specific atoms in the sun that absorb radiation.

Experimental observation of hydrogen atom

- ⊛ Hydrogen atom emission is “quantized”. It occurs at discrete wavelengths (and therefore at discrete energies).
- ⊛ The Balmer series results from four visible lines at 410 nm, 434 nm, 496 nm and 656 nm.
- ⊛ The relationship between these lines was shown to follow the Rydberg relation.



Atomic spectra

- ⊛ Atomic spectra consist of series of narrow lines.
- ⊛ Empirically it has been shown that the wavenumber of the spectral lines can be fit by

$$\tilde{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (n_2 > n_1)$$

where R is the Rydberg constant, and n_1 and n_2 are integers.

Electronic Structure of Hydrogen

- ⊛ The Schrödinger equation for hydrogen
- ⊛ Separation of variables
Radial and angular parts
- ⊛ Hydrogen atom wavefunctions
- ⊛ Expectation values
- ⊛ Spectroscopy of atomic hydrogen

Schrödinger equation for hydrogen: The kinetic energy operator

The Schrödinger equation in three dimensions is:

$$-\frac{\hbar^2}{2m} \tilde{\nabla}^2 \Psi + V\Psi = E\Psi$$

The operator del-squared is:

$$\tilde{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The procedure uses a spherical polar coordinate system. Instead of x, y and z the coordinates are θ , ϕ and r.

Schrödinger equation for hydrogen: The form of the potential

- ⊕ The Coulomb potential between the electron and the proton is $V = -Ze^2/4\pi\epsilon_0 r$
- ⊕ The hamiltonian for both the proton and electron is:

$$H = -\frac{\hbar^2}{2m_N}\tilde{N}_N^2 - \frac{\hbar^2}{2m_e}\tilde{N}_e^2 + V$$

- ⊕ Separation of nuclear and electronic variables results in an electronic equation in the center-of-mass coordinates: $H = -\hbar^2/2\mu\nabla^2 - Ze^2/4\pi\epsilon_0 r$ ($1/\mu = 1/m_e + 1/m_N$).

Separation of variables

It would be impossible to solve the equation with all three variables simultaneously. Instead a procedure known as separation of variables is used.

The steps are:

1. Substitute in $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$
2. Divide both sides by $R(r)Y(\theta,\phi)$
3. Multiply both sides by $2\mu r^2$

Solutions of the angular equation

- ⊕ The wavefunction solutions of the angular equation are spherical harmonics $Y_{lm}(\theta,\phi)$.
- ⊕ These functions describe the angular distribution of atomic orbitals and are the wavefunctions for the rigid rotor of polyatomic molecules.
- ⊕ The degeneracy of a given orbital is $2l+1$ and the angular momentum of the electron is $\sqrt{l(l+1)}\hbar$.

MAPLE

worksheet on spherical harmonics

- ⊕ The form of the spherical harmonics $Y_{lm}(\theta,\phi)$ is quite familiar. The shape of the s-orbital resembles the first spherical harmonic Y_{00} .
- ⊕ Attached to this lecture are three MAPLE worksheets that illustrate the s, p and d orbitals respectively. The idea is to obtain an interactive picture of the mathematical form and the plots of the functions.
- ⊕ Disclaimer: The spherical harmonics have been simplified by formation of linear combinations to remove any complex numbers.

MAPLE worksheet on spherical harmonics

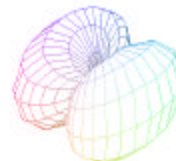
- ⊕ The Y_{00} spherical harmonic has the form of an s-orbital.



- ⊕ There is only one angular function for $l=0$.

MAPLE worksheet on spherical harmonics

- ⊕ The Y_{10}, Y_{11} , and $Y_{1,-1}$ spherical harmonics have the form of p-orbitals.



- ⊕ There are three angular functions for $l=1$.

MAPLE worksheet on spherical harmonics

- ⊕ The $Y_{20}, Y_{21}, Y_{2,-1}, Y_{22}$ and $Y_{2,-2}$ spherical harmonics have the form of d-orbitals.



- ⊕ There are five angular functions for $l=2$.

The effective potential: result of the solution of the angular part

- ⊕ The solutions for the angular part result in a term in potential energy equal to:

$$V' = \hbar^2 l(l+1)/2\mu r^2$$

- ⊕ This term contains the contributions to the energy from angular terms.
- ⊕ Together with the Coulomb potential the effective potential energy is:

$$V_{\text{eff}} = -Ze^2/4\pi\epsilon_0 r + \hbar^2 l(l+1)/2\mu r^2$$

The Bohr radius

The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2$ is known as the Bohr radius. The Bohr radius is $a_0 = 0.529 \text{ \AA}$. Since it emerges from the calculation of the wave functions and energies of the hydrogen atom it is a fundamental unit. In so-called atomic units the unit of length is the Bohr radius. So 1 \AA is approximately 2 Bohr radii.

You should do a dimensional (unit) analysis and verify that a_0 has units of length!

Normalization of the radial functions

Each of the radial equation solutions is a polynomial multiplying an exponential. The normalization is obtained from the integral:

$$\int_0^\infty R_{nl}^* R_{nl} r^2 dr = 1$$

The volume element here is $r^2 dr$ which is the "r" part of the spherical coordinate volume element $r^2 \sin\theta dr d\theta d\phi$.

MAPLE worksheet Normalization of the radial functions

A MAPLE worksheet attached to this lecture illustrates the normalization of the first three radial functions. The worksheet includes plots of the functions.

When examining a plot keep in mind that you can plot the wave function or the square of the wave function. We often plot the square of the wave function, because the integral of the square of the wave function gives the probability.

Energy levels of hydrogen atom

- ⊕ The energy levels of the hydrogen atom are specified by the principal quantum number n :

$$E = -\frac{\mu e^4}{32\pi^2\epsilon_0^2 \hbar^2 n^2}$$

- ⊕ All states with the same quantum number n have the same energy.
- ⊕ All states of negative energy are bound states, states of positive energy are unbound and are part of the continuum.

The Rydberg Constant

- ⊛ The energy levels calculated using the Schrödinger equation permit calculation of the Rydberg constant.
- ⊛ One major issue is units. Spectroscopists often use units of wavenumber or cm^{-1} . At first this seems odd, but $h\nu = hc/\lambda = hc\tilde{\nu}$ where $\tilde{\nu}$ is the value of the transition in wavenumbers.

$$R = \frac{1}{hc} \frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \quad \text{in cm}^{-1}$$

The simple form

- ⊛ Using the Rydberg constant the energy of the hydrogen atom can be written as:

$$E = -\frac{R}{n^2}$$

where $R = 107,636 \text{ cm}^{-1}$

Shells and subshells

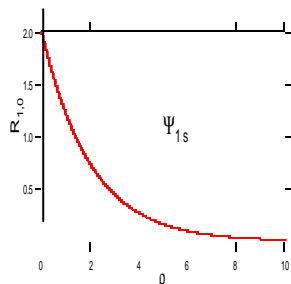
- ⊛ All of the orbitals of a given value of n for a shell.
- ⊛ $n = 1, 2, 3, 4 \dots$ correspond to shells K, L, M, N...
- ⊛ Orbitals with the same value of n and different values of l form subshells.
- ⊛ $l = 0, 1, 2, \dots$ correspond to subshells s, p, d ...
- ⊛ Using the quantum numbers that emerge from solution of the Schrödinger equation the subshells can be described as orbitals.

Hydrogenic orbitals

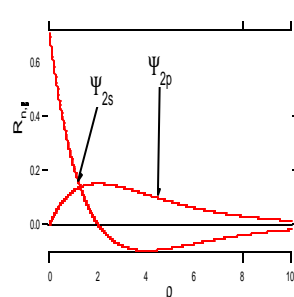
- ⊛ s orbitals are spherically symmetrical. The 1s wavefunction decays exponentially from a maximum value of $(1/\pi a_0^3)^{1/2}$ at the nucleus.
- ⊛ p orbitals have zero amplitude at $r=0$, and the electron possesses an angular momentum of $\hbar\sqrt{l(l+1)}$. The orbital with $m = 0$ has zero angular momentum about the z axis. The angular variation is $\cos\theta$ which can be written as z/r leading to the name p_z orbital.

Hydrogen 1s radial wavefunction

- ⊛ The 1s orbital has no nodes and decays exponentially.
- ⊛ $R_{1s} = 2(1/a_0)^{3/2} e^{-\rho/2}$
- ⊛ $n = 1$ and $l = 0$ are the quantum numbers for this orbital.



The Radial Distribution in Hydrogen 2s and 2p orbitals



Spectroscopy of atomic hydrogen

- ⊛ Spectra reported in wavenumbers, ...
- ⊛ Rydberg fit all of the series of hydrogen spectra with a single equation, ...
- ⊛ Absorption or emission of a photon of frequency ν occurs in resonance with an energy change, $\Delta E = h\nu$ (Bohr frequency condition).
- ⊛ Solutions of Schrödinger equation result in further selection rules.

Spectroscopic transitions

- ⊛ A transition requires a transfer from one state with its quantum numbers (n_1, l_1, m_1) to another state (n_2, l_2, m_2) .
- ⊛ Not all transitions are possible: there are selection rules, $\Delta l = \pm 1, m = 0, \pm 1$
- ⊛ These rules demand conservation of angular momentum. Since a photon carries an intrinsic angular momentum of 1.

Many-electron atoms: The orbital approximation

- ⊛ The orbital approximation to the total many-electron wavefunction $Y(r_1, r_2, \dots)$ is to rewrite it as a product of "one-electron" wavefunctions $\psi(r_1)\psi(r_2)\dots$ so that

$$Y(r_1, r_2, \dots) = \psi(r_1)\psi(r_2)\dots$$
- ⊛ The configuration of an atom is the list of occupied orbitals.
- ⊛ The Pauli exclusion principle states that the spins must be paired if two electrons are to occupy one orbital and no more than two electrons may occupy an orbital.

Penetration and shielding

- ⊛ In many-electron atoms the s, p, d etc. orbitals of each shell are not degenerate.
- ⊛ An electron distance r from the nucleus experiences the nuclear charge Z shielded by all of the other electrons. The effective charge is Z_{eff} .
- ⊛ $Z_{\text{eff}} = Z - \sigma$ where σ is the shielding parameter.
- ⊛ An s electron has a greater penetration through inner shells than a p electron of the same shell because the p electron has a node at the nucleus.

The Aufbau principle

- ⊛ Aufbau means "building-up" in German.
- ⊛ The configurations of atoms are built up by population of the hydrogenic orbitals.
- ⊛ Imagine a bare nucleus with charge Z and then add Z electrons to the orbitals in the following order:
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s etc.
- ⊛ Hund's rule an atom in its ground state adopts a configuration with the greatest number of unpaired spins.

The problem of multiple electrons

- ⊛ The central difficulty with application of the Schrödinger equation is the presence of electron-electron interaction terms in the potential energy:

$$V = - \sum_{i=1}^L \left(\frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i,j=1}^{L,L} \left(\frac{e^2}{4\pi\epsilon_0 r_{ij}} \right)$$

electron - nuclear electron - electron

- ⊛ No analytical solutions.
- ⊛ Hartree-Fock procedure. Find solutions that optimize the electron in each orbital in the presence of the field of all of the other orbitals.

Hartree-Fock procedure

As an example, for He we can write the two electron wave function as a product of orbitals.

$$\Psi(r_1, r_2) = \phi(r_1)\phi(r_2)$$

The probability distribution, $\phi^*(r_2)\phi(r_2)dr_2$ for electron 2 corresponds to a charge density in classical physics. Therefore, we can say that the effective potential felt by electron 1 is:

$$V_1^{eff}(r_1) = \int \phi^*(r_2) \frac{1}{r_{12}} \phi^*(r_2) dr_2$$

The self-consistent field method

The effective or average potential can be used in a one electron hamiltonian operator for electron 1

$$\hat{H}_1^{eff}(r_1) = -\frac{1}{2}\tilde{N}_1^2 - \frac{2}{r} + V_1^{eff}(r_1)$$

The Schrödinger equation is solved for electron 1

$$\hat{H}_1^{eff} \phi(r_1) = \epsilon_1 \phi(r_1)$$

Start with a trial function $\phi(r_2)$ and solve for $\phi(r_1)$. Using $\phi(r_1)$ calculate an effective potential for 2 and solve for $\phi(r_2)$. Continue until convergence is reached.

Atomic term symbols

- ⊕ The letter indicates the total orbital angular momentum quantum number of all electrons in an atom $L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \dots, |\ell_1 - \ell_2|$
- ⊕ The left superscript gives the multiplicity $2S+1$, where $S = s_1 + s_2 + s_3 + \dots$
- ⊕ The right subscript gives the total angular momentum $J = L + S, L + S - 1, \dots, |L - S|$
- ⊕ The term symbol is

$${}^{2S+1}L_J$$

Hund's rules determine the term symbol of the ground state

- ⊕ Each state is designated by a term symbol corresponds to a wave function that is an eigenfunction of L^2 and S^2 with unique energy.
- ⊕ The state with the largest value of S is the most stable.
- ⊕ For states with the same value of S , the state with the largest value of L is the most stable.
- ⊕ If the states have the same value of L and S
 - subshell less than half filled, smallest J is most stable
 - subshell more than half filled, the state with the largest value of J is the most stable.