Chemistry 882 Notes – Weliky

I.1 Introduction

Spectroscopy deals with the interaction of light with matter. Light and matter can be considered both as waves and as particles. First consider these two views for light.

Light as a Transverse Electromagnetic Wave: We consider light which propagates (moves) in the **x** direction. There are associated electric and magnetic fields which oscillate perpendicular to each other and to the propagation direction.

An electric field is created by any distribution of electric charges and exerts a force on other charges. For example, a point charge q_1 has an associated electric field:

$$\boldsymbol{\mathcal{E}}(\boldsymbol{r}) = (1/4\pi\varepsilon_0) \times (q_1/r^3) \times \boldsymbol{r} \tag{1.1.1}$$

where $\boldsymbol{r}$ is a vector whose origin is at the charge and $(1/4\pi\varepsilon_0) = 8.99 \times 10^9$ Newton-meter^2/coulomb^2. The × means "times". The constant ε_0 is the "permittivity of free space". An SI unit of $\boldsymbol{\mathcal{E}}$ is Newton/coulomb (N/C). The electric field of q_1 will exert a force on another charge q_2:

$$\boldsymbol{F}(\boldsymbol{r}) = q_2 \times \boldsymbol{\mathcal{E}} \tag{1.1.2}$$

The energy of the two charges:

$$E(\boldsymbol{r}) = \int_\infty^r -(\boldsymbol{F} \cdot d\boldsymbol{r}) = (1/4\pi\varepsilon_0) \times (q_1 q_2/r) \tag{1.1.3}$$

The "**.**" refers to the dot product between two vectors. The attractive negative force and energy of positively charged nuclei and negatively charged electrons is the basis of atomic and molecular stability.

The electric potential $V(\boldsymbol{r})$ of q_1:

$$V(\boldsymbol{r}) = \int_\infty^r -(\boldsymbol{\mathcal{E}} \cdot d\boldsymbol{r}) = (1/4\pi\varepsilon_0) \times (q_1/r) = E(\boldsymbol{r})/q_2 \tag{1.1.4}$$

The common SI unit of V is the Volt ≡ Joule/Coulomb (J/C) and the common SI unit of $\boldsymbol{\mathcal{E}}$ is Volt/meter (V/m).

The electric field of a charge exerts force on another charge and the electric potential of a charge gives rise to an electrostatic energy with another charge.

A magnetic field is created by moving charges (i.e. electric currents) and exerts a force on other moving charges. For example, a solenoid coil whose axis is along the **z** direction with N turns/length and counterclockwise current I_1 has a field $\boldsymbol{B} = \mu_0 N I_1 \mathbf{z}$ where μ_0 is the "permeability of free space" and equals $4\pi \times 10^{-7}$ kg-m/C^2. The SI unit of $\boldsymbol{B}$ is kg/C-s or "Tesla" (T).

Now consider a current loop of area A and counterclockwise current I_2. The current loop is considered to have "magnetic moment" $\boldsymbol{\mu}$ which is a vector with magnitude $|I_2A|$ and direction perpendicular to the plane of the loop. In the uniaxial magnetic field, there is a torque on the current loop:

$$\boldsymbol{N} = \boldsymbol{\mu} \times \boldsymbol{B} \qquad (1.1.5)$$

The "×" refers to the cross product between two vectors. The energy is:

$$E = -\boldsymbol{\mu} \,.\, \boldsymbol{B} \qquad (1.1.6)$$

$\boldsymbol{N} = 0$ and most negative E are achieved when $\boldsymbol{\mu}$ and $\boldsymbol{B}$ are parallel.

Let us return to electromagnetic radiation propagating along the **x** direction. The equations for the fields as a function of position and time are:

$$\boldsymbol{\epsilon}(x, t) = \epsilon_0 \cos[2\pi(kx - \nu t) + \delta]\, \mathbf{y} \qquad (\mathrm{I.1.7})$$
$$\boldsymbol{B}(x, t) = B_0 \cos[2\pi(kx - \nu t) + \delta]\, \mathbf{z} \qquad (\mathrm{I.1.8})$$

Note that there is an oscillation in both position and in time and δ is a "phase factor" and is just a number.

These equations contain the wavenumber k and frequency ν.

$k = 1/\lambda$ where λ is the wavelength of the light. (I.1.9)
$\nu = 1/T$ where T is the time period of the light. (I.1.10)

The unit of k is commonly cm^{-1} while that of ν is nearly always Hertz (Hz) or sec^{-1}.

The speed of the radiation is given:

$$c = \lambda / T = \lambda \nu \qquad (1.1.11)$$

In vacuum, $c = 2.997925 \times 10^8$ m/s in vacuum while in materials, the speed is reduced by $n_{\mathrm{material}} \geq 1$ where n is the index of refraction and has value 1 in vacuum. For example, $n = 1.40$ for KCl. The frequency of the radiation is constant in all materials. The wavelength changes proportionally with the speed.

ϵ_0 and B_0 are related:

$$B_0 = \epsilon_0 k/c \qquad (1.1.12)$$

The total energy of the wave is given:

$$E = \varepsilon_0 \epsilon_0^2 \cos^2[2\pi(kx - \nu t) + \delta] \qquad (1.1.13)$$

For $\langle \cos^2[2\pi(kx - \nu t) + \delta] \rangle = ½$ where $\langle\rangle \equiv$ the average value over one period of the wave, $\langle E \rangle = \varepsilon_0 \epsilon_0^2/2$. Thus, the average energy of the radiation is proportional to the (electric field)^2.

Very often, we are only interested in the time variation of the fields at a particular position ($x = 0$). We can then write a simplified set of equations:

$$\boldsymbol{\epsilon}(x, t) = \epsilon_0 \cos[2\pi \nu t + \delta]\, \mathbf{y} \tag{I.1.14}$$
$$\boldsymbol{B}(x, t) = B_0 \cos[2\pi \nu t + \delta]\, \mathbf{z} \tag{I.1.15}$$

The δ in Eqs. 1.1.14 and 1.1.15 have opposite sign to those in Eqs. 1.1.7 and 1.1.8.

Light as a Particle: We consider light as a stream of particles (photons). The energy of each photon is:

$$E = h\nu = hc/\lambda, \tag{I.1.16}$$

The h refers to Planck's constant and has value 6.626 x 10^{-34} Joule-sec.

The electromagnetic spectrum is the whole range of light frequencies and energies. Different regions of the spectrum can be used to excite different kinds of motion in molecules. You should consider the spectral frequencies typical for NMR, ESR, rotational transitions, vibrational transitions, electronic transitions, a microwave oven, the cosmic interstellar background, and room temperature.

Experimentally, it is known that energy levels in atoms and molecules are *quantized* (discrete). Light is used to excite transitions between these discrete energy levels. The energy level difference must satisfy the *Bohr condition*.

$$\Delta E = h\nu \tag{I.1.17}$$

The spectrum of a molecule is typically the energy *absorbed* or *emitted* by the molecule as a function of spectral frequency. *Emission* is divided into at least two categories, *fluorescence* and *phosphorescence*.

Fluorescence is emission from the initial excited state or a nearby excited state.

Sometimes, the initial excited state changes non-radiatively (without light) into a much lower energy state. This change is often the result of a collision with another molecule. The emission from this lower energy state is called phosphorescence and can last for ~ 1 sec. after the initial absorption.

I.2. Orders of Magnitudes of Energy (from T. Oka, Atkins)

I.2.A Atoms

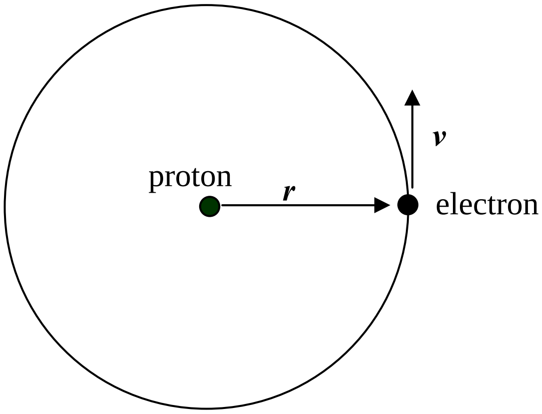
In looking at the electromagnetic spectrum, one obvious question is:

Why are certain electronic or nuclear motions excited by certain regions of the electromagnetic spectrum? I give a semiquantitative answer to the question and will provide you with a framework for estimating atomic and molecular spectral parameters.

We start with the Bohr (circular planetary orbit) model of the H atom. M is the mass of the proton and m is the mass of the electron.

$$M = 1.67239 \times 10^{-27} \text{ kg} \tag{I.2.1}$$
$$m = 9.10908 \times 10^{-31} \text{ kg} \tag{I.2.2}$$

Note that $M \sim 2000m$. Both the proton and electron have charge $e = 1.602 \times 10^{-19}$ Coulomb.



To zeroth order, the electron orbits around the proton.

In classical mechanics, this circular orbit requires equal magnitudes of centripetal and coulombic forces:

$$mv^2/r = (1/4\pi\varepsilon_0) \times e^2/r^2 \tag{I.2.3}$$

Bohr's insight was to quantize electronic orbital angular momentum in integral units of $\hbar = h/2\pi$.

$$|\,\boldsymbol{L}\,| = |\,\boldsymbol{r} \times \boldsymbol{p}\,| = |\,\boldsymbol{r} \times m\boldsymbol{v}\,| = mrv = n_e\hbar \qquad n_e \text{ is a positive integer} \tag{I.2.4}$$

Bohr's insight is consistent with the DeBroglie relationship:

$$\lambda = h/|\,\boldsymbol{p}\,| \tag{I.2.5}$$

This relationship is based on the hypothesis that a particle has an associated oscillation ("wave") and that the wavelength of the oscillation is given by Eq. 1.2.5. It is reasonable that an integer times the DeBroglie wavelength should equal the circumference of the orbit so that the particle forms a "standing wave" in the orbit; i.e. there is constructive interference of the wave at all points along the circumference with each orbital revolution.

$$2\pi r = n_e\lambda = n_e h/|\boldsymbol{p}| = n_e h/mv \Rightarrow mrv = n_e\hbar \qquad (1.2.6)$$

Combining Eqs. I.2.3 and I.2.4:

$$v = (1/4\pi\varepsilon_0) \times e^2/mrv = (1/4\pi\varepsilon_0) \times e^2/n_e\hbar \qquad (I.2.7)$$

$$r = (1/4\pi\varepsilon_0) \times e^2/mv^2 = (1/4\pi\varepsilon_0)^{-1} \times n_\mathrm{e}^2\hbar^2/me^2 \qquad (I.2.8)$$

Calculate total energy E by summing kinetic and potential energies using Eq. 1.2.3:

$$E = (mv^2/2) - [(1/4\pi\varepsilon_0) \times (e^2/r)] = -mv^2/2 = -(1/4\pi\varepsilon_0)^2 \times (1/n_e^2) \times me^4/2\hbar^2 \qquad (I.2.9)$$

The quantity $(1/4\pi\varepsilon_0)^2 \times me^4/2\hbar^2$ is known as a Rydberg and has energy 13.6 eV ≡ 2.18×10^{-18} J ≡ 314 kcal/mol. A more meaningful spectroscopic quantity is E/hc which has units 1/wavelength:

$$(1/4\pi\varepsilon_0)^2 \times me^4/4\pi\hbar^3 c = 109700\ \mathrm{cm}^{-1} \qquad (I.2.10)$$

The H atom transitions will occur between smaller n_{e1} and larger n_{e2} at wavenumber:

$$\Delta E/hc = 109700\ \mathrm{cm}^{-1} \times (1/n_{e1}^2 - 1/n_{e2}^2) \qquad (I.2.11)$$

The $\Delta E/hc$ calculated from this equation agree very well with the transition wavenumbers measured in experimental H atom spectra.

For n_{e1}=1, ΔE are in the ultraviolet, for n_{e1}=2, the visible, and n_{e1}=3, the near infrared. This gives us an order of magnitude about the spectral regions reasonable for electronic transitions.

It is observed that these spectral regions correlate with electronic transitions of all molecules which is consistent with the idea that electronic transitions are *localized* to particular functional groups in molecules. The electrons associated with the transition are contained in a region with dimension of order-of-magnitude of the H atom.

The Bohr atom equations show $v \propto 1/n_e$, $r \propto n_e^2$, and $E \propto -1/n_e^2$. As n_e increases, the velocity and kinetic energy decrease, the radius and potential energy increase, and the overall energy increases.

For the n_e=1 lowest energy state:

$$\alpha = v/c = (1/4\pi\varepsilon_0) \times e^2/\hbar c \sim 1/137 \qquad (I.2.12)$$

The small value of α suggests that relativistic effects are relatively minor. The proton-electron distance is known as the Bohr radius:

$$a_0 = (1/4\pi\varepsilon_0)^{-1} \times \hbar^2/me^2 = 0.529\ \text{Å} \qquad \text{(I.2.13)}$$

This provides a measure of atomic size.

In atoms and molecules, important quantities are *multipole moments*. Moments are a convenient means of expressing the electric or magnetic fields of a system of static or moving charges, respectively. The electric moments of molecules are calculated from the static charge distributions within the molecule while the magnetic moments are calculated from currents within the molecule. The total electric or magnetic field is the sum of the moment fields.

Consider the electric moments:

Moment ($\boldsymbol{M}$)	Order (j)	Order-of-Magnitude of Moment	Order-of-Magnitude of Electric Field of Moment
monopole	0	e	$(1/4\pi\varepsilon_0) \times \Sigma_j\, q_j /R^2$
dipole ($\boldsymbol{\mu}$)	1	ea_0	$(1/4\pi\varepsilon_0) \times \mu/R^3$
quadrupole ($\boldsymbol{Q}$)	2	ea_0^2	$(1/4\pi\varepsilon_0) \times Q/R^4$
octupole ($\boldsymbol{O}$)	3	ea_0^3	$(1/4\pi\varepsilon_0) \times O/R^5$
hexadecapole ($\boldsymbol{H}$)	4	ea_0^4	$(1/4\pi\varepsilon_0) \times H/R^6$

(I.2.14)

You can see from this table that $|\boldsymbol{M}_j| \sim e \times (a_0)^j$ and that the order-of-magnitude of the electric field of $\boldsymbol{M}_j$ is $(1/4\pi\varepsilon_0)(e)(a_0/R)^j(1/R^2)$. The R in this expression is the distance from the molecule to some point *far* from the molecule. Because $a_0 << R$, the fields decrease rapidly with increasing j. Thus, we typically only consider the lowest order moments when calculating the electric and magnetic fields of an atom or molecule.

The lowest order electric moment is the monopole and is the charge of the molecule.

The next order is the electric dipole moment which plays a large role in molecular interactions with radiative electric fields. The electric dipole moment reflects spatial separation of positive and negative charge in the molecule and is a vector from the center of the negative charge to the center of the positive charge of the molecule. The simplest example of such charge separation are heteronuclear diatomic molecules like HCl and the electric dipole moment is along the internuclear axis with vector head nearer the negatively charged Cl atom and tail nearer the positively charged H atom.

The order of magnitude of the electric dipole moment:

$$|\boldsymbol{\mu}_e| \sim ea_0 = 8.475 \times 10^{-30} \text{ Coulomb-meter} \equiv 2.55 \text{ Debye} \qquad (I.2.15)$$

The Debye is a commonly used “cgs” unit for dipole moment. Small molecule dipole moments are ~1 Debye while dipole moments in macromolecules can be much larger because the molecular dimensions are much greater than a_0.

There is an energy associated with an electric dipole moment in an electric field $\boldsymbol{\epsilon}$:

$$E_{\text{elec.dipole}} = -\boldsymbol{\mu}_e \cdot \boldsymbol{\epsilon} \qquad (I.2.16)$$

The lowest energy is associated with the dipole moment vector parallel to the electric field vector and the highest energy is associated with the dipole moment antiparallel with the electric field vector.

Consider a constant uniaxial electric field such as the one produced between two plates with different voltages. The $\boldsymbol{\epsilon}$ points from the higher voltage plate to the lower voltage plate. The most energetically favorable dipole orientation is the positive end of the dipole closest to the lower voltage plate and the negative end of the dipole closest to the higher voltage plate.

An achievable experimental field is 10^5 V/m and yields an electric dipole energy for the Bohr atom of ~.04 cm^{-1}, seven orders of magnitude smaller than the Rydberg. This result points out that electric fields internal to atoms and molecules are typically much greater than the fields achievable with laboratory apparatus.

Another interesting example is the radiative electric field. From Eq. I.1.7, we know that the radiative electric field oscillates symmetrically and periodically in time about zero so that for a static electric dipole, $\langle -\boldsymbol{\mu}_e \cdot \boldsymbol{\epsilon} \rangle = 0$. However, in the Bohr atom, $\boldsymbol{\mu}_e$ periodically changes direction as the electron orbits the proton. There can be a non-zero $\langle -\boldsymbol{\mu}_e \cdot \boldsymbol{\epsilon} \rangle$ when the $\boldsymbol{\mu}_e$ frequency and the $\boldsymbol{\epsilon}$ frequency are close to one another. This is an example of *resonance*.

The higher electric multipole moments correspond to more complex distributions of charge. For example, the electric quadrupole moment corresponds to two positive charges on a line and two negative charges on a line which bisects the positive charge line in a perpendicular fashion. The charge distributions of homonuclear diatomics such as H_2 are approximated by an electric quadrupole.

The quadrupole moment interacts with electric field gradients; i.e. the derivatives of the electric field with respect to position:

$$E_{\text{elec.quadrupole}} \sim (\boldsymbol{Q})(\nabla\boldsymbol{\epsilon}) \qquad (I.2.17)$$

This interaction is important in NMR of nuclei with large spin quantum numbers (e.g. ^{2}H, ^{14}N, ^{23}Na) . The $\boldsymbol{Q}$ is associated with the electric charge distribution in the nucleus and the $\nabla\boldsymbol{\epsilon}$ is associated with the chemical bonds of the nucleus.

There is no magnetic monopole moment. The *magnetic dipole moment* is a vector associated with electronic motion in the Bohr atom and is calculated as the product of the counter-clockwise electronic current and the area enclosed by the electronic orbit. If we consider that the electron orbit is in the *xy* plane, then $\boldsymbol{\mu}_m$ will be along the $-\mathbf{z}$ direction.

$$\boldsymbol{\mu}_m = (I \times A)\,\mathbf{z} = (-\,ev/2\pi r) \times (\pi r^2)\,\mathbf{z} = (-\,evr/2)\,\mathbf{z} = -\,e \times (e^2/n_e\hbar)(n_e^2\hbar^2/2me^2)\,\mathbf{z} =$$

$$-\,(n_e e\hbar/2m)\,\mathbf{z} \qquad \text{(I.2.18)}$$

For $n_e = 1$, $|\boldsymbol{\mu}_m| = \mu_B$ and is called the *Bohr magneton* and has value 9.28×10^{-24} C-m^2/s.

Both the nucleus and electron orbit about their center of mass so that there is also an electric current and magnetic dipole moment associated with the nucleus:

$$\boldsymbol{\mu}_m = (n_e e\hbar/2M)\,\mathbf{z} \qquad \text{(I.2.19)}$$

Note that $\boldsymbol{\mu}_m$ for the nucleus lies along the positive $\mathbf{z}$ direction because the nucleus is positively charged. For $n_e = 1$, $|\boldsymbol{\mu}_m| = \mu_N$ and is called the *nuclear magneton* and has value 5.05×10^{-27} C-m^2/s. Note that $\mu_N \sim \mu_B/2000$.

For the Bohr atom, $\boldsymbol{L}_e = n_e\hbar\,\mathbf{z}$ and in the center-of-mass frame $\boldsymbol{L}_N = n_e\hbar\,\mathbf{z}$. Eqs. 1.2.18 and 1.2.19 can be written:

$$\boldsymbol{\mu}_m = -(e/2m) \times \boldsymbol{L}_e \qquad \text{(I.2.20)}$$

$$\boldsymbol{\mu}_m = (e/2M) \times \boldsymbol{L}_N \qquad \text{(I.2.21)}$$

The sign difference between electrons and nuclei is due to their different charge signs. The key finding is that the electronic and nuclear magnetic moments are proportional and collinear with their respective angular momenta.

Consider the Bohr atom in a constant uniaxial magnetic field $B_0\mathbf{z}$. Using Eq. 1.1.6, the magnetic dipole energy of the atom:

$$E = -\,\boldsymbol{\mu}_m \,.\, \boldsymbol{B} = -(eB_0/2m) \times L_{ez} \qquad \text{(I.2.22)}$$

Spin

For electrons and nuclei, there is an additional angular momentum, *spin*, which also has an associated magnetic moment. This type of angular momentum is a result of relativistic effects which are not considered in the Bohr atom. Although it is tempting to think of the electrons and nuclei as ‘spinning’ as in a planetary model, this is not a correct physical picture.

For our purposes, we simply think of spin as another type of angular momentum. Unlike orbital angular momentum, spin angular momentum can have half-integral *n*.

Eqs. I.2.20 and 1.2.21 hold for spin with the inclusion of an extra "*g* factor" in the proportionality.

$$\boldsymbol{\mu}_m = -\, g \times (e/2m) \times \boldsymbol{L}_e \tag{I.2.23}$$

$$\boldsymbol{\mu}_m = \; g_N \times (e/2M) \times \boldsymbol{L}_N \tag{I.2.24}$$

The electron *g* factor is 2.0032 while the nuclear g_N factor is nucleus isotope-specific and varies from about –2 to +6 (e.g. 5.58 for ^{1}H, 1.40 for ^{13}C, –1.11 for ^{29}Si). The ratio $|\boldsymbol{\mu}|/|\boldsymbol{L}|$ is known as the *gyromagnetic ratio* and is usually denoted γ.

The magnitude of spin angular momentum:

$$|\boldsymbol{L}| = S(S+1) \times \hbar \tag{I.2.25}$$

S is the spin quantum number. S = ½ for an electron while S for a nucleus depends on the specific nuclear isotope. Some examples: $S = 0 \Rightarrow$ ^{12}C, ^{16}O; S = ½ $\Rightarrow$ ^{1}H, ^{13}C; $S = 1 \Rightarrow$ ^{2}H, ^{14}N; $S = 3/2 \Rightarrow$ ^{23}Na.

Spin interactions are typically probed in a uniaxial magnetic field $B_0\mathbf{z}$ and the energies are derived with Eq. 1.1.6. The $\boldsymbol{L}_z$ are quantized:

$$\boldsymbol{L}_z = m_S\hbar\,\mathbf{z} \qquad \text{with } m_S = -S, -S+1, \ldots, S \tag{1.2.26}$$

Eq. 1.1.6 yields:

$$E = -\boldsymbol{\mu} \,.\, \boldsymbol{B} = m_S\gamma\hbar B_0 \tag{1.2.27}$$

Spectroscopic transitions are observed for $\Delta m_S = \pm 1$ and yield:

$$\nu = |\Delta E|/h = |\gamma B_0|/2\pi \tag{1.2.28}$$

For electrons, $\gamma = -1.76 \times 10^{11}$ C/kg. One typical electron spin resonance magnetic field is B_0 = 0.32 kg/C-s ≡ 0.32 Tesla (T) and results in $\nu = 8.97 \times 10^9$ Hz which is in the microwave region of the spectrum. For protons, $\gamma = 2.675 \times 10^8$ C/kg. A typical nuclear magnetic resonance B_0 = 9.4 T which yields $\nu = 4.00 \times 10^8$ Hz in the radiofrequency region of the spectrum.

The magnetic field in Eq. I.2.28 is a sum of the large external field and smaller "local fields" due to the magnetic moments of the surrounding electrons and nuclei. For example, the electrons associated with the chemical bonds of a nucleus have a local field which typically has opposite direction to the external field. The magnitude of this shielding depends strongly on the functional group and creates "chemical shift" dispersion in the NMR frequencies.

Interactions between nuclear spins, between electron spins, and between electron and nuclear spins are typically both theoretically well-understood and largely decoupled from spatial electronic and nuclear motion (e.g. vibration). Electron and nuclear spin resonance spectroscopies provide useful information about the spatial configurations of electrons and nuclei in molecules while the couplings of spins to spatial motions provide information about the locations and magnitudes of these motions.

I.2.B Molecules

Small molecule dimensions are similar to atomic dimensions. For example, the H_2 equilibrium internuclear separation is 0.74 Å. So the electronic properties of small molecules should be similar to those of atoms. In macromolecules, it turns out that electrons are typically localized to functional groups containing 2 – 10 atoms and the electronic properties of the macromolecule can be considered as the properties of the "small molecule" functional groups.

For the analysis of molecular rotation and vibration, a useful constant is the Born-Oppenheimer constant $\kappa = (m/M)^{1/4} \sim 0.1$.

For molecular rotation, a simple model is a particle constrainted to move on a spherical surface. The particle mass is the molecular mass M and the sphere radius R reflects the radial dimension of the molecule. Consider a radial vector $\boldsymbol{R}$ from the origin to the particle and the particle momentum vector $\boldsymbol{P} = M\boldsymbol{V}$. Note that $\boldsymbol{R}$ and $\boldsymbol{P}$ are orthogonal. The rotational angular momentum $\boldsymbol{L} = \boldsymbol{R} \times \boldsymbol{P}$:

$$|\boldsymbol{L}| = |\boldsymbol{R} \times \boldsymbol{P}| = MRV \sim Ma_0V \sim n_r\hbar \qquad \text{(I.2.29)}$$

For this case, we consider that the molecule is small so that $R \sim a_0$. In addition, $\boldsymbol{L}$ is assumed to be quantized in a manner similar to the electronic angular momentum of Eq. 1.2.4. For $n_e = n_r = 1$, the electronic and rotational angular momenta are comparable:

$$Ma_0V = ma_0v \;\; \Rightarrow V = (m/M) \times v \qquad \text{(I.2.30)}$$

This result suggests that the molecular rotational velocity in a low energy rotational state is three to four orders of magnitude smaller than the electronic velocity in the ground electronic state.

There is a will usually be a relatively constant potential energy associated with molecular rotation and the large variations in rotational energy will associated with the kinetic contribution:

$$E_{rot} \sim MV^2/2 = M \times (m/M)^2 \times v^2/2 = (m/M) \times mv^2/2 \sim \kappa^4 |E_{electronic}| = 10\ \text{cm}^{-1} \qquad \text{(I.2.31)}$$

Rotational transition energies will be of order-of-magnitude of E_{rot} and for small molecules will generally occur in the microwave and far-infrared regions of the spectrum. For macromolecules, the transitions will occur at lower frequencies because of the larger M.

Vibrational motion is motion of nuclei about their equilibrium structural positions. This motion should be correlated with the chemical bonds between the nuclei. The simplest vibrational model is two nuclear masses connected by a spring representing their chemical bond. The separation of the two masses is denoted x and the equilibrium separation is x_e. The restoring force is:

$$F(x) = -k(x - x_e) \tag{I.2.32}$$

Note that the force constant k is different from the wavenumber k in Section I.1. The force constant will depend on the strength of the bonding between the two nuclei. For example, the force constant of a double bond will be larger than that of a single bond.

The potential energy:

$$V(x) = \int_{x_e}^{x} -F(x)\, dx = k/2 \times (x - x_e)^2 \tag{I.2.33}$$

This is harmonic (parabolic) in $(x - x_e)$. Newton's Second Law equation:

$$M \times (d^2x/dt^2) = -k(x - x_e) = -kx + kx_e$$

$$d^2x/dt^2 = (-k/M)x + (k/M)x_e \tag{I.2.34}$$

In this equation, M will be a "reduced mass" calculated by a mathematical expression including the masses of both nuclei.

One solution for Eq. I.2.34:

$$x(t) = x_e + A\cos(\omega t) \tag{I.2.35}$$

with $\omega = (k/M)^{1/2}$ and $A = x(0) - x_e$. For this solution, the initial velocity $(dx/dt)_{t=0} = 0$.

The mass oscillates in time about x_0. The angular frequency $\omega = 2\pi\nu$ where ν is 1/(period of the oscillation). Note that the vibrational frequency is larger for bigger k (stronger bonding) and for lighter atoms (smaller M).

For molecular vibration, consider the nuclei moving in a harmonic potential well of depth $E_{\text{electronic}} \sim 100000\ \text{cm}^{-1}$ and width $2a_0$. Using Eq. I.2.33, we define $E_e \sim ka_0^2/2$.

Approximate the angular vibrational frequency:

$$\omega = (k/M)^{1/2} \sim (2E_e/Ma_0^2)^{1/2} = (1/4\pi\varepsilon_0) \times (2E_e m^2 e^4/M\hbar^4)^{1/2} = 2(m/M)^{1/2}\, E_e/\hbar \tag{I.2.36}$$

We guess that vibrational energy will be quantized as $n_v\hbar\omega$ where n_v is a non-negative integer:

$$E_{vib} \sim 2n_v(m/M)^{1/2}\, E_e = 2n_v\kappa^2 E_e \sim 2n_v(10^{-2})(100000\ \text{cm}^{-1}) \sim n_v(2000\ \text{cm}^{-1}) \tag{I.2.37}$$

So vibrational energies are about two orders of magnitude smaller than electronic energies and about two orders of magnitude greater than rotational energies.

Transitions between vibrational energy levels will yield vibrational spectra which largely lie in the infrared, intermediate between the rotational and electronic spectral regions. Thus, different regions of the spectrum are appropriate for exciting different kinds of motion in molecules (electronic, rotation, vibration).

It is also possible to excite different kinds of motion simultaneously, for example electronic + vibrational motion.

A particular vibrational motion is typically confined to a single functional group so that the vibrational motion of a macromolecule can be approximated as a combination of independent vibrational motions of the individual functional groups of the molecule.

If we assume that vibrational energy is evenly divided between kinetic and potential energy, then the kinetic energy for the $n_v = 1$ state:

$$E_{kin} = MV^2/2 = (1/4\pi\varepsilon_0)^2 \times me^4/\hbar^2$$

$$V = (1/4\pi\varepsilon_0) \times 2^{½} \times (m/M)^{½} \times (e^2/\hbar) = 2^{½} \times \kappa^2 \times v$$

$$V/v = 2^{½} \times \kappa^2 \approx 0.01 \tag{I.2.38}$$

The v and V represent the electron and nuclear vibrational velocities in the $n_e = 1$ and $n_v = 1$ states. The small value of V/v means that the nuclei move much slower than the electrons. This ratio is the basis of the *Born-Oppenheimer approximation* which states that the electrons relocate instantaneously in response to changes in nuclear positions. This means that it is possible to separate calculations of electron and nuclear motions. First, the nuclei are fixed at particular locations and the electronic motion and energy are calculated. The nuclei are then fixed at different positions and the electronic motion and energy are recalculated. An “electronic potential” is determined by many such calculations. Vibrational motion and energy of the nuclei are then considered within this electronic potential.

Combining Eqs. I.2.30 and I.2.38:

$$V_{rot}/V_{vib} \sim (2)^{-½} \times \kappa^2 \approx 0.01 \tag{I.2.39}$$

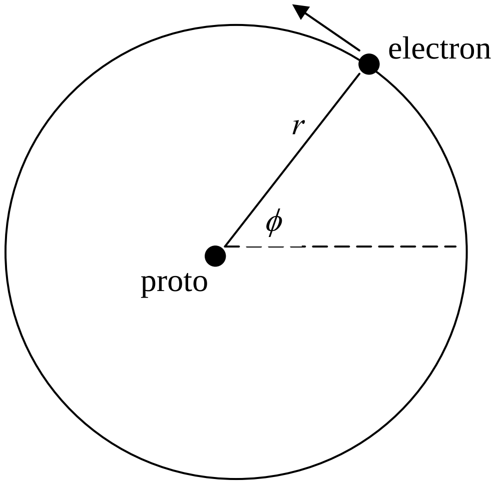
Because molecular rotation is much slower than molecular vibration, rotational and vibrational motion can also be calculated independently.

QUANTUM MECHANICAL METHODS

I. Postulates

We set out to give some description of quantum mechanics which is useful for spectroscopy.

1. The Postulates of Quantum Mechanics



A simple example will be used to illustrate the postulates of quantum mechanics. For the *radial atom*, an electron of mass m is constrained to move in an orbital of fixed radius r in the xy plane about the proton. The radial constraint makes the system different from that of the Bohr atom.

First Postulate: The state of an N-particle system is defined by a wavefunction $\Psi(\boldsymbol{q}, t)$. A wavefunction is single-valued and continuous. The coordinates for the N particles are $\boldsymbol{q} = \boldsymbol{q}_1, .., \boldsymbol{q}_N$ and t refers to time.

$$\boldsymbol{q}_j = x_j\,\mathbf{x} + y_j\,\mathbf{y} + z_j\,\mathbf{z} \equiv (x_j, y_j, z_j) \qquad \text{(II.1.1)}$$

For example, for the radial atom, $\boldsymbol{q}$ could be $(r, 0, 0)$ and would correspond to $\phi = 0$.

A set of wavefunctions for the radial atom:

$$\Psi(\phi, t) = (2\pi)^{-\frac{1}{2}}\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2m}\} \qquad \text{(II.1.2)}$$

The "k" can be any integer and $i = (-1)^{1/2}$. The first exponential describes the spatial dependence of the wavefunction and the second exponential describes the time dependence of the wavefunction. The k is integral so that $\Psi(\phi, t) = \Psi(\phi + 2\pi, t)$. The azimuthal positions ϕ and $\phi + 2\pi$ are experimentally indistinguishable and integral k is necessary to have a single-valued Ψ.

The k is an example of a *quantum number*. The wavefunction associated with each value of k would correspond to a different state of the atom with distinct properties (e.g. energy or angular momentum).

For some comparison, consider a classical description of the electron position:

$$\phi(t) = \omega t \qquad \text{(II.1.3)}$$

For this classical description, the electron orbits around the proton with uniform angular frequency ω.

All of the properties of the atom or molecule (e.g. energy, angular momentum, dipole moment) can be obtained from the wavefunction.

The quantity $\Psi(\boldsymbol{q}_m, \tau)^* \times \Psi(\boldsymbol{q}_m, \tau) = |\Psi(\boldsymbol{q}_m, \tau)|^2 = \mathcal{P}(\boldsymbol{q}_m, \tau)$ describes the relative probability for finding the system with the specific coordinates $\boldsymbol{q}_m$ at time τ.

The * refers to the complex conjugate. Consider a complex number $a + ib$. The product $(a + ib) \times (a + ib)^* = (a + ib) \times (a - ib) = a^2 + b^2$ which is a real number (good for a probability!).

For the radial atom:

$$\mathcal{P}(\phi_0, \tau) = \Psi(\phi_0, \tau)^* \times \Psi(\phi_0, \tau) = (2\pi)^{-1/2}\,\{e^{-ik\phi 0}\}\{e^{ik^2\hbar\tau/2m}\} \times (2\pi)^{-1/2}\,\{e^{ik\phi 0}\}\{e^{-ik^2\hbar\tau/2m}\}$$

$$= (2\pi)^{-1} \qquad \text{(II.1.4)}$$

For these radial atom wavefunctions, there is no dependence of electron density on ϕ or on time.

Note that we often normalize the probability integrated over all coordinates:

$$\int \Psi(\boldsymbol{q}, t)^* \, \Psi(\boldsymbol{q}, t) \, d\boldsymbol{q} = 1 \qquad \text{(II.1.5)}$$

This normalization is reasonable because it infers that at a given time, the particle has to be somewhere in space. The wavefunctions of Eq. II.1.2 are normalized.

Second Postulate: Every observable (measurable) property of the system is described by a corresponding *Hermitian operator A*.

Examples of these operators:

Position of a one particle system: x for position along the **x** direction
y for position along the **y** direction (II.1.6)
z for position along the **z** direction

Momentum in a one particle system: $(-i\hbar)d/dx$ for momentum along the **x** direction
$(-i\hbar)d/dy$ for momentum along the **y** direction (II.1.7)
$(-i\hbar)d/dz$ for momentum along the **z** direction

In classical mechanics, position would also be described by x, y, and z while momentum would be described by mv_x, mv_y, and mv_z.

Operators act on wavefunctions to yield new wavefunctions. So, a general operator expression for operator $A(\boldsymbol{q}, t)$ and wavefunctions $\Psi(\boldsymbol{q}, t)$ and $\Phi(\boldsymbol{q}, t)$:

$$A(\boldsymbol{q}, t)\ \Psi(\boldsymbol{q}, t) = \Phi(\boldsymbol{q}, t) \qquad \text{(II.1.8)}$$

The radial atom electron has angular momentum L_z along the **z** direction and the associated operator:

$$L_z \equiv (-i\hbar)\ d/d\phi \qquad \text{(II.1.9)}$$

$$L_z\Psi(\phi, t) = \{(-i\hbar)\ d/d\phi\}\ (2\pi)^{-½}\ \{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\} = (k\hbar)(2\pi)^{-½}\ \{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\}$$
(II.1.10)

For this case, the new wavefunction is a constant ($k\hbar$) times the old wavefunction. Note that classically, $L_z = mvr$ for the radial atom.

What is a Hermitian operator A?

Two equivalent ways to express this property:

$$\int \Psi^*(\boldsymbol{q}, t)\ A\ \Phi(\boldsymbol{q}, t)\ d\boldsymbol{q} = \int\{\Phi^*(\boldsymbol{q}, t)\ A\ \Psi(\boldsymbol{q}, t)\ d\boldsymbol{q}\ \}^* \qquad \text{(II.1.11)}$$

Take the complex conjugate of this equation and rearrange the terms.

$$\int\{A\ \Phi(\boldsymbol{q}, t)\}^*\ \Psi(\boldsymbol{q}, t)\ d\boldsymbol{q} = \int \Phi^*(\boldsymbol{q}, t)\ A\ \Psi(\boldsymbol{q}, t)\ d\boldsymbol{q} \qquad \text{(II.1.12)}$$

This is a good time to introduce the *bra/ket* vector notation. This notation contains no new physics but allows us to concisely write quantum mechanical expressions. The integral equations above are expressed in a shorthand way as:

$$\langle\Psi|A|\Phi\rangle = \langle\Phi|A|\Psi\rangle^* \qquad \text{(II.1.13)}$$

$$\langle(A\Phi)|\Psi\rangle = \langle\Phi|A\Psi\rangle \qquad \text{(II.1.14)}$$

The left-hand “bra” vector such as $\langle\Psi|$ contains implicitly a complex conjugate. The right-hand “ket” vector is not a complex conjugate. The intermediate operator position is also not a complex conjugate and allows greater clarity. For example:

$$\langle\Psi|A|\Phi\rangle = \langle\Psi|A\Phi\rangle \qquad \text{(II.1.15)}$$

$$\langle\Psi|A|\Phi\rangle = \langle\Psi A^*|\Phi\rangle \qquad \text{(II.1.16)}$$

When we have an expression with a bra followed by a ket as above, the expression contains an implicit integration over all of the spatial variables $\boldsymbol{q}$ of the wavefunctions. Otherwise, there is no implicit integration. For an expression such as $A|\Psi\rangle$, there is no integration.

In all quantum mechanical expressions, the expression is calculated from left to right. The order can be important so one cannot indiscriminately change the order of operators and wavefunctions. For example:

$$\langle\Psi|\Phi\rangle \neq |\Phi\rangle\langle\Psi| \tag{II.1.17}$$

The expression on the left is an integral (a number) while the expression on the right is an operator. Also, in general for an operator A and ket $|\Psi\rangle$:

$$A|\Psi\rangle \neq |\Psi\rangle A \tag{II.1.18}$$

A radial atom example:

$$L_z|\Psi\rangle = \{(-i\hbar)\, d/d\phi\}|(2\pi)^{-½}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\}\rangle = |(k\hbar)(2\pi)^{-½}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\}\rangle$$

$$|\Psi\rangle L_z = |(2\pi)^{-½}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2m}\}\rangle\{(-i\hbar)\, d/d\phi\} \tag{II.1.19}$$

In general for operators A and B:

$$AB|\Psi\rangle \neq BA|\Psi\rangle \tag{II.1.20}$$

The difference operator $AB - BA$ is written shorthand as $[A, B]$ and is called the *commutator*. If $[A, B] = 0$, the operators A and B are said to commute. If $[A, B] \neq 0$, then the operators A and B do not commute.

$$[\phi, L_z]|\Psi\rangle = \phi\,(-i\hbar)\,(d/d\phi)\,|\Psi\rangle - (-i\hbar)\,(d/d\phi)\phi\,|\Psi\rangle \;= (i\hbar)\{1 + \phi\,(d/d\phi) - \phi\,(d/d\phi)\}|\Psi\rangle =$$

$$(i\hbar)|\Psi\rangle \Rightarrow [\phi, L_z] = i\hbar \tag{II.1.21}$$

Consider some constant c in a bra:

$$\langle c\Psi| = \langle\Psi|c^* \tag{II.1.22}$$

I can take constant out of the bra but have to remember the implicit complex conjugate. Finally, for two wavefunctions $|\Phi\rangle$ and $|\Psi\rangle$:

$$\langle\Phi|\Psi\rangle = \langle\Psi|\Phi\rangle^* \tag{II.1.23}$$

Because there is simple multiplication between the two wavefunctions, I can switch their order.

I also introduce *eigenvalue/eigenfunction equations*:

$$A|\psi\rangle = \lambda\,|\psi\rangle \qquad \text{(II.1.24)}$$

In this equation, $|\psi\rangle$ is an eigenfunction of A and has eigenvalue λ which is a number. For the radial atom, an eigenvalue/eigenfunction equation for L_z:

$$L_z|\psi\rangle = \{(-i\hbar)\,d/d\phi\}|(2\pi)^{-1}e^{ik\phi}\rangle = (k\hbar)|(2\pi)^{-1}e^{ik\phi}\rangle \qquad \text{(II.1.25)}$$

For this example, $\lambda = k\hbar$ and $|\psi\rangle = |(2\pi)^{-1}e^{ik\phi}\rangle$ is the non-time-dependent part of Ψ in Eq. II.1.2.

Eigenvalue equations are at the core of quantum mechanics and spectroscopy. The operator for each physical observable has a set of eigenfunctions and eigenvalues associated with it and:

Third Postulate: The only possible result of the measurement of a physical observable is one of its eigenvalues of its associated operator.

Because the eigenvalues are what we measure, much effort goes into their calculation and into the calculation of their associated eigenfunctions. If our physical model of the molecule is reasonable, then the observed and calculated eigenvalues will be similar. Typical spectroscopically measurable observables are energy and dipole moments. In crystallography, the observable is electron density.

In the quantum mechanical radial atom, the only observable values of L_z are $k\hbar$, again where k is an integer. This is similar to the $n_e\hbar$ quantization condition for the semiclassical Bohr atom but there are some important differences. For example, $k = 0$ is allowed in the radial atom while $n_e = 0$ is not allowed in the Bohr atom. In addition, the radial atom has k values which are independent of r while the value of r in the Bohr atom depends on n_e (cf. Eq. I.2.8).

The eigenvalues associated with *Hermitian* operators are always *real*. You can see why physical observables would be associated with Hermitian operators – we can only measure real quantities.

Also, the eigenfunctions of a Hermitian operator associated with *different* eigenvalues are *orthogonal*, that is $\langle\psi_{\lambda_j}|\psi_{\lambda_k}\rangle = 0$ if $\lambda_j \neq \lambda_k$.

If our system is in a state which corresponds to the eigenfunction of the operator, then measurement of the observable associated with this operator would be the eigenvalue.

For example, if the radial atom $|\psi\rangle = |(2\pi)^{-1/2}\,e^{2i\phi}\rangle$, then the observed value of L_z will be $2\hbar$.

Suppose the system is not in an eigenfunction of its observable operator A. We will still measure only eigenvalues of the observable operator. But which eigenvalues and with what probabilities?

We express the wavefunction $|\psi\rangle$ as a linear combination of the *orthonormal* eigenfunctions $|\varphi_1\rangle$, $|\varphi_2\rangle$,… of A:

$$|\psi\rangle = \Sigma_j\, c_j\,|\varphi_j\rangle \qquad \text{(II.1.26)}$$

Don’t confuse the $|\varphi_j\rangle$ which is a function with the angular variable ϕ in our radial atom example.

Orthonormality (orthogonality + normality):

$$\langle\varphi_j|\varphi_k\rangle = \delta_{jk} \quad (0 \text{ if } j \neq k,\ 1 \text{ if } j = k) \tag{II.1.27}$$

The δ_{jk} is known as the *delta function*. Note that our radial atom L_z eigenfunctions are orthonormal:

$$\langle\varphi_j|\varphi_k\rangle = \langle(2\pi)^{-1/2}\, e^{ij\phi}|(2\pi)^{-1/2}\, e^{ik\phi}\rangle \;=\; \int_0^{2\pi} (2\pi)^{-1/2}\{e^{-ij\phi}\}(2\pi)^{-1/2}\{e^{ik\phi}\}d\phi$$

$$= \int_0^{2\pi} (2\pi)^{-1}\, e^{i(k-j)\phi}\, d\phi \;=\; \{1/2\pi i(k-j)\}\; e^{i(k-j)\phi}\,\Big|_0^{2\pi} \tag{II.1.28}$$

For $j \neq k$, the definite integral yields $0/2\pi i(k-j) = 0$, while for $j = k$, the integral yields 0/0 which can be shown to be 1 in this case.

Any particular c_k can be found by *projecting* $\langle\varphi_k|$ onto both sides of Eq. II.1.26. This means multiplying by φ_k^* and integrating over the coordinates $\boldsymbol{q}$:

$$\langle\varphi_k|\psi\rangle = \langle\varphi_k|\, \Sigma_j\, c_j\, |\varphi_j\rangle = \Sigma_j\, c_j\, \langle\varphi_k|\varphi_j\rangle = \Sigma_j\, c_j\, \delta_{jk} = c_k \tag{II.1.29}$$

We are now ready to answer the eigenvalue probability question.

Fourth Postulate: The probability of observing the eigenvalue λ_k is $\mathcal{P} = c_k{}^*c_k/\Sigma_j|c_j|^2$ $= |c_k|^2/\Sigma_j|c_j|^2$.

If $|\psi\rangle$ is normalized, then $\mathcal{P} = |c_k|^2$.

If the wavefunction of a molecule is not an eigenfunction of the observable property, it is possible to observe many different eigenvalues. However, for any single molecule, only one value will be observed.

We typically make measurements on many molecules (e.g. 10^{23} ~ Avogadro’s number) so that our measurements give statistical probabilites for the observed eigenvalues. These statistical probabilities are expressed by the fourth postulate.

Consider a normalized radial atom wavefunction:

$$|\psi\rangle = (3i/5)|e^{i\phi}\rangle \;+\; (4/5)|e^{-i\phi}\rangle \tag{II.1.30}$$

The probability of observing the angular momentum eigenvalues:

$$\mathcal{P}(\hbar) = (-3i/5)(3i/5) = 9/25$$

$$\mathcal{P}(-\hbar) = (4/5)(4/5) = 16/25 \tag{II.1.31}$$

For this approach, some linear combination of wavefunctions $|\varphi_j\rangle$ must completely describe any state of the molecule. In other words, the $|\varphi_j\rangle$ eigenfunctions must form a *complete* set which *span* the entire state space. *The eigenfunctions of an observable property always form a complete set.*

Completeness can be described mathematically with the *closure relation*:

$$\Sigma_j\, |\varphi_j\rangle\langle\varphi_j| = 1 \tag{II.1.32}$$

The sum of *projector operators* $\Sigma_j\, |\varphi_j\rangle\langle\varphi_j|$ has no effect on any wavefunction of the system.

Let's calculate the effect of the projector on $|\psi\rangle$:

$$\Sigma_k\, |\varphi_k\rangle\langle\varphi_k|\psi\rangle \;=\; \Sigma_k\, |\varphi_k\rangle\langle\varphi_{jk}|\, \Sigma_j\, c_j|\varphi_j\rangle \;=\; \Sigma_k\, \Sigma_j\, c_j|\varphi_k\rangle\langle\varphi_k|\varphi_j\rangle \;=\; \Sigma_k\, \Sigma_j\, c_j|\varphi_k\rangle\, \delta_{jk}$$

$$= \;\Sigma_j\, c_j|\varphi_j\rangle = |\psi\rangle \qquad \text{(No Effect!)} \tag{II.1.33}$$

The closure relation is used in many derivations and can be used to derive an important result about the average values of observable quantities.

The average value of the observable A for a wavefunction $|\psi\rangle$ is the probability weighted sum of the observable eigenvalues λ_j (cf. Postulate 4). Consider a normalized $|\psi\rangle$:

$$\langle A\rangle = \;\Sigma_j\, |c_j|^2\, \lambda_j \;=\; \Sigma_j\, c_j{}^*c_j\, \lambda_j \;=\; \Sigma_j\, \langle\varphi_j|\psi\rangle^*\, \lambda_j\, \langle\varphi_j|\psi\rangle \;=\; \Sigma_j\, \langle\psi|\varphi_j\rangle\, \lambda_j\, \langle\varphi_j|\psi\rangle$$

$$= \;\Sigma_j\, \langle\psi|A|\varphi_j\rangle\, \langle\varphi_j|\psi\rangle \;=\; \langle\psi|A\, \Sigma_j\, |\varphi_j\rangle\langle\varphi_j|\, \psi\rangle \;=\; \langle\psi|A|\psi\rangle \tag{II.1.34}$$

The importance of the wavefunction for predicting system properties is clearly demonstrated.

Consider $\langle L_z\rangle$ for the radial atom wavefunction of Eq. II.1.30:

$$\langle L_z\rangle = \langle\psi|(-i\hbar)\, d/d\phi\, |\psi\rangle = \{(-3i/5)\langle e^{i\phi}| + (4/5)\langle e^{-i\phi}|\}\, (-i\hbar)d/d\phi\, \{(3i/5)|e^{i\phi}\rangle + (4/5)|e^{-i\phi}\rangle\}$$

$$= (\hbar)\, \{(-3i/5)\langle e^{i\phi}| + (4/5)\langle e^{-i\phi}|\}\{(3i/5)|e^{i\phi}\rangle - (4/5)|e^{-i\phi}\rangle\} = \hbar\, (9/25 - 16/25) = \;(-7/25)\, \hbar \tag{II.1.35}$$

Although $\langle L_z\rangle = (-7/25)\, \hbar$, only $L_z = \hbar$ and $-\hbar$ will be observed.

How can we use wavefunctions to calculate the time evolution of our molecule?

Fifth Postulate: The time evolution of the wavefunction is described by the *time-dependent Schrodinger equation*:

$$i\hbar\, d\Psi(\boldsymbol{q}, t)/dt = \mathcal{H}\, \Psi(\boldsymbol{q}, t) \qquad \text{(II.1.36)}$$

$\mathcal{H}$ is the *Hamiltonian* operator for the system and is associated with the total energy. The eigenvalues of $\mathcal{H}$ are the possible energies of the system. $\mathcal{H}$ contains contributions from kinetic energy and potential energy terms.

$$\mathcal{H} = T(\boldsymbol{q}) + V(\boldsymbol{q}, t) \qquad \text{(II.1.37)}$$

Classically, $T = \Sigma_j\, m_j v_j^2/2m_j \;=\; \Sigma_j\, p_j^2/2m_j$ where $p_j^2 = p_{xj}^2 + p_{yj}^2 + p_{zj}^2$ is the squared momentum of particle j and m_j and v_j are the mass and velocity of particle j.

Using Eq. II.1.7:

$$\mathcal{H}\; \Psi(\boldsymbol{q}, t) = \Sigma_j\, (2m_j)^{-1} p_j^2\, \Psi(\boldsymbol{q}, t) \;+\; V(\boldsymbol{q}, t)\Psi(\boldsymbol{q}, t)$$

$$= -\hbar^2 \Sigma_j\, (2m_j)^{-1}\, \nabla_j^2\, \Psi(\boldsymbol{q}, t) \;+\; V(\boldsymbol{q}, t)\Psi(\boldsymbol{q}, t)$$

$$\nabla_j^2 = d^2/dx_j^2 + d^2/dy_j^2 + d^2/dz_j^2 \qquad \text{(II.1.38)}$$

The quantum mechanical $V(\boldsymbol{q}, t)$ are typically the same as the classical potential energy terms.

For the radial atom:

$$T = L_z^2/2mr^2 = L_z^2/2I \;= (-\hbar^2/2I\,)\; d^2/d\phi^2$$

$$V = (1/4\pi\varepsilon_0) \times (-e^2/r) \qquad \text{(II.1.39)}$$

For the radial atom, V is a constant because r is a constant. $I = 2mr^2$ corresponds to the “moment of inertia”.

Consider the case of a *time-independent* potential $V(\boldsymbol{q})$ for which $\mathcal{H}$ is also time-independent. Important examples of a time-independent potential include the electrostatic potential among nuclei and electrons and vibrational potentials among nuclei. The possible energies of the molecule are found by solving the *time-independent Schrodinger Equation*:

$$\mathcal{H}(\boldsymbol{q})\; |\varphi_k(\boldsymbol{q})\rangle = E_k\; |\varphi_k(\boldsymbol{q})\rangle \qquad \text{(II.1.40)}$$

In absorption or emission spectroscopy, we are observing energy differences between the energy eigenvalues of the system. Because the energy eigenvalues are typically quantized (discrete) we only observe absorption or emission at discrete frequencies. The experimental spectrum is compared to the results of solving the Schrodinger Equation for some model of the molecule. An important requirement for a model is good agreement between some of the model energy eigenvalue differences and the observed frequencies.

In many cases, the model is parameterized and the model parameters are determined by fitting to the experimental frequencies. Examples of fitting parameters include internuclear distances and angles and vibrational force constants.

Neglecting V, the time-independent Schrodinger Equation for the radial atom:

$$(L_z^2/2I)\,|\varphi_k(\phi)\rangle = (-\hbar^2/2I)\, d^2/d\phi^2\, |\varphi_k(\phi)\rangle = E_k\,|\varphi_k(\phi)\rangle$$

$$|\varphi_k(\phi)\rangle = |\,(2\pi)^{-1/2}\, e^{ik\phi}\rangle$$

$$E_k = (-k^2\hbar^2/2I) \qquad \text{(II.1.41)}$$

For the radial atom, there are the same eigenfunctions for the $\mathcal{H}$ and the L_z operators. The same energy will be observed for k values of equal magnitude and opposite sign (e.g. 1 and –1). These two values correspond in classical mechanics to the electron moving with the same speed but in opposite directions around the ring. In classical mechanics, these two types of motion would also have the same energy.

The predicted spectrum of the radial atom will depend in part on *selection rules* which provide information about the possible final k values given an initial k value.

Assume the selection rule is $\Delta k = \pm 1$. Some absorption transitions:

$$\begin{array}{ll} k = 1 \leftarrow 0 \ \text{ or } \ k = -1 \leftarrow 0 & \Delta E/hc = \hbar/4\pi Ic \\ k = 2 \leftarrow 1 \ \text{ or } \ k = -2 \leftarrow -1 & \Delta E/hc = 3\hbar/4\pi Ic \\ k = 3 \leftarrow 2 \ \text{ or } \ k = -3 \leftarrow -2 & \Delta E/hc = 5\hbar/4\pi Ic \end{array} \qquad \text{(II.1.42)}$$

With the assumption $r = a_0$, $\Delta E/hc = 1.098 \times 10^5\ \text{cm}^{-1} \equiv 1$ Rydberg for the $k = 1 \leftarrow 0$ or $k = -1 \leftarrow 0$ transitions.

Think about how well the radial atom model fits with the experimental H atom spectrum. What are some possible reasons for disagreement between the model and experiment?

We now return to the general treatment of a time-independent potential. Although $\mathcal{H}$ is time-independent, the wavefunction can still be time-dependent as governed by the time-dependent Schrodinger Equation II.1.36.

Energy is an observable and its $|\varphi_j\rangle$ eigenfunctions form a complete set for the system:

$$|\Psi(\boldsymbol{q}, t)\rangle = \Sigma_j\, c_j(t)\, |\varphi_j(\boldsymbol{q})\rangle \qquad \text{(II.1.43)}$$

Because $\mathcal{H}$ is time-independent, its eigenfunctions are time-independent and the c_j contain all of the time dependence.

Eq. II.1.44 is incorporated into the time-dependent Schrodinger equation:

$$i\hbar\, d/dt\, \Sigma_j\, c_j(t)\, |\varphi_j(\boldsymbol{q})\rangle = H(\boldsymbol{q})\, \Sigma_j\, c_j(t)\, |\varphi_j(\boldsymbol{q})\rangle$$

$$i\hbar\, \Sigma_j\, dc_j/dt\, |\varphi_j\rangle = \Sigma_j\, c_j\, E_j\, |\varphi_j\rangle \qquad \text{(II.1.44)}$$

To solve for a particular $c_k(t)$, project $\langle\varphi_k|$ onto both sides of Eq. II.1.44:

$$i\hbar\, \langle\varphi_k|\, \Sigma_j\, dc_j/dt\, |\varphi_j\rangle = \langle\varphi_k|\, \Sigma_j\, c_j\, E_j\, |\varphi_j\rangle$$

$$i\hbar\, \Sigma_j\, dc_j/dt\, \delta_{jk} = \Sigma_j\, c_j\, E_j\, \delta_{jk}$$

$$dc_k/dt = (-iE_k/\hbar)\, c_k$$

$$c_k(t) = c_k(0)\, e^{-iE_k t/\hbar} = c_k(0)\, \mathrm{e}^{-i\omega_k t} = \mathrm{c}_k(0)\, \{\cos(\omega_k t) - i \sin(\omega_k t)\} \qquad \text{(II.1.45)}$$

For a time-independent potential, the coefficient associated with each energy eigenfunction oscillates with a characteristic angular frequency $\omega_k = E_k/\hbar$.

Consider an initial radial atom wavefunction:

$$|\Psi(0)\rangle = (1/4\pi)^{1/2}\, |e^{i\phi}\rangle \ + \ (1/4\pi)^{1/2}\, |e^{2i\phi}\rangle \qquad \text{(II.1.46)}$$

This is a linear combination of two energy eigenfunctions with energy eigenvalues $\hbar^2/2mr^2$ and $2\hbar^2/mr^2$. If $\beta = \hbar/2mr^2$, the wavefunction at time τ:

$$|\Psi(\tau)\rangle = (1/4\pi)^{1/2}\, e^{-\beta\tau}|e^{i\phi}\rangle \ + \ (1/4\pi)^{1/2}\, \mathrm{e}^{-4\beta\tau}|\mathrm{e}^{2i\phi}\rangle \qquad \text{(II.1.47)}$$

If $c_k(0) = 0$ except for $k = n$:

$$|\Psi(\boldsymbol{q}, t)\rangle = c_n(0)\, \mathrm{e}^{-i\omega_n t}\, |\varphi_n(\boldsymbol{q})\rangle \qquad \text{(II.1.48)}$$

with $|c_n(0)|^2 = 1$ as the normalization condition. The system is in a *stationary* (time-independent) state. That is, the average value of any observable A (associated with a time-independent operator) is time-independent. Using Eq. II.1.34:

$$\langle A\rangle = \langle c_n(0)\, \mathrm{e}^{-i\omega_n t}\, \varphi_n\, |\, A\, |\, c_n(0)\, \mathrm{e}^{-i\omega_n t}\, \varphi_n\rangle = |c_n(0)|^2\, \langle\varphi_n|\, A\, |\varphi_n\rangle = \langle\varphi_n|\, A\, |\varphi_n\rangle \qquad \text{(II.1.49)}$$

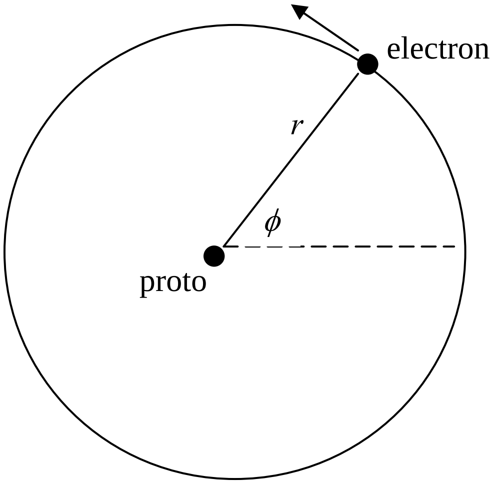
Because of the Schrodinger Equation, the energy eigenstates have a special status.

QUANTUM MECHANICAL METHODS

I. Postulates

We set out to give some description of quantum mechanics which is useful for spectroscopy.

1. The Postulates of Quantum Mechanics



A simple example will be used to illustrate the postulates of quantum mechanics. For the *radial atom*, an electron of mass m is constrained to move in an orbital of fixed radius r in the xy plane about the proton. The radial constraint makes the system different from that of the Bohr atom.

First Postulate: The state of an N-particle system is defined by a wavefunction $\Psi(\boldsymbol{q}, t)$. A wavefunction is single-valued and continuous. The coordinates for the N particles are $\boldsymbol{q} = \boldsymbol{q}_1,.., \boldsymbol{q}_N$ and t refers to time.

$$\boldsymbol{q}_j = x_j\,\mathbf{x} + y_j\,\mathbf{y} + z_j\,\mathbf{z} \equiv (x_j, y_j, z_j) \qquad \text{(II.1.1)}$$

For example, for the radial atom, $\boldsymbol{q}$ could be $(r, 0, 0)$ and would correspond to $\phi = 0$.

A set of wavefunctions for the radial atom:

$$\Psi(\phi, t) = (2\pi)^{-1/2}\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2m}\} \qquad \text{(II.1.2)}$$

The “k” can be any integer and $i = (-1)^{1/2}$. The first exponential describes the spatial dependence of the wavefunction and the second exponential describes the time dependence of the wavefunction. The k is integral so that $\Psi(\phi, t) = \Psi(\phi + 2\pi, t)$. The azimuthal positions ϕ and $\phi + 2\pi$ are experimentally indistinguishable and integral k is necessary to have a single-valued Ψ.

The k is an example of a *quantum number*. The wavefunction associated with each value of k would correspond to a different state of the atom with distinct properties (e.g. energy or angular momentum).

For some comparison, consider a classical description of the electron position:

$$\phi(t) = \omega t \tag{II.1.3}$$

For this classical description, the electron orbits around the proton with uniform angular frequency ω.

All of the properties of the atom or molecule (e.g. energy, angular momentum, dipole moment) can be obtained from the wavefunction.

The quantity $\Psi(\boldsymbol{q}_m, \tau)^* \times \Psi(\boldsymbol{q}_m, \tau) = |\Psi(\boldsymbol{q}_m, \tau)|^2 = \mathcal{P}(\boldsymbol{q}_m, \tau)$ describes the relative probability for finding the system with the specific coordinates $\boldsymbol{q}_m$ at time τ.

The * refers to the complex conjugate. Consider a complex number $a + ib$. The product $(a + ib) \times (a + ib)^* = (a + ib) \times (a - ib) = a^2 + b^2$ which is a real number (good for a probability!).

For the radial atom:

$$\mathcal{P}(\phi_0, \tau) = \Psi(\phi_0, \tau)^* \times \Psi(\phi_0, \tau) = (2\pi)^{-½} \{e^{-ik\phi_0}\}\{e^{ik^2\hbar\tau/2m}\} \times (2\pi)^{-½} \{e^{ik\phi_0}\}\{e^{-ik^2\hbar\tau/2m}\}$$

$$= (2\pi)^{-1} \tag{II.1.4}$$

For these radial atom wavefunctions, there is no dependence of electron density on ϕ or on time.

Note that we often normalize the probability integrated over all coordinates:

$$\int \Psi(\boldsymbol{q}, t)^* \, \Psi(\boldsymbol{q}, t) \, d\boldsymbol{q} = 1 \tag{II.1.5}$$

This normalization is reasonable because it infers that at a given time, the particle has to be somewhere in space. The wavefunctions of Eq. II.1.2 are normalized.

Second Postulate: Every observable (measurable) property of the system is described by a corresponding *Hermitian operator A*.

Examples of these operators:

Position of a one particle system:	x	for position along the **x** direction	
	y	for position along the **y** direction	(II.1.6)
	z	for position along the **z** direction	

Momentum in a one particle system:	$(-i\hbar)d/dx$	for momentum along the **x** direction	
	$(-i\hbar)d/dy$	for momentum along the **y** direction	(II.1.7)
	$(-i\hbar)d/dz$	for momentum along the **z** direction	

In classical mechanics, position would also be described by x, y, and z while momentum would be described by mv_x, mv_y, and mv_z.

Operators act on wavefunctions to yield new wavefunctions. So, a general operator expression for operator $A(\boldsymbol{q}, t)$ and wavefunctions $\Psi(\boldsymbol{q}, t)$ and $\Phi(\boldsymbol{q}, t)$:

$$A(\boldsymbol{q}, t)\,\Psi(\boldsymbol{q}, t) = \Phi(\boldsymbol{q}, t) \tag{II.1.8}$$

The radial atom electron has angular momentum L_z along the **z** direction and the associated operator:

$$L_z \equiv (-i\hbar)\, d/d\phi \tag{II.1.9}$$

$$L_z\Psi(\phi, t) = \{(-i\hbar)\, d/d\phi\}\, (2\pi)^{-1/2}\, \{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\} = (k\hbar)(2\pi)^{-1/2}\, \{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\} \tag{II.1.10}$$

For this case, the new wavefunction is a constant ($k\hbar$) times the old wavefunction. Note that classically, $L_z = mvr$ for the radial atom.

What is a Hermitian operator A?

Two equivalent ways to express this property:

$$\int \Psi^*(\boldsymbol{q}, t)\, A\, \Phi(\boldsymbol{q}, t)\, d\boldsymbol{q} = \int \{\Phi^*(\boldsymbol{q}, t)\, A\, \Psi(\boldsymbol{q}, t)\, d\boldsymbol{q}\,\}^* \tag{II.1.11}$$

Take the complex conjugate of this equation and rearrange the terms.

$$\int \{A\, \Phi(\boldsymbol{q}, t)\}^*\, \Psi(\boldsymbol{q}, t)\, d\boldsymbol{q} = \int \Phi^*(\boldsymbol{q}, t)\, A\, \Psi(\boldsymbol{q}, t)\, d\boldsymbol{q} \tag{II.1.12}$$

This is a good time to introduce the *bra/ket* vector notation. This notation contains no new physics but allows us to concisely write quantum mechanical expressions. The integral equations above are expressed in a shorthand way as:

$$\langle\Psi|A|\Phi\rangle = \langle\Phi|A|\Psi\rangle^* \tag{II.1.13}$$

$$\langle(A\Phi)|\Psi\rangle = \langle\Phi|A\Psi\rangle \tag{II.1.14}$$

The left-hand “bra” vector such as $\langle\Psi|$ contains implicitly a complex conjugate. The right-hand “ket” vector is not a complex conjugate. The intermediate operator position is also not a complex conjugate and allows greater clarity. For example:

$$\langle\Psi|A|\Phi\rangle = \langle\Psi|A\Phi\rangle \tag{II.1.15}$$

$$\langle\Psi|A|\Phi\rangle = \langle\Psi A^*|\Phi\rangle \tag{II.1.16}$$

When we have an expression with a bra followed by a ket as above, the expression contains an implicit integration over all of the spatial variables $\boldsymbol{q}$ of the wavefunctions. Otherwise, there is no implicit integration. For an expression such as $A|\Psi\rangle$, there is no integration.

In all quantum mechanical expressions, the expression is calculated from left to right. The order can be important so one cannot indiscriminately change the order of operators and wavefunctions. For example:

$$\langle\Psi|\Phi\rangle \neq |\Phi\rangle\langle\Psi| \tag{II.1.17}$$

The expression on the left is an integral (a number) while the expression on the right is an operator. Also, in general for an operator A and ket $|\Psi\rangle$:

$$A|\Psi\rangle \neq |\Psi\rangle A \tag{II.1.18}$$

A radial atom example:

$$L_z|\Psi\rangle = \{(-i\hbar)\, d/d\phi\}|(2\pi)^{-1/2}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\}\rangle = |(k\hbar)(2\pi)^{-1/2}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2mr^2}\}\rangle$$

$$|\Psi\rangle L_z = |(2\pi)^{-1/2}\,\{e^{ik\phi}\}\{e^{-ik^2\hbar t/2m}\}\rangle\{(-i\hbar)\, d/d\phi\} \tag{II.1.19}$$

In general for operators A and B:

$$AB|\Psi\rangle \neq BA|\Psi\rangle \tag{II.1.20}$$

The difference operator $AB - BA$ is written shorthand as $[A, B]$ and is called the *commutator*. If $[A, B] = 0$, the operators A and B are said to commute. If $[A, B] \neq 0$, then the operators A and B do not commute.

$$[\phi, L_z]|\Psi\rangle = \phi\,(-i\hbar)\,(d/d\phi)\,|\Psi\rangle - (-i\hbar)\,(d/d\phi)\phi\,|\Psi\rangle = (i\hbar)\{1 + \phi\,(d/d\phi) - \phi\,(d/d\phi)\}|\Psi\rangle =$$

$$(i\hbar)|\Psi\rangle \Rightarrow [\phi, L_z] = i\hbar \tag{II.1.21}$$

Consider some constant c in a bra:

$$\langle c\Psi| = \langle\Psi|c^* \tag{II.1.22}$$

I can take constant out of the bra but have to remember the implicit complex conjugate. Finally, for two wavefunctions $|\Phi\rangle$ and $|\Psi\rangle$:

$$\langle\Phi|\Psi\rangle = \langle\Psi|\Phi\rangle^* \tag{II.1.23}$$

Because there is simple multiplication between the two wavefunctions, I can switch their order.

I also introduce *eigenvalue/eigenfunction equations*:

$$A|\psi\rangle = \lambda\,|\psi\rangle \qquad \text{(II.1.24)}$$

In this equation, $|\psi\rangle$ is an eigenfunction of A and has eigenvalue λ which is a number. For the radial atom, an eigenvalue/eigenfunction equation for L_z:

$$L_z|\psi\rangle = \{(-i\hbar)\,d/d\phi\}|(2\pi)^{-1}e^{ik\phi}\rangle = (k\hbar)|(2\pi)^{-1}e^{ik\phi}\rangle \qquad \text{(II.1.25)}$$

For this example, $\lambda = k\hbar$ and $|\psi\rangle = |(2\pi)^{-1}e^{ik\phi}\rangle$ is the non-time-dependent part of Ψ in Eq. II.1.2.

Eigenvalue equations are at the core of quantum mechanics and spectroscopy. The operator for each physical observable has a set of eigenfunctions and eigenvalues associated with it and:

Third Postulate: The only possible result of the measurement of a physical observable is one of its eigenvalues of its associated operator.

Because the eigenvalues are what we measure, much effort goes into their calculation and into the calculation of their associated eigenfunctions. If our physical model of the molecule is reasonable, then the observed and calculated eigenvalues will be similar. Typical spectroscopically measurable observables are energy and dipole moments. In crystallography, the observable is electron density.

In the quantum mechanical radial atom, the only observable values of L_z are $k\hbar$, again where k is an integer. This is similar to the $n_e\hbar$ quantization condition for the semiclassical Bohr atom but there are some important differences. For example, $k = 0$ is allowed in the radial atom while $n_e = 0$ is not allowed in the Bohr atom. In addition, the radial atom has k values which are independent of r while the value of r in the Bohr atom depends on n_e (cf. Eq. I.2.8).

The eigenvalues associated with *Hermitian* operators are always *real*. You can see why physical observables would be associated with Hermitian operators – we can only measure real quantities.

Also, the eigenfunctions of a Hermitian operator associated with *different* eigenvalues are *orthogonal*, that is $\langle\psi_{\lambda_j}|\psi_{\lambda_k}\rangle = 0$ if $\lambda_j \neq \lambda_k$.

If our system is in a state which corresponds to the eigenfunction of the operator, then measurement of the observable associated with this operator would be the eigenvalue.

For example, if the radial atom $|\psi\rangle = |(2\pi)^{-1/2}\,e^{2i\phi}\rangle$, then the observed value of L_z will be $2\hbar$.

Suppose the system is not in an eigenfunction of its observable operator A. We will still measure only eigenvalues of the observable operator. But which eigenvalues and with what probabilities?

We express the wavefunction $|\psi\rangle$ as a linear combination of the *orthonormal* eigenfunctions $|\varphi_1\rangle$, $|\varphi_2\rangle$,… of A:

$$|\psi\rangle = \Sigma_j\, c_j\, |\varphi_j\rangle \qquad \text{(II.1.26)}$$

Don't confuse the $|\varphi_j\rangle$ which is a function with the angular variable ϕ in our radial atom example.

Orthonormality (orthogonality + normality):

$$\langle\varphi_j|\varphi_k\rangle = \delta_{jk} \quad (0 \text{ if } j \neq k,\ 1 \text{ if } j = k) \qquad \text{(II.1.27)}$$

The δ_{jk} is known as the *delta function*. Note that our radial atom L_z eigenfunctions are orthonormal:

$$\langle\varphi_j|\varphi_k\rangle = \langle(2\pi)^{-\frac{1}{2}} e^{ij\phi}|(2\pi)^{-\frac{1}{2}} e^{ik\phi}\rangle = \int_0^{2\pi} (2\pi)^{-\frac{1}{2}}\{e^{-ij\phi}\}(2\pi)^{-\frac{1}{2}}\{e^{ik\phi}\}d\phi$$

$$= \int_0^{2\pi} (2\pi)^{-1} e^{i(k-j)\phi}\, d\phi = \{1/2\pi i(k-j)\}\, e^{i(k-j)\phi}\Big|_0^{2\pi} \qquad \text{(II.1.28)}$$

For $j \neq k$, the definite integral yields $0/2\pi i(k-j) = 0$, while for $j = k$, the integral yields 0/0 which can be shown to be 1 in this case.

Any particular c_k can be found by *projecting* $\langle\varphi_k|$ onto both sides of Eq. II.1.26. This means multiplying by φ_k^* and integrating over the coordinates $\boldsymbol{q}$:

$$\langle\varphi_k|\psi\rangle = \langle\varphi_k|\, \Sigma_j\, c_j\, |\varphi_j\rangle = \Sigma_j\, c_j\, \langle\varphi_k|\varphi_j\rangle = \Sigma_j\, c_j\, \delta_{jk} = c_k \qquad \text{(II.1.29)}$$

We are now ready to answer the eigenvalue probability question.

Fourth Postulate: The probability of observing the eigenvalue λ_k is $\mathcal{P} = c_k{}^*c_k/\Sigma_j|c_j|^2$
$= |c_k|^2/\Sigma_j|c_j|^2$.

If $|\psi\rangle$ is normalized, then $\mathcal{P} = |c_k|^2$.

If the wavefunction of a molecule is not an eigenfunction of the observable property, it is possible to observe many different eigenvalues. However, for any single molecule, only one value will be observed.

We typically make measurements on many molecules (e.g. 10^{23} ~ Avogadro's number) so that our measurements give statistical probabilites for the observed eigenvalues. These statistical probabilities are expressed by the fourth postulate.

Consider a normalized radial atom wavefunction:

$$|\psi\rangle = (3i/5)|e^{i\phi}\rangle + (4/5)|e^{-i\phi}\rangle \qquad \text{(II.1.30)}$$

The probability of observing the angular momentum eigenvalues:

$$\mathcal{P}(\hbar) = (-3i/5)(3i/5) = 9/25$$

$$\mathcal{P}(-\hbar) = (4/5)(4/5) = 16/25 \qquad \text{(II.1.31)}$$

For this approach, some linear combination of wavefunctions $|\varphi_j\rangle$ must completely describe any state of the molecule. In other words, the $|\varphi_j\rangle$ eigenfunctions must form a *complete* set which *span* the entire state space. *The eigenfunctions of an observable property always form a complete set.*

Completeness can be described mathematically with the *closure relation*:

$$\Sigma_j\, |\varphi_j\rangle\langle\varphi_j| = 1 \qquad \text{(II.1.32)}$$

The sum of *projector operators* $\Sigma_j\, |\varphi_j\rangle\langle\varphi_j|$ has no effect on any wavefunction of the system.

Let's calculate the effect of the projector on $|\psi\rangle$:

$$\Sigma_k\, |\varphi_k\rangle\langle\varphi_k|\psi\rangle \;=\; \Sigma_k\, |\varphi_k\rangle\langle\varphi_{jk}|\, \Sigma_j\, c_j|\varphi_j\rangle \;=\; \Sigma_k \Sigma_j\, c_j|\varphi_k\rangle\langle\varphi_k|\varphi_j\rangle \;=\; \Sigma_k \Sigma_j\, c_j|\varphi_k\rangle\, \delta_{jk}$$

$$=\; \Sigma_j\, c_j|\varphi_j\rangle = |\psi\rangle \qquad \text{(No Effect!)} \qquad \text{(II.1.33)}$$

The closure relation is used in many derivations and can be used to derive an important result about the average values of observable quantities.

The average value of the observable A for a wavefunction $|\psi\rangle$ is the probability weighted sum of the observable eigenvalues λ_j (cf. Postulate 4). Consider a normalized $|\psi\rangle$:

$$\langle A\rangle = \;\Sigma_j\, |c_j|^2\, \lambda_j \;=\; \Sigma_j\, c_j{}^*c_j\, \lambda_j \;=\; \Sigma_j\, \langle\varphi_j|\psi\rangle^*\, \lambda_j\, \langle\varphi_j|\psi\rangle \;=\; \Sigma_j\, \langle\psi|\varphi_j\rangle\, \lambda_j\, \langle\varphi_j|\psi\rangle$$

$$=\; \Sigma_j\, \langle\psi|A|\varphi_j\rangle\, \langle\varphi_j|\psi\rangle \;=\; \langle\psi|A\, \Sigma_j\, |\varphi_j\rangle\langle\varphi_j|\, \psi\rangle \;=\; \langle\psi|A|\psi\rangle \qquad \text{(II.1.34)}$$

The importance of the wavefunction for predicting system properties is clearly demonstrated.

Consider $\langle L_z\rangle$ for the radial atom wavefunction of Eq. II.1.30:

$$\langle L_z\rangle = \langle\psi|(-i\hbar)\, d/d\phi\, |\psi\rangle = \{(-3i/5)\langle e^{i\phi}| + (4/5)\langle e^{-i\phi}|\}\, (-i\hbar)d/d\phi\, \{(3i/5)|e^{i\phi}\rangle + (4/5)|e^{-i\phi}\rangle\}$$

$$= (\hbar)\, \{(-3i/5)\langle e^{i\phi}| + (4/5)\langle e^{-i\phi}|\}\{(3i/5)|e^{i\phi}\rangle - (4/5)|e^{-i\phi}\rangle\} = \hbar\, (9/25 - 16/25) = \;(-7/25)\, \hbar$$

$$\text{(II.1.35)}$$

Although $\langle L_z\rangle = (-7/25)\, \hbar$, only $L_z = \hbar$ and $-\hbar$ will be observed.

How can we use wavefunctions to calculate the time evolution of our molecule?

Fifth Postulate: The time evolution of the wavefunction is described by the *time-dependent Schrodinger equation*:

$$i\hbar\, d\Psi(\boldsymbol{q}, t)/dt = \mathcal{H}\,\Psi(\boldsymbol{q}, t) \qquad \text{(II.1.36)}$$

$\mathcal{H}$ is the *Hamiltonian* operator for the system and is associated with the total energy. The eigenvalues of $\mathcal{H}$ are the possible energies of the system. $\mathcal{H}$ contains contributions from kinetic energy and potential energy terms.

$$\mathcal{H} = T(\boldsymbol{q}) + V(\boldsymbol{q}, t) \qquad \text{(II.1.37)}$$

Classically, $T = \Sigma_j\, m_j v_j^2/2m_j \;=\; \Sigma_j\, p_j^2/2m_j$ where $p_j^2 = p_{xj}^2 + p_{yj}^2 + p_{zj}^2$ is the squared momentum of particle j and m_j and v_j are the mass and velocity of particle j.

Using Eq. II.1.7:

$$\mathcal{H}\;\Psi(\boldsymbol{q}, t) = \Sigma_j\,(2m_j)^{-1}\, p_j^2\,\Psi(\boldsymbol{q}, t) \;+\; V(\boldsymbol{q}, t)\Psi(\boldsymbol{q}, t)$$

$$= -\hbar^2\Sigma_j\,(2m_j)^{-1}\,\nabla_j^2\,\Psi(\boldsymbol{q}, t) \;+\; V(\boldsymbol{q}, t)\Psi(\boldsymbol{q}, t)$$

$$\nabla_j^2 = d^2/dx_j^2 + d^2/dy_j^2 + d^2/dz_j^2 \qquad \text{(II.1.38)}$$

The quantum mechanical $V(\boldsymbol{q}, t)$ are typically the same as the classical potential energy terms.

For the radial atom:

$$T = L_z^2/2mr^2 = L_z^2/2I = (-\hbar^2/2I\,)\; d^2/d\phi^2$$

$$V = (1/4\pi\varepsilon_0) \times (-e^2/r) \qquad \text{(II.1.39)}$$

For the radial atom, V is a constant because r is a constant. $I = 2mr^2$ corresponds to the “moment of inertia”.

Consider the case of a *time-independent* potential $V(\boldsymbol{q})$ for which $\mathcal{H}$ is also time-independent. Important examples of a time-independent potential include the electrostatic potential among nuclei and electrons and vibrational potentials among nuclei. The possible energies of the molecule are found by solving the *time-independent Schrodinger Equation*:

$$\mathcal{H}(\boldsymbol{q})\,|\varphi_k(\boldsymbol{q})\rangle = E_k\,|\varphi_k(\boldsymbol{q})\rangle \qquad \text{(II.1.40)}$$

In absorption or emission spectroscopy, we are observing energy differences between the energy eigenvalues of the system. Because the energy eigenvalues are typically quantized (discrete) we only observe absorption or emission at discrete frequencies. The experimental spectrum is compared to the results of solving the Schrodinger Equation for some model of the molecule. An important requirement for a model is good agreement between some of the model energy eigenvalue differences and the observed frequencies.

In many cases, the model is parameterized and the model parameters are determined by fitting to the experimental frequencies. Examples of fitting parameters include internuclear distances and angles and vibrational force constants.

Neglecting V, the time-independent Schrodinger Equation for the radial atom:

$$(L_z^2/2I)\,|\varphi_k(\phi)\rangle = (-\hbar^2/2I)\,d^2/d\phi^2\,|\varphi_k(\phi)\rangle = E_k\,|\varphi_k(\phi)\rangle$$

$$|\varphi_k(\phi)\rangle = |\,(2\pi)^{-1/2}\,e^{ik\phi}\rangle$$

$$E_k = (-k^2\hbar^2/2I) \qquad \text{(II.1.41)}$$

For the radial atom, there are the same eigenfunctions for the $\mathcal{H}$ and the L_z operators. The same energy will be observed for k values of equal magnitude and opposite sign (e.g. 1 and –1). These two values correspond in classical mechanics to the electron moving with the same speed but in opposite directions around the ring. In classical mechanics, these two types of motion would also have the same energy.

The predicted spectrum of the radial atom will depend in part on *selection rules* which provide information about the possible final k values given an initial k value.

Assume the selection rule is $\Delta k = \pm 1$. Some absorption transitions:

$$\begin{array}{lll} k = 1 \leftarrow 0 \text{ or } k = -1 \leftarrow 0 & \Delta E/hc = \hbar/4\pi Ic & \\ k = 2 \leftarrow 1 \text{ or } k = -2 \leftarrow -1 & \Delta E/hc = 3\hbar/4\pi Ic & \\ k = 3 \leftarrow 2 \text{ or } k = -3 \leftarrow -2 & \Delta E/hc = 5\hbar/4\pi Ic & \text{(II.1.42)} \end{array}$$

With the assumption $r = a_0$, $\Delta E/hc = 1.098 \times 10^5\ \text{cm}^{-1} \equiv 1$ Rydberg for the $k = 1 \leftarrow 0$ or $k = -1 \leftarrow 0$ transitions.

Think about how well the radial atom model fits with the experimental H atom spectrum. What are some possible reasons for disagreement between the model and experiment?

We now return to the general treatment of a time-independent potential. Although $\mathcal{H}$ is time-independent, the wavefunction can still be time-dependent as governed by the time-dependent Schrodinger Equation II.1.36.

Energy is an observable and its $|\varphi_j\rangle$ eigenfunctions form a complete set for the system:

$$|\Psi(\boldsymbol{q}, t)\rangle = \Sigma_j\, c_j(t)\,|\varphi_j(\boldsymbol{q})\rangle \qquad \text{(II.1.43)}$$

Because $\mathcal{H}$ is time-independent, its eigenfunctions are time-independent and the c_j contain all of the time dependence.

Eq. II.1.44 is incorporated into the time-dependent Schrodinger equation:

$$i\hbar\, d/dt\, \Sigma_j\, c_j(t)\, |\varphi_j(\boldsymbol{q})\rangle = H(\boldsymbol{q})\, \Sigma_j\, c_j(t)\, |\varphi_j(\boldsymbol{q})\rangle$$

$$i\hbar\, \Sigma_j\, dc_j/dt\, |\varphi_j\rangle = \Sigma_j\, c_j\, E_j\, |\varphi_j\rangle \qquad \text{(II.1.44)}$$

To solve for a particular $c_k(t)$, project $\langle\varphi_k|$ onto both sides of Eq. II.1.44:

$$i\hbar\, \langle\varphi_k|\, \Sigma_j\, dc_j/dt\, |\varphi_j\rangle = \langle\varphi_k|\, \Sigma_j\, c_j\, E_j\, |\varphi_j\rangle$$

$$i\hbar\, \Sigma_j\, dc_j/dt\, \delta_{jk} = \Sigma_j\, c_j\, E_j\, \delta_{jk}$$

$$dc_k/dt = (-iE_k/\hbar)\, c_k$$

$$c_k(t) = c_k(0)\, e^{-iE_kt/\hbar} = c_k(0)\, \mathrm{e}^{-i\omega_kt} = \mathrm{c}_k(0)\, \{\cos(\omega_kt) - i\sin(\omega_kt)\,\} \qquad \text{(II.1.45)}$$

For a time-independent potential, the coefficient associated with each energy eigenfunction oscillates with a characteristic angular frequency $\omega_k = E_k/\hbar$.

Consider an initial radial atom wavefunction:

$$|\Psi(0)\rangle = (1/4\pi)^{1/2}\, |e^{i\phi}\rangle\; +\; (1/4\pi)^{1/2}\, |e^{2i\phi}\rangle \qquad \text{(II.1.46)}$$

This is a linear combination of two energy eigenfunctions with energy eigenvalues $\hbar^2/2mr^2$ and $2\hbar^2/mr^2$. If $\beta = \hbar/2mr^2$, the wavefunction at time τ:

$$|\Psi(\tau)\rangle = (1/4\pi)^{1/2}\, e^{-\beta\tau}|e^{i\phi}\rangle\; +\; (1/4\pi)^{1/2}\, \mathrm{e}^{-4\beta\tau}|\mathrm{e}^{2i\phi}\rangle \qquad \text{(II.1.47)}$$

If $c_k(0) = 0$ except for $k = n$:

$$|\Psi(\boldsymbol{q}, t)\rangle \;=\; c_n(0)\, \mathrm{e}^{-i\omega_nt}\, |\varphi_n(\boldsymbol{q})\rangle \qquad \text{(II.1.48)}$$

with $|\, c_n(0)|^2 = 1$ as the normalization condition. The system is in a *stationary* (time-independent) state. That is, the average value of any observable A (associated with a time-independent operator) is time-independent. Using Eq. II.1.34:

$$\langle A\rangle = \langle c_n(0)\, \mathrm{e}^{-i\omega_nt}\, \varphi_n\, |\, A\, |\, c_n(0)\, \mathrm{e}^{-i\omega_nt}\, \varphi_n\rangle = |\, c_n(0)|^2\, \langle\varphi_n|\, A\, |\varphi_n\rangle \;=\; \langle\varphi_n|\, A\, |\varphi_n\rangle \qquad \text{(II.1.49)}$$

Because of the Schrodinger Equation, the energy eigenstates have a special status.

IV. Electronic Spectroscopy, Angular Momentum, and Magnetic Resonance

The foundation of electronic spectroscopy is the exact solution of the time-independent Schrodinger equation for the hydrogen atom. This is the only atomic or molecular system for which there is an exact solution.

In section I, the Bohr model of the hydrogen atom yielded correct energies with correlation of energy levels with the z-component of electronic orbital angular momentum. Greater angular momentum correlated with higher energy.

The potential energy contribution to the Hamiltonian is the Coulombic interaction $-(1/4\pi\varepsilon_0)(e^2/r)$. Polar coordinates (r, θ, ϕ) are good for the hydrogen atom Schrodinger equation because the potential is radial:

$$(2mr^2)^{-1}\{-\hbar^2[d/dr(r^2 d\psi/dr)] - \hbar^2[(1/sin\theta)\, d/d\theta\,(sin\theta\, d\psi/d\theta)] - \hbar^2[(1/sin^2\theta)\, d^2\psi/d\phi^2]\}$$

$$- (1/4\pi\varepsilon_0)(e^2/r)\psi = E\psi \qquad \text{(IV.1)}$$

The kinetic energy term in braces is split between the first term which only contains derivatives with respect to r and the second two terms which contain derivatives with respect to θ, ϕ. These second two terms are the squared angular momentum of the electron:

$$(2mr^2)^{-1}\{[(-\hbar^2)d/dr\,(r^2 d\psi/dr)] + L^2\psi\} - (1/4\pi\varepsilon_0)(e^2/r)\psi = E\psi \qquad \text{(IV.2)}$$

$$L^2 = \boldsymbol{L} \,.\, \boldsymbol{L} = (\boldsymbol{r} \times \boldsymbol{p}) \,.\, (\boldsymbol{r} \times \boldsymbol{p}) \qquad \text{(IV.3)}$$

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = (x\,\mathbf{x} + y\,\mathbf{y} + z\,\mathbf{z}) \times -i\hbar\,\{(d/dx)\,\mathbf{x} + (d/dy)\,\mathbf{y} + (d/dz)\,\mathbf{z}\} \qquad \text{(IV.4)}$$

L^2 can be written in spherical polar coordinates using the following equations:

$$x = r\, sin\theta\, cos\phi \qquad \text{(IV.5)}$$

$$y = r\, sin\theta\, sin\phi \qquad \text{(IV.6)}$$

$$z = r\, cos\theta \qquad \text{(IV.7)}$$

In Eq. IV.2, the kinetic energy operator $L^2/2mr^2$ corresponds to the kinetic energy operator for an electron moving on a sphere of radius r. This operator is analogous to the kinetic energy operator of the radial atom Hamiltonian (Eq. II.39). The other kinetic energy operator in Eq. IV.2 corresponds to kinetic energy along the r direction.

Eq. IV.2 is solved by separation of variables:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad \text{(IV.8)}$$

$$(2mr^2)^{-1}\{[(-\hbar^2 Y)d/dr\,(r^2 dR/dr)] + RL^2Y\} - (1/4\pi\varepsilon_0)(e^2/r)RY = E(RY) \qquad \text{(IV.9)}$$

Note that L^2 operates on Y which includes taking derivatives. Multiply Eq. IV.9 by $2mr^2/(RY)$:

$$(-\hbar^2/R)d/dr(r^2 dR/dr) - (1/4\pi\varepsilon_0)(2mre^2) - 2mr^2E + L^2Y/Y = 0 \tag{IV.10}$$

The first three terms depend only on r while the last term depends only on θ and ϕ. Eq. (IV.10) is only possible for all r, θ, ϕ when the sum of the first three terms is equal to a constant and the last term is equal to –1 times that constant. With foresight, the constant is called $-l(l + 1)\hbar^2$ so that an equation can be written for the last term:

$$L^2(Y) = l(l + 1)\hbar^2 Y \tag{IV.11}$$

Consider:

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi) \tag{IV.12}$$

Eq. IV.12 is rewritten using the expression for L^2 from Eq. IV.1:

$$-\hbar^2\{[(1/sin\theta)\, d/d\theta\,(sin\theta\, d(\Theta\Phi)/d\theta)] + [(1/sin^2\theta)\, d^2(\Theta\Phi)/d\phi^2]\} = l(l + 1)\hbar^2(\Theta\Phi) \tag{IV.13}$$

Multiply Eq. IV.13 by $-sin^2\theta/(\Theta\Phi)$:

$$\hbar^2(sin\theta/\Theta)\, d/d\theta\,(sin\theta\, d\Theta/d\theta) + l(l + 1)\,\hbar^2 sin^2\theta + \hbar^2(1/\Phi)\, d^2\Phi/d\phi^2 = 0 \tag{IV.14}$$

The first two terms depend only on θ and the last term depends only on ϕ. In order for the sum to be 0 for all θ, ϕ , the first two terms and last term must be constants with opposite sign. Set the constants as $m^2\hbar^2$ and $-m^2\hbar^2$. For the third term:

$$\hbar^2 d^2\Phi/d\phi^2 = -m^2\hbar^2\,\Phi \tag{IV.15}$$

$$(-i\hbar\, d/d\phi)^2\,\Phi = m^2\hbar^2\,\Phi \tag{IV.16}$$

$$L_z^2\,\Phi = m^2\hbar^2\,\Phi \tag{IV.17}$$

The eigenvalues and eigenfunctions for this equation are taken from Eqs. II.25 and II.41.

$$\Phi_m(\phi) = (2\pi)^{-1/2}\, e^{im\phi}, \qquad m = \text{integer} \tag{IV.18}$$

These are the eigenfunctions of the angular momentum along the z direction. The eigenvalue for the projection of rotational angular momentum on the space-fixed z axis is $m\hbar$. This is the only cartesian projection of angular momentum which we know with certainty.

The Θ eigenfunctions are the *Legendre polynomials* and are functions of $cos\theta$:

$$\Theta_{lm} = P_l^{|m|}(cos\,\theta) \qquad l, m \text{ are integers with } l \geq 0 \tag{IV.19}$$

$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ are known as the *spherical harmonics* and a few representative normalized Y_{lm} are presented:

$$|Y_{00}\rangle = (1/4\pi)^{1/2}$$

$$|Y_{10}\rangle = (3/4\pi)^{1/2}\, cos\,\theta$$

$$|Y_{1\pm1}\rangle = -+(3/8\pi)^{1/2}\, sin\,\theta\, e^{\pm i\phi}$$

$$|Y_{20}\rangle = (5/16\pi)^{1/2}\,(3cos^2\theta - 1) \tag{IV.20}$$

$$|Y_{2\pm1}\rangle = -+(15/8\pi)^{1/2}\, cos\,\theta\, sin\,\theta\, e^{\pm i\phi}$$

$$|Y_{2\pm2}\rangle = (15/32\pi)^{1/2}\, sin^2\theta\, e^{\pm 2i\phi}$$

Note:

$$L^2\,|Y_{lm}\rangle = l(l+1)\hbar^2|Y_{lm}\rangle \tag{IV.21}$$

$$L_z\,|Y_{lm}\rangle = m\hbar|Y_{lm}\rangle \tag{IV.22}$$

$$L_z^2\,|Y_{lm}\rangle = m^2\hbar^2|Y_{lm}\rangle \tag{IV.23}$$

Note that $\langle L_z^2\rangle \leq \langle L^2\rangle$ because the magnitude of angular momentum along one axis cannot be greater than the total magnitude of angular momentum. This physical limitation leads to the restriction $|m| \leq l$. For example, for $l = 2$, m = –2, –1, 0, 1, 2.

Y_{lm} are commonly denoted by letters with l = 0, 1, 2, 3 referred to as *s*, *p*, *d*, and *f* orbitals.

The *parity* or space inversion of Y_{lm} has a $(-1)^l$ dependence. The parity operation is described in cartesian coordinates by the operation $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$ or $\boldsymbol{r} \rightarrow -\boldsymbol{r}$. In polar coordinates, the parity operation is described by $\theta \rightarrow \pi - \theta$, $\phi \rightarrow \phi + \pi$ and:

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l\, Y_{lm}(\pi, \phi) \tag{IV.24}$$

The Y_{lm} with even l have even parity and the Y_{lm} with odd l have odd parity. The even parity Y_{lm} do not change with coordinate inversion while the odd parity Y_{lm} change sign with space inversion.

The parity of the Y_{lm} can be useful in calculating integrals over the angular θ, ϕ coordinates. An integral can only be non-zero if the parity of the total product of the wavefunctions and the operator function is even. For two functions, odd × odd = even, even × even = even, and even × odd = odd.

Consider the dipole selection rules for transition intensities between different RY_{lm} (Eq. III.21):

$$I \propto |\langle RY_{l_2m_2}|\mu_x|RY_{l_1m_1}\rangle|^2\,\epsilon_x{}^2 + |\langle RY_{l_2m_2}|\mu_y|RY_{l_1m_1}\rangle|^2\,\epsilon_y{}^2 + |\langle RY_{l_2m_2}|\mu_z|RY_{l_1m_1}\rangle|^2\,\epsilon_z{}^2 \qquad \text{(IV.25)}$$

$$\langle RY_{l_2m_2}|\mu_x|RY_{l_1m_1}\rangle = -\langle RY_{l_2m_2}|er\sin\theta\cos\phi|RY_{l_1m_1}\rangle = -\langle R|er|R\rangle\langle Y_{l_1m_1}|\sin\theta\cos\phi|Y_{l_1m_1}\rangle$$
(IV.26)

$$\langle RY_{l_2m_2}|\mu_y|RY_{l_1m_1}\rangle = -\langle RY_{l_2m_2}|er\sin\theta\sin\phi|RY_{l_1m_1}\rangle = -\langle R|er|R\rangle\langle Y_{l_2m_2}|\sin\theta\sin\phi|Y_{l_1m_1}\rangle \qquad \text{(IV.27)}$$

$$\langle RY_{l_2m_2}|\mu_z|RY_{l_1m_1}\rangle = -\langle RY_{l_2m_2}|\cos\theta|RY_{l_1m_1}\rangle = -\langle R|er|R\rangle\langle Y_{l_2m_2}|\cos\theta|Y_{l_1m_1}\rangle \qquad \text{(IV.28)}$$

The integrals in Eqs. IV.26-28 are separated into r and θ, ϕ integrals. The dipole moment operator $\boldsymbol{\mu} = -e\boldsymbol{r}$ and its three components μ_x, μ_y, and μ_z have odd parity and one dipole selection rule is that transitions only occur between Y_{lm} with opposite parity. This is shown by Eqs. IV.26-28. Further analysis shows there are only non-zero transition dipole moments for $\Delta l = \pm 1$.

The m selection rule can be derived from considering only the ϕ part of the transition dipole moment integrals. For the μ_x component for a $m_2 \leftarrow m_1$ transition:

$$\int_0^{2\pi} \Phi_{m_2}{}^* \cos\phi\, \Phi_{m_1}\, d\phi = (2\pi)^{-1} \int_0^{2\pi} e^{-im_2\phi} \cos\phi\, e^{im_1\phi}\, d\phi =$$

$$(4\pi)^{-1} \left\{ \int_0^{2\pi} e^{-im_2\phi} e^{i\phi} e^{im_1\phi}\, d\phi + \int_0^{2\pi} e^{-im_2\phi} e^{-i\phi} e^{im_1\phi}\, d\phi \right\} =$$

$$(4\pi)^{-1} \left\{ \int_0^{2\pi} e^{i(m_1 - m_2 + 1)\phi}\, d\phi + \int_0^{2\pi} e^{i(m_1 - m_2 - 1)\phi}\, d\phi \right\} \qquad \text{(IV.29)}$$

Each integral is only non-zero if the argument of the exponential is 0 and results in a $\Delta m = \pm 1$ selection rule. Analysis of the μ_y component also results in a $\Delta m = \pm 1$ selection rule and analysis of the μ_z component results in a $\Delta m = 0$ selection rule. The overall m selection rule is then $\Delta m = 0, \pm 1$.

Magnetic Resonance

Much of the quantum mechanics of angular momentum described for the electron can be directly applied to nuclear and electron spin magnetic resonance. Recall Eqs. I.2.23 and I.2.24 for the spin magnetic moment:

$$\boldsymbol{\mu} = \gamma \boldsymbol{L} = \gamma \hbar \boldsymbol{S} = \gamma \hbar (S_x \mathbf{x} + S_y \mathbf{y} + S_z \mathbf{z}) \quad \text{(IV.30)}$$

$\boldsymbol{S} = \boldsymbol{L}/\hbar$ is the "spin operator" and is unitless. Assuming that Eqs. IV.21 and IV.22 are general for any angular momentum:

$$S^2 |S, m\rangle = L^2/\hbar^2 |S, m\rangle = S(S+1)|S, m\rangle \quad \text{(IV.31)}$$

$$S_z |S, m\rangle = m|S, m\rangle \quad \text{(IV.32)}$$

There is a confusing convention that " S " refers both to the spin operator and to the spin quantum number $S \equiv l$.

Unlike the orbital angular momentum of the electron which can have any integral $l \geq 0$, S has a single integer or half-integer value specific to the electron or particular nuclear isotope. For example, $S = ½$ for e^-, ^{1}H, and ^{13}C, $S = 1$ for ^{2}H and ^{14}N, and $S = 3/2$ for ^{23}Na. The $| m | \leq S$ so that for ^{2}H, $m = -1, 0, 1$.

A time-independent Schrodinger Equation for magnetic resonance in an external magnetic field $\boldsymbol{B}_{ext} = B_0 \mathbf{z}$ (Eq. I.2.22):

$$\mathcal{H} |S, m\rangle = \{-\boldsymbol{\mu} \,.\, \boldsymbol{B}_{ext}\} |S, m\rangle = E_m |S, m\rangle \quad \text{(IV.33)}$$

$$\{-\gamma \hbar (S_x \mathbf{x} + S_y \mathbf{y} + S_z \mathbf{z}) \,.\, B_0 \mathbf{z}\}|S, m\rangle = E_m |S, m\rangle \quad \text{(IV.34)}$$

$$-\gamma \hbar B_0 S_z |S, m\rangle = E_m |S, m\rangle \quad \text{(IV.35)}$$

$$E_m = -\gamma \hbar B_0 m \quad \text{(IV.36)}$$

Determination of selection rules is aided by raising and lowering operators:

$$S_+ = L_+ / \hbar = S_x + i S_y \qquad \text{(raising operator)} \quad \text{(IV.37)}$$

$$S_- = L_- / \hbar = S_x - i S_y \qquad \text{(lowering operator)} \quad \text{(IV.38)}$$

These operators have the properties:

$$S_+ |S, m\rangle = [S(S+1) - m(m+1)]^{1/2} |S, m+1\rangle \quad \text{(IV.39)}$$

$$S_- |S, m\rangle = [S(S+1) - m(m-1)]^{1/2} |S, m-1\rangle \quad \text{(IV.40)}$$

The μ_x transition dipole moment integral for the $|S, m_2\rangle \leftarrow |S, m_1\rangle$ transition:

$$\langle S, m_2|\mu_x|S, m_1\rangle = (\gamma\hbar/2)\{\langle S, m_2|S_+|S, m_1\rangle + \langle S, m_2|S_-|S, m_1\rangle\}$$

$$= (\gamma\hbar/2)\{[S(S+1) - m(m+1)]^{1/2}\langle S, m_2|S, m_1+1\rangle + [S(S+1) - m(m-1)]^{1/2}\langle S, m_2|S, m_1-1\rangle\}$$

(IV.41)

The first integral is non-zero for $m_2 = m_1 + 1$ and the second integral is non-zero for $m_2 = m_1 - 1$ and result in a $\Delta m = \pm 1$ selection rule. This result is confirmed by the μ_y and the μ_z transition dipole moment integrals.

The magnetic resonance transition frequency:

$$\nu = \gamma B_0/2\pi \tag{IV.42}$$

In addition to the large external field $B_0\mathbf{z}$, there are smaller internal magnetic fields within the molecule that vary with chemical and geometric structure. These internal or “local” fields are different for different nuclei and electrons and determination of these fields from the magnetic resonance spectrum provides most of the chemical and structural information.

The most important internal fields are along the z direction:

$$\boldsymbol{B} = (B_0 + B_{int})\mathbf{z} \tag{IV.43}$$

$$\nu = (\gamma/2\pi)(B_0 + B_{int}) \tag{IV.44}$$

For nuclear spins, the most important internal fields are due to *chemical shielding*. There are electronic currents induced by the external field and the chemical shielding fields are the magnetic fields of the induced currents (see page 1). The induced currents, chemical shielding, and NMR frequency depend on the chemical bonds of the nucleus:

$$\boldsymbol{B}_{shield} = -\sigma B_0\mathbf{z} \tag{IV.45}$$

where σ is typically positive and $10^{-6} < \sigma_{typical} < 10^{-3}$. Note that $\boldsymbol{B}_{shield}$ is typically antiparallel to $\boldsymbol{B}_{ext}$ and therefore reduces ν.

The induced currents and σ will also depend on the orientation of the chemical bonds in the magnetic field and this dependence is called the *chemical shielding anisotropy*.

Inclusion of B_{shield} in Eq. IV.44:

$$\nu_{shield} = \gamma\hbar B_0(1 - \sigma) \tag{IV.46}$$

Experimental determination of σ as defined in Eq. IV.44 is difficult because measurement of ν in a compound with $\sigma = 0$ corresponds to the nucleus with no electrons. It is more practical to measure $\Delta\nu$ and therefore σ relative to some reference compound:

$$\Delta\nu_{shield} = -\gamma B_0 \sigma / 2\pi \qquad \text{(IV.47)}$$

$$\delta = -\sigma = 2\pi \Delta\nu_{shield} / \gamma B_0 \qquad \text{(IV.48)}$$

The δ is called the *chemical shift* and is typically reported in ppm.

Another significant internal field is *scalar* or *J-coupling*:

$$\boldsymbol{B}_{scalar} = -(2\pi JM/\gamma)\ \mathbf{z} \qquad \text{(IV.49)}$$

$$\nu_{scalar} = JM \qquad \text{(IV.50)}$$

In these equations, M refers to the m value of a nearby nuclear spin which has chemical bond connectivity with the nuclear spin undergoing a transition and J is a “coupling constant” particular to the two spins and their chemical bond connectivity. For example, $J \sim 150$ Hz for a directly bonded ^{1}H-^{13}C spin pair.

In a typical sample, the nearby spin has nearly equal probabilities of being in any of its M states. A multiplet of transitions are observed and each transition corresponds to a different M value. For example, consider detection of ^{13}C in a ^{1}H-^{13}C spin pair. $S(^1\text{H}) = ½$ and $J = 150$ Hz:

$$\begin{aligned} &M = ½ \qquad && \nu_{scalar} = J/2 = 75 \text{ Hz} \\ &M = -½ \qquad && \nu_{scalar} = -J/2 = -75 \text{ Hz} \end{aligned} \qquad \text{(IV.51)}$$

$$\Delta\nu_{scalar} = J = 150 \text{ Hz} \qquad \text{(IV.52)}$$

The scalar fields result in splittings in the spectra.

The chemical shift and scalar couplings are both sensitive to the local bonding of the nucleus and measurement of these parameters in the NMR spectrum is helpful in assignment of individual peaks to specific nuclei. Because the chemical shifts and scalar couplings of particular functional groups are well-known, NMR spectra are also very useful for determination of the chemical structures of unknown compounds.

Distinguishing between $\Delta\nu_{shield}$ and $\Delta\nu_{scalar}$ is most straightforwardly done by taking NMR spectra at two different B_0 fields. Note that $\Delta\nu_{shield} \propto B_0$ while $\Delta\nu_{scalar}$ is independent of B_0.

Return to Hydrogen Atom

The radial part of the time-independent Schrodinger equation for the hydrogen atom will now be solved. The first three terms of Eq. IV. 10:

$$(-\hbar^2/R)\; d/dr(r^2 dR/dr) - (1/4\pi\varepsilon_0)(2mre^2) - 2mr^2E \;=\; -\hbar^2\, l(l+1) \tag{IV.53}$$

Multiply by $R\,/\,2mr^2$ and rearrange terms:

$$(-\hbar^2/\,2mr^2)\; d/dr(r^2 dR/dr) + [(\hbar^2/\,2mr^2)\, l(l+1) - (1/4\pi\varepsilon_0)(e^2/r)]R \;=\; ER \tag{IV.54}$$

The first term in this equation is the radial kinetic energy, the second term is the *centrifugal potential*, and the third term is the Coulomb potential. The centrifugal potential reflects the “conservation” of angular momentum; i.e. $L^2 = \hbar^2\, l(l+1) \equiv$ constant. In order for $L^2 = |\boldsymbol{r} \times \boldsymbol{p}|^2$ to be independent of $\boldsymbol{r}$, p^2 and the kinetic energy associated with angular motion (centrifugal potential) are proportional to r^{-2}. The centrifugal potential is also apparent in the classical mechanics solution of two particles with an attractive radial potential.

The R eigenfunctions are the associated Laguerre Polynomials $R_{nl}(r)$ which are indexed by the radial or “principal” quantum number n, an integer greater to or equal to 1 and the angular momentum or “azimuthal” quantum number l with $n > l$, $l = 0 \equiv s$, $l = 1 \equiv p$, $l = 2 \equiv d$.

$$1s \qquad R_{10} \;=\; (a_0)^{-3/2}\, 2\, e^{-r/a_0} \tag{IV.55}$$

$$2s \qquad R_{20} \;=\; (a_0)^{-3/2}\, (1/8)^{1/2}\, [2 - (r/a_0)]\; e^{-2r/a_0} \tag{IV.56}$$

$$2p \qquad R_{21} \;=\; (a_0)^{-3/2}\, (1/24)^{1/2}\, (r/a_0)\; e^{-2r/a_0} \tag{IV.57}$$

$$3s \qquad R_{30} \;=\; (a_0)^{-3/2}\, (1/243)^{1/2}\, [6 - (4r/a_0) + (4r^2/9a_0^{\,2})]\; e^{-3r/a_0} \tag{IV.58}$$

$$3p \qquad R_{31} \;=\; (a_0)^{-3/2}\, (1/486)^{1/2}\, [4 - (2r/3a_0)]\; e^{-3r/a_0} \tag{IV.59}$$

$$3d \qquad R_{32} \;=\; (a_0)^{-3/2}\, (1/2430)^{1/2}\, (r/a_0)^2\; e^{-3r/a_0} \tag{IV.60}$$

The total eigenfunction:

$$\psi_{nlm}(r,\, \theta,\, \phi) = R_{nl}(r)\; Y_{lm}(\theta,\, \phi) \tag{IV.61}$$

It is interesting to calculate the integrated probability for the electron over a spherical shell of radius r. This “radial probability density” is independent of θ, ϕ and is proportional to the surface area of the sphere = $4\pi r^2$:

$$(\text{Radial probability density})_{nl} \;\propto\; r^2 R_{nl}^{\;2} \tag{IV.62}$$

$$(\text{Angular probability density})_{lm} \;\propto\; Y_{lm}^{\;2} \tag{IV.63}$$

The hydrogen atom enegy eigenvalues:

$$E = -(1/4\pi\varepsilon_0)^2 \times (1/n^2) \times me^4/2\hbar^2 \qquad \text{(IV.64)}$$

This is the same solution as the Bohr atom semiclassical approach, Eq.1.2.9. Note though that the 'n' in the Bohr atom is the component of angular momentum along the z axis. In the quantum mechanical solution, the Bohr atom 'n' is the "magnetic" quantum number 'm' whose value has no effect on the energy. In the quantum mechanical approach, the energy for a give n is independent of l and m. So, the energy (although not the wavefunction) is independent of the angular momentum. Note that as n increases, $\langle r \rangle$ increases, $\langle V_{coulomb} \rangle$ increases, and E increases.

Different eigenfunctions with the same energy are "degenerate". For example, $n = 1$ has a degeneracy of 1 (1s), $n = 2$ has a degeneracy of 4 (1s, 2p), and $n = 3$ has a degeneracy of 9 (3s, 3p, 3d).

The selection rule for changes in the radial quantum number n are calculated from the integration over r in Eqs. IV.26-IV.28 along with incorporation of the $\Delta l = \pm 1$ selection rule:

$$-\langle R_{n_2,\, l+1} | er | R_{n_1,\, l} \rangle \qquad \text{(IV.65)}$$

$$-\langle R_{n_2,\, l-1} | er | R_{n_1,\, l} \rangle \qquad \text{(IV.66)}$$

The radial quantum number selection rule:

$$\Delta n = \text{anything} \qquad \text{(IV.67)}$$

This selection rule and energy levels are consistent with the experimental hydrogen atom spectrum.

One interesting aspect of the hydrogen atom is that although there is kinetic energy associated with θ, ϕ motion, the total energy is only dependent on the the radial quantum number n:

$$\langle L_z^2/2mr^2 \rangle_{nl} = [l(l+1)\hbar^2/2m][\langle r^{-2} \rangle_{nl}] \qquad \text{(IV.68)}$$

$$\langle -(1/4\pi\varepsilon_0)(e^2/r) \rangle_{nl} = -(e^2/4\pi\varepsilon_0)(\langle r^{-1} \rangle_{nl} \qquad \text{(IV.69)}$$

In order for the 2s ($l = 0$) and 2p ($l = 1$) orbitals to have the same energy, $\langle r \rangle_{21} < \langle r \rangle_{20}$. In general, as l increases for fixed n, $\langle r \rangle_{nl}$ decreases. The decreased Coulomb energy compensates for the increased angular kinetic energy.

Because $S = ½$ for electrons, the total electron wavefunction is $|\psi_{nlm}\rangle|½\,, m\rangle$ where the first part is the spatial function and the second part is the electron spin function. Each spatial function can be associated with either the $m = ½$ or the $m = -½$ spin function.

The orbitals for atoms with larger numbers of electrons are based on the hydrogen atom orbitals. Electrons are *fermions* which means that there can be only one electron per hydrogen atom wavefunction. For example, the ten electrons in neon are considered to occupy all of the $n = 1$ and $n = 2$ orbitals (5 spatial orbitals: $1s$, $2s$, $2p$ ($m = -1, 0, 1$).

The independence of energy on l for the hydrogen atom is not obtained for other atoms. The difference is interelectron repulsion.

Understanding electronic structure in molecules begins with creation of atomic orbitals whose spatial orientations are the same as those of the chemical bonds. These orbitals are linear combinations of the hydrogen atom orbitals. For example, the $l = 1$, $m = \pm1$ hydrogen orbitals have no preferred orientation in the xy plane but defined direction can be created by linear combinations of these orbitals. In particular:

$$\psi_{px} \propto (\psi_{1,+1} + \psi_{1,-1}) \propto sin\theta(e^{i\phi} + e^{-i\phi})/2 = sin\theta cos\phi \qquad \text{(IV.70)}$$

$$\psi_{py} \propto (\psi_{1,+1} - \psi_{1,-1}) \propto sin\theta(e^{i\phi} - e^{-i\phi})/2 = sin\theta sin\phi \qquad \text{(IV.71)}$$

Some molecular electronic spectra are interpreted in terms of perturbed atomic orbitals. For example, visible spectra of first-row transition metal complexes are often interpreted in terms of $3d \leftarrow 3d$ transitions of the metal ion. Directional $3d$ hydrogen atom orbitals are perturbed by the ligands of the complex. Note that these transitions violate the $\Delta l = 1$ selection rule for hydrogen atom transitions.

Most molecular electronic spectra are understood as transitions between “molecular orbitals” which are linear combinations of atomic orbitals of different different atoms in the molecule. The individual atomic orbitals may be “hybridized” as linear combinations of the hydrogen atom orbitals which point along the chemical bond directions. A specific example is the tetrahedrally oriented $2sp^3$ orbitals of carbon which are formed from linear combinations of the $2s$, $2p_x$, $2p_y$, and $2p_z$ ($l = 1$, $m = 0$) orbitals.

$$\tfrac{1}{2}\, 2s + (3/4)^{1/2}\, 2p_z \quad \text{points along } z \text{ direction} \qquad \text{(IV.72)}$$

$$\tfrac{1}{2}\, 2s - (1/12)^{1/2}\, 2p_z + (2/3)^{1/2}\, 2p_x \quad \text{lies in } xz \text{ plane} \qquad \text{(IV.73)}$$

$$\tfrac{1}{2}\, 2s - (1/12)^{1/2}\, 2p_z - (1/6)^{1/2}\, 2p_x + (\tfrac{1}{2})^{1/2}\, 2p_y \qquad \text{(IV.74)}$$

$$\tfrac{1}{2}\, 2s - (1/12)^{1/2}\, 2p_z - (1/6)^{1/2}\, 2p_x - (\tfrac{1}{2})^{1/2}\, 2p_y \qquad \text{(IV.75)}$$

Note that the four sp^3 orbitals are orthonormal and that the total number of hybridized orbitals equals the number of input hydrogen atom orbitals.

The hydrogen molecule with hydrogen atoms A and B is the simplest example of molecular orbitals:

$$1s\sigma \propto 1s_A + 1s_B \qquad \text{(IV.76)}$$

$$1s\sigma^* \propto 1s_A - 1s_B \tag{IV.77}$$

An electron in the $1s\sigma$ "bonding" orbital has a higher probability of being between the two hydrogen nuclei than does an electron in the $1s_A$ or the $1s_B$ orbital. Electrons in this in-between region experience the attractive Coulomb interaction with both hydrogen nuclei and leads to lower overall energy relative to the atomic orbitals.

An electron in the $1s\sigma^*$ "anti-bonding" orbital has lower probability of being between the two nuclei and has higher energy relative to the atomic orbitals.

Because they have opposite values of the spin quantum number m, the two electrons can both be in the $1s\sigma$ orbital and form the chemical bond, i.e. a region of significant electron density between two nuclei.

A π molecular orbital is formed by a linear combination of p atomic orbitals whose direction is perpendicular to the internuclear axes.

Electronic spectral transitions are typically localized to molecular orbitals of a specific functional group within the molecule. In this context, the functional group is called a "chromophore".