

# Review of Zumdahl: Quantum Mechanics

Problems worth doing:

## Chapter 12

1, 2, 5, 6, 10, 16, 17, 22-24, 26, 27, 30, 32, 34, 36, 38, 40, 42, 47, 49, 50, 53, 54, 60, 62 (what is the energy of an H atom in the ground state), 65, 66, 72, 75, 78.

## Chapter 13

1, 3, 4, 9, 10, 11, 12, 20, 48, 50, 72, 76.

## Chapter 14

1, 2, 3 (Goes to the heart of the MO order), 5, 9, 13, 15, 16, 22, 26, 28, 43, 45

Doing problems is the single most important learning activity.

# Course Goal

- We will learn how to compute the energies of atoms and molecules
  - Compute bond energies and the energy stored in the chemical bond
  - Compute energy of a chemical reaction and energy of batteries.
  - Compute the way molecules absorb and emit light (EM Radiation).
  - Compute any molecular property you want.
- Spectroscopy is the way we compare our computations with the real systems. (By observing the light absorbed and emitted).

# QM and Atomic Theory: A Review of Ch 12-14 Zumdahl

- What is light?
- When is light a particle (and a wave)?
- How does light interact with matter?
  - (electrons, protons, atoms and molecules)
- All properties follow from Coulomb's Law
- Simple calculation of energy of H atom and H<sub>2</sub> molecule
- Find the allowed energy levels for a particle in a box (as an example of how a confining potential gives rise to quantization).
- Describe H-like orbitals
- Electron Spin
- Aufbau Principle of Atoms and the Periodic Table
- The chemical bond (it's origin and energy)
- The wave function for electrons in molecules and molecular orbitals.

# Light; The Spectrum; and Spectroscopy

Light as a Wave: Contains an oscillating Electric Field  
(and magnetic field)

Wave length,  $\lambda$  frequency,  $\nu$  or  $\omega$  and the speed,  $c$ , are all connected

$$\nu\lambda = c$$

$$\omega = 2\pi\nu$$

$$\omega = ck$$

$$k = 2\pi/\lambda$$

Oscillating (time dependent) Electric Field:  $E(t) = E_o \cos(\omega t + \phi)$

$E(t)$  oscillates perpendicular to the direction of propagation.

Includes a phase delay (arbitrary number)  $\phi$  Think Radians

Light as a Particle: Made up of individual Photons.

Planck's famous formula:  $E = h\nu = \hbar\omega$

same frequency as in the wave picture

Spectrum: Choice of  $\nu$  OR  $\lambda$  (we go back and forth)

# Light and Matter

- How does light interact with electrons and protons?
- Light has an electric field,  $E(t)$ , which is time dependent.
- That field is just like having charges; electrons are also charged. An electron is at position  $r$  and has charge  $q$ .
- The charges interact with the field. The energy of the interaction is  $E = E(t) \cdot q \cdot r$
- $E(t)$  and  $r$  are vectors (with  $x, y$  and  $z$  components)

$$E(t) \cdot r = E_x(t) \cdot r_x + E_y(t) \cdot r_y + E_z(t) \cdot r_z$$

$$E(t) \cdot r = \vec{E}(t) \cdot \vec{r} = \begin{pmatrix} E_x(t) & E_y(t) & E_z(t) \end{pmatrix} \cdot \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix}$$

- Work out a dipole and an Electric field:

# A dipole and the $E(t)$ field of light

- A dipole is two charges of equal magnitude and opposite sign separated by a fixed distance,  $d$ .
- This is the simplest example of a typical molecule which has positive and negative charges but is overall electrically neutral.
- This dipole interacts with the  $E(t)$  of light, and we can compute its energy of interaction using the formula from before:  $E = q_1 r_1 \cdot E(t) + q_2 r_2 \cdot E(t) = q(r_1 - r_2) \cdot E(t) = -\mu \cdot E(t)$

$$\mu = \bar{\mu} = q(r_2 - r_1) = (qd) \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix}$$

- Neutral molecules have an interaction with the field that leads to preferential alignment (or orientation; no trans)
- An oscillating field will cause dipoles to rotate.

# Coulomb's Law and an Electric Field

- Q is charge that generates the field  $Q = Q_o \sin(\omega t)$
- A charge of +Q is at -L and -Q at +L
- q is the charge of an electron at position z away from the center between the two (large) charges, Q.
- Use Coulomb's Law and obtain the energy of interaction that looks like  $qzE(t)$ .  $L \gg z$

$$V = \frac{qQ}{|-L-z|} + \frac{-qQ}{|z-L|} = \left(\frac{qQ}{L}\right) \left[ \frac{L}{L+z} - \frac{L}{L-z} \right]$$
$$= \left(\frac{qQ}{L}\right) \frac{\left[1 - \frac{z}{L} - 1 - \frac{z}{L}\right]}{1 - \left(\frac{z}{L}\right)^2} \approx -qz \cdot \left(\frac{2Q}{L^2}\right)$$

$$E(t) = \frac{2Q}{L^2} = \frac{2Q_o}{L^2} \sin(\omega t)$$

# Energy of particles

- Particles have energy. Two types: Kinetic and Potential
- Kinetic energy. The energy due to mass and velocity

$$KE = T = \frac{1}{2}mv^2 = \frac{1}{2}m\vec{v}\cdot\vec{v} = \frac{1}{2m}p^2$$

$$p = mv \text{ (momentum)} \quad v = \frac{dx}{dt}$$

- Angular Kinetic energy
  - I the moment of inertia, that is the angular analogue to mass (or linear inertia),  $I = mr^2$
  - Omega is the angular velocity, (analogue to v).
  - Angular velocity is the change in angle with time

$$E = \frac{1}{2}I\omega^2 \quad \omega = r \times v = \frac{d\phi}{dt}$$

- Potential Energy
  - The energy associated with interaction. The main one for us is coulombic interaction:  $PE = V = \frac{q_1q_2}{r}$  (careful of units)

- Show that Coulomb's law is similar to gravity and consistent with the interaction of a charged particle with the light field  $E(t)$ .

# The energy of the H atom

- What is the energy of the H atom?
  - The H atom has one proton and one electron.
  - The energy of an H atom is relative to the electron and the proton separated by an infinite distance but moving as a unit with a center of mass. (So the translational kinetic energy of the two particle unit is not part of the energy of the H atom).
- The first energy is the potential. Let's assume that the electron is in an orbit at distance,  $a_o$ , from the nucleus.  
Then: 
$$V = -\frac{e^2}{a_o}$$
- (this is the attraction that binds the two together)
- To be in stationary orbit (like a planet) the K.E. (T) balances the P.E. (V).  $T = -(1/2)V$ . The total energy then is

$$E = T + V = (1/2)V \text{ (notice it is bound, } E < 0)$$

# The Energy of the H atom

- Compute in the S.I. units the energy of the H atom (in the ground state).
- Virial Theorem for Planets:  $E = -T = \frac{1}{2}V$
- Problem 13.12 (Zumdahl) gives the numbers
- If an electron circled the nucleus at the distance given by Bohr (the Bohr radius) then the charge, attraction potential can be computed (using SI units):

$$V = -\frac{e^2}{4\pi\epsilon_0 a_o} = \frac{K}{a_o} = -2.31 \cdot 10^{-19} \frac{1}{a_o} \text{ nm} - J$$

$$V = -2.31 \cdot 10^{-19} \frac{1}{0.05292} J = -43.65 \cdot 10^{-19} J$$

$$E = \frac{1}{2}V = -21.78 \cdot 10^{-19} J$$

# Energy of the H atom

- Put some numbers in and compute the energy. Use the Bohr radius. Convert to kJ/mole

$$E = -21.8 \cdot 10^{-19} \text{ J} = -N_A \cdot 21.8 \cdot 10^{-22} \text{ kJ / mole} = -1.3 \text{ MJ / mole}$$

- Compare with spectroscopy, which measures the energy of the photon released when the electron binds to the nucleus (in the ground state)
  - This is Bohr's great insight: Spectroscopy tells us what is going on in the atom because the energy of the photon must exactly match the energy change of the atom (system). This is a universally true statement, which is why spectroscopy is so important to understand atoms and molecules.

# The Atomic Spectrum

- The specific lines coming from the H atom (and other atoms) gives clues about the possible energy states of the electron. Not all energies are in fact possible.
- The conservation of energy says that the energy of the photon must equal the energy change of the atom:

$$E_{\text{photon}} = h\nu = \Delta E_{\text{Atom}} = hR_y \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Using the Balmer-Rydberg way to reduce all possible spectral lines to the difference of integers:  $n_1$  and  $n_2$

The convention: If the system absorbs a photon  $\Delta E$  goes up, and the photon energy is positive (going into the atom). Go from 1 to 2.

$$n_2 > n_1$$

$$hR_y = 21.78 \cdot 10^{-19} \text{ J/molecule}$$

$$hR_y N_A = 1.312 \cdot 10^6 \text{ J/mole}$$

# Atomic Spectra

- The frequencies of light that come from H atom are discrete.
  - The Balmer-Rydberg Formula predicts all of them
  - The discrete frequencies tell that bound states are finite in number (a property of localization of electrons).
  - Quantum numbers ( $n$ ) keep track of the states of the H atom.
- Same question; different ways to write it
  - What is the energy of the H atom in the ground state?
  - What is the ionization energy of the H atom?
  - What frequency of light is emitted for the H atom going to the ground state (what are  $n_1$  and  $n_2$ )?
    - Show the light is in the UV band of the spectrum.
  - What is the largest energy Balmer line?
    - What quantum numbers are used?
    - Show the light is in the visible region?

# The Energy of H<sub>2</sub> (the energy of a bond)

- Use H atom as a reference.
- Now make a molecule (problem 13.12, Zumdahl)
- Keep the electrons at the Bohr Radius from each of the nuclei and make a “diamond” arrangement so that the two nuclei are the same distance from each other as the two electrons (which is  $\sqrt{2} \cdot a_0$  or 1.4\*Bohr Radius).
- Amazingly, the H<sub>2</sub> bond distance is almost exactly 1.4\*Bohr Radius; determined from spectroscopy.
- This configuration is just made up to illustrate how the electrostatics give a bond energy IF the electrons would go to these places.
- Ernshaw’s theorem tells us there is no place to put the charges as a stable arrangement, therefore the electrons must be moving to balance electrostatics (the virial theorem holds for H<sub>2</sub> molecule as it does for H atom)

# How the “diamond” arrangement of H<sub>2</sub> gives a different energy than two H atoms

- Compare potential and total energy (use virial theorem) for molecule and two atoms
- Get a bond energy (B.E.) that is 1/4 the energy of H atom and is 65% greater than the experimental value
- The negative B.E. indicates that the system is more stable sharing the electrons.
- Gives insight how Coulomb attraction helps make a molecule.

$$V_{H_2} = K \left\{ \frac{1}{\sqrt{2}a_0} + \frac{1}{\sqrt{2}a_0} - \frac{4}{a_0} \right\}$$

$$V_{H_2} = -2 \frac{K}{a_0} \left\{ 2 - \frac{1}{\sqrt{2}} \right\} = -2 \frac{K}{a_0} \cdot 1.29$$

$$E_{H_2} = \frac{1}{2} V_{H_2} = -\frac{K}{a_0} \cdot 1.29$$

$$E_{2H} = \frac{1}{2} V_{2H} = -\frac{K}{a_0} = -2 \cdot 21.78 \cdot 10^{-19} \text{ J}$$

$$B.E. = E_{H_2} - E_{2H} = -\frac{K}{a_0} \cdot 0.29 = -12.6 \cdot 10^{-19} \text{ J}$$

$$B.E._{exp} = -7.6 \cdot 10^{-19} \text{ J}$$

Chemical energy (like bond energy) comes from Kinetic and Potential Energy, and the Potential is Coulomb’s law (and nothing more).

# Q.M. Particle in a box:

## How Q.M. Handles a Simple Problem

- All of the problems are like this one: You have a particle held by a potential, the particle can move, so you have kinetic energy of the particle and the potential energy (which depends only on the position of the particle).
- For the particle in a box the potential is a bit quirky because it's job is to keep the particle inside a box. So the potential is zero inside the box, and infinite (or infinitely repulsive) outside the box. That should keep a particle in the box. All other potentials are much smoother functions of position.
- Q.M. replaces the usual kinetic energy by a kinetic energy operator, and the usual position by a distributed position amplitude (or wave function).

# Particle in a Box (Zumdahl, 12.6)

- Classically the total energy is the sum of the kinetic and potential energy.  $E=T+V$
- This is replaced by:  $\hat{H} \equiv \hat{T} + \hat{V}$  and  $E\psi = \hat{H}\psi$
- For the particle in the box the potential is zero and the kinetic energy operator is:  $\hat{V} = 0$  and  $\hat{H} = \hat{T} = \frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$
- The equation of motion (which does not have time in it) is a second-order ordinary differential equation (2<sup>nd</sup>-ODE).

$$0 \leq x \leq L \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E\psi$$

# Particle in a Box

- This second order differential equation has a solution. We will use rules like this a lot in this course.
- As a summary: We solve the wave function, in terms of a quantum number,  $k$ .
- Then by a boundary condition on the wave function, which brings in physical reality on what wave functions are physically allowable, we find only discrete values of  $k$  are allowed.
- The discrete values follow from the confinement of the particle (i.e. electron) via the boundary condition.

# Solution to Wave Function for Particle in a Box

- We use the known form of the wave function and put it into the differential equation and relate  $k$ , the unknown constant to the energy,  $E$ , also unknown.
- $k$  is the wave vector (related to the wave length) just like the quantity for light.  $A$  is the amplitude (a constant)

$$\psi = A \sin kx$$

$$-A \frac{\hbar^2}{2m} \frac{d^2 \sin kx}{dx^2} = EA \sin kx$$

$$\frac{\hbar^2 k^2}{2m} \sin kx = E \sin kx$$

$$E = \frac{\hbar^2 k^2}{2m}$$

# Boundary Condition for Particle in Box

- The wave function must be zero outside the box, so it must be zero at the walls of the box.
- The wave function is always zero at the origin.
- The wave function can be zero at the other end ( $x=L$ ) only for certain values of  $k$ .

$$\sin kL = 0 \quad \Rightarrow \quad kL = \pi n \quad \Rightarrow \quad k = \frac{\pi n}{L}$$

- $n$  is an integer (not zero). So the wave vector is proportional to an integer and the energy goes as the wave vector squared:

$$E = \frac{(\hbar k)^2}{2m} = \frac{(\hbar \pi n)^2}{2mL^2} = E_n$$

# Meaning of QM and Wave Function

- Square of Wave Function tells us where the electron (or particle) is located (a probability distribution).
- Can't say anything about motion or change in time (no time in the answer).
- The confining potential causes electron localization and this leads to discrete-only energies for the electron.
- The three problems we will do are those for different potentials. They all work the same.
  - Particle in a box potential
  - Particle in a harmonic confining potential (not done in Zumdahl)
  - Particle confined by Coulomb's law potential (attraction).
- There is a lowest energy state (the ground state); no temperature in the answer.

# Wave Functions and Energies for Hydrogen atom

- For hydrogen we have a different potential than for the particle in a box, now the potential is the attraction of electrons for nucleus, using Coulomb's Law. So we know the potential operator: 
$$\hat{V} = -\frac{Ze^2}{r}$$
- The wave functions solve the motion of an electron held by the nucleus (charge  $Ze$ ). Nothing is time dependent, just like the particle in the box.
- Now in three dimensions:  $Cart \Rightarrow Polar \Rightarrow Q.N.$

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \Rightarrow \begin{Bmatrix} r \\ \theta \\ \phi \end{Bmatrix} \Leftrightarrow \begin{Bmatrix} n \\ l \\ m_l \end{Bmatrix}$$

# Hydrogenic energy and Orbitals (Table 12.1)

- The energy depends only on the  $n$  quantum number; the principle quantum number.

$$E = -\frac{1}{2} \frac{e^2}{a_0} \cdot \left( \frac{Z}{n} \right)^2 = -21.78 \cdot 10^{-19} \cdot \left( \frac{Z}{n} \right)^2 \text{ J}$$

- Notice  $E$  goes up (increases) as  $n$  goes up, and that all  $E$ 's are negative, so going up means going closer to zero. All energies are negative, indicating bound.
- The energy depends on  $Z^2$  not  $Z$ .
- The wave functions all decay exponentially, they go further out as  $n$  increases, and are pulled in as  $Z$  increases.

$$\Psi_{n,\ell,m} \propto e^{-\frac{Zr}{na_0}}$$

# The Shape of Atomic Orbitals

- The  $\ell$ , or angular momentum, quantum number determines the shape of the atomic orbital.

- The orbital angular, momentum squared is:

$$L^2 = \hbar^2 \ell(\ell + 1)$$

- The angular quantum number can be zero, and must be less than the principal quantum number:

$$0 \leq \ell < n$$

- The values are given names; there are  $2\ell + 1$  different orbitals for each value of  $\ell$ ; the  $m$ (magnetic) quantum number tracks the different  $\ell$  orbitals:  $-\ell \leq m \leq \ell$

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$\ell$ value	0	1	2	3
name	s	p	d	f
number	1	3	5	7

# Electron Spin

- In addition to the three quantum numbers for each atomic orbital, an electron has its own quantum number, the spin quantum number. For electrons there are two values (and only two values),  $m_s = \pm \frac{1}{2}$
- An electron in a given state then has associated with it 4 quantum numbers.
- Pauli Exclusion requires that each electron, in a multi-electronic atom, must have a unique set of quantum number; therefore only two electrons can occupy a given atomic orbital.

# Aufbau Principle and the Periodic Table

- The set of quantum numbers (and allowed values) explains the structure of the periodic table.
- Aufbau means build up. The atoms are made by putting the electrons in the lowest possible energy states (ground state). For atomic number  $Z$ , there are  $Z$  electrons in the neutral atom.
- The electronic configuration is the list of all quantum numbers for each electron in an atom. There are shortcuts to writing all this out.
- Two-s electrons on the left; six-p electrons on the right and ten-d, transition electrons in the middle of P.T.
- Inert atoms correspond to filling the p orbitals.
- The chemistry of many atoms is related to achieving locally an electronic structure of an inert atom.
- The lanthanides and actinides each have 14 electrons to fill the f orbitals.

# Atomic Properties: I.P. and E.A.

- Consider trends in the ionization potential (I.P.) and the electron affinity (E.A.) of atoms.
- I.P. is the energy needed to remove the most easily removed electron from an atom. (figure 12.35)  
*e.g.  $I.P.(H) = 21.8 \cdot 10^{-19} J = 1,300 kJ / mole$*
- I.P.(He) is much larger because the 1s level is filled (it is inert). Locally, all noble gasses have relatively high I.P.s.
- I.P.(Li) is much smaller so that Li (or Li<sup>+</sup>) can become pseudo-He.
- Halogens have the largest Electron Affinities, taking up an electron to become iso-electronic with noble gasses.

# The covalent Bond

- Consider again the simple picture (based on QM) of the  $H_2$  molecule.
- Molecular Orbitals (MOs) work just like AO. They are places where the electrons reside.
- MOs place electrons between nuclei to generate a bond.
- For  $H_2$  two 1s AOs overlap to form a bonding and an anti-bonding orbital.
- Examine the MOs energy diagram:
- Explain why  $H_2$  is stable but  $He_2$  is not stable.
- Others work the same.
- Go through the diatomic molecules:  $Li_2$  to  $F_2$ ; predicting paramagnetism.
- Compare  $CH_4$ ,  $NH_3$ ,  $OH_2$ ,  $FH$   $sp^3$  type hybrid orbitals.

# Spectroscopies

- Electronic Spectroscopy
  - Direct electron excitation, UV/Vis transitions.
- Vibrational Spectroscopy
  - The librations (wiggling) and bond stretching (of nuclei)
- Rotational Spectroscopy
  - The inertia (rotational mass) of molecules
- Nuclear Magnetic Resonance (NMR) Spectroscopy
  - Local electronic environment of nuclei.
- Electron Paramagnetic Resonance (EPR) Spectroscopy
  - The wave function of unpaired electrons in molecules.

All spectroscopies have in common that the frequency of the light matches the energy difference of the transition between the levels of the molecule or atom.

# Electronic Transitions

- Use the “Particle in a Box” model to show how spectroscopy can tell about energy levels.
- A one dimensional box (1 nanometer long) can be like the confining potential of beta carotene (See page 536, and 683 and problem 12.42 in Zumdahl)
- Consider a transition from  $n$  to  $n+1$ .
- Match the energy difference in the two levels with the energy of light:  $E_{n,box} = \frac{p^2}{2m}$  where  $p = \hbar k$  and  $kL = n\pi$

$$\Delta E_{n,box} = \frac{(\pi\hbar)^2}{2mL^2} \left[ (n+1)^2 - n^2 \right] = \frac{h^2}{2mL^2} \frac{1}{4} (2n+1)$$

$$h\nu_{photon} = \Delta E_{n,box} = h \frac{1}{2} \frac{h}{2mL^2} \left( n + \frac{1}{2} \right)$$

$$\frac{h}{2mL^2} = \frac{2\pi \cdot 10^{-34}}{2 \cdot 10^{-30} \cdot 10^{-18}} = \pi \cdot 10^{14} \text{ sec}^{-1}$$

$$\text{For } n=1 \Rightarrow \nu_{photon} = 2 \cdot 10^{14} \text{ sec}^{-1} \text{ (visible light)}$$

# Atoms Vibrate in Molecules

- Electrons hold molecules together (using QM principles)
- Nuclei in stable molecules can vibrate about the equilibrium (lowest energy) positions.
- Approximate the binding of two nuclei in a diatomic molecule by a Harmonic Force (simple spring) P.E. is:  $V = \frac{1}{2} k_o (r - r_{eq})^2$
- Classical mechanics tells us that the frequency of oscillation is related to the reduced mass and the force constant by:

$$\omega_o = \sqrt{\frac{k_o}{\mu}} \text{ where } \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

- The possible Q.M. energies are:  $E_{HO,n} = \hbar\omega_o \left(n + \frac{1}{2}\right)$
- So the transition between any two levels different by one quantum is:  $\Delta E_{HO,n} = \hbar\omega_o \left[ \left(n \pm 1 + \frac{1}{2}\right) - \left(n + \frac{1}{2}\right) \right] = \pm \hbar\omega_o$

$$h\nu_{light} = E_{photon} = \Delta E_{HO,n} = \hbar\omega_o$$

# Vibrational Energy

- Vibrations are in the infrared (Zumdahl pg 686)

$$k_o = 500 \text{ J / m}^2 \text{ and } \mu(\text{HCl}) = 1.5 \cdot 10^{-27} \text{ kg}$$

$$\omega_o = \sqrt{\frac{k_o}{\mu}} = 5.8 \cdot 10^{14} \text{ sec}^{-1}$$

$$h\nu_{light} = E_{photon} = \Delta E_{HO,n} = \hbar\omega_o$$

$$\nu_{light} = \frac{1}{2\pi} \omega_o = 1 \cdot 10^{14} \text{ sec}^{-1} \text{ (InfraRed)}$$

$$\lambda_{light} = \frac{c}{\nu_{light}} = 3 \cdot 10^{-6} \text{ m}$$

$$\frac{1}{\lambda_{light}} = \frac{1}{3} \cdot 10^6 \text{ m}^{-1} = 3,000 \text{ cm}^{-1}$$

# How far do nuclei vibrate?

- The mean square amplitude of displacement can be found using the Virial Theorem for the Harmonic Oscillator:

$$E = \hbar\omega_o \left(n + \frac{1}{2}\right) = 2\langle V \rangle = 2\frac{1}{2}k_o \langle x^2 \rangle$$

$$\langle x^2 \rangle = \frac{\hbar \sqrt{\frac{k_o}{\mu}}}{k_o} \left(n + \frac{1}{2}\right) = \frac{\hbar}{\sqrt{\mu k_o}} \left(n + \frac{1}{2}\right)$$

$$\langle x^2 \rangle = \frac{1 \cdot 10^{-34}}{\sqrt{\frac{1}{2} \cdot 10^3 \cdot 1.6 \cdot 10^{-27}}} \left(n + \frac{1}{2}\right) = \left(n + \frac{1}{2}\right) \cdot 10^{-22} m^2$$

$$\sigma_x = \sqrt{\langle x^2 \rangle} = \sqrt{\left(n + \frac{1}{2}\right) \cdot 10^{-11} m}$$

The rms extent of oscillation about the mean is then about 0.1 of the bond length itself (which is on the order of an angstrom).

# Molecules Rotate

- The rotation of molecules is in the microwave range.
- The rotation of water in a microwave heats the water (and whatever the water is part of) by absorbing microwaves.
- How rotational energy (the energy in a spinning merry-go-round) works; consider a diatomic (or two body rotation).
- Linear energy:  $E = K.E. = \frac{1}{2}mv^2 = \frac{1}{2m}p^2$
- Angular motion (and energy):

$$I = \mu r_e^2 \quad \text{and} \quad \omega = r_e \times p$$

$$v \Rightarrow \omega \text{ (angular velocity)}$$

$$m \text{ ( or } \mu \text{ )} \Rightarrow I \text{ (rotational inertia)}$$

$$p = mv \Rightarrow L = I\omega \text{ (angular momentum)}$$

$$E = \frac{1}{2}I\omega^2 = \frac{1}{2I}L^2$$

# Angular Momentum Q.M. Style

- In Q.M. Angular Momentum comes in multiples of Planck's constant. (Remember Bohr's insight for Atoms?)

$$L^2 = \hbar^2 \ell(\ell + 1)$$

- Therefore Rotational Energy is:  $E_\ell = \frac{1}{2I} L^2 = \frac{\hbar^2}{2I} \ell(\ell + 1)$

- Compare with the Particle in a box equation (L for the box is the length of the box not the angular momentum)

$$\Delta E_{n,box} = \frac{(\pi\hbar)^2}{2mL^2} n^2$$

parallels:  $\pi n \Leftrightarrow \ell$  and  $mL^2 \Leftrightarrow I = \mu r_e^2$

- Spectroscopists like to rewrite the rotational energy to parallel the harmonic oscillator so that the rotational constant (B) is easily related to the frequency of the light driving rotations.

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell + 1) = hB\ell(\ell + 1) \quad \text{where} \quad B = \frac{\hbar}{4\pi I}$$

# Angular Momentum and Light

- Connect the rotation transitions with the light frequency:
- We have a transition where the quantum number increases by 1.

$$h\nu_{\text{photon}} = \Delta E_{\ell,+1} = hB [(\ell + 1)(\ell + 2) - \ell(\ell + 1)]$$

$$\frac{c}{\lambda} = \nu_{\text{photon}} = 2B(\ell + 1)$$

- Compute B assuming a bond distance of 1.2 Ang or 126 pm for HCl, and everything else is known (pg 690 Zumdahl).
- Obtain a photon frequency  $\sim 10^{+12} \text{ Hz}$  (which is microwave).

$$2B = \frac{\hbar}{2\pi I} = \frac{1 \cdot 10^{-34}}{6.3 \cdot 1.5 \cdot 10^{-27} \cdot (1.26 \cdot 10^{-10})^2} = 0.7 \cdot 10^{12} \text{ Hz}$$

# Magnetic Resonance and Spin

- Protons and electrons have spin  $\frac{1}{2}$ .
- Any transition from the lower to the upper spin state then is a change of 1 quantum number (just as all other examples).

$$\Delta S_z = 1$$

- Magnetic resonance uses a magnetic field to split the spin states and then the light energy used to drive transitions must match the energy difference imposed by the magnetic field.
- The energy of the spin states is given by the magnet, the effect of local fields and the presence of other nuclei that have their own magnetic states and interact with the nucleus of interest.

$$E = \hbar \left[ \omega_o (1 + \delta) + aI_z \right] S_z$$

$$h\nu_{\text{photon}} = \Delta E = \hbar \left[ \omega_o (1 + \delta) + aI_z \right] \Delta S_z$$

$$\nu_{\text{photon}} = \frac{1}{2\pi} \left[ \omega_o (1 + \delta) + aI_z \right]$$