

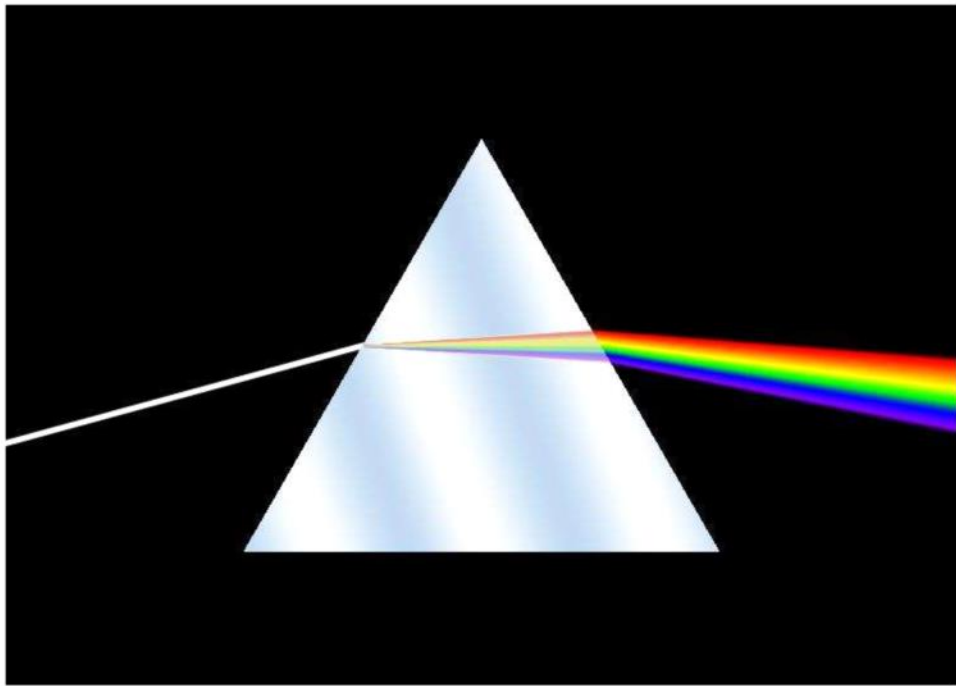
Spectroscopy

Chem 401 / 519

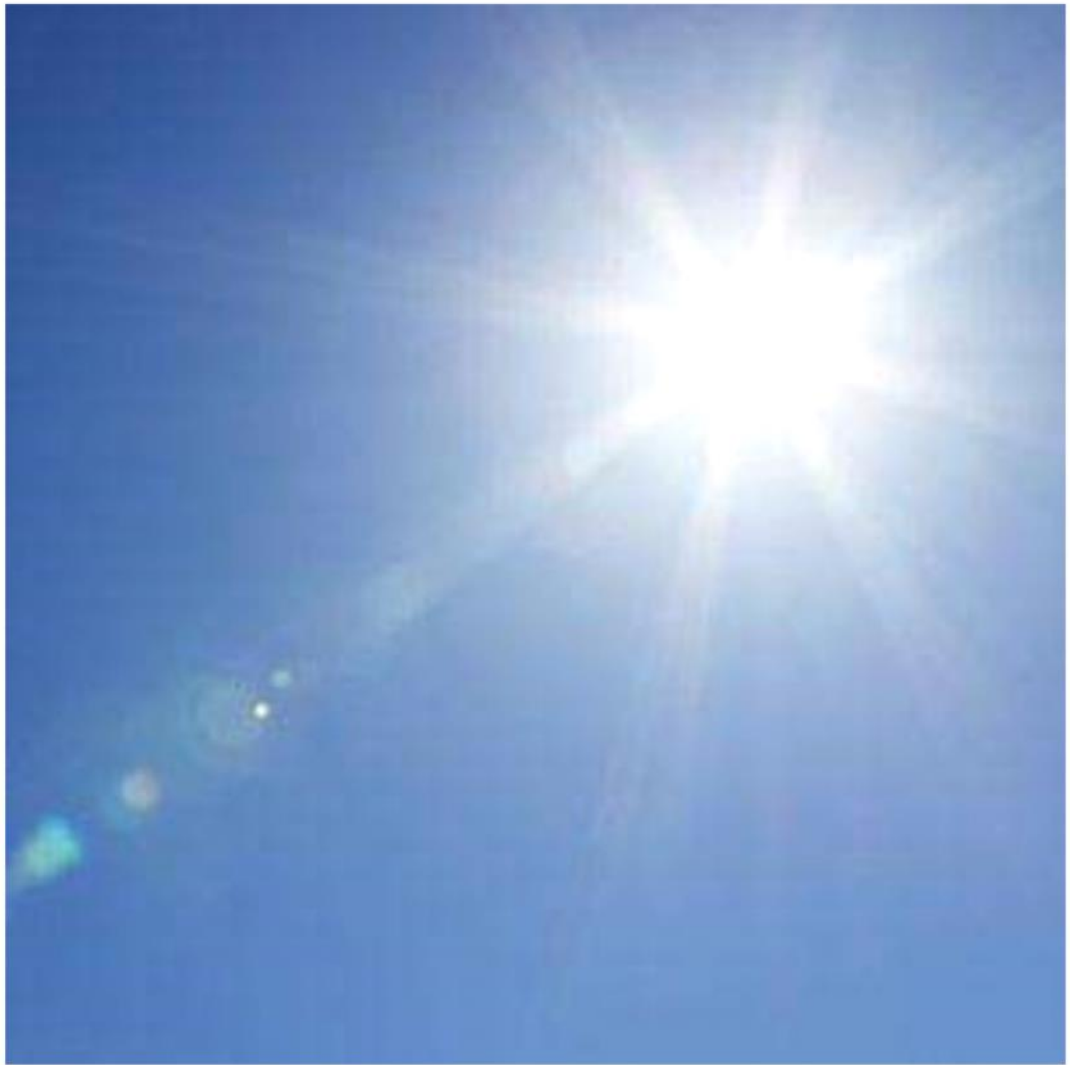
W.A. MacFarlane

Jan 2016

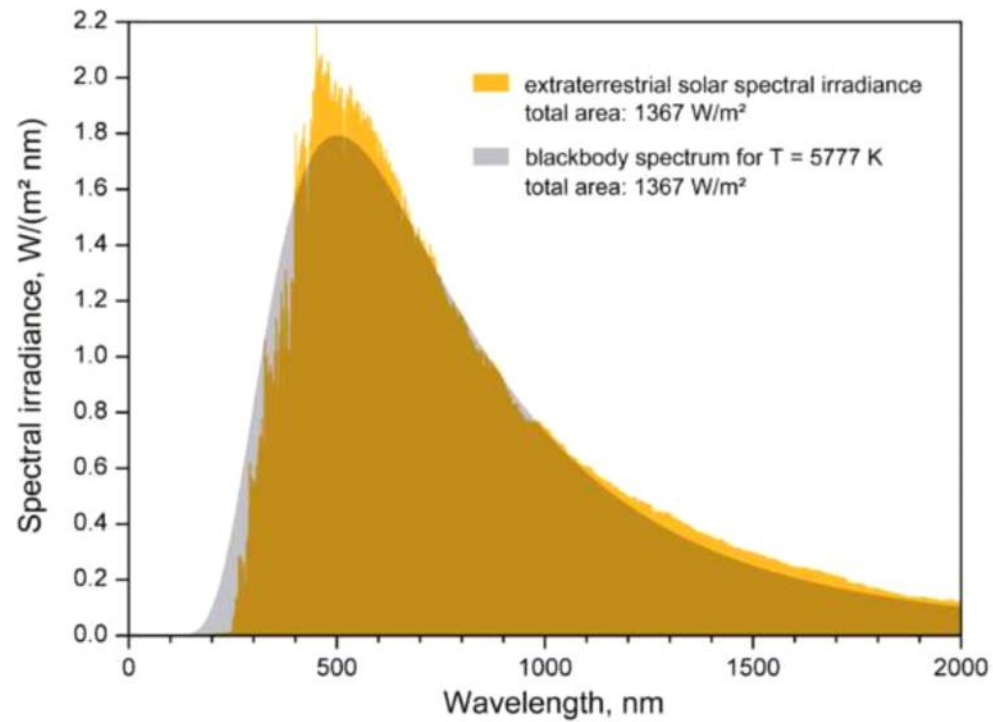
Prism, a dispersive optical element



$$n = n(\lambda)$$



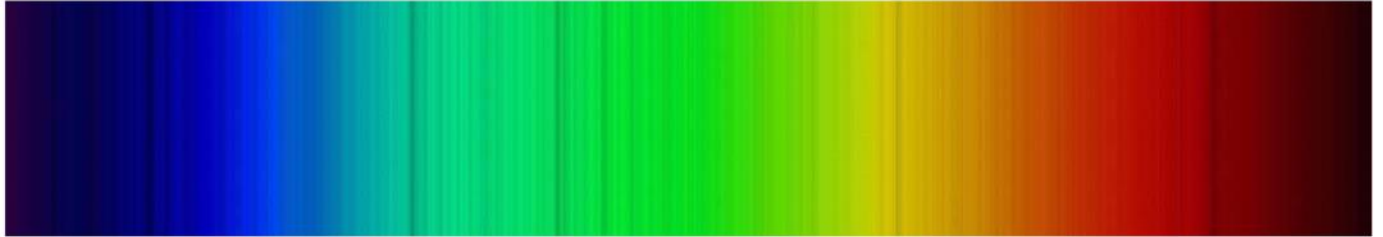
Solar Spectrum approx. a blackbody with surf. temperature 5800 K



Planck blackbody spectrum depends only on temperature

Solar Spectrum

UV



Fraunhofer lines

- absorption at characteristic wavelength
- due to cooler atomic gases in the solar atmosphere
- e.g. 587.49 nm line of *Helium*

Absorption by Terrestrial Atmosphere

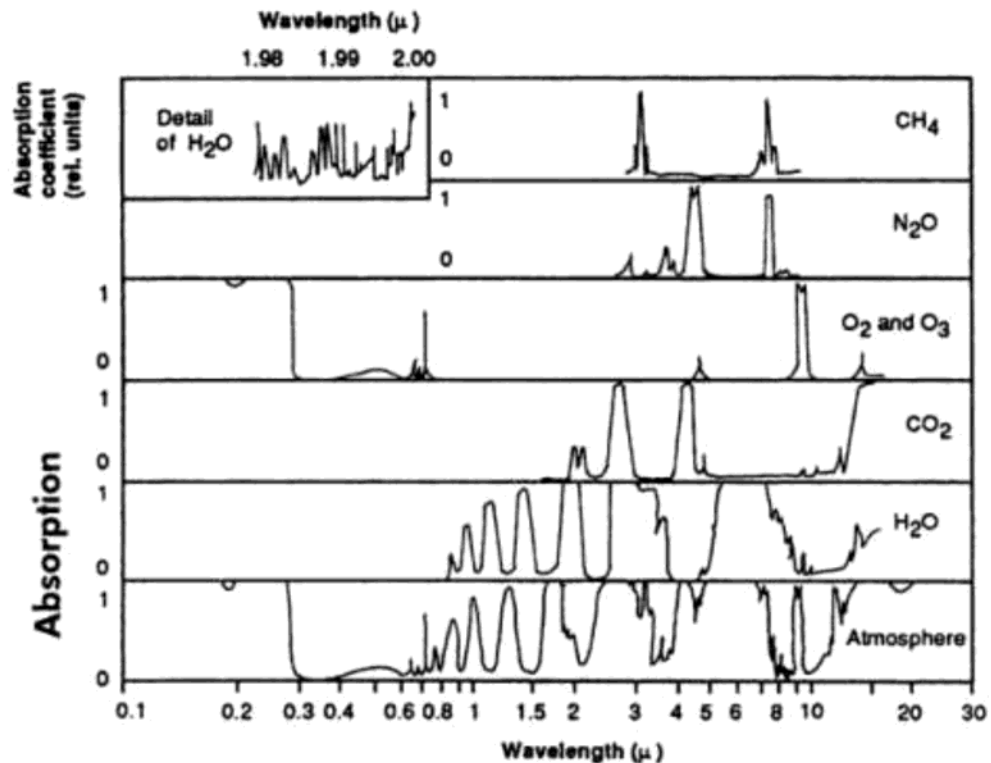
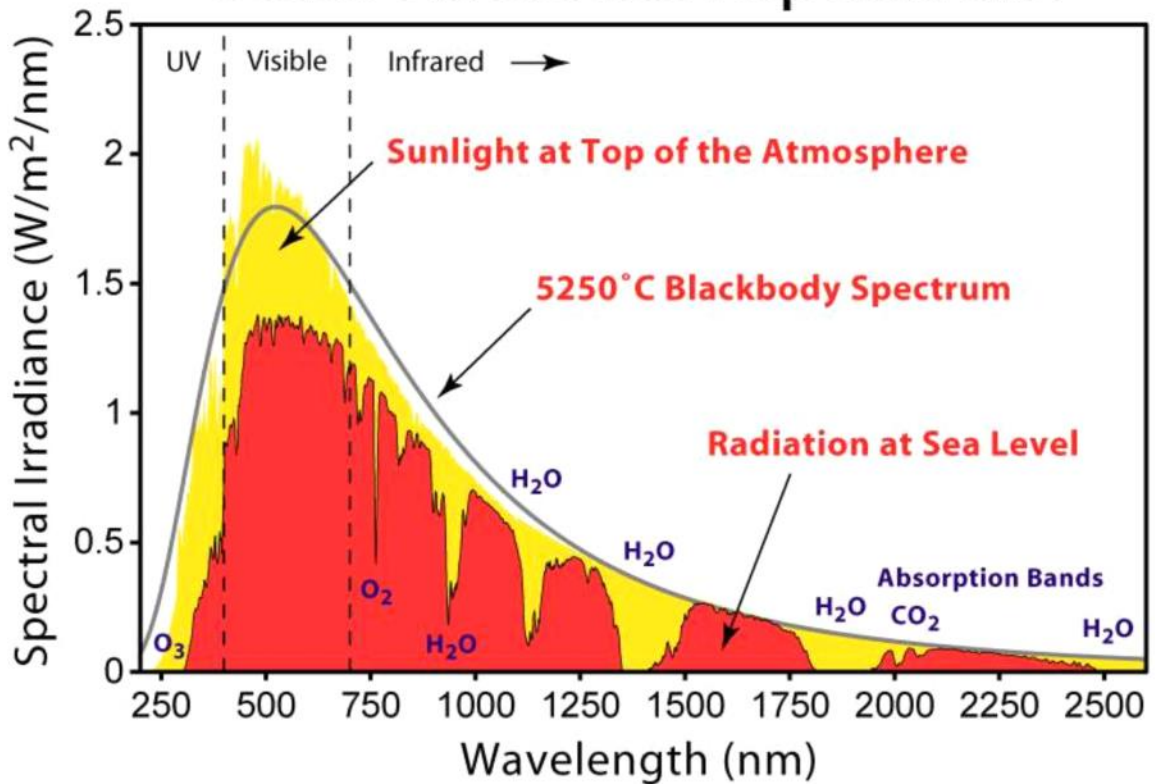


Figure 5-2. Absorption spectra for CH₄, NO₂, O₂, O₃, CO₂, and H₂O, and of the atmosphere. (From R. G. Fleagle and J. A. Businger [2006] after J. H. Howard [519] and R. M. Goody and G. D. Robinson [514])

Solar Radiation Spectrum



importance: photosynthesis, photovoltaic power, global climate, ...

Quantum Mechanics

Saturday, April 16, 2016 10:15 PM

Review of Quantum Mechanics

System: This is usually an atom or molecule composed of nuclei and electrons

A. The wavefunction

- This describes the state of the system
- Based on probability

A. Classically

- Based on macroscopic systems that behave predictably determine momentum, position and energy

The QM description is delocalized

- Simplest system: 1 particle system an e^- in a H atom
- $\psi(x, y, z, t)$

Postulates

The system is describe by its wavefunction ψ

Valid wavefunction

The wavefunction is

- Single valued
- Continuous
- Remain finite

Also $\left(\frac{\partial \psi}{\partial x}\right)$ must be defined in all space

Recall Complex numbers

$$z \in \mathbb{C}$$

$$z = a + ib, \quad \text{where } a \text{ and } b \text{ are real numbers}$$

$$i = \sqrt{-1}, \quad a \text{ is the real component, } b \text{ is the imaginary}$$

$$r = \text{modulus of } z = \sqrt{a^2 + b^2}$$

$$\theta = \text{phase of } z$$

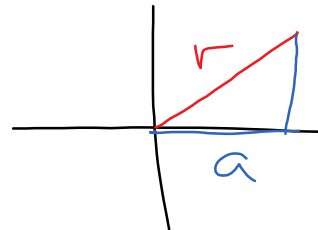
$$z^* = a - ib, \quad \text{this is know as the complex conjugate}$$

$$|z|^2 = r^2 = z \cdot z^*$$

$$z = r e^{i\theta}$$

$$z^* = r e^{-i\theta}$$

$$e^{i\theta} = \cos \theta + i \sin \theta$$



Normalization of wavefunction

Its probability in all space must be 1, ie finite and normalizable

$$\int |\psi|^2 d^3r = 1$$

Observable Quantity has a corresponding Hermitian operator linear operator

The eigenvalues of \hat{A} are the possible measured values

Operators

Operates on the space of a wave function

$$\hat{A}\psi_n(x, y, z, t) = G_n\psi_n(x, y, z, t)$$

Operators are linear

$$af + bg$$

$$\hat{A}(af + bg) = a\hat{A}f + b\hat{A}g$$

Hermitian Operator is equal to its Hermitian conjugate

$$\hat{A} = \hat{A}^*$$

$$\int g \hat{A} h^* d^3r = \left(\int h^* \hat{A} g d^3r \right)^* = \int h \hat{A}^* g^* d^3r$$

Eigenvalues

eigenvalues equation

$$\hat{A}\psi_n(x, y, z, t) = a_n \psi_n(x, y, z, t)$$

ψ is an eigenfunction of \hat{A} with eigenvalue with many solutions

$$\hat{A}\psi_n = a_n \psi_n$$

Any given measurement of quantity corresponding to \hat{A} will result in a measured value that is exactly the a_n eigenvalue

Repeated measurements

$$\text{Average value, } \bar{a} = \sum_i^N \frac{a_i}{N}$$

The average is given by the expectation value of \hat{A}

$$\langle \hat{A} \rangle = \int_{\text{all space}} \psi^* \hat{A} \psi d\tau$$

For the system as prepared in state ψ

C. Schrodinger Equation

The state of the system is an Eigen function of the time dependent Schrodinger equation

$$\hat{H}\Phi(x, y, z, t) = i\hbar \frac{\partial}{\partial t} \Phi$$

\hat{H} is the Hamiltonian operator corresponding to the total energy

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}, \quad p = -i\hbar \vec{\nabla}$$

$$= -\frac{\hbar^2}{2m} \nabla^2$$

$V(x, y, z)$ is potential energy

$$\hat{V}\psi = V(x, y, z, t)\psi$$

If \hat{H} is not explicitly a function of time.

$$\Phi(x, y, z, t) = \Psi(x, y, z)T(t)$$

$$T(t) = e^{-\frac{iEt}{\hbar}}$$

In absorption spectroscopy, the system (atom/molecule) is coupled to the electromagnetic field of radiation

This coupling leads to a small time dependent term in \hat{H}

Usually this is so small in the case of small electric fields, small concentration of photons

Can result in nonlinear effects with lasers

Some Examples

| | \hat{H} | E |
|---------------|---|--------------------|
| Free particle | $\hat{T}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ | $\frac{p_x^2}{2m}$ |

| | | |
|---------------------|---|--|
| Particle in Box | $\left\{ \begin{array}{l} \hat{T}_x \text{ from } 0 < x < L \\ \hat{T}_x + \text{infinity, otherwise} \end{array} \right\}$ | $\frac{\hbar^2 n^2}{8mL^2}$ |
| Rigid Rotor | $\hat{T} = -\frac{\hbar^2}{2\mu} \nabla^2(r, \theta, \psi)$ | $\frac{\hbar^2}{2\mu R^2} j(j+1), \quad j = 0, 1, 2, 3, 4 \dots$ |
| Harmonic Oscillator | $\hat{T}_x + \frac{1}{2} k_f x^2$ | $\left(m + \frac{1}{2}\right) \hbar \omega, \quad \omega = 2\pi \sqrt{\frac{k_f}{\mu}},$ $m = 0, 1, 2, 3 \dots$ |
| Hydrogen Atom | $\hat{T} - \frac{Ze^2}{R}$ | $-\frac{\mu e^4 Z^2}{2\hbar} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}$ |

Bra – Ket notation

$|ket\rangle$, ket "vector"

$\langle bra|$, bra "vector"

$$\Psi_n(\vec{r}) \Rightarrow |n\rangle$$

$$\Psi_n^*(\vec{r}) \Rightarrow \langle n| = |n\rangle^*$$

Matrix Elements or an operator

$$A_{nm} = \langle n|\hat{A}|m\rangle = \int \psi_n^* \hat{A} \psi_m d\tau$$

$$A = \begin{bmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{bmatrix}$$

Inner Product

$$\text{recall } \vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z = |\vec{a}| |\vec{b}| \cos \theta$$

$$\langle n|m\rangle = \int \Psi_n^* \Psi_m d\tau = \delta_{nm}$$

$$\langle n|n\rangle = 1$$

$$\hat{H}|n\rangle = E_n |n\rangle$$

Any state can be expanded in terms of a complete set of $|k\rangle$ set of states (this is the entire basis of the wavefunction)

Like in 3D, \vec{a} can be expanded in terms of its components along a set of unit vectors

$$\vec{a} = \langle a_x, a_y, a_z \rangle$$

$$|n\rangle = \sum_k c_{nk} |k\rangle, \quad \text{the sum maybe be infinite}$$

If the $|k\rangle$ are an orthonormal basis then $\langle k_i | k_j \rangle = \delta_{ij}$

This expansion can be useful to calculate for example matrix element

$$\langle m|n\rangle = \langle m| \left(\sum_k c_{nk} |k\rangle \right) = \sum_k c_{nk} \langle m|k\rangle$$

Commutativity of operators

In algebra $xy = yx$

In matrix/operator algebra

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = ?$$

eg $[\hat{x}, \hat{p}_x] = i\hbar$, a fundamental aspect of quantum mechanics

$$(\Delta A)(\Delta B) \geq \frac{1}{2} |\langle [A, B] \rangle|$$

$$\text{eg } \Delta x \Delta p_x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} \sqrt{\langle (p_x - \langle p_x \rangle)^2 \rangle} \geq \frac{1}{2} |i\hbar| = \frac{\hbar}{2}$$

When 2 operators do not commute, we cannot make a simultaneous determination of their observables with equal accuracy

When 2 operators do commute, we can measure both properties with arbitrary accuracy

Energy time uncertainty

$$\Delta E \Delta t = \text{something look up}$$

This is not a special case of the above

There is no QM operator for time

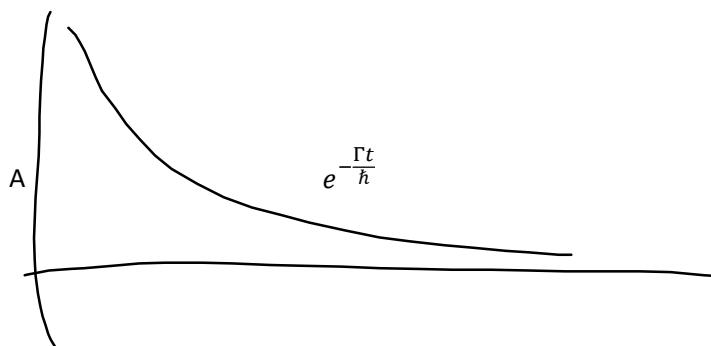
Recall

$$\Phi = \psi E^{-\frac{iEt}{\hbar}}$$

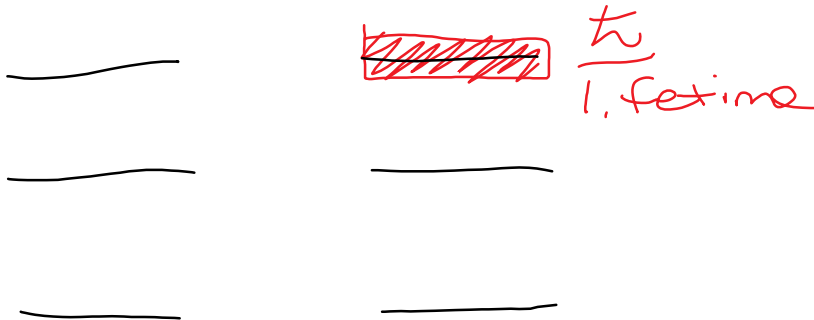
For example in an energy eigenstate E is exactly specified $\Delta E = 0$

Therefore the time dependence goes off to -infinity to infinity

If instead, we are in a quantum state whos lifetime is finite



$\Delta E \geq \Gamma$, this is lifetime broadening



Born Oppenheimer Approximation

Electron are much lighter than the proton

$$\frac{m_p}{m_e} \approx 1840$$

Lead to the approximate separator of the electronic and nuclear wavefunctions

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

Sum of energies. V are interactions

We assume e^- adjust instantaneously to the positive of the nuclei

$\psi = \psi_e(q; Q)\psi(Q)$, Q is the nuclear coordinates, q is the electron coordinate

For the electrons

$$\hat{H}_e = \hat{T}_e + \hat{V}_{en}(Q) + \hat{V}_{ee}$$

For the nuclei

$$\hat{H}_n = T_n + \hat{V}_{nn} + E_e$$

The nuclear motion is often further split into rotation and vibration

$$\psi = \psi_e \psi_{n,v} \psi_{n,r}$$

$$E = E_e + E_v + E_r$$

Electron spin and nuclear spin

Electron and many nuclei have internal angular momentum, called spin we need to expand our QM theory to account for it

Electron spin

$$\hat{S}_z |\alpha\rangle = \frac{1}{2} \hbar |\alpha\rangle$$

$$\hat{S}_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle$$

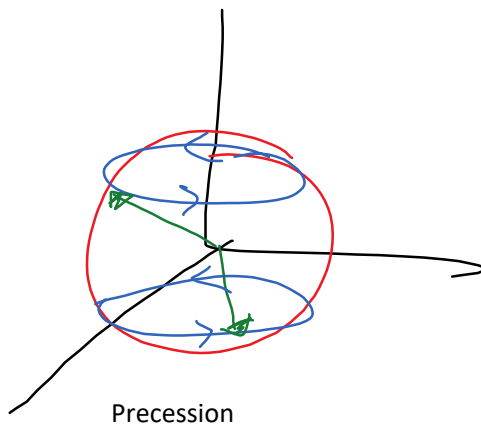
The basis set are alpha and beta

$|- \rangle$ for spin down

$|+ \rangle$ for spin up

$$\hat{S}^2 \begin{Bmatrix} |\alpha\rangle \\ |\beta\rangle \end{Bmatrix} = \hbar s(s+1) \begin{Bmatrix} |\alpha\rangle \\ |\beta\rangle \end{Bmatrix}$$

$$\sqrt{\hat{S}^2} = \sqrt{3} \frac{\hbar}{2}$$



Hydrogen

Tuesday, January 12, 2016 11:00 AM

Total electron wavefunction for a single electron is indexed by 4 quantum numbers

$$\Phi_{n,l,m_l,m_s}(r, \theta, \phi) \\ = R_{nl}(\vec{r})Y_{lm_l}(\theta, \phi)$$

Level degeneracy

$$g = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2, \quad 2 \text{ for electron spins}$$

Review Spin orbit coupling causes splitting on energy levels

Nuclei Spin

Internal angular momentum

$$I\hbar \text{ where } I = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

Even A then I is an integer Bosonic

Odd A results in half integers Fermionic

Effect on intensity patterns in some spectra

Examples. Hydrogen Atom

Single electron system

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \psi = E\psi$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e \text{ since } m_p \gg m_e$$

This is most easily solved in spherical coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\partial_x = \partial_r (\partial_x r) \dots$$

$$\nabla^2 = \partial_r^2 + \frac{2}{r} \partial_r + \frac{1}{r^2} \partial_\theta^2 + \frac{1}{r^2} \cot \theta \partial_\theta + \frac{1}{r^2 \sin^2 \theta} \partial_\phi^2$$

$$\text{Define } \hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] \\ = \text{square of orbital angular momentum}$$

SE

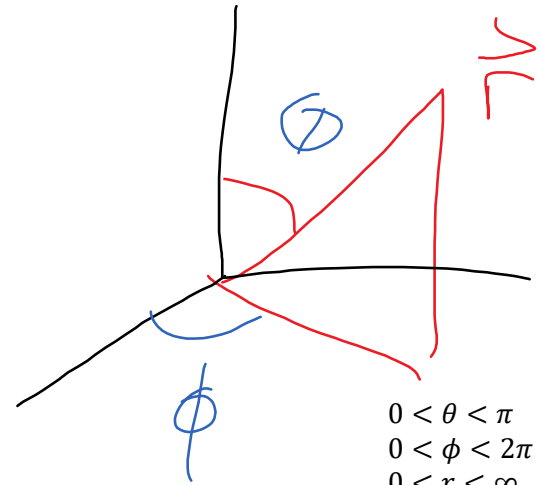
$$-\frac{\hbar^2}{2\mu} \partial_r (r \partial_r \psi) + \frac{1}{2\mu r^2} \hat{L}^2 \psi - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \psi = E\psi$$

Separation of variables

$$\psi(r, \theta, \phi) = R_{nl}(r)Y_{lm_l}(\theta, \phi)$$

$$\text{Note } \hat{L}^2 |Y_{lm}\rangle = \hbar^2 l(l+1) |Y_{lm}\rangle$$

$$\hat{L}_z |Y_{lm}\rangle = \hbar m_l |Y_{lm}\rangle$$



The spherical Harmonics are eigenfunctions of \hat{H}, \hat{L}^2, L_z

$$E = E_n = -\frac{Z^2 e^2}{4\pi\epsilon_0} \frac{1}{a_0 n^2} \cong -\frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = 0.529 \text{ \AA}, \quad \text{bohr radius of the hydrogen atom}$$

$$-\frac{\hbar^2}{2\mu^2} \partial_r(r^2 \partial_r R) + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) \right] R = ER$$

$$R_{nl} = N_{nl} r^l e^{-\frac{r}{na_0}} L_{n+l}^{l+1} \left(\frac{2r}{na_0} \right)$$

$$L_{n+l}^{l+1}$$

Spherical Harmonics

$$|Y_{lm}(\theta, \phi)\rangle = (-1)^m N_{lm} P_l^m(\cos \theta) e^{im\phi}$$

$$N_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}$$

P_l^m are associated with Legendre polynomial

$$P_0^{+1} = -\sin \theta$$

$$P_1^0 = \cos \theta$$

$$P_1^{-1} = \frac{1}{2} \sin \theta$$

$$P_2^2 = 3 \sin^2 \theta$$

$$P_2^1 = -3 \sin \theta \cos \theta$$

$$P_2^0$$

Look these up in quantum chem book

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$$

Can transform using linear recombination's to return real valued solutions

$$\widetilde{Y}_{lm} \Rightarrow \tilde{Y}_{l0} = Y_{l0}$$

$$\tilde{Y}_{lm} = \begin{cases} \frac{1}{\sqrt{2}} (Y_{l-m} + (-1)^m Y_{lm}), & \text{for } m > 0 \\ \frac{i}{\sqrt{2}} (Y_{l-m} - (-1)^m Y_{lm}), & \text{for } m < 0 \end{cases}$$

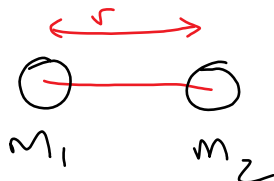
$$Y_{00} = \frac{1}{\sqrt{4\pi}} \quad \tilde{Y}_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad \tilde{Y}_{10}, \text{ no change}$$

$$Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}, \quad \tilde{Y}_{11} = \frac{1}{\sqrt{2}} (Y_{1-1} - Y_{1+1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r}$$

$$\tilde{Y}_{1-1} = \sqrt{\frac{3}{4\pi}} \frac{y}{r}$$

I. The rigid Rotor



$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

Moment of Inertia

$$\sum m_i r_i^2$$

r_i is \perp direction of m_i from the rotation axis

Here $I_{\text{rotation axis}} = 0$

$$I_{\perp} = m_1 r_1^2 + m_2 r_2^2 = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Rotational Hamiltonian

$$\hat{H}_{\text{rot}} = \frac{\hat{L}^2}{2I}$$

$$\hat{H}_{\text{total}} = \hat{H}_{\text{rot}} + \hat{H}_{\text{trans of cm}} + \frac{p_{\text{cm}}^2}{2(m_1 + m_2)}$$

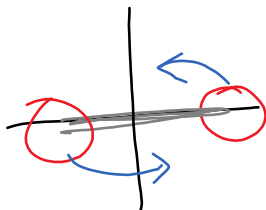
$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

Rigid molecule

$J = 0, 1, 2, \dots$ like l

Angular Momentum Operator

$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} \Leftarrow$ cross product \vec{r} and \vec{p} are perpendicular



$$L_x = -\frac{\hbar}{i} [\sin \phi \partial_{\theta} + \cot \theta \cos \phi \partial_{\phi}]$$

$$L_y = \frac{\hbar}{i} [\cos \phi \partial_{\theta} - \cot \theta \sin \phi \partial_{\phi}]$$

$$L_z = \frac{\hbar}{i} \partial_{\phi}$$

$$\hat{L}^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \partial_{\theta} (\sin \theta \partial_{\theta}) + \frac{1}{\sin^2 \theta} \partial_{\phi}^2 \right]$$

Computation relations

$$[A, B] = AB - BA$$

$$[L_x, L_y] = i\hbar \epsilon_{xyz} L_z \text{ and cyclic permutation}$$

$$[L_y, L_x] = -i\hbar \epsilon_{yxz} L_z$$

$$[L^2, L_i] = 0$$

Eigenstates of $H = H_{rot}$ are spherical harmonics

$$Y_{lm}(\theta, \phi)$$

$$L^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

Can define Ladder operators

$$L_{\pm} = L_x \pm iL_y$$

The harmonic oscillator

$$F = -kx \text{ hooks law}$$

$$V = \frac{1}{2} kx^2$$

$$F = -\vec{\nabla} V = -\partial_x V$$

Solution

$$x = x_o \cos(\omega_o t), \quad \omega_o = 2\pi v_o = \sqrt{\frac{k}{m}}$$

$$V = \frac{1}{2} kx^2 = \frac{1}{2} kx_o^2 \cos^2(\omega_o t)$$

$$T = \frac{1}{2} kx_o^2 \sin^2(\omega_o t)$$

$$T + V = \frac{kx_o^2}{2}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \partial_x^2 + \frac{1}{2} kx^2$$

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega_o, \quad \text{with } v = 0, 1, 2, 3, \dots$$

$$v_o = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\hat{H}|v\rangle = E_v|v\rangle$$

$$\Psi_v = N_v H_v(\sqrt{\alpha} x) e^{-\frac{\alpha x^2}{2}}$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

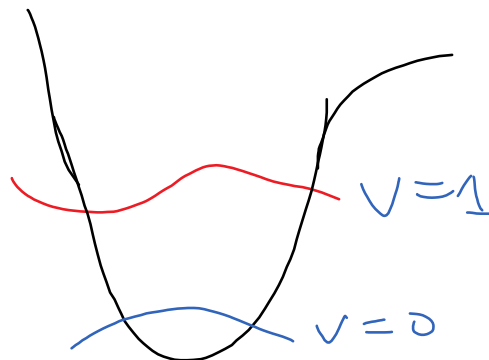
$$N_v = \frac{1}{(2^v v!)^{\frac{1}{2}}} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

H_v are the hermite polynomial

$$H_0 = 1, H_1 = 2x, H_2 = 4x^2 - 2$$

$$\int dx H_v(x) H_{v'}(x) e^{-x^2} = \delta_{vv'}$$

$$E_0 = \frac{1}{2} \hbar \omega_o \text{ zero point energy}$$



Operators

Thursday, January 14, 2016 11:01 AM

$$H = -\frac{\hbar^2}{2\mu}\partial_x^2 + \frac{1}{2}kx^2$$

$$\left(-\frac{\hbar^2}{2\mu}\partial_x^2 + \frac{1}{2}kx^2\right)\psi = E\psi$$

$$\psi = N_v H_v(\sqrt{\alpha}x) e^{-\frac{\alpha x^2}{2}}$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

$$N_v = \frac{1}{\sqrt{2^v v} \pi^{\frac{1}{4}}}$$

Ladder operator solution of Harmonic Oscillator

$$a^+ = \sqrt{\frac{\mu\omega_o}{2\hbar}} \left(x - i\frac{p}{\mu\omega_o}\right), \quad \text{rename } x \text{ to } p \text{ and momentum to } p \text{ to generalize coordinates}$$

$$a = \sqrt{\frac{\mu\omega_o}{2\hbar}} \left(x + i\frac{p}{\mu\omega_o}\right)$$

$a^+ \neq a$, these operators are not hermitian thus do not result in real observables

$$x = \sqrt{\frac{\hbar}{2\mu\omega_o}}(a + a^+), \quad p = -i\left(\frac{\mu\hbar\omega_o}{2}\right)^{\frac{1}{2}}(a - a^+)$$

One can show that

$$[a, a^+] = 1, \quad \text{using } [x, p] = i\hbar$$

$$\hat{H}_{vib} = \frac{p^2}{2\mu} + \frac{\mu\omega_o}{2}x^2 = \hbar\omega_o \left(a^+a + \frac{1}{2}\right) \text{ simple form}$$

Number operator

$N = a^+a$ and $N^+ = (a^+a)^+ = a^+a = N$ which means that this is hermitian

$$(AB)^+ = B^+A^+$$

$$N|v\rangle = v|v\rangle$$

$$H|v\rangle = \hbar\omega_o \left(v + \frac{1}{2}\right)|v\rangle$$

a^+ creation operator, creates a vibrational excitation. Raising operator

a : annihilation operator, removes one vibrational quantum level. Lowering operator

$$a^+|v\rangle = c|v+1\rangle, \quad a|v\rangle = c|v-1\rangle$$

$$Na|v\rangle = a^+aa|v\rangle, \quad [a, a^+] = 1 = aa^+ - a^+a \Rightarrow a^+a = aa^+ - 1$$

$$= [aa^+ - 1]a|v\rangle$$

$$= a(a^+a - 1)|v\rangle$$

$$= a(N - 1)|v\rangle$$

$$= a(v - 1)|v\rangle$$

$$= (v - 1)a|v\rangle$$

w with Eigenvalue $(v-1)$

$$a|v\rangle = \text{constant } |v-1\rangle$$

$$Na^+|v\rangle = (v+1)a^+|v\rangle$$

$$a|v\rangle = |\psi\rangle$$

$$\langle \psi | \psi \rangle \geq 0$$

$$(a|v\rangle)^+ = \langle v|a^+$$

$$\langle v|a^+a|v\rangle = v\langle v|v\rangle = v$$

Therefore $v \geq 0$

Normally we consider operators to operator on $|ket\rangle$ to the right

$$|b\rangle = A|a\rangle$$

$$\langle b| = (A|a\rangle)^+ = \langle a|A^+$$

matrix element

$$\langle \psi | A | \psi \rangle = \langle \psi | (A | \psi \rangle)$$

$$= (\langle \psi | A^+) | \psi \rangle$$

Ambiguous except if A is Hermitian $A^+ = A$

$$a|v\rangle = \sqrt{v} |v-1\rangle$$

$$a^+|v\rangle = \sqrt{v+1} |v+1\rangle$$

Lower the ground state

Integrate

$$|0\rangle = N e^{-\frac{m\omega_0 x^2}{2\hbar^2}}$$

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^+)^n |0\rangle$$

The eigenfunctions of a Hermitian operator with different eigenvalues, then the wavefunctions are orthogonal

$$A\psi_1 = a_1\psi_1$$

$$A\psi_2 = a_2\psi_2$$

$$a_1 \neq a_2$$

$\langle 1|2\rangle = 0$ then ψ_1 and ψ_2 are orthogonal

Molecular Symmetry

Why is it important

The basic task is to solve $H|\psi\rangle = E|\psi\rangle$

Often easy to write down

The problem of solving the S.E. can be enormously simplified by using symmetry

These simplification are rigorous

Zero by symmetry is not an approximation but exact

Strategy -fully exploit symmetry first then use approximations such as SALC

$$\Pi|\psi(\vec{r})\rangle = |\psi(-\vec{r})\rangle$$

Use the machinery of group theory \Rightarrow systematic and complete account of symmetry

It's the symmetry of H that is k

Transformation operators that results in a change of coordinates

Such operators will be symmetries of H if H looks the same before/after the operator

Eg if the potential energy order is even like $\frac{kx^2}{2}$

Then it is invariant under the change of coordinates $x \Rightarrow -x$

$$T = \frac{1}{2} m \left(\frac{\partial x}{\partial t} \right)^2 \text{ is also even}$$

The harmonic oscillator H_{vib} is inversion symmetric

If an operator \hat{R} leaves the Hamiltonian Invariant

$$\hat{R}\hat{H}|\psi\rangle = \hat{H}\hat{R}|\psi\rangle \text{ for all } |\psi\rangle$$

$$[\hat{R}, \hat{H}] = 0, \text{ they commute}$$

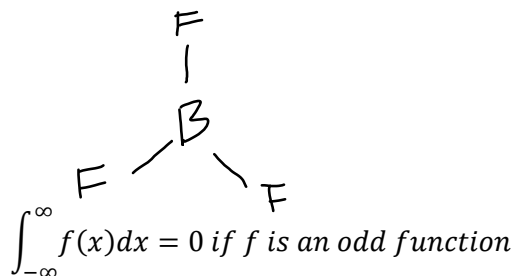
$\hat{H}|\psi\rangle$ does not mix states with different eigenvalues of R

Inversion symmetry $\Rightarrow |\psi\rangle$ is a state of definite parity

$$\pi = \pm 1$$

Rotation system H atom $\Rightarrow |\psi\rangle$ have fixed values l, m $|l, m\rangle$

BF_3 is symmetric



symmetry

–MO $|\psi\rangle$ SALC

–Selection Rules symmetry constraints on matrix transition elements which are integrals

–classify normal modes of vibrations

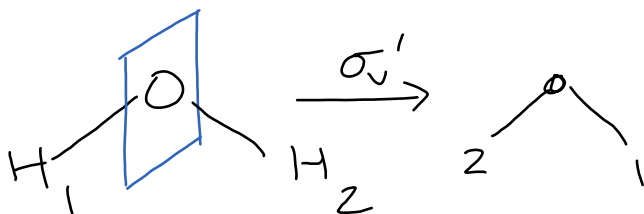
–crystallography is enormously simplified by symmetry

–optical activity, handedness of molecules

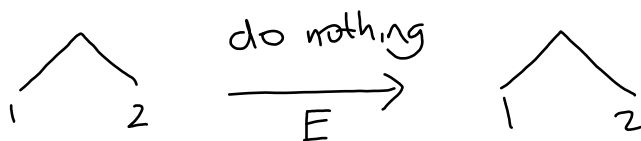
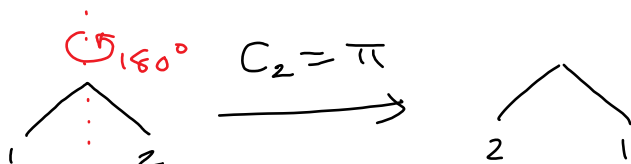
Point Symmetry (Molecules)

At least one point is left unchanged by the symmetry operation

What are the symmetries of H_2O



"spiegel" is german for mirror



Symmetry Operator

Geometrical operator that leaves the molecules in equivalent positions

5 types of operation

E : identity

σ : reflection through plane

C_n : rotation by axis via $\frac{2\pi}{n}$

S_n : rotation + reflection

i : inversion

2) \hat{C}_n rotate by $\frac{2\pi}{n}$ radians about a specific axis

a. The axis must pass through the origin of the center of mass

b. Principle axis is C_n with largest n

Rotation can be repeated

$$\hat{C}_k^k = \hat{C}_k \hat{C}_k \hat{C}_k \dots \hat{C}_k = 1$$

Counter clockwise rotation is \hat{C}_n^{-1}

$$\text{Note: } \hat{C}_n C_n^{-1} = E = \hat{C}_n^{-1} \hat{C}_n$$

Symmetry

Saturday, April 16, 2016 10:24 PM

If an operator \hat{R} leaves the Hamiltonian Invariant

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$[\hat{R}, \hat{H}] = 0$, they commute

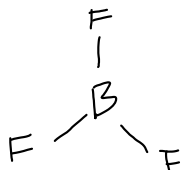
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$$\int_{-\infty}^{\infty} f(x)dx = 0 \text{ if } f \text{ is an odd function}$$

symmetry

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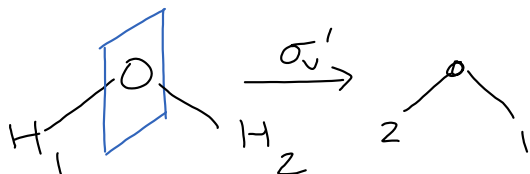
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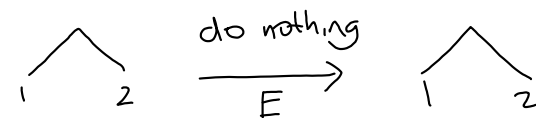
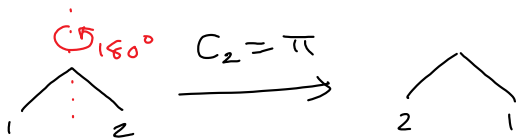
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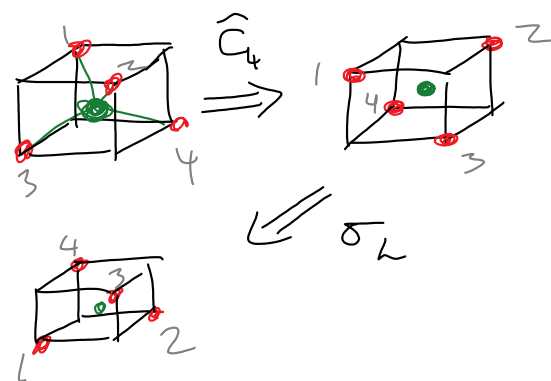
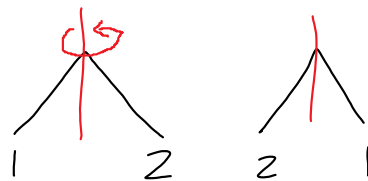
σ : reflection through plane

C_n : rotation by axis via $\frac{2\pi}{n}$

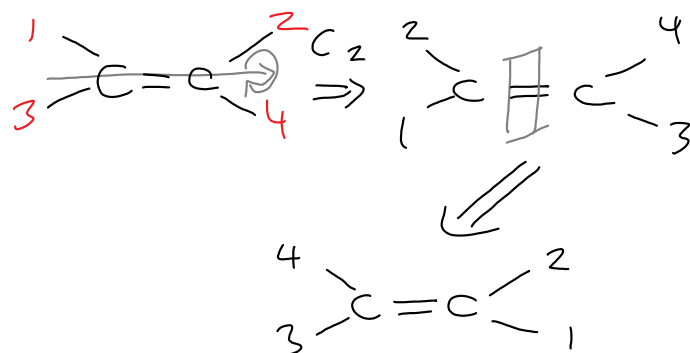
S_n : rotation + reflection

i : inversion

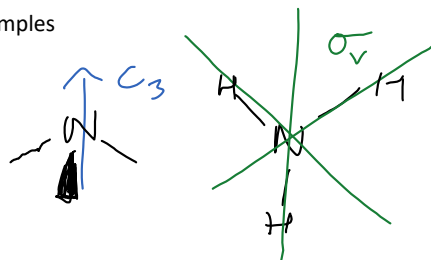
- 1) \hat{C}_n rotate by $\frac{2\pi}{n}$ radians about a specific axis
 - a. The axis must pass through the origin of the center of mass
 - b. Principle axis is C_n with largest n
 - c. Rotation can be repeated
 - d. $\hat{C}_k^k = \hat{C}_k \hat{C}_k \hat{C}_k \dots \hat{C}_k = 1$
 - e. Counter clockwise rotation is \hat{C}_n^{-1}
 - f. Note: $\hat{C}_n \hat{C}_n^{-1} = E = \hat{C}_n^{-1} \hat{C}_n$
- 2) reflection through a plane at the COM
 - a. eg yz plane
 - b. $x, y, z \rightarrow \sigma x, -y, z$
 - c. $\hat{\sigma}^2 = \hat{E} \iff \hat{\sigma} = \hat{\sigma}^{-1}$
 - d. B types of mirror planes
 - e. $\hat{\sigma}_v$ contains principle rotation axis
 - f. $\hat{\sigma}_v$ contains principle rotation axis
 - g. $\hat{\sigma}_h$ contains \perp to principle axis
 - h. $\hat{\sigma}_d$ dihedral – vertical that bisects adjacent C_2 axes (\perp principle axis)
- 3) Roto-reflection \hat{S}_n (improper rotation)
 - a. $\hat{S}_n = \hat{\sigma}_n \hat{C}_n$, rotation clockwise by $\frac{2\pi}{n}$ followed by reflection
 - b. $\hat{S}_1 = \hat{\sigma}_1$



- 4) Inversion \hat{i}
 - a. Reflection through origin
 - b. $x, y, z \Rightarrow -x, -y, -z$
 - c. Center of symmetry or centre of measure
 - d. The center is the point corresponding to origin
 - e. $\hat{i} = \hat{S}_2 = \hat{\sigma}_h \hat{C}_2$



Examples



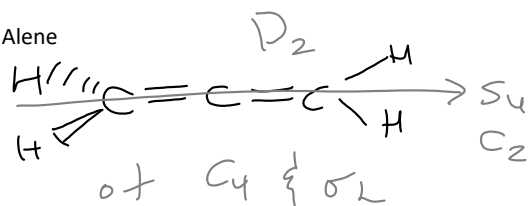
The available operations on this molecule are

$\hat{E}, \hat{C}_3, \hat{C}_3^2, \sigma_v', \sigma_v'', \sigma_v'''$

Alene



Alene



Perturbation Theory

Thursday, January 28, 2016 11:06 AM

Perturbation Theory in QM

In linear spectroscopy, the EM field can be treated as a weak perturbation on the Hamiltonian of a molecule

Time independent Perturbation

Some \hat{H}_o for which we know

$$\hat{H}_o |\psi_n^{(o)}\rangle = E_n^{(o)} |\psi_n^{(o)}\rangle$$

$$\hat{H} = \hat{H}_o + \lambda \hat{H}'$$

The problem is the sum of 2 terms. The latter is small compared to the unperturbed Hamiltonian

Here λ is a unitless book keeping parameter

$\lambda \rightarrow 0$ for unperturbed problem

$\lambda \rightarrow 1$ for problem

Call the solution to the full problem

$$\hat{H} |\psi_n^{(o)}\rangle = E_n^{(o)} |\psi_n^{(o)}\rangle$$

Assume the solution can be expanded in a series of progressively smaller terms

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots + \lambda^m |\psi_n^{(m)}\rangle$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots + \lambda^m E_n^{(m)}$$

The first order correction to the energy eigen values are

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = H'_{nn}$$

$$\begin{aligned} |\psi_n^{(1)}\rangle &= \sum_{j \neq i} \frac{\langle \psi_j^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle \\ &= \sum_{j \neq i} \frac{H'_{ij}}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle \end{aligned}$$

The has to be modified in the case of degeneracy

Example Anharmonic oscillator

$$\hat{H}_{vib} = \frac{p^2}{2\mu} + \frac{1}{2} kx^2$$

$$H'_{anharmonic} = \frac{1}{3!} \gamma_5 x^3 + \frac{1}{4!} \gamma_6 x^4$$

2) Time dependent perturbation theory

a. General case

- Important for time dependent phenomena like transitions

3) $H = H_o + H'(t)$, where H_o is time independent

To include the time dependent schrodinger equation

$$H|\Psi\rangle = i\hbar \partial_t |\Psi\rangle$$

$$H_0 |\psi_i^{(0)}\rangle = E_i^{(0)} |\psi_i^{(0)}\rangle$$

$$|\Psi_i^0\rangle = |\psi_i^0\rangle e^{-i\frac{E_i^0}{\hbar}t}$$

$$|\Phi\rangle = \sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t} |\psi_n\rangle$$

$$\begin{aligned} H|\Phi\rangle &= \sum_n c_n(t) e^{-i\left(\frac{E_n}{\hbar}\right)t} (H + H') |n\rangle \\ &= i\hbar \sum_n \partial_t c_n e^{-i\frac{E_n}{\hbar}t} |n\rangle \end{aligned}$$

$$\langle m|H|\Phi\rangle = i\hbar \sum_n \partial_t c_n e^{-i\frac{E_n}{\hbar}t} \langle m|n\rangle = \sum_n c_n(t) e^{-i\left(\frac{E_n}{\hbar}\right)t} (H_{mn} + H'_{mn})$$

$$\langle m|n\rangle = \delta_{mn}$$

$$\langle m|H_0|n\rangle = E_{mn}\delta_{mn}$$

$$\langle m|H'(t)|n\rangle = V_{mn}(t)$$

$$E_m c_m(t) e^{-i\frac{E_m}{\hbar}t} + \sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t} V_{mn}(t) = i\hbar (\partial_t c_m) e^{-i\frac{E_m}{\hbar}t} + i\hbar \left(-\frac{iE_m}{\hbar}\right) e^{-i\frac{E_m}{\hbar}t} c_m(t)$$

$$\sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t} V_{mn}(t) = i\hbar (\partial_t c_m) e^{-i\frac{E_m}{\hbar}t}$$

$$\frac{d}{dt} c_m(t) = -\frac{i}{\hbar} \sum_n c_n(t) e^{-i\frac{\omega_{mn}}{\hbar}t} V_{mn}(t)$$

$$\hbar\omega_{mn} = E_m - E_n = -\omega_{nm}\hbar$$

B) First Order Approximation

Assume an initial state $C_n(t=0)\delta_{ni}$

Put constant value(s) on RHS

$$C_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' e^{i\omega_{fi}t'} V_{fi}(t')$$

$$|c_f(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{mn}t'} V_{mn}(t') dt' \right|^2$$

$$v_{fi}(t) = V_{fi} \cos(\omega t)$$

e.g. EM waves

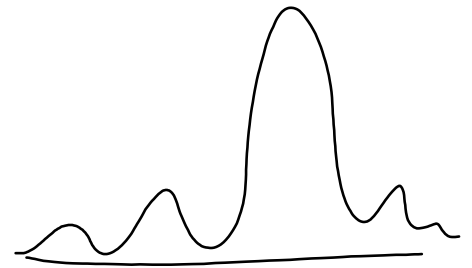
$$V_{fi}(t) = V_{fi} \delta(t - t_i) \text{ eg collisions}$$

Harmonic Perturbations

First order result

$$c_f(t) = -\frac{i}{\hbar} \frac{V_{fi}}{2} \int_0^t e^{i\omega_{fi}t'} (e^{i\omega t} + e^{-i\omega t}) dt'$$

$$P_{fi}(t) = |c_f|^2 = \frac{4|V_{fi}|^2}{\hbar^2(\omega_{fi} - \omega)^2} \sin^2\left(\frac{1}{2}(\omega_{fi} - \omega)t\right), \text{ sinc function}$$



States in a range ΔE

$$\Delta E = \hbar(\omega_{if} - \omega) < \frac{2\pi}{t} \hbar \text{ will be populated after } t \text{ seconds}$$

Constant with energy time uncertainty

C) Limits:

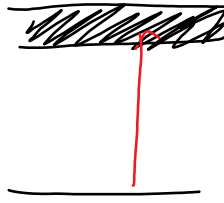
At long times

$$P_{if} \Rightarrow \frac{2\pi}{\hbar^2} t |V_{fi}|^2 \delta(\omega_{if} \neq \omega) \Leftarrow \text{energy conservation bohrrate}$$

D) Transition rate $= W_{if} = \frac{P_{if}}{t}$

At short times $P_{if} = \frac{|V_{if}|^2}{\hbar^2} t^2$

The transition rate from i to the band of width dE at E_f



$$g(E) dE = dN$$

density of states

$$W_{if} = \frac{2\pi}{\hbar} g(E_f) |V_{fi}|^2 \Leftarrow \text{very useful in general}$$

Electromagnetic waves as a perturbation

1) Maxwell equations govern the E and B fields

2) In free space

a. $\vec{\nabla} \cdot \mathbf{E} = 0$

b. $\nabla \cdot \mathbf{B} = 0$

c. $\nabla \times \mathbf{E} = \partial_t \mathbf{B}$

d. $\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}$

3) The solutions of the Electric and Magnetic fields are not independent

4) Refer to notes in EM 2

Potentials

In electrostatics it is well known that E can be considered to arise from electrostatic potential

$$\mathbf{E} = -\nabla \phi$$

$$e\phi = V$$

Point charge

$$\phi = \frac{ke}{r}$$

Similarly in magnetostatics

$\mathbf{B} = \nabla \times \mathbf{A}$ where A is the vector potential

Instead of E and B we can use ϕ & A

We need to generalize when there is a time dependence

$$\vec{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}$$

Nonuniqueness of Potentials

$$\phi_o = \phi_a + \text{constant}$$

gives the same E field

$$\phi \rightarrow \phi - \partial_t f$$

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla f$$

$$(\nabla \times \nabla f) \equiv 0$$

f is the gauge and we are free to choose it so (this is called the gauge freedom)

Use this to simplify the math

In free space, we can choose f to make $\phi = 0$

This leads (via Maxwell equation) to

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial A}{\partial t} = 0$$

EM and Quantum

Tuesday, February 2, 2016 11:03 AM

Magnetic Vector Potential \vec{A} for a wave equation is

$$A(r, t) = A_o e^{i(kr - \omega t)}$$

$$k = |k| = \frac{2\pi}{\lambda} = \frac{\omega}{c} \text{ wave vector}$$

In free space, the fields are

$$E = -\frac{\partial A}{\partial t} = -\omega A_o \sin(kr - \omega t), E \text{ and } A \text{ are parallel}$$

$$B = \nabla \times A = -(k \times A_o) \sin(kr - \omega t)$$

$$|E_o| = \omega A_o$$

$$|B_o| = k A_o = \frac{\omega}{c} A_o = \frac{E_o}{c}$$

Total average energy density

$$U = \frac{1}{2} \epsilon_o E_o^2 \left\{ \frac{\text{energy}}{\text{volume}} \right\}$$

$$I = Uc = \frac{1}{2} \epsilon_o E_o^2 c \left\{ \frac{\text{power}}{\text{area}} \right\}$$

Poynting Vector

$$S = \frac{1}{\mu_o} E \times B$$

The effect of EM fields on a charge particle

E causes a force on a charge q

$$F = ma = qE$$

The magnetic contribution results in

$$F = q(E + v \times B) = \frac{dp}{dt}$$

To include these interactions in QM we replace the momentum

$$\vec{p} = -i\hbar \vec{\nabla} \text{ by the canonical momentum}$$

$$\vec{p} \Rightarrow \vec{p} - q\vec{A}$$

Make this substitution, has units of kg m/s

$$\begin{aligned} H = T + V &= \frac{p^2}{2m} + V = \frac{(p - qA)^2}{2m} + V \\ &= \frac{1}{2m} (-i\hbar \vec{\nabla} - qA)^2 + V \\ &= -\frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar}{2m} q(\nabla \cdot A + A \cdot \nabla) + \frac{q^2}{2m} A^2 + V \\ \nabla \cdot A &= \partial_x A_x + \partial_y A_y + \partial_z A_z \\ A \cdot \nabla &= A_x \partial_x + A_y \partial_y + A_z \partial_z \end{aligned}$$

b) Weak Fields

Linear spectroscopy, the EM waves are weak compared to internal E field in atom and molecules in this case neglect

$$A \cdot A \approx 0$$

Not valid when they are intense, for example a focused laser beam

Can result in non linear effects

One can further specify the gauge (beyond $\psi = \varphi = 0$)

$$\vec{\nabla} \cdot A \psi + A \cdot \nabla \psi = 2A \cdot \nabla \psi$$

Coulomb Gauge

The full hamiltonian is the

$$H = H_o + H'$$

$$H_o = -\frac{\hbar^2}{2m} \nabla^2 + V \text{ (no EM field)}$$

$$H'(t) = -\frac{q}{m} A \cdot p = \frac{iq\hbar}{m} A(t) \cdot \nabla \Leftarrow \text{this is time dependent}$$

$$A = A_o \cos(kr - \omega t) = \text{Re}(e^{i(kr - \omega t)})$$

H' is a small harmonic time dependent perturbation

On H_o We can use perturbation theory

C) The long wavelength (molecular) limit

The size of a molecule $\sim 1nm$ is typically much smaller than λ ,

The wavelength is $\lambda > 100nm$

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{c}, \quad kr = \frac{2\pi r}{\lambda} \ll 1$$

Taylor series

$$e^{ikr} = 1 + ikr + \frac{1}{2!}(ikr)^2 + \dots$$

$$\text{here } H'(t) = \frac{iq\hbar}{m} 2\text{Re}[e^{i\omega t}] A_o(t) \cdot \nabla$$

$$\begin{aligned} A_o \parallel z \\ &= \frac{iq\hbar}{m} A_{oz} 2\text{Re}[e^{-i\omega t}] \frac{\partial}{\partial z} \\ V_{fi} &= \langle f | H'(t) | i \rangle \end{aligned}$$

$$H' = g(t) \frac{\partial}{\partial z} = g(t) \frac{p_z}{-i\hbar}$$

$$V_{fi} = \frac{ig(t)}{\hbar} \langle f | p_z | i \rangle$$

$$\begin{aligned}\langle f|p_z|i\rangle &= \frac{im}{\hbar} \langle f|[H_o, z]|i\rangle = \frac{im}{\hbar} \langle f|H_o z - z H_o|i\rangle \\ &= \frac{im}{\hbar} (E_f - E_i) \langle f|z|i\rangle \\ \text{By definition } \mu_{ez} &= -ez, \text{ the electric dipole moment} \\ \langle f|p_z|i\rangle &= im \frac{\omega_{fi}}{-e} \langle f|\mu|i\rangle\end{aligned}$$

Electric dipole moment transition matrix element

$$\begin{aligned}V_{fi}(t) &= -\frac{e}{m} 2\text{Re}[e^{-i\omega t}] \langle f|A_o \cdot p|i\rangle \\ &= i\omega_{fi} z \text{Re}[e^{i\omega t}] \langle f|A_o \cdot \mu|i\rangle \\ &= -i\omega_{fi} (e^{i\omega t} + e^{-i\omega t}) (\mu_{fi} \cdot E_o), \quad \mu_{fi} = \langle f|\mu|i\rangle\end{aligned}$$

This H' describes the electric dipole transition $E1$

EL is electric 2^L fold

ML is magnetic 2^L fold

Higher order terms

$e^{ikr} = 1 + ikr \leftarrow$ use this extra term

$$H' = \left\langle f \left| y \frac{d}{dz} \right| i \right\rangle$$

$$\begin{aligned}\frac{1}{2} \left(\left\langle f \left| y \frac{d}{dz} - z \frac{\partial}{\partial y} \right| i \right\rangle + \left\langle f \left| y \frac{d}{dz} + z \frac{\partial}{\partial y} \right| i \right\rangle \right), \quad L = r \times p \\ = \frac{i}{2\hbar} \langle f|L_x|i\rangle - \frac{m\omega}{\hbar} \langle f|z_y|i\rangle\end{aligned}$$

The first term is related to magnetic dipole moment, M transitions

The 2nd term corresponds to the electric quadrupole moment E2

Can apply all the formulas to a time dependent perturbation theory

$$P_{if} = \frac{\sin^2\left(\frac{1}{2}(\omega_f - \omega)t\right)}{(\omega_f - \omega)^2}, \text{ for monochromatic light}$$

$$\int_{-\infty}^{\infty} P_{if}(\omega) g(\omega) d\omega = \frac{|V_{if}|^2}{\hbar^2} g(\omega_{fi}) \text{ in long time limit}$$

Now we know that we need matrix elements like

$\langle f|\mu|i\rangle$ to describe a spectroscopy experiment

But symmetry considerations are useful to understand why in some cases

$\langle f|\mu|i\rangle = 0$, indentionally

Can either use brute force or use symmetry

To predict zeros $\langle f|\mu|i\rangle$ we need a systematic account of symmetry

Group theory

Recall symmetry operations

- Mechanical operations that result in an identical operation or indistinguishable configuration

Recall 5 types

E, i, σ, C_n, S_n we will see that the two sets of symmetry operations form a group

A set of elements $\{A, B, C, \dots\}$

Together with a product operation that associates uniquely 1 element to one of the objects in the set with every ordered pair of elements

$AB = C$

Is a group provided

- 1) Closure
 - a. every AB is in the group
- 2) Associativity
 - a. $(PQ)R = P(QR)$ $\forall P, Q, R$ in group
- 3) Identity element called e
 - a. $\forall S \quad S R = S$ in group
 - b. $ER = R$
- 4) $\forall R$ in the group there is an inverse R^{-1}
 - a. $RR^{-1} = R^{-1}R = E$

Some groups have a finite number of elements. Finite groups

The number of elements is the order of the group, h

The product operation may or may not be commutative

$AB=BA$ is commutative for all members, this group is ABELIAN

Point groups

Groups whose elements are the point symmetry operations of a rigid body

The group product is just a sequential operation

AB do B then A, ie, order matters

Generally noncommutative

For most molecules, point symmetry group is finite so it has some number of order associated with it

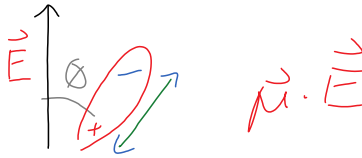
Exception: very high symmetry molecules such as atoms and linear molecules

Example

Called $C_{3v}(NH_3)$

$\{E, C_3, C_3^{-1}, \sigma_v, \sigma_v'', \sigma_v'''\}, h = 6$

full structure of group is given by an $h \times h$ ordered square matrix



Quantum theory by david Bohm

forall
C

Electromagnetism

Tuesday, January 5, 2016 10:04 AM

Light from that of conventional light source composed of EM waves of many wavelengths/frequencies

- Visible light ranges from 400nm to 700nm
- a dispersive optical element: prism or diffraction grating that decomposes EM radiation into its various k contribution
- spectroscopy is an experimental science for decomposing light into its components and interacting them with matter
- this is further generalized masses \Rightarrow mass spectroscopy

Here we will study traditional spectroscopy (light)

Quantum mechanics provides theoretical frame for interpreting spectra

Draw photon absorption and spontaneous emission

Historically

Newton "Opticks" (1666) prism could separate light

Fraunhofer improved glassmaking and optical instrumentation

- This proved to increase resolution

This revealed many features or spectra that had no classical interpretation

| Spectroscopy | Quantum Mechanics |
|--|---|
| <ul style="list-style-type: none">• Experimental• Light sources<ul style="list-style-type: none">◦ Optics◦ Detectors• Gas phase | <ul style="list-style-type: none">• Electrical• Rotational• Vibrational• Sharply defined energy levels With a particular structure |

Application

- 1) Characteristic spectra for qualitative and quantitative analysis
- 2) Detailed high resolution spectroscopy
 - a. Gas phase
 - b. Gives information about structure
 - i. Bond length
 - ii. Bond angles
- 3) Time resolution
 - a. Kinetic phenomenon
 - b. Reaction kinetics
- 4) Remote sensing
 - a. b/c light interacts relatively weakly w/ matter can study systems at a distance
 - i. Atomic gases
 - ii. Interstellar gases

Reflection and refraction of EM radiation

In a medium speed of light $c = \frac{c_0}{n}$

The frequency $\Rightarrow v = v_o \Rightarrow \text{wavelength } \lambda = \frac{\lambda_o}{n}$

Geometric Optics

Ray tracing lines corresponds to the propagation direction of the wave

Reflection

$$\theta_{inc} = \theta_{refl}$$

Snell's Law

$$n_1 \sin \theta_{inc} = n_2 \sin \theta_{trans}$$

Polarization and Reflection correlation

-reflectivity is dependent on the polarization of the wave

P polarized for along plane perpendicular to surface

S polarized for along plane parallel to surface

Fresnel Equation (1818)

$$R_s = \left| \frac{n_1 \cos \theta_{inc} - n_2 \cos \theta_t}{n_1 \cos \theta_{inc} + n_2 \cos \theta_t} \right|^2$$

$$R_p = \left| \frac{n_1 \cos \theta_t - n_2 \cos \theta_{inc}}{n_1 \cos \theta_t + n_2 \cos \theta_{inc}} \right|^2$$

$$\text{At } \theta_{inc} = \theta_{tra} = 0$$

$$R = R_s = R_p = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$$

$$R(n_1 = 1, n_2 = 1.5) \approx 4\%$$

Google total reflection

When $n_1 > n_2$ there exists optical angles above which

$$R_s, R_p = 1$$

-Total internal reflection

Brewsters Angle

$$\theta_t + \theta_{inc} = \frac{\pi}{2}$$

$$R_p \Rightarrow 0, T_p = 1$$

We get $R_{reflect} = 0$ and $T = 1$

Total transmittance

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right), \quad n_1 = 1, n_2 = 1.5 \quad \theta_B = 56.3^\circ$$

Mostly P polarized

Dispersion: $n = n(\lambda)$

In visible range, $n(\text{blue}) > n(\text{red}) > 1$

$$n^2(\lambda) = 1 + \sum_i \frac{B_i \lambda^2}{\lambda^2 - C_i}$$

Where B_i and C_i are tabulated for each material

Radiation Density and Light Intensity

Volume Density of energy in light waves

ρ has units of $\frac{J}{m^3}$

-spectrally resolved

$\rho(v) = \rho$ in range $v, v + dv$

$$\rho(v) \Rightarrow \frac{J}{m^3 Hz} \Rightarrow \rho = \int_0^\infty \rho(v) dv$$

Intensity of Light

Irradiance

I works in units of $\frac{W}{m^2}$

Spectrally resolved Irradiance I has units of $\frac{W}{m^2 Hz} = \frac{W}{m^2} s$

$$I = \int_0^\infty dv I(v)$$

Flux of photons

The number of photons flowing

$$F = \frac{I(v)}{hv} = \Phi \Rightarrow \frac{1}{m^2 s} \left(\frac{1}{Hz} \right)$$

Relations

$$I(v) = \rho(v)c = \rho(v) \frac{c_0}{n}$$

$$\rho(v) = \frac{1}{2} \epsilon_0 E^2$$

$E = |\vec{E}_0| = \text{electric field amplitude of the light waves}$

$$I(v) = \frac{1}{2} \epsilon_0 E^2 c = \langle S \rangle$$

Example: 1 watt laser beam with 1mm diameter

$$\text{Then the } I = 1.3 \times 10^6 \frac{W}{m^2}$$

$$E_{field} \Rightarrow E = 27.4 \sqrt{I} = 3.1 \times 10^4 \frac{V}{m}$$

Absorption and Emission

-Basic general consideration that yield important and useful results

Consider a two level system

We need to consider 3 process, absorption, emission and stimulated emission

$$\text{Absorption rate} = N_1 B_{12} \rho(v)$$

$$\text{Emission rate} = N_2 A_{21}$$

$$\text{Stimulated Emission rate} = N_2 B_{21} \rho(v)$$

Can also polarized light with molecules that are aligned in a certain direction

Planck distribution

The distribution of the radiation

Boltzmann (thermal equilibrium)

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{E_2-E_1}{k_b T}} = \frac{g_2}{g_1} e^{-\frac{h\nu}{k_b T}}$$

Without radiation ($\rho(\nu) = 0$)

$$\frac{dN_2}{dt} = -A_{21}N_2$$

$$N_2(t) = N_2(0)e^{-A_{21}t}$$

$$\tau_{rad} = \frac{1}{A_{21}}$$

With radiation

Upward rate

$$W_{12} = N_1 B_{12} \rho(\nu)$$

Downward rate

$$W_{21} = N_2 B_{21} \rho(\nu) + N_2 A_{21}$$

In kinetic equilibrium

$$W_{12} = W_{21}$$

$$N_1 B_{12} \rho(\nu) = N_2 B_{21} \rho(\nu) + N_2 A_{21}$$

$$\rho(\nu) = \frac{A_{21} N_2}{N_1 B_{12} - N_2 B_{21}} = \frac{A_{21}}{\frac{N_1}{N_2} B_{12} - B_{21}}$$

$$\rho(\nu) = \frac{A_{21}}{\frac{g_1}{g_2} e^{\frac{h\nu}{k_b T}} B_{12} - B_{21}}$$

$\rho(\nu)$ must also be equal to the Planck distribution in thermal equilibrium

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_b T}} - 1} = \frac{A_{21}}{\frac{g_1}{g_2} e^{\frac{h\nu}{k_b T}} B_{12} - B_{21}}$$

$$g_1 B_{12} = g_2 B_{21}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h \nu^3}{c^3}$$

For higher frequency $\nu \Rightarrow$ spontaneous radiation is more important

For lower frequency $\nu \Rightarrow$ stimulated radiation becomes more important

Transition Dipole Moment

$$\vec{\mu}_{mn} = \int \psi_m^* \hat{\mu} \psi_n$$

Where $\hat{\mu}$ is the dipole moment operator

$$\vec{\mu} = \sum q_i \vec{r}_i$$

For atoms and molecules, the transition rates are dependent on this quantity by μ_{mn}

Other processes

Eg involving magnetic dipole moment operator or electric quadrupole moment
 In NMR its purely magnetic dipole moments
 Gamma ray is due to nuclear excitation, can be due to electric quadrupole and magnetic moments etc

To a good approximation

$$B_{12}^v = \frac{1}{g_1} \frac{2\pi^2}{3\epsilon_0 h^2} (\mu_{21})^2$$

$$A_{21} = \frac{1}{g_2} \frac{16\pi^3 \nu^3}{3\epsilon_0 h c^3} (\mu_{21})^2$$

Beer's Law

Absorption of light by macroscopic amount of matter

Assume Spontaneous Emission A_{21} is negligible

$$\frac{dN_2}{dt} = -B_{21}N_2\rho(\nu) + B_{12}N_1\rho(\nu)$$

$$= B_{12} \left(\frac{h\nu}{c} \right) \left(N_1 - \frac{g_1}{g_2} N_2 \right) F(\nu)$$

$$\rho(\nu) = \frac{h\nu}{c} F$$

Now transition rate is a function of frequency

$B_{12} = B_{21}(\nu) = B_{12}f(\nu - \nu_{12})$ spectral line shape,
 $f(\nu - \nu)$ can be any function that represents the peak shape

Define the ABSORPTION CROSS SECTION

$$\sigma[m^2] = B_{12} \frac{h\nu}{c} f(\nu - \nu_{12})$$

$$\frac{dN_2}{dt} = \sigma F \left(N_1 - \frac{g_1}{g_2} N_2 \right)$$

The change in the flux of photons in a thin slice dx

Some homogenous

sample

$$dF = -\frac{dN_2}{dt} dx = -\sigma F \left(N_1 - \frac{g_1}{g_2} N_2 \right) dx, \text{ solve this differential}$$

$$\ln \left(\frac{F}{F_0} \right) = \ln \left(\frac{I}{I_0} \right) = -\sigma \left(N_1 - \frac{g_1}{g_2} N_2 \right) l$$

assume $N_2 \approx 0$ ($N_2 \ll N_1$)

$$I = I_0 e^{-\sigma N_1 l} = I_0 10^{-\epsilon \cdot c \cdot l} = I_0 e^{-\alpha l}$$

ϵ is the molar absorption coefficient

α is the absorption coefficient

$$\alpha = \sigma N_1 = B_{12} \frac{h\nu}{c} f(\nu - \nu_{21}) N_1$$

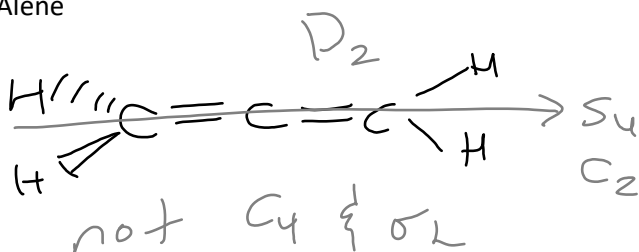
Lecture 5

Tuesday, January 19, 2016 11:03 AM

The available operations on this molecule are

$$\hat{E}, \hat{C}_3, \hat{C}_3^2, \sigma_v', \sigma_v'', \sigma_v'''$$

Alene

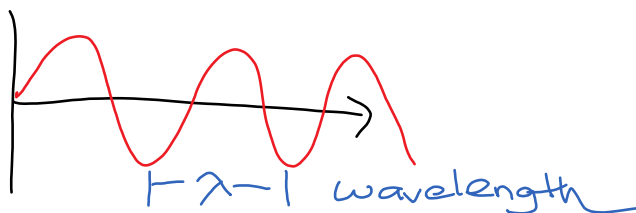


Electromagnetic radiation and Interaction with matter

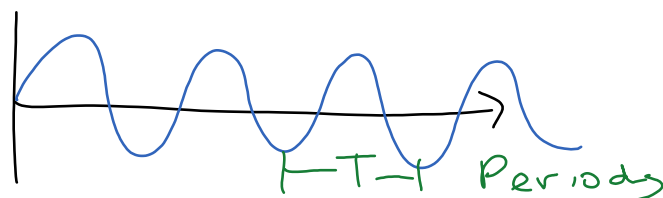
-Light is an EM wave

-Fields \vec{E} \vec{B} that pervade all space

Light in all forms is a wave excitation of these fields



At fixed x , the electric field oscillates as a function of time



$$v = \frac{1}{T} \Rightarrow, \quad \omega = 2\pi v = \frac{2\pi}{T}$$

For all waves

$\lambda v = \text{speed of propagation}$

For light $\lambda v = c = \text{speed of light}$

in vacuum $c = c_0 \approx 2.998 \times 10^8 \frac{\text{m}}{\text{s}}$

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i(\omega t - \vec{k} \cdot \vec{r})}$$

$$\vec{k} = \frac{2\pi}{\lambda} \frac{\langle a, b, c \rangle}{\sqrt{a^2 + b^2 + c^2}}$$

$$\vec{k} \cdot \vec{r} = k_x x + k_y y + k_z z$$

Unit Conversions of Plankk

$$E = h\nu = \hbar\omega = \frac{hc}{\lambda}$$

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda} = \frac{E}{hc} = \frac{\nu}{c} \text{ in the gigahertz range}$$

$$\tilde{\nu} = 1\text{cm}^{-1} \Rightarrow \nu = 30\text{GHz}$$

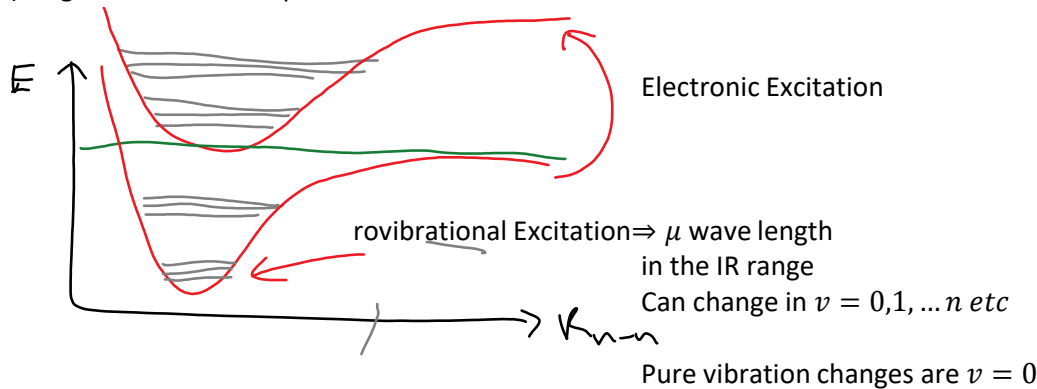
$$\lambda = 1\mu\text{m} \Rightarrow \tilde{\nu} = 10000\text{cm}^{-1}$$

$$1\text{eV} = 1.602 \times 10^{-19}\text{J}$$

$$1\mu\text{m} \Rightarrow 1.24\text{eV}$$

$$1\text{eV} \Rightarrow \tilde{\nu} = 80865.54\text{cm}^{-1}$$

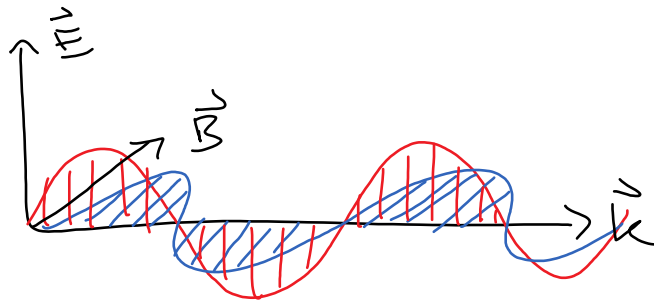
B) Light and molecular processes



Polarization of Light

Light is a purely transverse wave oscillation of \vec{E} and \vec{B} are \perp in direction of propagation

$$\vec{k} \cdot \vec{E} = 0, \vec{E} \cdot \vec{B} = 0, \vec{k} \cdot \vec{B} = 0$$



$$\vec{E} = E_0 \langle 0, 0, 1 \rangle e^{i(\omega t - \vec{k} \cdot \vec{r})}$$

$$\vec{B} = B_0 \langle 1, 0, 0 \rangle e^{i(\omega t - \vec{k} \cdot \vec{r})}, B_0 = \frac{E_0}{c}$$

Unpolarized light has no preferred electric field direction

2) Plane polarized light

a. Linearly polarized

b. \vec{E} is always in the same direction

3) More generally, the polarization can change direction, be in a mix state and out of phase

a.
$$\vec{E}(\vec{r}, t) = \frac{\langle E_x^*, E_y^*, 0 \rangle}{\sqrt{|E_x^*|^2 + |E_y^*|^2}} e^{i(\omega t - \vec{k} \cdot \vec{r})} \text{ where } \alpha \text{ and } \beta \text{ are complex numbers}$$

b. For circularly polarized light where α and β have a phase difference by $\pm \frac{\pi}{2}$ and are equal in magnitude $|E_x^*| = |E_y^*|$

c. elliptically polarized light $|E_x^*| \neq |E_y^*|$ with a phase difference of $\pm \frac{\pi}{2}$

4) D photons have spin 1

—L and R circularly polarized photons have spin S_z

$= \pm 1(\hbar)$ where z is propagation direction

There is no spin $s_z = 0$ since light is a transverse wave

Unpolarized light is a random statistical mixture of Left and Right polarized light
 Linearly polarized light is as linear combination of L and R polarized light
 Both these two cases have no net angular momentum

Propagation of Light

$$c = c_o \text{ in a vacuum}$$

$$= \frac{1}{\sqrt{\epsilon_o \mu_o}} \text{ in a vacuum}$$

$$= \frac{1}{\sqrt{\epsilon \mu}}$$

Define refractive index of material

$$n = \frac{c_o}{c} \geq 1$$

$$= \sqrt{\frac{\epsilon \mu}{\epsilon_o \mu_o}}$$

For nonmagnetic media

$$\mu \approx \mu_o$$

$$n \approx \sqrt{\frac{\epsilon}{\epsilon_o}} = \sqrt{\epsilon_r} \text{ the relative dielectric permativity}$$

Static \vec{E} or maybe low frequency

Only some of the polarizability of a material can respond to the high frequency of light

| | ϵ_r | $\mu_{mol}(D)$ |
|-----------|--------------|----------------|
| Vacuum | 1 | 1 |
| Benzene | 2.28 | 0 |
| Acetone | 20.7 | 2.88 |
| Formamide | 111.0 | 3.73 |
| | | |

Radiation

Thursday, January 21, 2016 11:01 AM

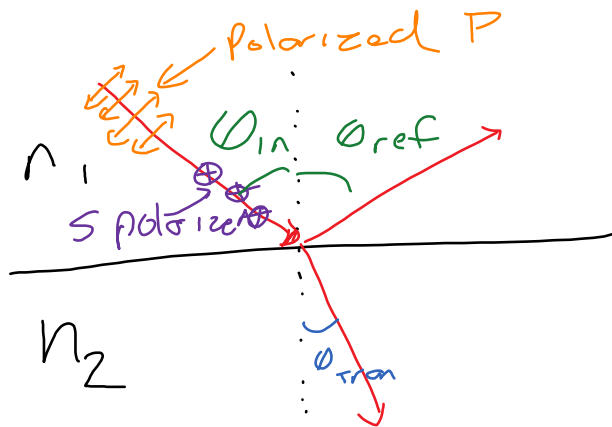
Reflection and refraction of EM radiation

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The frequency $\Rightarrow \nu = \nu_0 \Rightarrow \text{wavelength } \lambda = \frac{\lambda_0}{n}$

Geometric Optics

Ray tracing lines corresponds to the propagation direction of the wave



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P polarized for along plane perpendicular to surface

S polarized for along plane parallel to surface

Fresnel Equation (1818)

$$R_s = \left| \frac{n_1 \cos \theta_{inc} - n_2 \cos \theta_t}{n_1 \cos \theta_{inc} + n_2 \cos \theta_t} \right|^2$$

$$R_p = \left| \frac{n_1 \cos \theta_t - n_2 \cos \theta_{inc}}{n_1 \cos \theta_t + n_2 \cos \theta_{inc}} \right|^2$$

At $\theta_{inc} = \theta_{tra} = 0$

$$R = R_s = R_p = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$$

$$R(n_1 = 1, n_2 = 1.5) \approx 4\%$$

Google total reflection

When $n_1 > n_2$ there exists optical angles above which

$$R_s, R_p = 1$$

-Total internal reflection

Brewsters Angle

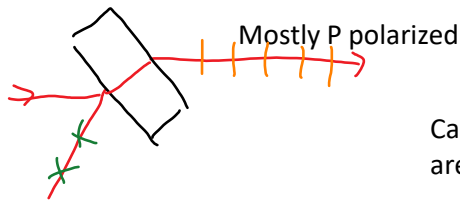
$$\theta_t + \theta_{inc} = \frac{\pi}{2}$$

$$R_p \Rightarrow 0, T_p = 1$$

We get $R_{reflect} = 0$ and $T = 1$

Total transmittance

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right), \quad n_1 = 1, n_2 = 1.5 \quad \theta_B = 56.3^\circ$$



Can also polarized light with molecules that are aligned in a certain direction

Dispersion: $n = n(\lambda)$

In visible range, $n(blue) > n(red) > 1$

$$n^2(\lambda) = 1 + \sum_i \frac{B_i \lambda^2}{\lambda^2 - C_i}$$

Where B_i and C_i are tabulated for each material

Radiation Density and Light Intensity

Volume Density of energy in light waves

ρ has units of $\frac{J}{m^3}$

-spectrally resolved

$\rho(v) = \rho$ in range $v, v + dv$

$$\rho(v) \Rightarrow \frac{J}{m^3 Hz} \Rightarrow \rho = \int_0^\infty \rho(v) dv$$

Intensity of Light

Irradiance

I works in units of $\frac{W}{m^2}$

Spectrally resolved Irradiance I has units of $\frac{W}{m^2 Hz} = \frac{W}{m^2} s$

$$I = \int_0^\infty dv I(v)$$

Flux of photons

The number of photons flowing

$$F = \frac{I(v)}{h\nu} = \Phi \Rightarrow \frac{1}{m^2 s} \left(\frac{1}{Hz} \right)$$

Relations

$$I(v) = \rho(v)c = \rho(v) \frac{c_0}{n}$$

$$\rho(\nu) = \frac{1}{2} \epsilon_0 E^2$$

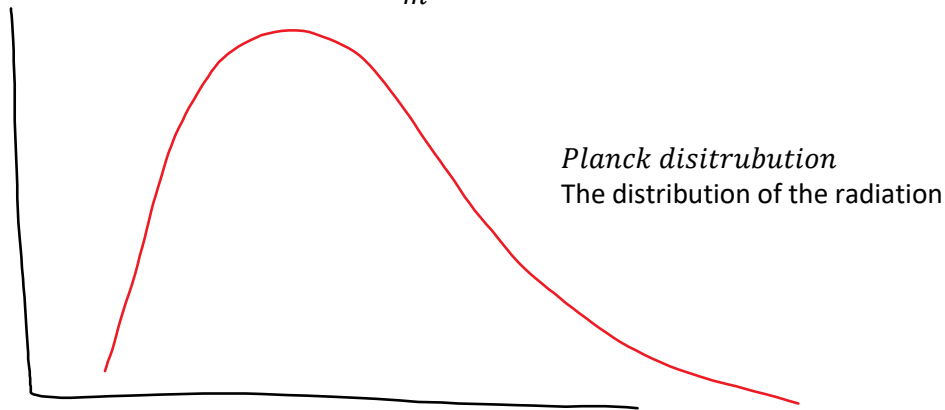
$E = |\vec{E}_0| = \text{electric field amplitude of the light waves}$

$$I(\nu) = \frac{1}{2} \epsilon_0 E^2 c = \langle S \rangle$$

Example: 1 watt laser beam with 1mm diameter

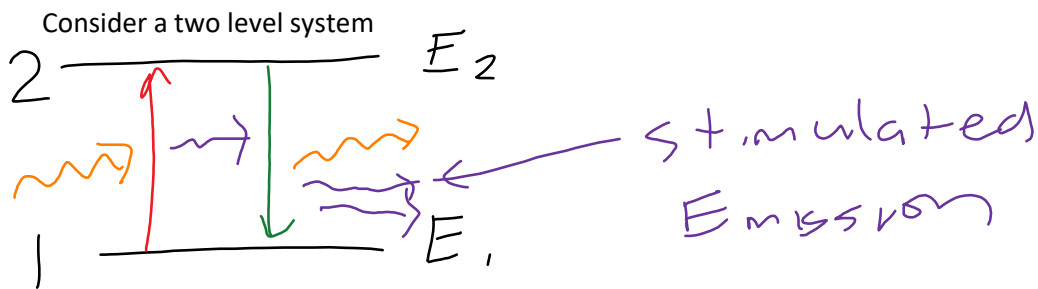
Then the $I = 1.3 \times 10^6 \frac{W}{m^2}$

$$E_{\text{field}} \Rightarrow E = 27.4 \sqrt{I} = 3.1 \times 10^4 \frac{V}{m}$$



Absorption and Emission

-Basic general consideration that yield important and useful results



We need to consider 3 process, absorption, emission and stimulated emission

$$\text{Absorption rate} = N_1 B_{12} \rho(\nu)$$

$$\text{Emission rate} = N_2 A_{21}$$

$$\text{Stimulated Emission rate} = N_2 B_{21} \rho(\nu)$$



Boltzmann (thermal equilibrium)

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{E_2-E_1}{k_b T}} = \frac{g_2}{g_1} e^{-\frac{h\nu}{k_b T}}$$

Without radiation ($\rho(\nu) = 0$)

$$\frac{dN_2}{dt} = -A_{21}N_2$$

$$N_2(t) = N_2(0)e^{-A_{21}t}$$

$$\tau_{rad} = \frac{1}{A_{21}}$$

With radiation

Upward rate

$$W_{12} = N_1 B_{12} \rho(\nu)$$

Downward rate

$$W_{21} = N_2 B_{21} \rho(\nu) + N_2 A_{21}$$

In kinetic equilibrium

$$W_{12} = W_{21}$$

$$N_1 B_{12} \rho(\nu) = N_2 B_{21} \rho(\nu) + N_2 A_{21}$$

$$\rho(\nu) = \frac{A_{21} N_2}{N_1 B_{12} - N_2 B_{21}} = \frac{A_{21}}{\frac{N_1}{N_2} B_{12} - B_{21}}$$

$$\rho(\nu) = \frac{A_{21}}{\frac{g_1}{g_2} e^{\frac{h\nu}{k_b T}} B_{12} - B_{21}}$$

$\rho(\nu)$ must also be equal to the planck distributn in thermal equilibrium

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_b T}} - 1} = \frac{A_{21}}{\frac{g_1}{g_2} e^{\frac{h\nu}{k_b T}} B_{12} - B_{21}}$$

$$g_1 B_{12} = g_2 B_{21}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

For higher frequency $\nu \Rightarrow$ spontaneous radiation is more important

For lower frequency $\nu \Rightarrow$ stimulated radiation becomes more important

Transition Dipole Moment

$$\vec{\mu}_{mn} = \int \psi_m^* \hat{\mu} \psi_n$$

Where $\hat{\mu}$ is the dipole moment operator

$$\vec{\mu} = \sum q_i \vec{r}_i$$

For atoms and molecules, the transition rates are dependent on this quantity by μ_{mn}

Other processes

Eg involving magnetic dipole moment operator or electric quadrupole moment

In NMR its purely magnetic dipole moments

Gamma ray is due to nuclear excitation, can be due to electric quadrupole and magnetic moments etc

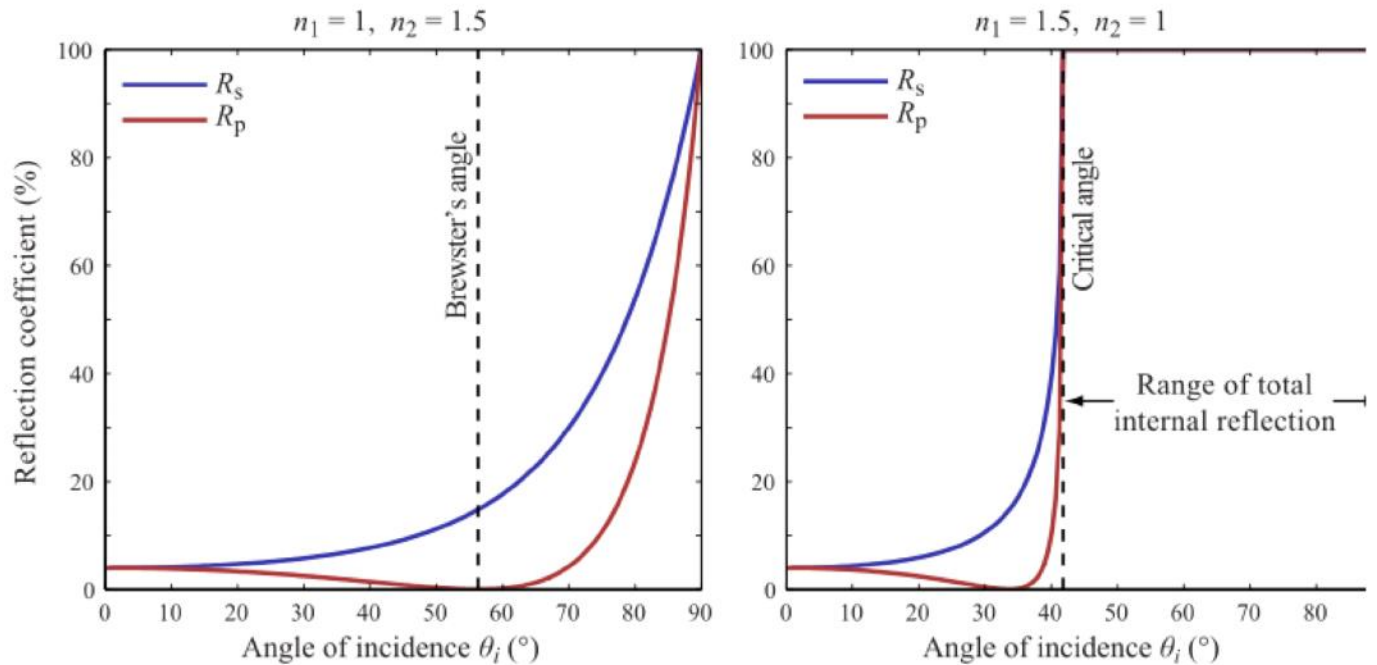
To a good approximation

$$B_{12}^v = \frac{1}{g_1} \frac{2\pi^2}{3\epsilon_o h^2} (\mu_{21})^2$$

$$A_{21} = \frac{1}{g_2} \frac{16\pi^3 v^3}{3\epsilon_o h c^3} (\mu_{21})^2$$

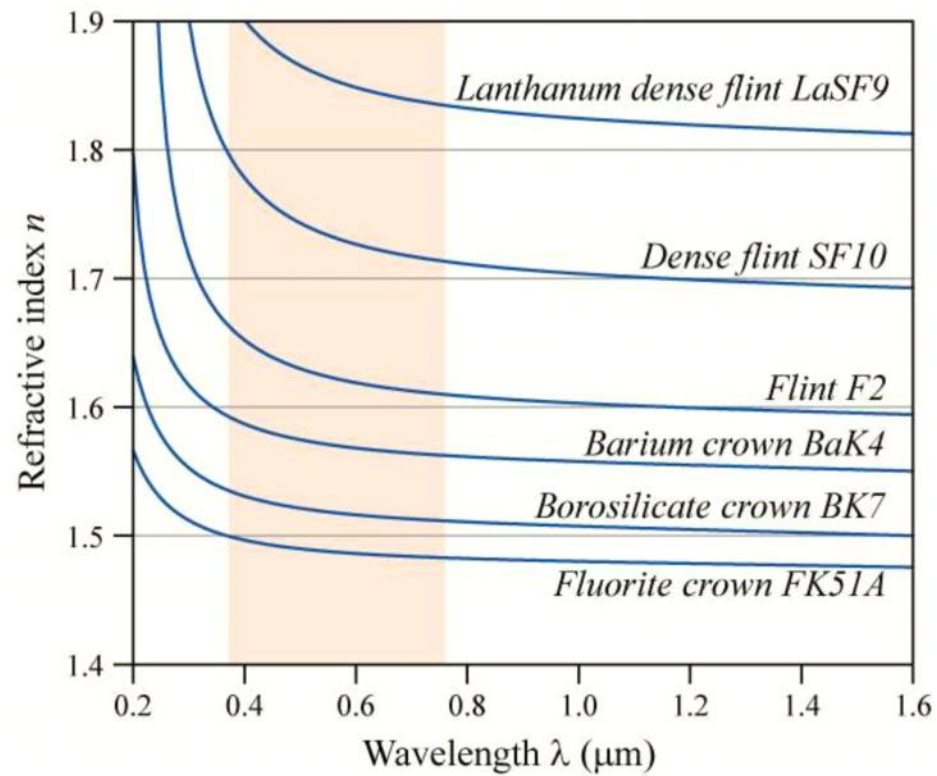
Optics

Fresnel Reflection



wikiped

Dispersion of Common Glasses



Printout

Friday, January 22, 2016 4:19 PM

Blackbody Spectrum

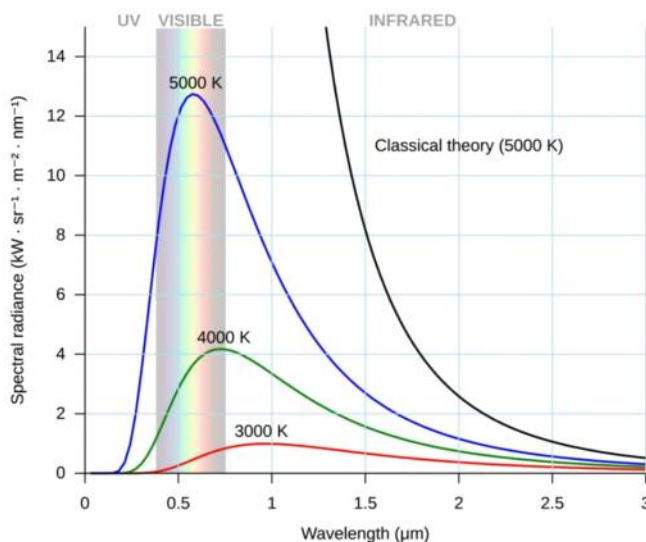


Figure 1: The Planck spectrum $(c/4)\rho(\lambda)$ at a few temperatures, graphic from wikipedia. The evident failure of the classical theory shown is called the “ultraviolet catastrophe”. Planck’s quantum solution to this catastrophe was one of the early indications that classical physics had to be revised to account for quantum discreteness.

The spectrum of electromagnetic radiation emitted by a blackbody (or contained in a closed cavity) held at absolute temperature T is given by the Planck spectrum,

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5 (e^{h\nu/kT} - 1)},$$

where $\nu = c/\lambda$. This is the photon energy per unit volume per unit wavelength of the radiation in SI in J/m³/m, here integrated over 4π sr. Matter cannot be isolated from the electromagnetic field which permeates all space, so this radiation is always present. It depends only on the temperature (and fundamental constants). It is plotted in Figure 1 for a few temperatures where it has appreciable intensity in the visible range. As a hot object’s temperature is increased, the peak of the spectrum sweeps through the visible, and the glow changes from red to white to blue. At room temperature, the entire spectrum is in the infrared range, λ longer than visible light. In this case, the Planck distribution is not zero in the visible range, it is just extremely small.

One can show generally,

$$\frac{c}{4} \int_0^\infty \rho(\lambda) d\lambda = \sigma T^4,$$

i.e. the Stefan-Boltzmann law with Stefan’s constant $\sigma = 5.670 \times 10^8 \text{ Wm}^{-2}\text{K}^{-4}$.

One can also easily show an equivalent distribution in frequency $\tilde{\rho}(\nu)$ by recognizing that the energy density in a small range of λ is the same as the energy density in the corresponding range of ν , i.e.

$$dE = \rho(\lambda)d\lambda = \tilde{\rho}(\nu)d\nu.$$

Spectral Data

Tuesday, January 26, 2016 11:02 AM

Line Profiles of Spectral Lines $f(v - v_{12})$

Emission and absorption is never perfectly monochromatic

Mathematically monochromatic: $\delta(v - v_{12})$

In practice each line has a shape or a profile characterized by a width

$\delta v = FWHM$

There is a resolution limit on the spectrum lines spaced apart by less than the width δv cannot be resolved

Source of linewidth

- natural lifetime of the states involved in the transition
 - doppler broadening
 - collisional broadening
- } gas phase

Common Lineshapes

Lorentian,
$$L(v - v_{12}) = \frac{1}{\pi} \frac{\Gamma/2}{(v - v_o)^2 + (\Gamma/2)^2}$$

peaked at v_o

Height = $\frac{2}{\pi\Gamma}$

FWHM = Γ

This is normalized

$$\int_{-\infty}^{\infty} L(v - v_{12}) dv = 1$$

Gaussian,
$$G(v - v_o) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(v-v_o)^2}{2\sigma^2}}$$

Height = $\frac{1}{\sigma\sqrt{2\pi}}$

FWHM = $2\sigma\sqrt{2 \ln 2}$

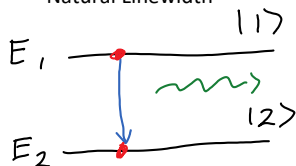
Also normalized

Voigt Profile

Convolution of the Gaussian and Lorentian

$$V(v - v_o) = \int_{-\infty}^{\infty} G(v)L(v - v') dv'$$

Natural Linewidth



Assume a molecule is at some excited state and loses energy by emitting a photon after an average lifetime of τ
 $\hbar\omega = E_1 - E_0$

If the initial state is $|1\rangle$, we will never have a transition/decay

$|initial\rangle = a_0|0\rangle + a_1|1\rangle$, this is the time independent probability of finding in states $|0\rangle$ is $|a_0|^2 = a_0^* a_0$

The time dependent

$$|initial(t)\rangle = a_0|0\rangle e^{-\frac{iE_0 t}{\hbar}} + a_1|1\rangle e^{-\frac{iE_1 t}{\hbar}}$$

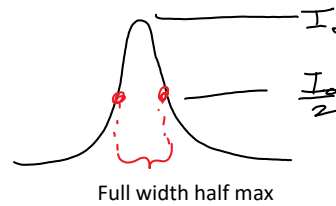
Calculate the electric dipole moment

$$\vec{M} = \langle init(t) | \vec{\mu} | init(t) \rangle = \mu_{10} (a_0^* a_1 e^{-i(\omega_{10})t} + a_1^* a_0 e^{-i(\omega_{10})t})$$

Here we have neglected $\mu_{00} = \langle 0 | \mu | 0 \rangle$, $\mu_{11} = \langle 1 | \mu | 1 \rangle$

$$\vec{M} = 2|a_0||a_1|\mu_{10} \cos(\omega_{10}t)$$

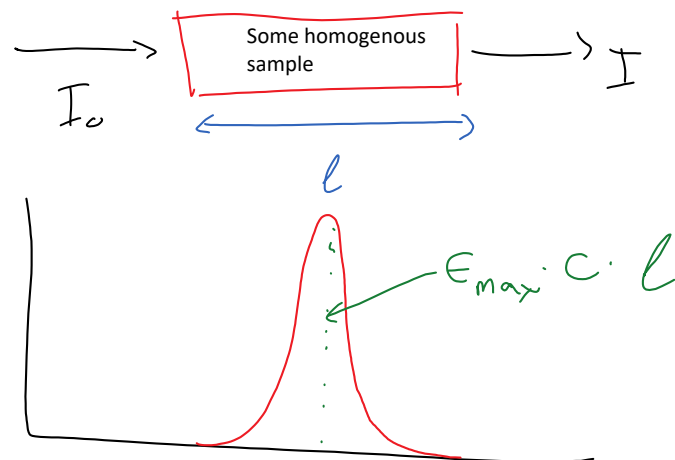
Natural Linewidth



Full width half max

Beer's Law

Absorption of light by macroscopic amount of matter



Assume Spontaneous Emission A_{21} is negligible

$$\begin{aligned} \frac{dN_2}{dt} &= -B_{21}N_2\rho(v) + B_{12}N_1\rho(v) \\ &= B_{12}\left(\frac{hv}{c}\right)\left(N_1 - \frac{g_1}{g_2}N_2\right)F(v) \end{aligned}$$

$$\rho(v) = \frac{hv}{c} F$$

Now transition rate is a function of frequency

$B_{12} = B_{21}(v) = B_{12}f(v - v_{12})$ spectral line shape, $f(v-v)$ can be any function that represents the peak shape

Define the ABSORPTION CROSS SECTION

$$\sigma[m^2] = B_{12}\frac{hv}{c} f(v - v_{12})$$

$$\frac{dN_2}{dt} = \sigma F \left(N_1 - \frac{g_1}{g_2}N_2\right)$$

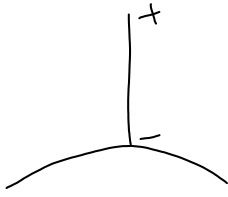
The change in the flux of photons in a thin slice dx



$$\vec{M} = 2|a_0||a_1|\mu_{10} \cos(\omega_{10}t)$$

Natural Linewidth

What we have described is not a transition but a coherent oscillation



An oscillating electric dipole is an antenna (classically) it should radiate waves

If the excited state "population" $|a_1|$ decays exponentially at a rate slow compared to $\frac{1}{\omega_{10}}$

We can approximate the energy radiation
 $a_1(t) = a_1(0)e^{-\frac{\gamma}{2}t}$

$$\vec{M} = M_0 e^{-\frac{\gamma}{2}t} \cos(\omega_{10}t)$$

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$

$$\begin{aligned} F(\omega) &= \int_{-\infty}^{\infty} e^{-\frac{\gamma}{2}t} \cos(\omega_{10}t) e^{-i\omega t} dt \\ &= \frac{1}{2} \int_{-\infty}^{\infty} e^{-\frac{\gamma}{2}t} (e^{i(\omega_{10}-\omega)t} + e^{-i(\omega_{10}+\omega)t}) dt \\ &= \frac{1}{2} \left[\frac{1}{\frac{\gamma}{2} + i(\omega - \omega_{10})} + \frac{1}{\frac{\gamma}{2} + i(\omega + \omega_{10})} \right] \\ &\approx \frac{1}{2} \left[\frac{1}{\frac{\gamma}{2} + i(\omega - \omega_{10})} \right], \end{aligned}$$

Classically the antenna would radiate power via $|\vec{\mu}_{10}(t)|$

$$|F(\omega)|^2 = \frac{1}{4} \frac{1}{\left[\left(\frac{\gamma}{2}\right)^2 + (\omega - \omega_{10})^2\right]} = \text{laurentian}$$

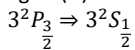
$$\Delta v_{\frac{1}{2}} = \frac{\gamma}{2\pi} = \frac{1}{2\pi\tau_{\text{spent}}}, \text{ from the exponential decay}$$

$$\Delta E \Delta t \geq \hbar$$

$$\Delta E \Delta t = \hbar$$

A measurement of the width is a measurement of the life time

Eg Na(D)

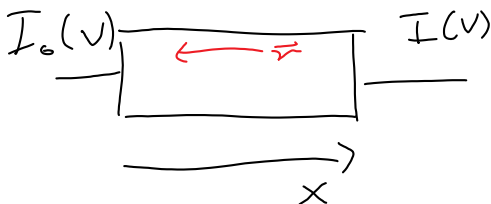


$$\tau = 16\text{ns}$$

$$\Delta v_{\frac{1}{2}} = 10\text{MHz}$$

If you measure homogenous lifetime broadened linewidth, you have measured $\tau_{\text{spontaneous}}$

Doppler broadening due to relativity



Due to distributions in velocity, there is going to be a distribution in frequency

u_x is velocity distribution of the gas molecules, atoms

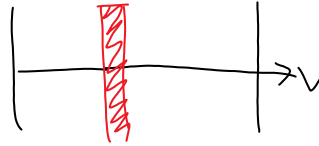
$$v = v_0 \left(1 + \frac{u_x}{c}\right) \text{ Doppler shift}$$

$$\text{Emission at } v_0 \left(1 + \frac{u_x}{c}\right)$$

Absorption at

$$u_x = \left(\frac{v - v_0}{v_0}\right) c$$

For a gas in thermal equilibrium at T, velocity is distributed according to the Maxwellian



$$dF = -\frac{dN_2}{dt} dx = -\sigma F \left(N_1 - \frac{g_1}{g_2} N_2\right) dx, \text{ solve this differential}$$

$$\ln\left(\frac{F}{F_0}\right) = \ln\left(\frac{I}{I_0}\right) = -\sigma \left(N_1 - \frac{g_1}{g_2} N_2\right) l$$

assume $N_2 \approx 0$ ($N_2 \ll N_1$)

$$I = I_0 e^{-\sigma N_1 l} = I_0 10^{-\epsilon \cdot c \cdot l} = I_0 e^{-\alpha l}$$

ϵ is the molar absorption coefficient

α is the absorption coefficient

$$\alpha = \sigma N_1 = B_{12} \frac{h\nu}{c} f(v - v_{21}) N_1$$

$\partial \bar{a}_x l$

$$n(u_x)du_x = \frac{N}{u^*\sqrt{\pi}} e^{-\left(\frac{u_x}{u^*}\right)^2} du_x$$

$$v^* = \sqrt{\frac{2k_B T}{m}}, \quad m \text{ is the molecular mass}$$

$$du_x = \frac{c}{v_o} dv$$

$$n(v)dv = \frac{Nc}{v^*v_o\sqrt{\pi}} e^{-\left[\left(\frac{c}{v^*}\right)\frac{v-v_o}{v_o}\right]^2} dv, \quad \text{this is}$$

Obtained from plugging in u_x and du_x into $n(u_x)du_x$

This whole transformation is still gaussian

$$f(v - v_o) = \frac{Nc}{v^*v_o\sqrt{\pi}} e^{-\left[\left(\frac{c}{v^*}\right)\frac{v-v_o}{v_o}\right]^2}$$

Lineshape

$$I(\omega) = I(\omega_o) e^{-\left[\left(\frac{c}{v^*}\right)\frac{\omega-\omega_o}{\omega_o}\right]^2} dv$$

$$FWHM = \delta\omega_o = 2\sqrt{\ln 2} \frac{\omega_o v^*}{c} = \frac{\omega_o}{c} \sqrt{\frac{8k_B T \ln 2}{m}}$$

$$\delta v_D = \frac{2v_o}{c} \sqrt{\frac{2RT \ln 2}{M}}, \quad M = mN_a$$

Na_2 molecules in vapor electronic transition at 500k

$$\delta v_o = 1.4 \text{GHz}$$

Collisional/ Pressure Broadening

-Several processes involved

- a) Intermolecular interaction shift electronic energy levels

As molecules collides, there is going to be some electronic interaction that causes shifts in energy levels up and down

This causes shift/broadening of the spectrum

- b) Inelastic collision

-shorten lifetime of the excited state

$$\frac{1}{\tau} = \frac{1}{\tau_{spont}} + \frac{1}{\tau_{inelastic}} = \frac{\tau_{spont} + \tau_{in}}{\tau_{spont}\tau_{in}}$$

- c) Elastic collision

Coherent oscillation can be randomized

Phenomenological Lorentian

$$I_o = \frac{\left(\left[\frac{\gamma + \gamma_{in}}{2}\right]^2 + Nu\sigma_o\right)^2}{(\omega - \omega_o - Nu\sigma)^2 + [\quad]^2}$$

The $Nu\sigma$ term can shift resonance

$$\gamma_{inelastic} = 1/\tau_{inelastic}$$

σ_b = broadening cross section

σ_s = shift cross section

roughly $FWHM = b \times p$, p is the partial pressure

$$b \approx \frac{10 \text{MHz}}{\text{torr}}$$

Group theory

Thursday, February 4, 2016 11:00 AM

Group theory
Recall symmetry operations
- Mechanical operations that result in an identical operations or indistinguishable configuration

Recall 5 types
 E, i, σ, C_n, S_n we will see that the two set of symmetry operations from a group
A set of elements $\{A, B, C, \dots\}$
Together with a product operation that associates uniquely 1 element to one of the objects in the set with every ordered pair of elements
 $AB = C$
Is a group provided
1) Closure
a. every AB is in the group
2) Associativity
a. $(PQ)R = P(QR)$ $\forall P, Q, R$ in group
3) Identity element called e
a. $\forall S \ S R = R$
b. $ER = RE = R$
4) $\forall R$ in the group there is an inverse R^{-1}
a. $RR^{-1} = R^{-1}R = E$

Some groups have a finite number of elements. Finite groups
The number of elements is the order of the group, h

The product operation may or may not be commutative
 $AB = BA$ is commutative for all members, this group is ABELIAN

B point groups
Groups whose elements are the point symmetry operations of a rigid body
The group product is just a sequential operation
 AB do B then A , ie, order matters

Generally noncommutative
For most molecules, point symmetry group is finite so it has some number of order associated with it
Exception: very high symmetry molecules such as atoms and linear molecules

Example
Called $C_{3v}(NH_3)$
 $\{E, C_3, C_3^{-1}, \sigma'_v, \sigma''_v, \sigma'''_v\}, h = 6$
full structure of group is given by an $h \times h$ ordered square matrix

Correction
$$U = \frac{1}{2} \epsilon_o E^2 + \frac{1}{2 \mu_o} B^2$$
$$u = \epsilon E^2$$

Concepts of Abstract Group Theory
These ideas aim to reveal the structure of groups
Many of these ideas rely on forming a group into subsets

The rows and columns of the multiplication table contains each element exactly once
Each row and columns is just a rearranged list of the elements

Cycles
For a finite group, if we have some element X we can construct a sequence
 $X, X^2, X^3 \dots X^N$
Due to finiteness, the sequence must reach the identity operator at some point
 $X^N = E$ for some n
The sequence then repeats or cycles
 N order of the elements

Subgroups
 G is a subgroup
If there is a subset of G , (contains E), that satisfies all properties of a group then it is a subgroup
 $\{E\}$ is a trivial subgroup of every group
 $\{X, X^2, \dots, X^{N-1}, E\}$ is a subgroup of G for every X in G . If it is the whole group then G is a cyclic group

symmetry operations are often cyclic
 $C_N^N = E, \sigma^2 = E, i^2 = E$
There are also non cyclic groups

Cosets
If G is a subgroup of \mathbb{G} and we consider any element $X \in \mathbb{G}$ but $X \notin G$ but $X \in G$
 XG and GX are left and right coset of X wrt \mathbb{G}

$g_1, g_2 \in G$
 $g_1 X = g_2$
 $X = g_1^{-1} g_2$, therefore $X \in G$
But we stated that $X \notin G$ so therefore there are no common elements in GX and G
ie that means g_2 is not a common element in GX

They are sets of g elements where g is the order G
Cosets are not subgroups
Cosets have no elements in G
They divide the remaining elements \mathbb{G}
The division is complete

Let G be the cyclic group Z_8 whose elements are
 $G = \{0, 2, 4, 6, 1, 3, 5, 7\}$
and whose group operation is addition modulo eight.
Its Cayley table is

| + | 0 | 2 | 4 | 6 | 1 | 3 | 5 | 7 |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 2 | 4 | 6 | 1 | 3 | 5 | 7 |
| 2 | 2 | 4 | 6 | 0 | 3 | 5 | 7 | 1 |
| 4 | 4 | 6 | 0 | 2 | 5 | 7 | 1 | 3 |
| 6 | 6 | 0 | 2 | 4 | 7 | 1 | 3 | 5 |
| 1 | 1 | 3 | 5 | 7 | 2 | 4 | 6 | 0 |
| 3 | 3 | 5 | 7 | 1 | 4 | 6 | 0 | 2 |
| 5 | 5 | 7 | 1 | 3 | 6 | 0 | 2 | 4 |
| 7 | 7 | 1 | 3 | 5 | 0 | 2 | 4 | 6 |

This group has two nontrivial subgroups: $J = \{0, 4\}$ and $H = \{0, 2, 4, 6\}$, where J is also a subgroup of H . The Cayley table for H is the top-left quadrant of the Cayley table for G . The group G is cyclic, and so are its subgroups. In general, subgroups of cyclic groups are also cyclic.

Abelian group is a set A whose elements a_1, a_2, \dots, a_n when operating on each other, form another element in the group

Closure
For all a, b in A , the result of the operation $a \bullet b$ is also in A .

Associativity
For all a, b and c in A , the equation $(a \bullet b) \bullet c = a \bullet (b \bullet c)$ holds.

Identity element
There exists an element e in A , such that for all elements a in A , the equation $e \bullet a = a \bullet e = a$ holds.

Inverse element
For each a in A , there exists an element b in A such that $a \bullet b = b \bullet a = e$, where e is the identity element.

Commutativity
For all a, b in A , $a \bullet b = b \bullet a$.

If XG and YG are 2 left Cosets then $XG=YG$ or XG and YG have no elements in common

$$g_1X = g_2Y \text{ with } g_1, g_2 \in G$$

$$XY^{-1} = g_1^{-1}g_2 \Rightarrow XY^{-1} \in G$$

$$GXY^{-1} = G$$

$GX = GY$ or no elements in common

The order of a subgroup G , g must be an integral division of the order of G , h

Ie $l = \frac{h}{g}$, must be an integer called the index of G in G

Examples

| H | Groups |
|-----------|--|
| 1 | $\{E\}$ |
| 2 | $\{A, A^2 = E\}$ |
| 3 | $\{A, A^2, A^3 = E\}$ |
| 4 | $\{A, A^2, A^3, A^4 = E\}$ Vierengruppe: abelian not cyclic 3 orthogonal C_2 axes rotation |
| Any prime | Group is a cyclic or abelian |
| $n!$ | One group is the permutation group no objects and can reorder them |

Conjugation and Classes

An element of a group B is a conjugate to A

$$B = XAX^{-1} \text{ or } A = X^{-1}BX$$

Conjugation is reciprocal is transitive

A conjugate to B

A is conjugate to C

then B is conjugate to C

The class of an element A in G is the set of all elements of G conjugate to A

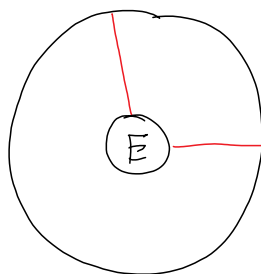
$$EAE^{-1} = A, BAB^{-1} \dots$$

The Identity E is always in the a class by itself

The only class that is a subgroup

Generally classes are not subgroups

For abelian groups, each element is in its own class



If the group elements are MATRICES with matrix product is the group multiplication then the trace of every matrix in a class must be the same

In terms of symmetry operations

$$B = X^{-1}AX$$

Means operate with respect to X , eg $C_N = \frac{2\pi}{N} \text{ rot}$

Then operator A with X^{-1} eg $C_N^{-1} = -\frac{2\pi}{N}$

A and B must be of similar types of operations

Isomorphism and Homomorphism

Isomorphism

Two groups that have the same multiplication table are isomorphic

any fact about one is true about the other

Homomorphism is weaker

| G | H |
|-----|-----------------------|
| A | $A_1, A_2, A_3 \dots$ |
| B | $B_1, B_2, B_3 \dots$ |
| C | C_1, C_2, C_3 |

$AB=C$ then $A_iB_j = C_k$, can be any ijk

This is a many to 1 correspondence, not 1 to 1

Eg $\{E\}$ is homomorphic to every group

There are many important quantities

Invariant subgroups contain complete classes

Representation of Groups

Here the elements of an abstract group are represented by a set of matrices

Review of matrices

M is a table of m rows and n columns and each entry is a complex number

Square matrices $m=n$

Compatible sized matrices can be multiplied and added

\xrightarrow{n}

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 0 + 0$$

Review of matrices

M is a table of m rows and n columns and each entry is a complex number

Square matrices m=n

Compatible sized matrices can be multiplied and added

$$M_{ik} = \sum_{j=1}^n A_{ij} B_{jk}$$

Matrices can act on vectors matrix with columns

Some unary matrix operations

A^* complex conjugate $(A^*)_{ij} = A_{ij}^*$

A^t matrix transpose $(A^t)_{ij} = A_{ji}$

A^+ hermitian conjugate $(A^+)_{ij} = A_{ji}^*$

Some matrices are invertible

A is invertible

Then there exist another matrix A^{-1}

$$\Rightarrow AA^{-1} \text{ or } A^{-1}A = I$$

In general matrix multiplication is not commutative

Trace

$tr(A) = \text{a number}$

= the sum of diagonal elements

$$= \sum_{i=1}^n A_{ii}$$

Determinant

$\det(A) = |A|$ another number

Special types

Symmetrics: $A^t = A$

Hermitian: $A^+ = A$

Orthogonal $A^{-1} = A^t$

Unitary $A^+ = A^{-1}$

Identity matrix $A_{ij} = \delta_{ij} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

Transformation of vectors

$$\vec{v}' = A\vec{v}$$

A n dimension vector operated on by a $n \times n$ matrix results in a n dimension vector

If A is orthogonal (unitary for complex) \vec{v}' is not changed in length, just a change in direction

$$|\vec{v}|^2 = (\vec{v} \cdot \vec{v}) = v_x v_x + v_y v_y + v_z v_z$$

$$|\psi|^2 = \int d\tau \psi^* \psi = 1$$

Similar transformation

One can use an invertible matrix Z to transform matrix A into $B = Z^{-1}AZ = YAY^{-1}$ ($Y = Z^{-1}$)

A and B are similar matrixes

They have the same

- 1) Trace
- 2) Determinant
- 3) Eigenvalues

If B is diagonal then Z diagonalize A

A Hermitian matrix is diagonalize by a unitary transformation

A group \mathbb{G} is represented by another group H if H is homoprhic to \mathbb{G}

In practice we use a set of square matrices as a representation

$$VA \in \mathbb{G}$$

$\Gamma(A)$ is the square matrix representing A

Homomorphism means

$$\Gamma(AB) = \Gamma(A)\Gamma(B)$$

$$VA, b \in \mathbb{G}$$

The identity is represent by I

$$\Gamma(E) = I \text{ non unit matrix}$$

Dimension of the rep is just n

$$\text{If } \Gamma(A) = \text{an } n \times n \text{ matrix } \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$n = Tr(\Gamma(E))$$

Faithful representations

For each A in \mathbb{G} , $\Gamma(A)$ is a different matrix the representation is true or faithful or it is isomorphic

Unfaithful reppsentations

Have fewer distinct matrices than the group order

$$A, B \in \mathbb{G} \quad A \neq B, \quad \Gamma(A) = \Gamma(B)$$

The set of all in \mathbb{G} with $\Gamma(A) = I$ is an invariant subgroup \mathbb{G}

Identical Rep

A trivial (usually unfaithful) rep associates I with every group number

$$\Gamma(A) = IVA \text{ in } \mathbb{G} [1], \quad \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Totally symmetric rep

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 0 + 0$$

$$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 0 + 0$$

$$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = i - i = 0$$

Similar Transformation and Representation

Tuesday, February 9, 2016 11:02 AM

For finite groups we have h matrices in a rep.

If $M = \Gamma(A)$ then we can define another matrix (one for each $A \in \mathbb{G}$)

$$M' = S^{-1}MS$$

For S some compatible sized invertible matrix

Then the set M' is also a representation of the group and it is equivalent to the group represent $\Gamma(A)$

They are the same up to some arbitrary choice of coordinates

Eg $C = AB$

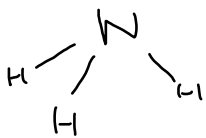
$$C' = S^{-1}CS = S^{-1}ABS = S^{-1}ASS^{-1}BS = A'B'$$

Then M' are a representation

An example

To find a representation, we need h matrices that satisfy the x-table

If the group is a point symmetry group, there is a natural way to generate a 3d representation



Consider the effect of the symmetry operation on an arbitrary point $\bar{x} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$

Here the origin is $\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$ is the point symmetry of the group

Eg Reflection through xz plane

$$\begin{bmatrix} x \\ -y \\ z \end{bmatrix} = A \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$A = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Rotation by θ about z axis

$$A = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Inversion

$$A = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Usually we consider only unitary matrices

One can show if $\Gamma(A)$ is a representation $|\Gamma(A)| \neq 0$

Then $\Gamma(A)$ are similar to a aset of unitary matrices

Rotoreflection through xy plane

$$A = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$I = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We can always generate such a representation for every point system group

A single representation - doesn't tell us everything about a group structure (may not even be faithful)

We need special representation called irreducible (few in numbers)

- A little like prime factors in an integer

$C_{3v}(NH_3)$

$E \rightarrow I$

$$a = \frac{1}{2}, \quad b = \frac{\sqrt{3}}{2}$$

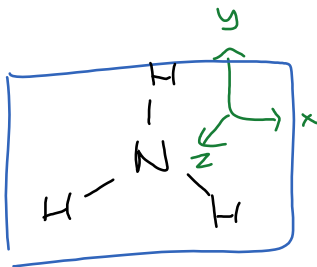
$$C_3 \Rightarrow \begin{bmatrix} -a & b & 0 \\ -b & -a & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3^{-1} \Rightarrow \begin{bmatrix} -a & -b & 0 \\ b & -a & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma'_v = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad yz \text{ plane } y$$

$$\sigma''_v = \begin{bmatrix} a & -b & 0 \\ -b & -a & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma'''_v = \begin{bmatrix} a & b & 0 \\ b & -a & 0 \\ 0 & 0 & 1 \end{bmatrix}$$



Check if these are unitary (orthogonal)

Reducible and Irreducible Representations

Any representation can be combined to form a higher dimension representation of the same group using direct sum

If we have 2 matrices

$\Gamma^{(1)}(A)$ $m \times m$

$\Gamma^{(2)}(A)$ $n \times n$

For each $A \in G$ then

$$\Gamma'(A) = \Gamma^{(1)}(A) \oplus \Gamma^{(2)}(A) = \begin{bmatrix} \Gamma^{(1)}(A) & 0 \\ 0 & \Gamma^{(2)}(A) \end{bmatrix}, \quad \text{a block diagonal } (m+n) \times (m+n) \text{ matrix}$$

This gives us a set of bigger matrices that is another representation

But this representation is reducible

A representation $\Gamma(A)$ is reducible if there is a similarity transform

$$S^{-1}\Gamma(A)S$$

That takes the h matrices into h block diagonal matrices of the same form

$$\begin{bmatrix} 2 \times 2 & 0 \\ 0 & 1 \times 1 \end{bmatrix}$$

If this cannot be done with any S then the representation is irreducible

There are generally a small number (sh) of irreducible representation of a finite group

The Great Orthogonality Theorem

Let $\Gamma^{(i)}(R)$, $i = 1, \dots, h$, be the set of all irreducible representation of a finite group $R \in \mathbb{G}$ of order h (inequivalent and unitary)

$$\sum_{\text{all } R \text{ in } \mathbb{G}} \left(\Gamma_{(R)}^{(i)*} \right)_{uv} \left(\Gamma_{(R)}^{(j)} \right)_{\alpha\beta} = \frac{h}{l_i} \delta_{ij} \delta_{u\alpha} \delta_{v\beta}$$

where l_i is the dimension of the i th irreducible representation

Orthogonality is \perp

$$a \cdot b = a_x b_x + a_y b_y + a_z b_z = 0 \text{ for } a \perp b$$

LHS of (*) is like $a \cdot b$ but for some h - dimensional vector whose

Elements are the matrix element of $\Gamma^{(i)}, \Gamma^{(j)}$

RHS of (*) has a product of 3 kronecker δ symbols many ways to make a RHS=0

But only one way to make it nonzero

$$i = j, \quad u = \alpha, \quad v = \beta$$

In this case

$$\sum_{\text{all } R \text{ in } \mathbb{G}} \Gamma_{aa}^{(i)*}(R) \Gamma_{aa}^{(j)}(R) = \frac{h}{l_i}$$

But recall

For an h dimensional vector space, you can only have h mutually orthogonal vectors

Character

$$\text{Recall } \text{tr}(M) = \sum_i M_{ii}$$

$$\text{for } \text{tr}(I) = l$$

Trace is invariant under similarity transforms

The characters of a representation $\Gamma(A)$ is the trace

$$\chi(\Gamma(A)) = \text{tr}(\Gamma(A)) = \sum_{\mu=1}^l (\Gamma(A))_{\mu\mu}$$

Consequences

a) The dimensionality theorem

The sum of the squares of the dimensions l of all the irreducible representation of a group is equal to the order of the group h

$$\sum_{\text{irre} > i} l_i^2 = h$$

b) The sum of χ^2 for an irreducible representation

$$\sum_{R \in \mathbb{G}} (\chi(\Gamma(R)))^2 = h$$

c) The vectors whose components are characters of 2 different irreducible representations are orthogonal h - dimensional vectors

$$\begin{aligned}
 &(\chi^{(i)}(A), \chi^{(i)}(B), \dots) \\
 &(\chi^{(j)}(A), \chi^{(j)}(B), \dots) \\
 &\dots \\
 &\sum_{R \in \mathbb{G}} \chi^{(i)}(R) \chi^{(j)}(R) = 0, \quad i \neq j
 \end{aligned}$$

d) In any representation characters of operations of the same (group element)

Class are identical

If A & B are in same class

$$B = R^{-1}AR \text{ for some } R \in \mathbb{G}$$

$$\Gamma(B) = \Gamma(R^{-1}AR) = \Gamma(R^{-1})\Gamma(A)\Gamma(R)$$

$$\text{But } \Gamma(R^{-1}) = \Gamma^{-1}(R)$$

$$\Gamma(E) = I = \Gamma(R^{-1}R) = \Gamma(R^{-1})\Gamma(R)$$

$$\Gamma(B) = S^{-1}\Gamma(A)S, \text{ where } S = \Gamma(R)$$

$$\text{Tr}(\Gamma(B)) = \text{Tr}(\Gamma(A))$$

$$\chi_{(B)} = \chi_{(A)}$$

e) The number of irreducible representation of a group is the number of classes in the group

f) Decomposing reducible representation

A reducible representation consists of matrices similar to block diagonal matrices where each block is an irreducible of the group

$$\chi(R) = \sum_{\text{irreps } i} a_i \chi^{(i)}(R)$$

The number of times the block $\chi^{(i)}$ occurs in the reducible representation $\chi(R)$ is a_i .
one can further show that

$$a_i = \frac{1}{h} \sum_{R \in \mathbb{G}} \left(\chi^{(i)}(R) \right)^* \chi(R)$$

Characters of R in the i^{th} irreducible representation

If we have the characters $\chi(R)$ of the reducible representation and the characters of the irreducible representation

$\chi^{(i)}(R)$ then we can just compute a_i

These consequences motivate construction of character tables that distill the structure of the group

Lecture 12

Thursday, February 11, 2016 11:04 AM

An example of a character table is $C_{3v}, n = 6$

First step? How many classes?

E (a class by itself)

C_3^{-1} takes one of the σ_v

if element = element $i \times$ element j

The left most element is the row while the right most element is the column

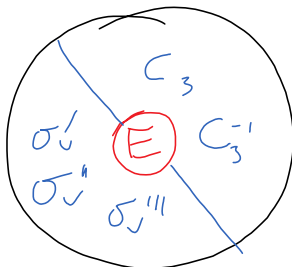
$$\sigma_v^{-1} C_3^{-1} \sigma_v = \sigma_v C_3^{-1} \sigma_v = \sigma_v \sigma_v'' = C_3$$

C_3^{-1} and C_3 are in the same class, same kind

$$\sigma_v'' \sigma_v \sigma_v'' = \sigma_v'' C_3 = \sigma_v'''$$

$\sigma_v, \sigma_v'', \sigma_v'''$ are in the same class

Class Structure



Column structure of a character table

All groups elements in the same class have the same character in a given representation

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | $\sum_{elements} = h \text{ (the order)}$ |
|----------|---|--------|-------------|---|
|----------|---|--------|-------------|---|

Row structures if character table

-1 rows for each irreducible representation

of irreducible representation = # of classes

Character table is square

For now, label these $\Gamma^{(1)}$

There is a notation (mulliken)

We do not group elements into subgroups but into classes instead

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | $\sum_{elements} = h \text{ (the order)}$ |
|----------------|---|--------|-------------|---|
| $\Gamma^{(1)}$ | | | | |
| $\Gamma^{(2)}$ | | | | |
| $\Gamma^{(3)}$ | | | | |

Each entry is a χ of that element in that representation

Generate Character table

Column 1 corresponds to E

$$\chi(E) = Tr(I_{l_i \times l_i}) = l_i$$

Where l_i = dimensions of representation of $\Gamma^{(i)}$

$$\sum l_i^2 = h$$

$$\sum_{i=1}^3 l_i^2 = l_1^2 + l_2^2 + l_3^2 = 6$$

$$l_1 = 1, \quad l_2 = 1, \quad l_3 = 2$$

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | $\sum_{elements} = h \text{ (the order)}$ |
|----------------|---|--------|-------------|---|
| $\Gamma^{(1)}$ | 1 | | | |
| $\Gamma^{(2)}$ | 1 | | | |
| $\Gamma^{(3)}$ | 2 | | | |

$R \rightarrow [1]$ every element represented by 1×1 unit matrix

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | $\sum_{elements} = h \text{ (the order)}$ |
|----------------|---|--------|-------------|---|
| $\Gamma^{(1)}$ | 1 | 1 | 1 | |
| $\Gamma^{(2)}$ | 1 | | | |
| $\Gamma^{(3)}$ | 2 | | | |

Normalization

The rows (weighted by N_j , the number of elements per class) are normalized to h

$$\sum_{\text{classes}} N_c \times \chi^2(R_c)$$

$$\text{row } 1 = 1 * 1^2 + 2 * 1^2 + 3 * 1^2 = 6$$

The columns are normalized by $\frac{h}{N_{\text{class}}}$

$$\sum_{\text{irr rep}} \chi^2(R) = \frac{h}{N_{\text{class}}}$$

Orthogonality

G. O. T implies that the row weighted by N_{class} are orthogonal vectors

The columns are also orthogonal

| C_{3v} | E | $2C_3$ | $3\sigma_v$ | $\sum_{\text{elements}} = h \text{ (the order)}$ |
|----------------|---|--------|-------------|--|
| $\Gamma^{(1)}$ | 1 | 1 | 1 | |
| $\Gamma^{(2)}$ | 1 | 1 | -1 | |
| $\Gamma^{(3)}$ | 2 | -1 | 0 | |

EG row 2

Normalized $1 * 1^2 + 2 * a^2 + 3 * b^2 = h$

Orthogonal $1 * 1 * 1 + 1 * 2 * a + 3 * 1 * b = 0$

$a = -b = 1$

Group \Rightarrow subgroup \Rightarrow class

Column Vectors must be orthogonal

Symbols used to identify irreducible representations of groups:

A = singly degenerate state which is symmetric with respect to rotation about the principal C_n axis,

B = singly degenerate state which is antisymmetric with respect to rotation about the principal C_n axis,

E = doubly degenerate,

T = triply degenerate,

X_g = (gerade, symmetric) the sign of the wavefunction does not change on inversion through the center of the atom,

X_u = (ungerade, antisymmetric) the sign of the wavefunction changes on inversion through the center of the atom,

X₁ = (on a or b) the sign of the wavefunction does not change upon rotation about the center of the atom,

X₂ = (on a or b) the sign of the wavefunction changes upon rotation about the center of the atom,

' = symmetric with respect to a horizontal symmetry plane σ_h ,

" = antisymmetric with respect to a horizontal symmetry plane σ_h .

Connecting group theory to quantum mechanics

1) Symmetry operators

- Consider a point symmetry operation R, we have a simple intuitive way of generating a representation of R

by the effect of R on a point (x,y,z) yields a 3x3 matrices

QM is based on wave functions and operators that both depend on (x,y,z)

$$\text{Eg } \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$

$$|\psi\rangle = \psi(r)$$

It is useful to formulate symmetry operations as operators on the space of a wavefunction

$$\vec{x}' = M\vec{x} = \begin{bmatrix} \square & \square & \square \\ \square & \square & \square \\ \square & \square & \square \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \Rightarrow \text{here the basis for the representation is } \hat{i}, \hat{j}, \text{ and } \hat{k},$$

We need to generalize this to a basis of orthonormal functions

With respect to $M = \Gamma(R)$ is a 3×3 transformation matrix correspond to point symmetry R

We define P_R by

$$P_R |\psi\rangle = P_R |\psi(x, y, z)\rangle$$

$$= |\psi(M^{-1}\vec{x})\rangle$$

Here the arguments are replaced by x', y', z'

The operator $P(r)$ just compensates for the coordinate change (M), ψ is the same functional form in \vec{x}'

$P_R: \forall R$ interpret point system group is a group

$P_R P_{R_2} |\psi\rangle$

Of operators on $|\psi\rangle$ that is isomorphic to the point group - it is a representation

As the M are orthogonal matrices

P_R are unitary operators

If $|\psi_i\rangle$ are an orthonormal basis of the space of $|\psi\rangle$

$$|\psi\rangle = \sum_i a_i |\psi_i\rangle$$

$$(P_R)_{ij} = \langle i | R | j \rangle$$

Is a unitary matrix \rightarrow a square unitary matrix representation of R

The dimension of this representation is the dimension of the space $|\psi\rangle$

Often we are interested not in the whole space of functions but a finite dimensional subspace

Eg space spanned by $5 \times 3d$ orbitals

An obvious choice of basis $|\psi\rangle$ is the set of solutions to the schrodinger equations eigen functions of energy

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = \frac{\hbar^2}{2m} \nabla^2 = \frac{\hbar^2}{2m} (\partial_x^2 + \partial_y^2 + \partial_z^2)$$

The same function for any orthogonal coordinate transform

\rightarrow spherically symmetric

The potential $V(r)$ has a point symmetry of the molecule

The combination of the two has to have the point symmetry of the two

$$P_R \hat{H} |\psi\rangle = \hat{H} P_R |\psi\rangle \text{ for any } |\psi\rangle$$

$$[\hat{H}, \hat{P}_R] = 0$$

$$\hat{H} |i\rangle = E_i |i\rangle$$

$$\hat{P}_R |i\rangle = p_R^i |i\rangle$$

We can classify the wavefunctions $|i\rangle$ according to the values of (P_R^i) eigenvalues of the symmetry operators

These are known as the good quantum numbers in that they stay fixed

The group $\{P_R\}$ is the symmetry point group of the schrodinger equation

We can classify the S.E. by their behavior under symmetry operations

e.g. $R = i$

$$R = i$$

$P_R = \Pi$ parity operator

$$\Pi|\psi_i\rangle = \pm|\psi_i\rangle$$

If the system is inversion - symmetric, the wavefunction must be stations or definite parity

Even (+), gerade

Odd (-), ungerade

Degeneracy and Representation of P_R

A set of functions $|\psi_n^i\rangle$ are degenerate

$$\hat{H}|\psi_n^i\rangle = E_n|\psi_n^i\rangle$$

For each $i = 1 - l_n$

The space spanned by $|\psi_n^i\rangle$ a subset of solutions to S.E. is an l_n dimensional subspace

$$\text{The function in this subspace is } |\psi_n\rangle = \sum_{i=1}^{l_n} b_{ni} |\psi_n^i\rangle$$

All such functions are eigenfunctions of H with eigenvalues E_n

We often call this a "manifold of degenerate states of dimension l_n "

Let $|\psi_n\rangle$ be any wavefunction with energy E_n

$P_R|\psi_n\rangle$ is another wavefunction with energy E_n

If this leads to all other degenerate $|\psi_n\rangle$ with E_n that is normal degeneracy

Additional states at $E = E_n$ are accidentally degenerate

If the $|\psi_n^i\rangle$ are orthonormal

The action of P_R on this basis produces an l_n dimensional irreducible representation

$$P_R|\psi_n^i\rangle = \sum_{j=1}^{l_n} b_{ij} |\psi_n^j\rangle$$

$$b_{ij} = \Gamma(R)$$

The $l_n |\psi_n^i\rangle$ are a basis of an l_n dimensional representation if that symmetry group

This leads to the matrices being unitary

We can label wave functions of \hat{H} by the irreducible representation to which they corresponds

Non degenerate wavefunctions must corresponds to 1 dimensional irreducible representation

Lecture 13

Tuesday, February 23, 2016 11:04 AM

Recall for the symmetry operator R of a molecule can define "transformation operator are the space of the wavefunctions with

$$P_R |\psi(\vec{x})\rangle = |\psi(M^{-1}\vec{x})\rangle$$

Where M is the 3x3 matrices (orthogonal) corresponding to the effect of R on a point (x,y,z)

Eg. If R is a 90° is a rotation by $\left(\frac{2\pi}{4}\right)$

$$M \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ z \\ -y \end{bmatrix} \Rightarrow M = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$$

$$M^{-1} = M^T = M^+ = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$M^{-1}\vec{x} = M^{-1} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -z \\ y \end{bmatrix}$$

$$P_R |\psi(x, y, z)\rangle = |\psi(x, -z, y)\rangle$$

Degeneracy and Reperations of symmetry operators (P_R)

$$\hat{H} |\psi_n^i\rangle = E_n |\psi_n^i\rangle$$

$|\psi_n^i\rangle$ span the subspace of solutions of the schrodinger equation of of dimension l_n

Any function of this subspace can be written as $|\psi_n\rangle$

$$|\psi_n\rangle = \sum_{i=1}^{l_n} b_n^i |\psi_n^i\rangle$$

Here we have a general wave equation spanning the Hilbert space of elements ψ_n^i

Such a function is also a degenerate solution with E_n

A manifold of degenerate states of dimension l_n

Because $[P_R, H] = 0$

$P_R |\psi_n\rangle = \text{another solution of energy } E_n$

Assuming $|\psi_n^i\rangle$ are orthonormal

$$\langle \psi_n^i | \psi_n^j \rangle = \int (\psi_n^i)^* \psi_n^j = \delta^{ij}$$

an orthonormal basis for the subspace, like unit vectors

Then for each $|\psi_n^i\rangle$

$$P_R |\psi_n^i\rangle = \sum_{j=1}^{l_n} b_n^{ij} |\psi_n^j\rangle$$

Look up unitary

$b^{ij} = \Gamma(R)$ and irreducible representation of the symmetry group (also unitary)

- We can thus label the wavefunctions (eigenfunctions of \hat{H}) by the irreducible representation they belong to
- Non degenerate wavefunctions must corresponds to 1D irreducible representation.

Up to similarity, there is a unique representation of the symmetry group for each eigenvalue/vector of the Hilbert space of \hat{H}

The $|\psi_n^i\rangle$ are the basis of the representations (i, j, k) were for the M matrices

NH_3 $|\psi\rangle$ might be totally symmetric \Rightarrow belong to A_1 (Each R is represented by the [1] unit matrix)

$$P_R |\psi\rangle = +|\psi\rangle$$

Functions that possess symmetry properties compatible with the symmetry groups are called symmetry adapted functions

- Useful in numerical approximation solution of S.E.

Projection Operators

For an orthonormal basis set $|\psi_i\rangle$

The operator, $|\psi_i\rangle\langle\psi_i|$

That is a projection operator along $|\psi_i\rangle$

$$\text{Define another type of projection operator } P^\mu = \sum_R \chi^\mu(R) P_R$$

The operator projects an arbitrary function onto the μ^{th} irreducible representation of the symmetry group

$$P^\mu |\psi\rangle = |\eta\rangle \Leftarrow \text{has symmetry of the irreducible } \mu$$

Direct Product Representation

Multiparticle wavefunctions are often expressed as products of single particle functions b/c SE is often approximately

separable

Eg $\Phi = \psi_{el} \times \chi_{nuc}$

In such products, each function has definite symmetry properties under the symmetry of the SE

One can ask: to which rep does Φ belong to?

Besides this application, the symmetry properties of products of wavefunctions are important in deriving selection rules

We saw that electric dipoles transitions

We saw that electric dipole transition have intensity

$$I \propto \left| \int \psi_f^* \vec{\mu} \psi_i \right|^2$$

$\vec{\mu} = e\vec{r} = e(x, y, z)$ is the electric dipole moment operator

Here the integrand is the product of 3 factors with particular symmetries

If we know how each factor behaves under symmetry operators P_R , can we decide how P_R affect products

Consider $\Phi = \psi_1 \psi_2$

If ψ_1 belong to Γ^μ then

$$\psi_1 = \sum_{i=1}^{l_\mu} a_i \psi_i$$

where ψ_2 belongs to Γ^ν

$$\psi_2 = \sum_{j=1}^{l_\nu} b_j \eta_j$$

Gramschmidt process

Then the set $\psi_i \eta_j$ is a basis set for a larger ($l_\mu \times l_\nu$ dimensional) space

One obtain a matrix representation of the symmetry group

With this basis by taking a matrix direct product of the corresponding irreducible representation of ψ_1 and ψ_2

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{bmatrix} a_{11}b_{11} & a_{11}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} \end{bmatrix} \begin{bmatrix} a_{12}b_{11} & a_{12}b_{12} \\ a_{12}b_{21} & a_{12}b_{22} \\ a_{22}b_{11} & a_{22}b_{12} \\ a_{22}b_{21} & a_{22}b_{22} \end{bmatrix}$$

Look at trace

$$\chi(A \otimes B) = \chi(A)\chi(B)$$

The character of direct product matrix is the product of the character of the factors

The direct product must be a reducible representation of the symmetry group - but usually a reducible one

Reducible means it can be expressed as a direct product of irreducible representation

$$\Gamma^{\nu \otimes \mu} = \Gamma^\nu \otimes \Gamma^\mu = a_1 \Gamma^1 \oplus a_2 \Gamma^2 \oplus \dots \oplus a_n \Gamma^n$$

When a_1 = the number of times irreducible representation 1 appears along the diagonal blocks (integers)

$$a_i = \frac{1}{h} \sum_R \chi^{\nu \otimes \mu}(R) \chi^i(R)$$

Where the sum is a product of characters

Integrals of Selection Rules

Essentially generalizes

$$\int f(x) dx = 0 \text{ for } f(x) = -f(-x) \text{ where } f \text{ is an odd function like } x \text{ and } \sin$$

Consider the integral

$$\int \psi_1 \psi_2 \psi_3$$

Where each factor belongs to an irreducible representation of a symmetry group called μ, λ, ν

The integrand belongs to the direct product

$$\Gamma^\mu \otimes \Gamma^\lambda \otimes \Gamma^\nu = \oplus \sum_{irr \text{ reps}} a_i \Gamma^i$$

If this decompositions does not contain the totally symmetry irr. Rep A_1 , then the integral is totally zero by symmetry

recall A_i all $R \rightarrow [1]$

means a_{A_1}

Note the $\chi(\text{character})$ usually contains extra columns at right to show symmetry prop of simple functions

like x, y, z

???

Thursday, March 10, 2016 10:15 AM

$P_R |\psi_n\rangle$ is another wavefunction with energy E_N

If this leads to all other degenerate $|\psi_n\rangle$ with E_n that is normal degeneracy

Additional states at $E = E_n$ are accidentally degenerate

If the $|\psi_n^i\rangle$ are orthonormal

The action of P_R on this basis produces an l_n dimensional irreducible representation

$$P_R |\psi_n^i\rangle = \sum_{j=1}^{l_n} b_{ij} |\psi_n^j\rangle$$

Spin Statistics

Thursday, March 10, 2016 11:07 AM

9. Nuclear Spin Statistics

Multiparticle QM: We face the problem of describing multiples indistinguishable particles
→ arbitrary labelling

If $\hat{H} = H_1 + H_2$ for particle 1 and 2

For $\psi = \psi_1(r_1) + \psi_2(r_2)$

But if the particles are identical, we should observe no change if we label the particles

$$\psi = \psi_1(r_2) + \psi_2(r_1) = \psi_1(r_1) + \psi_2(r_2)$$

Here we have an exchange of two identical particles

$2e^-, 2p^+, 2(C^{12})$

$C^{12} \neq C^{13}$

This can be treated mathematically as an operators

$$\hat{P}_{12}\psi(r_1, r_2) = \psi(r_2, r_1)$$

$$\hat{P}_{12}\psi(\sigma_1, \sigma_2) = \psi(\sigma_2, \sigma_1)$$

Is a bit like our symmetry transformation operators P_R but it doesn't act on whole molecule, just a pair of particles

There are 2 cases

1) Fermions

A particle w/ spin which is $\frac{1}{2}$ integers

e^-, p^+, F^{12}, Li^7

$$\hat{P}_{ij}\psi(\dots r_i, r_j \dots) = \psi(\dots r_j, r_i \dots) = -\psi(\dots r_i, r_j \dots)$$

2) Bosons

Particles w/ integers including zero

Deuteron 1

He⁴ atom 0

Photon 1

C^{12} nuclei \Rightarrow any even mass number nucleus

$$P_{ij}\psi^B(\dots r_i, r_j \dots) = +\psi(\dots r_1, r_2 \dots) \text{ symmetrically even under exchange}$$

$$P_{ij}\psi = e^{i\theta}\psi \text{ where } \theta = \pi \text{ for fermions and } \theta = 0 \text{ for bosons}$$

Anyons \rightarrow Fractional quantum hall effect

Consequence of Symmetry and Antisymmetric

Pauli Exclusion Principle

For electronic states

$$\psi = \psi(x, y, z) \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

$2e^-$ has spin $\frac{1}{2}$ wavefunction

$$\psi = \psi_1(r_1)\chi(m_1)\psi_2(r_2)\chi(m_2)$$

spin w. f. = α or β

Spin orbital "spinors"

$$P_{12}\psi = -\psi(r_1)\chi(m_1)\psi(r_2)\chi(m_2)$$

$$\psi(2,1) = \hat{P}_{12}\psi(1,2) = -\psi(1,2)$$

choose

$$\psi' = \frac{\psi(1,2) - \psi(2,1)}{\sqrt{2}}, \text{ this is automatically antisymmetric}$$

Slater determinant

Rows and columns swapped in a matrix

Quantum Statistical Distribution

Statistical limit: many particles

$f(E)$ = probability that a state with energy E is occupied in thermal eqb



Classically

$f(E)$ = Maxwell Boltzmann

$$= \frac{1}{e^{\alpha} e^{\frac{E}{k_B T}}}$$

This is or at High T, low density but only approximately

Eg. It will violate Pauli Exclusion

| | | |
|---------|-------------|---|
| Boson | f_{bose} | $\frac{1}{e^{\alpha} e^{\frac{E}{k_B T}} - 1}$ Super fluid helium, bose einstein condensation |
| Fermion | f_{fermi} | $\frac{1}{e^{\alpha} e^{\frac{E}{k_B T}} + 1}$, e^- in condensed matter physics, |

Homonuclear atomics

- Apply to symmetric linear molecules
 - o BeF_2
- Especially high symmetry
- We need to consider the effect of identical nuclei
 - o Eg Dihydrogen $H_2 \neq HD \neq D_2$
 - o $\Phi = \psi_{el} \cdot \psi_{rot} \cdot \psi_{vib} \cdot \psi_{nuc}$
 - o $P_{12}\Phi = -\Phi$

2 types of H_2 – distinguished by nuclear spins

Nuclear Spin State

Ortho
1 1
Triplet

$\alpha(1)\alpha(2)$ for spin 1

$\beta(1)\beta(2)$ for spin 2

$\alpha(1)\alpha(2)$ for spin 1

$\beta(1)\beta(2)$ for spin 2

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$ for spin 0

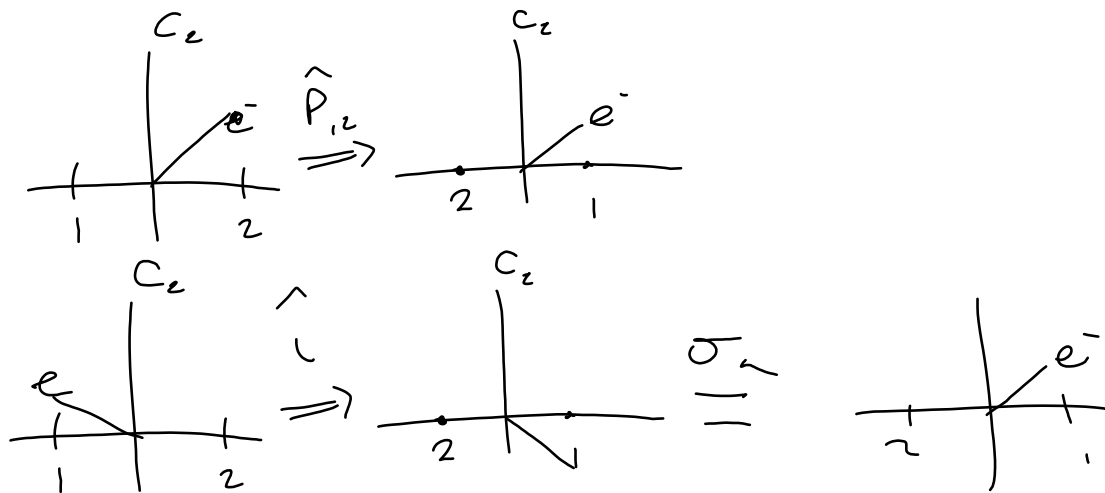


$$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

Under $\hat{P}_{12} \psi_{nuc} = -\psi$

| P_{12}^{proton} | Φ | ψ_{el} | ψ_{vib} | ψ_{rot} | ψ_{nuc} | g |
|-------------------|--------|-------------|--------------|--------------|--------------|-----|
| Ortho | - | + | + | - | + | 3 |
| Para | - | + | + | + | - | 1 |

P_{12}^{proton} can be related to point symmetry



$$\hat{P}_{12}^P = \sigma_h^{el} i^{el} C_2$$

Are I except on ψ_{el}

The electronic state ψ_{el} , (α its symmetry) is abbreviated by the diatomic term symbol

$$(2s + 1 \text{ deg}) 1 \sum_{g \text{ inversion } i}^{+ (o_h)} \quad \square \text{ this is the total something} = 0$$

For H_2 in ground ψ_{el}^0

$$\sigma_h^{el} i^{el} \psi_{el}^0 = (+)(+)\psi_{el}^0$$

$$C_2 \psi_{rot} = (-1)^J \psi_{rot}$$

$$Y_{JM} = \psi_{rot}$$

$$\theta \Rightarrow \pi - \theta$$

$$\psi = \psi + \pi$$

Kraztler relation

ortho H_2 - combines only with odd J

Para H_2 - combines only with even J

Similarly $C^{12} - C^{12}, O^{16} - O^{16}$, no odd J states

$O^{16} - O^{17} \rightarrow$ state of low abundance

$O^{16} - O^{18}$

Rovibrational Spectroscopy

Tuesday, March 15, 2016 11:03 AM

Vibrational Spectroscopy

Vibrations of Diatomics

$$H = T_N + T_e + V_{nn} + V_{ne} + V_{ee}$$

In the Born oppenheimer approximation

$$T_n \cong 0$$

$$V_{nn} \cong \text{constant}$$

$$\hat{H} = T_E + V_{ee} + V_{en}$$



$$H_{el}\psi_i(r, R) = E_i(R)\psi(r, R)$$

$\psi_i = i^{th}$ electronic eigen state w nuclei R

$$H_n = T_n + V_i(R)$$

$V_i(R)$ is the effective potential between the two nuclei

$$V_i(R) = E_i(R) + V_{nn} = E_i(|R|) + \frac{ke^2Z_1Z_2}{R}, \quad k = \frac{1}{4\pi\epsilon_0}$$

The T_n term contains the rotational KE included

Schrodinger Equation for nuclei

$$H_n\psi_{(rot)}^{(vib)} = E_{vr}\psi_{vr}$$

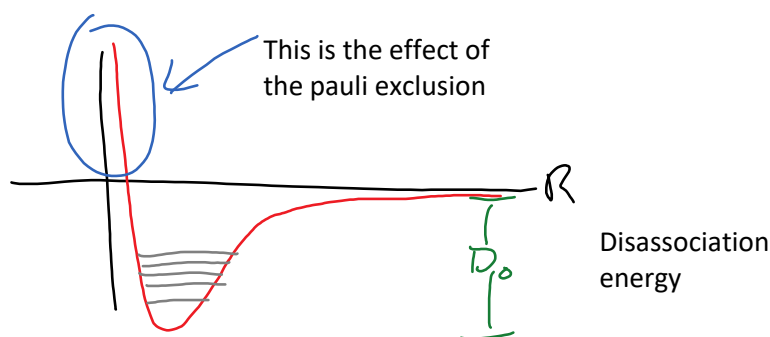
$$\psi_{(rot)}^{(vib)} = \psi_{vib} \times \psi_{rot}$$

$$\psi_{rot} = Y_{JM}(\theta, \phi)$$

$$\psi_{vib} = \chi_v^i(R)$$

Total vibronic wave function

$$\Phi(r, R) = \psi(r, R)\chi_v^i(R)$$



To find $V_i(R)$ —need detailed quantum chemical calculation

e.g. C_2 molecule

A reasonable mathematical form to represent the potential is the **Morse Potential**

A Morse potential

$$V_{morse}(R) = D_e[e^{-2\beta q} - 2e^{-\beta q}]$$

Where $q = R - R_e$

—pure phenomenology depth of well

$$q = 0, \rightarrow V_m = -D_e$$

$$q \rightarrow \infty \rightarrow V_m = 0$$

Harmonic Approximation

Take a Taylor series expansion of $V_i(R)$ close to its minimum at $R = R_e$

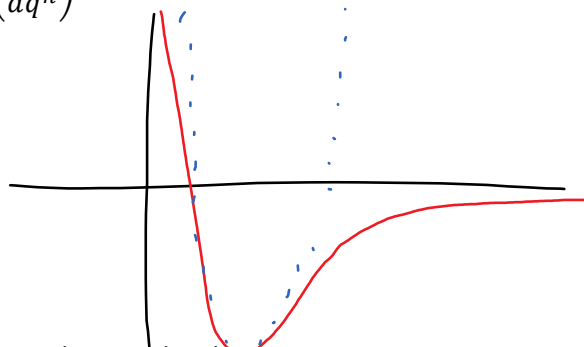
$$V(q) = V(0) + \left(\frac{dV}{dq}\right)_{q=0} q + \frac{1}{2} \left(\frac{d^2V}{dq^2}\right)_{q=0} q^2 + \dots + \frac{1}{n} \left(\frac{d^n V}{dq^n}\right) q^n$$

$$\frac{d^2V}{dq^2} = \text{curvature of potential at } q = 0$$

Harmonic approximation: truncate after q^2

$$V(q) \cong \text{constant} + \frac{1}{2} \left(\frac{d^2V}{dq^2}\right)_{q=0} q^2 = V_o + \frac{1}{2} k q^2$$

$V(q)$ = a parabola like a spring



The blue curve is the harmonic approximation

The harmonic approximation is accurate for low vibrational energy levels

$$\begin{aligned} \frac{dV}{dq} &= D_e [-2\beta e^{-2\beta q} + 2\beta e^{-\beta q}] \\ &= 2\beta D_e [e^{-\beta q} - e^{-2\beta q}] \end{aligned}$$

$$\left(\frac{dV}{dq}\right)_{q=0} = 0 = 2\beta D_e [e^{-\beta q} - e^{-2\beta q}] = 1 - 1 = 0$$

$$\begin{aligned} \frac{d^2V}{dq^2} &= 2\beta D_e [-\beta e^{-\beta q} + 2\beta e^{-2\beta q}] \\ &= 2\beta^2 D_e [2e^{-2\beta q} - e^{-\beta q}] \end{aligned}$$

RoVibrational Coupling

Tuesday, April 19, 2016 12:59 PM

Rotational Raman Scattering

An electric field can induce an electric dipole moment provided the polarizability is anisotropic

$$\mu_i = \alpha_{ij} E_j$$

$$L_i = I_{ij} \omega_j$$

α is the polarizability tensor just like I is the moment of inertia tensor

Choose a set of coordinates to diagonalize it

If all 3 diagonal are equal then the molecule is isotropic

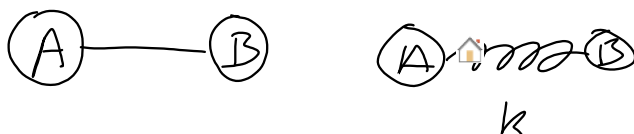
For linear molecules - molecular axis \neq other axes

\rightarrow rotational raman possible

For spherical tops $CH_4 \Rightarrow \alpha_{ij}$ is isotropic

Nonrigidity of Molecules Rotors

Centrifugal Distortion



-The faster A - B rotates, the longer the bond length

-The stretching depends on K the spring constant

Equilibrium

$$F_c (\text{stretching}) = \frac{\mu v^2}{r} = \frac{J^2}{\mu r^3}, \text{ where } J \text{ is classical angular momentum}$$

$$F_r (\text{restoring}) = -K(r - r_e)$$

$$\text{Equilibrium } F_c + F_r = 0$$

$r_c = r$ in the distorted state

$$\frac{J^2}{\mu r_c^3} = k(r_c - r_e)$$

How big a stretch?

e.g. $Cl^{35} - Cl^{35}$

$$k \sim 319 \frac{N}{m}$$

$$\mu = 17.5 \mu$$

$$r_e = 1.99 \text{ \AA}$$

Consider $J = 1 \rightarrow (1)(2)\hbar^2$

$$F_c = \frac{2\hbar^2}{17.5\mu(1.99\text{\AA})^3} \cong 9.7 \times 10^{-14} N \text{ or } 0.1 pN$$

$$|F_r| = kqc = F_c$$

$$q_c \sim 3 \times 10^{-60} \text{ A}$$

$$I = \mu r^2$$

$$\frac{\mu r^2 v^2}{r}$$

$$J^2 = I^2 \omega^2$$

$$v = r\omega$$

$$v^2 = r^2 \omega^2$$

$$I = \mu r \times v$$

$$J^2 = (\mu r v)^2 \omega^2$$

$$v = r\omega$$

$$v^2 = r^2 \omega^2$$

Transitions labeling

Thursday, March 17, 2016 11:02 AM

Rovibrational Transitions in Diatomics

$$E_{rv} = E_{vib} + E_{rot} = \left(v + \frac{1}{2}\right) h\nu_o + hB_e J(J + 1)$$

Rotational: $\mu_o \neq 0$, $\Delta J = \pm 1$, $\Delta M = 0, \pm 1$

Vibrational transformations occur, $\Delta v = \pm 1$

| | | | |
|----------|-----------------|----------------------|---|
| P branch | $\Delta J = -1$ | $\Delta v \pm 1$ | $h\nu_{J-1 \leftarrow J} = h\nu_e - 2hB_e J$ |
| R branch | $\Delta J = 1$ | $\Delta v = \pm 1$ | $h\nu_{J+1 \leftarrow J} = h\nu_e + 2hB_e(J + 1)$ |
| Q branch | $\Delta J = 0$ | Not normally bounded | $h\nu = h\nu_e (J \leftarrow J)$ |

Another example NO ground state 2Π

The 2 corresponds to the spin states

$$L_z = A = 1\hbar$$

This angular momentum corresponds to the unpaired electron in the HOMO

The A is analogous to the prolate symmetric top therefore resulting in $\Delta J = 0$

$$V = \frac{1}{2} \sum_{n=1}^{3N} \lambda_n Q_n^2$$

$\Rightarrow 3N$ harmonic oscillators

This formulation includes overall translation motion of the CM and Rigid Body Rotation KE

6(5) of the λ_n are zero

Linear molecules

The corresponding Q_n to these zeros describes overall translation and rotation of molecules

The $3N - 6(5)$ coordinates are vibrations

An example – a linear triatomic

\hat{x}_1

\vec{x}_2

\vec{x}_3



time t \rightarrow C \leftarrow O

Symmetric stretch
of the molecule

Alternation extension
& compression along

reflection plane
containing axis

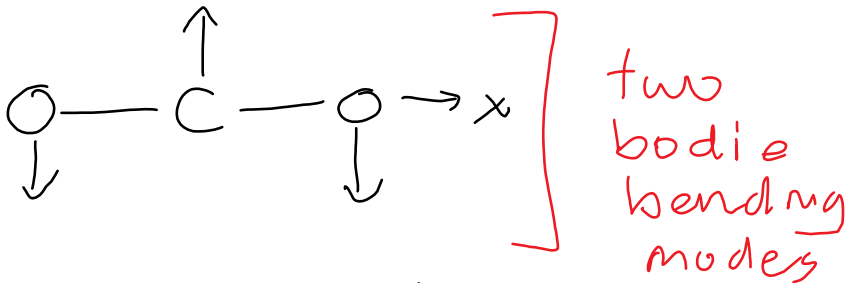
$\rightarrow t$

Alternation extension
& compression along
molecular axis
 $\tilde{\nu} = 1354 \text{ cm}^{-1}$

\sum^t
 \sum^g ← symmetry
under
inversion
g-gerade

$\leftarrow \text{O} - \text{C} - \text{O} \rightarrow$
corresponds to λ_z
 $\tilde{\nu}_2 = 2396 \text{ cm}^{-1}$
antisymmetric stretch

\sum_u^t



$\tilde{\nu} = 673 \text{ cm}^{-1}$

(non linear triatomic
 H_2O
 $3N-6$ modes { one bending
mode is missing

Quantum treatment
Classically

$$E_{tot} = T + V = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2 + \frac{1}{2} \sum_{j=1}^{3N} \lambda_j Q_j^2$$

$$E_{tot}^{vib} = \frac{1}{2} \sum_{i=1}^{3N-6(5)} \dot{Q}_i^2 + \frac{1}{2} \sum_{j=1}^{3N-6(5)} \lambda_j Q_j^2, \text{ subtract the translation and rotational}$$

$$\hat{H} = \sum_{j=1}^{3N-6} \left(-\frac{\hbar^2}{2} \partial_{Q_i}^2 + \lambda_i Q_i^2 \right)$$

Some $3N - 6$ independent Q.H. Osc. solutions of the Schrodinger Equation

$$\psi_{vib}(Q_1, \dots, Q_{3N-6(5)}) = \chi_{v_1}(Q_1) \chi_{v_2}(Q_2) \dots \chi_{v_{3N-6(5)}}(Q_{3N-6(5)})$$

each

$$\chi_{v_i}(Q_i) = N_{v_i} H(\sqrt{\alpha_i} Q_i) e^{-\frac{\alpha_i Q_i^2}{2}}$$

$$\alpha_i = \frac{2\pi v_i}{\hbar}$$

The vibrational state of molecule is specified by $3N - 6$ vibrational quantum #'s

v_i' each $0, 1, 2, 3, \dots \infty$

The corresponding energy

$$E_{vib} = \sum_{i=1}^{3N-6(5)} \left(N_i + \frac{1}{2} \right) h v_i$$

The vibrational spectrum difference is the sum of $3N - 6$ individual vibrational spectra

The harmonic oscillator model

Sunday, April 17, 2016 7:49 PM

The nuclear KE

$$T_n = -\frac{\hbar^2}{2\mu} \nabla_R^2 = \frac{\hbar^2}{2\mu} \left(\partial_R^2 + \frac{2}{R} \partial_R + \frac{L^2}{R^2 \hbar^2} \right),$$

We now assume the case where R is a variable and is the free motion of the center of mass
S. Eq

$$H_n \Phi = -\frac{\hbar^2}{2\mu} \nabla_R^2 \Phi + V(R) \Phi = E_{vr} \Phi$$

Where E_{vr} is the rovibrational energy level

Seperation of rotation and vibrational

$$\Phi(R, \theta, \phi) = \psi(R) Y_{JM}(\theta, \phi)$$

$$V(R) = V(R) \text{ not } V(r, \theta, \phi)$$

$$-\frac{\hbar^2}{2\mu} \left(\partial_R^2 + \frac{2}{R} \partial_R - \frac{J(J+1)}{R^2} + V(R) \right) \psi(R) = E_{vr} \psi(R)$$

$$\text{define } \psi(R) = R \chi(R)$$

$$q = R - R_e$$

$$R = q + R_e$$

$$\left[\partial_R^2 \psi + \frac{2}{R} \partial_R \psi \right] = \frac{1}{R} \partial_q^2 \chi$$

$$-\frac{\hbar^2}{2\mu} \left[\partial_q^2 \chi - \frac{J(J+1)}{(q + R_e)^2} + V(q) \right] \chi(q) = E_{vr} \chi$$

$$\frac{\hbar^2 (J(J+1))}{2\mu (q + R_e)^2} \rightarrow \frac{\hbar^2 J(J+1)}{2\mu R_e^2} = E_{rot}(J)$$

$$-\frac{\hbar^2}{2\mu} \partial_q^2 \chi + V(q) \chi = E_{vib} \chi(q)$$

$$E_{vib} = E_{rovib} - E_{rot}(J)$$

The rotational energy simply adds to vibrational energy

Now we make the harmonic approximation

$$V(q) = \frac{1}{2} k q^2$$

Recall the QM harmonic oscillator

$$H = -\frac{\hbar^2}{2\mu} \partial_q^2 + \frac{1}{2} k q^2$$

$$E_v = \left(v + \frac{1}{2} \right) h \nu_e$$

ν_e fundamental frequency

$$k = (2\pi)^2 \mu \nu_e^2 = \mu \omega_e^2$$

$$v = 0, 1, 2, \dots$$

$$\text{wavefunctions} \rightarrow -\frac{\alpha q^2}{2}$$

$$\chi_v = N_v e^{-\frac{\alpha q^2}{2}} H_v(\sqrt{\alpha} q)$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar}}, v_v = \sqrt{\frac{\sqrt{\alpha}}{2^v v! \sqrt{\pi}}}$$

$H_v(x)$ is the hermite polynomial

$$H_{v+1}(x) = 2xH_v(x) - 2vH_{v-1}(x)$$

$$H_0 = 1 \text{ even}$$

$$H_1 = x \text{ odd}$$

$$H_2 = 4x^2 - 2 \text{ even}$$

$$H_3 = 8x^3 - 12x \text{ odd}$$

We now have an approximate picture for the rovibrational states of a diatomic

$$E_{vib} = E_{vib} + E_{rot}$$

$$E_{vib} \approx h\nu_e \left(v + \frac{1}{2} \right)$$

We expect this to be good approximation provided v is not too large, the frequency quantum number

Selection Rules

Assume no change to i electronic state

$$\Phi_{v,j,m}(R, \theta, \phi) = \psi_{vib} \psi_{rot} = \frac{1}{R} \chi_v(q) Y_{JM}$$

$$\vec{\mu}_{\chi,i} = \left\langle \Phi_{(v'',j'',m'')} | \vec{\mu}_{nuc} | \Phi_{(v',j',m')} \right\rangle$$

$$= \int_0^\infty R^2 dR \int_0^{2\pi} \sin \theta d\theta \int_0^\pi d\phi \left[\Phi_{(v'',j'',m'')}^* \vec{\mu}_{nuc} \Phi_{(v',j',m')} \right]$$

$$= \left(\int_0^\infty \chi_{v''}^*(q) \mu_o \chi_{v'}(q) dq \right) \times \left(\int \sin \theta d\theta \int d\phi Y_{(j'',m'')}^* \vec{\Omega}_{\theta,\phi} Y_{(j',m')} \right)$$

Because $\chi(q) \neq 0$ near $q = 0$

Falls strongly as e^{-q^2}

Can integrate $R \in [-\infty, \infty]$ instead of $R \in [0, \infty]$

Note $\mu_o = \mu_o(q)$

The nuclear dipole moment depends on separation

Taylor expand since we are only interested close to $q = 0$

$$\mu_o(q) = \mu_o(0) + \frac{d\mu_o}{dq} \Big|_{(q=0)} + \dots$$

First term $\vec{\mu}_o(0)$

$\vec{\mu}_{fi} \propto \delta_{v'',v'} \times \text{angular term because } \chi_v(q) \text{ are orthogonal}$
vibrational state doesn't change

2. Second term

$$\mu_o = \frac{d\mu_o}{dq} \Big|_{q=0} \left[\int_{-\infty}^{\infty} dq \chi_{v''}(q) q \chi_{v'}(q) \right] \times \text{angular} = \sqrt{\frac{\hbar}{2\mu\omega_e}} (\sqrt{v+1} \delta_{v'',v'+1} + \sqrt{v} \delta_{v'',v-1})$$

vibrational selection rule

$$\frac{d\mu_o}{dq} \neq 0 \Delta v = \pm 1$$

fundamental

$1 \leftarrow 0$ ground state

Hotbands

$3 \leftarrow 2$

$2 \leftarrow 1$

not normally thermally occupied

$2 \leftarrow 0$

$3 \leftarrow 0$

requires anharmonicity

Overtone

Vibration Polyatomic

Tuesday, April 19, 2016 2:17 PM

Vibration in Polyatomic

Equations of Motion

$$T = \frac{1}{2} \sum_{i=1}^N m_i \dot{r}_i^2$$

$$V(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2; \text{morse potential}$$

Each i^{th} atom has position x_i, y_i, z_i and velocity v_{xi}, v_{yi}, v_{zi}

Define mass-weighted generalized (σ – ordinates)

$$\Delta x_i = x_i - x_i^e$$

$$q_i = \sqrt{m_i} \Delta x_i$$

$$\text{This makes } T = \frac{1}{2} \sum_{j=1}^{3N} \dot{q}_j^2$$

$$\dot{q}_j = \frac{d}{dt} q_j$$

$$V = PE = V(q_i, i = 1, \dots, 3N)$$

Taylor expand V about equilibrium

$$q_j = 0 \forall j$$

$$V = V_0 + \sum_{j=1}^{3N} \left(\frac{\partial V}{\partial q_j} \right)_0 q_j + \frac{1}{2} \sum_{j,k=1}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_k} \right)_0 q_i q_k$$

At equilibrium, the first order terms are all 0 since we are near the minimum

$$V = V_0 + \frac{1}{2} \sum_{j,k=1}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_k} \right)_0 q_i q_k$$

$$V(\vec{q}) = \sum_{j,k=1}^{3N} b_{jk} q_j q_k$$

$$b_{jk} = \frac{1}{2} \left(\frac{\partial^2 V}{\partial q_j \partial q_k} \right)_0 \text{ a } 3N \times 3N \text{ matrix}$$

So far its just a generalization of diatomic

The Lagrangian Equation of Motion, a reformulation of Newtons equation of Motion

$$L = T - V$$

$$\frac{\partial}{\partial t} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0, \quad 3N \text{ 2nd order ODE equations}$$

$$\ddot{q}_j + \sum_{k=1}^{3N} b_{jk} q_k = 0$$

Imagine b_{jk} is diagonal $b_{jk} = b_{jk} \delta_{jk}$

Then the equation simplifies to

$$\ddot{q}_j + b_{jj} q_j = 0$$

This is simple harmonic oscillator

$$q_j = A_j e^{\omega_j t + \phi_j}$$

In general, if b_{jk} is nondiagonal we have a $3N$ coupled differential equations

The solutions are called normal modes

Choose a coordinate system that makes b_{jk} diagonal

$$\ddot{\vec{q}} + B\vec{q} = 0$$

Q_n is some linear combination of the q_i that results in transforming b_{jk} into a diagonal matrix B

$$B\vec{q} = \lambda\vec{q}$$

$$\det(B - \lambda I) = 0$$

λ_j are the $3N$ eigenvalues of B

in terms of the $Q_n \rightarrow \ddot{Q}_n + \omega_n^2 Q_n = 0$

$$Q_n = A_n \sin(\omega_n t + \psi_n), \quad \omega_n = \sqrt{\lambda_n}$$

$$T = \frac{1}{2} \sum_{n=1}^{3N} \dot{Q}_n^2$$

$$V = \frac{1}{2} \sum_{n=1}^{3N} \lambda_n Q_n^2$$

$\Rightarrow 3N$ harmonic oscillators

This formulation includes overall translation motion of the CM and Rigid Body Rotation KE

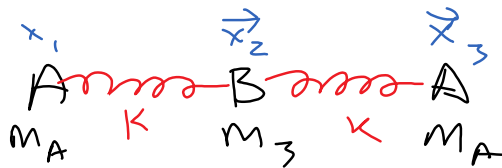
6(5) of the λ_n are zero

Linear molecules

The corresponding Q_n to these zeros describes overall translation and rotation of molecules

The $3N - 6(5)$ coordinates are vibrations

An example – a linear triatomic



The potential here is

$$V(x_1, x_2, x_3) = \frac{1}{2} k(x_2 - x_1)^2 + \frac{1}{2} k(x_3 - x_2)^2$$

B matrix

$$b_{11} = b_{33} = \frac{k}{m_A}, \text{ both particles 1 and 3 are attached to particle B}$$

$$b_{12} = b_{23} = -\frac{k}{\sqrt{m_A m_B}}, \text{ something standard deviation}$$

$$b_{22} = \frac{2k}{M_B} \text{ there are 2 masses connected to particle B}$$

$$b_{13} = 0, \text{ 1 and 3 are not connected}$$

$$B - \lambda I = \begin{bmatrix} b_{11} - \lambda & b_{12} & 0 \\ b_{12} & b_{22} - \lambda & b_{12} \\ 0 & b_{12} & b_{11} - \lambda \end{bmatrix}$$

$$\det[B - \lambda I] = (b_{11} - \lambda)^2 (b_{22} - \lambda) - 2(b_{11} - \lambda)b_{12}^2 = 0$$

$$\lambda_1 = \frac{k}{m_A} \rightarrow v_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m_A}}$$

$$\lambda_2 = k_{m_A} + \frac{2k}{m_B} \rightarrow v_2 = \frac{1}{2\pi} \sqrt{\frac{k}{m_A} + \frac{2k}{m_B}}$$

$$\lambda_3 = 0$$

The normal modes

Orthogonal eigenvectors of B

$$\sum_k |l_{ik}|^2 = \sum_k l_{ik}^* l_{ik} = 1$$

$$\vec{l}_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}, \quad \vec{l}_2 = \begin{bmatrix} b \\ 2a \\ b \end{bmatrix}, \quad \vec{l}_3 = \begin{bmatrix} a \\ b \\ a \end{bmatrix}$$

$$a = \sqrt{\frac{m_A}{2M}}, \quad M = M_A + M_A + M_B$$

$$b = \sqrt{\frac{m_b}{2M}}$$

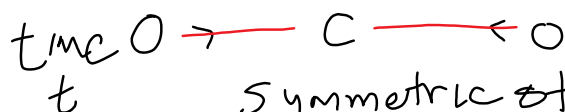
S = unitary orthogonal matrix of these columns
 \Rightarrow unitary transformation to diagonalize B

Recall $q_i = \sqrt{m_i}(x_i)$

$$\vec{Q} = S^t \vec{q}$$

$$Q_1 = \sqrt{\frac{m_A}{2}}(x_1 - x_3)$$

$$CO_2, \quad 3N - 5 = 9 - 5 = 4$$



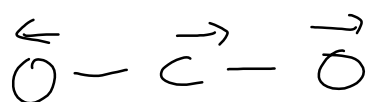
Symmetric stretch
of the molecule

Alternation extension
& compression along
molecular axis

$$\tilde{\nu} = 1354 \text{ cm}^{-1}$$

reflection plane
containing axis

$\left\{ \begin{array}{l} t \\ g \end{array} \right.$ symmetry
under
inversion
g-gerade

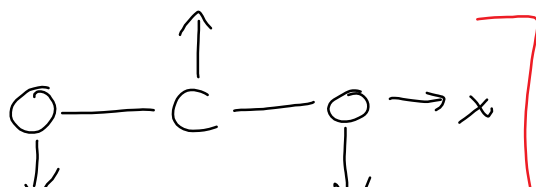


corresponds to λ_2

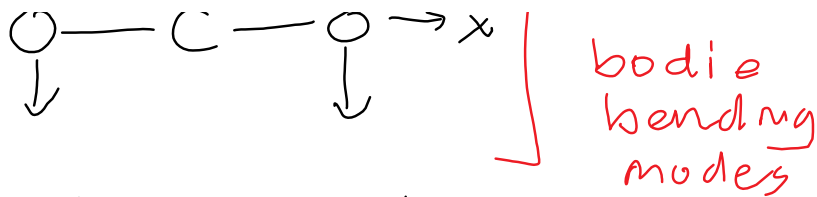
$$\tilde{\nu}_2 = 2396 \text{ cm}^{-1}$$

antisymmetric stretch

$$\sum_u^t$$



two
bodies



$$\tilde{\nu} = 673 \text{ cm}^{-1}$$

(non linear triatomic
H₂O
3N-6 modes { one bending
mode is missing

Quantum treatment

Classically

$$E_{tot} = T + V = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2 + \frac{1}{2} \sum_{j=1}^{3N} \lambda_j Q_j^2$$

$$E_{tot}^{vib} = \frac{1}{2} \sum_{i=1}^{3N-6(5)} \dot{Q}_i^2 + \frac{1}{2} \sum_{j=1}^{3N-6(5)} \lambda_j Q_j^2, \text{ subtract the translation and rotational}$$

$$\hat{H} = \sum_{j=1}^{3N-6} \left(-\frac{\hbar^2}{2} \partial_{Q_i}^2 + \lambda_i Q_i^2 \right)$$

Some $3N - 6$ independent Q.H. Osc. solutions of the Schrodinger Equation

$$\psi_{vib}(Q_1, \dots, Q_{3N-6(5)}) = \chi_{v_1}(Q_1) \chi_{v_2}(Q_2) \dots \chi_{v_{3N-6(5)}}(Q_{3N-6(5)})$$

each

$$\chi_{v_i}(Q_i) = N_{v_i} H(\sqrt{\alpha_i} Q_i) e^{-\frac{\alpha_i Q_i^2}{2}}$$

$$\alpha_i = \frac{2\pi v_i}{\hbar}$$

The vibrational state of molecule is specified by $3N - 6$ vibrational quantum #'s

v_i' each $0, 1, 2, 3, \dots, \infty$

The corresponding energy

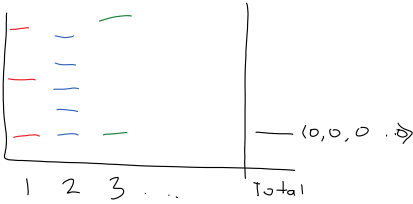
$$E_{vib} = \sum_{i=1}^{3N-6(5)} \left(N_i + \frac{1}{2} \right) h v_i$$

The vibrational spectrum difference is the sum of $3N - 6$ individual vibrational spectra

Transitions Polyatomics

Tuesday, March 22, 2016 11:02 AM

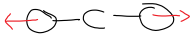
$$E_{vib} = \sum_{i=1}^{3N-6(s)} \left(N_i + \frac{1}{2} \right) h\nu_i$$



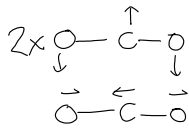
Rotational Structure

Vibrational transitions actually are bands consisting of many rotational transitions $J \rightarrow J \pm 1$

E.g. CO_2



$$\Sigma_g^+, \quad \bar{\nu}_1 = 1354 \text{ cm}^{-1}$$



$$\Pi_u(E_{1u}), \quad \bar{\nu}_2 = 673 \text{ cm}^{-1}$$

$$\Sigma_g^+ (A_{1g}), \quad \bar{\nu}_3 = 2396$$

IR spectrum CO_2

| | |
|---------|--|
| ν_1 | Displacement of this symmetry maintains $\mu_o = 0 \Rightarrow \left(\frac{d\mu_o}{dq_1} \right)_0 = 0$ No transition (forbidden) CO_2 symmetric stretch is no IR active |
| ν_3 | Under this displacement μ becomes no zero $Q_3 \neq 0 \Rightarrow \left(\frac{\partial \mu}{\partial Q_3} \right)_0 \neq 0$ Molecules remains linear $\Delta J = \pm 1$ branches \Rightarrow at the IR frequency ν_3 results in P and R branch |
| ν_2 | Under this displacement $\mu \Rightarrow$ non zero $\left(\frac{\partial \mu}{\partial Q_2} \right)_0 \neq 0$ But molecule is only quasi-linear $\Delta J = 0$ is possible (like the symmetric top) b -type asymmetric top selection rule $\Delta J = 0, \pm 1$ $\Delta v = \pm 1$ |

Labelling Irreducible Reps

Mulliken Notation

- A_1 for the totally symmetric representation
- one dimensional reps $\chi(E) = 1$
 - They are labelled A or B depending on $\chi(C_n \text{ or } S_n) = \begin{cases} +1 \Rightarrow A \\ -1 \Rightarrow B \end{cases}$
 - No rotational axis $\rightarrow A$
- Two dimensional representation E
- 3D representation T
- 4D, SD for I_h G or H

If there is a center of symmetry add $\frac{g}{u}$ as a post script $\chi(\tau) \pm 1, \frac{g}{u}$

Linear Molecules ($C_{\infty v}, D_{\infty h}$)

Differential labelling conventions

Labelled with capital greek letters for $\Lambda = |L_z|$ follow spectroscopic notes

| Λ | 1 | 2 | 3 | 4 |
|-----------|----------|-------|----------|-----|
| | s | p | d | f |
| | Σ | Π | Δ | |

$\Lambda > 0$

2 fold degenerate $L_z = \pm \Lambda$

Λ is a quantum that specifies the behavior under rotation about molecule axis $\psi \Rightarrow e^{i\Lambda\phi}$

The super script \pm refers to symmetry

Under mirror reflection σ_h

σ_v if no h plane

$\chi(C_2) = \text{Re}(e^{\pm i\Lambda\phi})$

$\chi(\sigma_v) = \pm 1, 0$

$\chi(I) = \pm 1, \frac{g}{u}$

Symmetries of Normal Modes

The normal modes of vibrations can be classified in terms of irreducible representation of the point group

Example H_2O



$$A_1 \Rightarrow a_1, \quad \text{use a lower case to denote mode symmetry}$$



$$A_1 \Rightarrow a_1$$



$$b_1, C_{2v}$$

Recall our normal mode decompositions

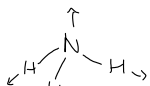
3N coordinates includes $\begin{bmatrix} \text{translation (cm)} \\ \text{rotation (rigid body)} \end{bmatrix}$

Translation and Rotations also have symmetry characters

translation - x, y, z

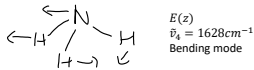
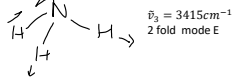
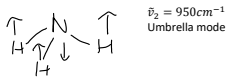
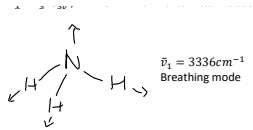
rotation - R_x, R_y, R_z

$$E_x NH_3 \quad C_{3v}, \quad 3 \cdot 4 - 6 = 6 \text{ normal modes}$$



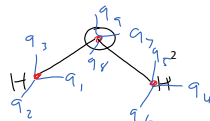
$$\bar{\nu}_1 = 3336 \text{ cm}^{-1}$$

Breathing mode



What symmetries of normal modes are possible?

- Group theory
- Normal modes of H2O

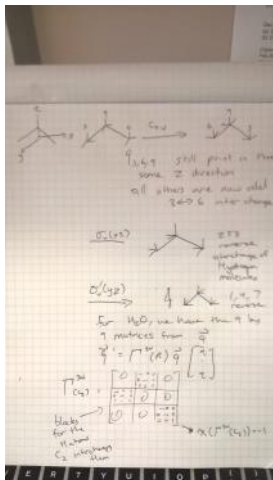
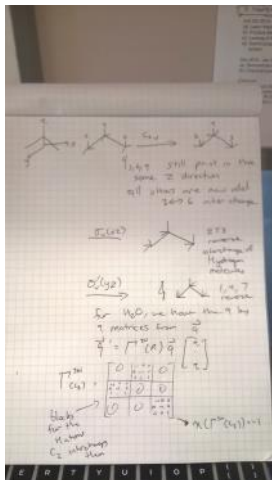


We have $3N=9$ coordinates of the molecules

From this construct, we construct a $3N \times 3N$ representation of the point group Γ^{3N}

Consider each symmetry operations

How does it affect the coordinates



The $3N$ reducible rep Γ^{3N}

Has the following character table

| | E | C_2 | σ_v | σ_v' |
|---------------|---|-------|------------|-------------|
| Γ^{3N} | 9 | -1 | +1 | 3 |

This is reducible so

$$\Gamma^{3N} = \sum a_l \Gamma^l$$

$$\Gamma^{3N} = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus 3\Gamma^{B_2}$$

The possible symmetry of an arbitrary motion of molecules

(3N degrees of Freedom)

A subset are the $3N - 6$ normal modes but the other 6 are rotating/translation

To get the symmetry of normal modes we need to find and subtract the symmetry characters of translation/rotation

Translation, we can find from the 3d representation for symmetry operators

$$C_{2z}: \Gamma^{trans} = \Gamma^{A_1} (\text{for } z) \oplus \Gamma^{B_1} (\text{for } x) \oplus \Gamma^{B_2} (\text{for } y)$$

$$\text{similarly } \Gamma^{rot} = \Gamma^{A_2} \oplus \Gamma^{B_1} \oplus \Gamma^{B_2}$$

$$C_2 R_z = R_z$$

$$\sigma_v R_z = -R_z$$

$$\sigma_v' R_z = -R_z$$

$$E R_z = R_z$$

R_z has symmetry character A_2 subtracting these from Γ^{3N}

$$\Gamma^{vib} = 2\Gamma^{A_1} \oplus \Gamma^{B_2}$$

This leaves 2 modes for A_1 and 1 mode for B_2 symmetry

For simple modes \Rightarrow assign mode symmetry by inspection

Systematically

One can use the symmetry projection operators

$$P^\mu = \sum_R \chi_R^\mu P_R$$

P^μ are displacement = displacement with respect to symmetry of μ

P^μ arbitrary wavefunction = w.f. with symmetry μ

Character table for C_{3v} point group

| | E | $2C_3(z)$ | $3\sigma_v$ | linear, rotations | quadratic |
|-------|---|-----------|-------------|-----------------------|--------------------------|
| A_1 | 1 | 1 | 1 | z | x^2+y^2, z^2 |
| A_2 | 1 | 1 | -1 | R_z | |
| E | 2 | -1 | 0 | (x, y) (R_x, R_y) | (x^2-y^2, xy) (xz, yz) |

Product table for C_{3v} point group

| | A_1 | A_2 | E |
|-------|-------|-------|-------------|
| A_1 | A_1 | A_2 | E |
| A_2 | A_2 | A_1 | E |
| E | E | E | A_1+A_2+E |

Lecture 20

Thursday, March 24, 2016 11:06 AM

Heizberg Ordering

v_1 – highest frequency A_1

v_2 – decreasing $v \Rightarrow A_2, \dots, B_1, \dots, B_2$

G. Abbreviated Rules for $\Gamma^{3N}\chi$

Distinguish between atoms that are moved or unmoved by the point symmetry operations

To be unmoved, the atom must lie on the symmetry element: point of inversion, axis of rotation, plane of reflection

Contribution to χ of atoms that are moved is zero since the entire 3×3 block is off diagonal

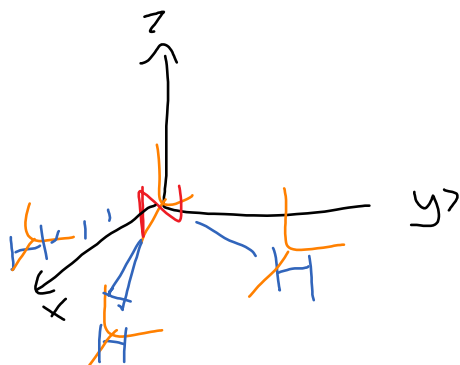
Each moved atom will change to its 3 coordinates like ± 1

Character contribution $\Rightarrow \chi = \pm 1$

| Symmetry | χ |
|-----------|--------|
| E | 3 |
| σ | 1 |
| \hat{i} | -3 |
| C_2 | -1 |
| C_3 | 0 |
| C_4 | 1 |
| S_3 | -2 |
| S_4 | -1 |
| S_6 | 0 |

We do not need to calculate Γ^{3N} matrices in most cases, just $\chi(\Gamma^{3N})$

Normal modes of NH_3



| | | | |
|---------------|----|--------|-------------|
| 1 | E | $2C_3$ | $3\sigma_v$ |
| Γ^{3N} | 12 | | |

C_3 : Only N atom is unmoved

$$\vec{x'} = \Gamma_{C_3} \vec{x}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) & 0 \\ -\sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

$$\chi(C_3) = -\frac{1}{2} - \frac{1}{2} + 1 = 0$$

$$\cos\left(\frac{2\pi}{3}\right) = -\frac{1}{2}$$

$\sigma_v(xz)$: 2 atoms N and H_3 dont move

$$\Gamma_{\sigma_v} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \Rightarrow \chi(\sigma_v) = 2$$

$$\Gamma^{3N} = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 4\Gamma^E$$

But this contains both the symmetry of the normal modes, rotational and translation

Translation consider an arbitrary point (x,y,z)

$\Rightarrow 3D$ representation

$$\Gamma(E) = I, \quad \Gamma(C_3) = \frac{1}{2} \begin{bmatrix} -1 & \sqrt{3} & 0 \\ -\sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}, \quad \Gamma(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

| | | | |
|---------------|---|-------|------------|
| 1 | E | C_3 | σ_v |
| Γ^{2D} | 3 | 0 | 1 |

$$\Gamma^{A_1} \oplus \Gamma^E$$

For rotation

$$\Gamma^{A_2} \oplus \Gamma^E$$

Symmetry of Vibrational ψ

1D/diatomic $v = \text{even} \Rightarrow \psi_{vib} \text{ even}$

$v = \text{odd} \Rightarrow \psi_{vib} \text{ odd}$

Recall the normal mode decomposition

$$\psi_{vib}(\vec{Q}) = \chi_{v_1}(Q_1) \chi_{v_2}(Q_2) \dots \chi_{v_{3N-6}}(Q_{3N-6})$$

$$\prod_{i=1}^{3N-6} \chi_{v_i}(Q_i)$$

$$\text{Each factor } \chi_{v_1}(Q_1) = N_{v_1} H_{v_1} e^{-\frac{\alpha}{2} Q_1^2}$$

$$\alpha = \frac{2\pi}{\hbar} v_1$$

$H_{v_1} = \text{Hermite polynomial}$

$$\psi_{vib} = N e^{-\frac{1}{2} \sum \alpha_i Q_i^2} \prod_{i=1} H_{v_i}(\sqrt{\alpha_i} Q_i)$$

Exponential term is $\sum Q_i^2 \Rightarrow \text{the same form as } V(Q), \text{ the P.E.} \Rightarrow \text{Most have symmetry } A_1$

Symmetry $\Rightarrow \psi_{vib}$ is that or $\prod_i H_i(Q_i)$

For the ground state

$$v_i = 0 \forall i$$

$$H_0 = 1 \Rightarrow \psi_{vib} = A_1$$

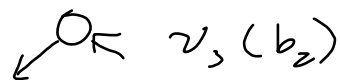
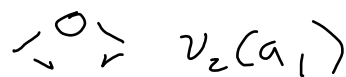
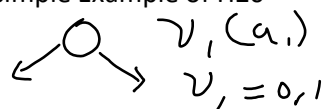
Single Excited mode

$$v_j = 1, v_i = 0, \quad \forall i \neq j$$

$$H_1(x) = x$$

ψ_{vib} has symmetry of Q_j

A simple Example of H₂O



ψ_{vib} is induced
by $3v_1$

| Vibrational state | Symmetry |
|-------------------|-------------------------|
| (v_1, v_2, v_3) | |
| (0,0,0) | A_1 |
| (1,0,0) | A_1 |
| (0,1,0) | A_1 |
| (0,0,1) | B_2 |
| (1,1,0) | $A_1 \otimes A_1 = A_1$ |
| (1,0,1) | $A_1 \otimes B_2 = B_2$ |
| (2,0,0) | A_1 |
| (0,0,2) | $B_2 \otimes B_2 = A_1$ |
| (0,2,1) | B_2 |
| (0,0,3) | B_2 |

For non-degenerate normal modes

$$\Gamma_{\{v\}} = \bigotimes_{i=1}^{3N-6} \Gamma_{v_i}$$

$$\chi(\Gamma_{\{v\}}) = \prod_{i=1} \chi(\Gamma_{v_i})$$

For even v : Γ_v is A_1 symmetric

odd v : Γ_v is symmetry or Q_v the normal mode

Vibrational Selection Rule

As before, we have transition matrix element

$$\begin{aligned} \vec{\mu}_{fi} &= \int \psi_f^* \vec{\mu} \psi_i d\tau_1 \dots d\tau_N \\ &= \int \psi_f^*(\vec{Q}) \vec{\mu}(\vec{Q}) \psi_i(\vec{Q}) dQ \end{aligned}$$

As before, we Taylor expand μ

$$\begin{aligned} \vec{\mu} &= \sum e\vec{r} = \vec{\mu}_0 + \sum_{k=1}^{3N-6} \left(\frac{\partial \mu}{\partial Q_k} \right) Q_k + \dots + O(3) \\ \vec{\mu}_{fi} &= \vec{\mu}_0 \int \psi_f^* \psi_i + \sum_{k=1}^{3N-6} \left(\frac{\partial \mu}{\partial Q_k} \right) \int \psi_f^* Q \psi_i \end{aligned}$$

For transitions or just the J^{th} mode

$$I_{f \leftarrow i} \propto |\mu_{fi}|^2 \propto \left| \frac{\partial u}{\partial Q} \right|^2 \left| \int \psi_{v_1} Q_j \psi_{v_2} dQ_j \right|^2$$

$$Q = (a + a^+) \times \text{constant}$$

$$\Delta v_j = \pm 1 \text{ for } J^{th} \text{ modes}$$

$$\Delta v_i = 0 \text{ for } j \neq 1$$

For $\vec{\mu}_{fi} \neq 0$ we must have an integrand that is totally symmetry A_1

$$\Gamma(\psi_f^*) \otimes \Gamma(\vec{\mu}) \times \Gamma(\psi_i) \text{ must contain } A_1$$

ie the a_i for Γ^{A_i} in the irreducible representation decomposition the direct must be $\neq 0$

If it is nonzero then the mode is IR active

$$\Delta v_j = \pm 1 \text{ selection rule}$$

For fundamental transitions from ground vibrational state

$$\Gamma(\psi_1) = A_1$$

$$\Gamma(\psi_f^*) \otimes \Gamma(\vec{\mu})$$

Q_j and x, y, z symmetry

Overtone transitions

Arise from higher order terms

$$\vec{\mu}_2 = \left(\frac{\partial^2 \mu}{\partial Q_j \partial Q_u} \right) Q_j Q_u$$

Transitions at $v_j + v_u$

$$\text{We require } \langle \psi_f | Q_j Q_k | \psi_i \rangle$$

Direct product tables

Tabulate symmetries of direct product under each point group

Examples

H_2O

| 1 | E | C_2 | σ_v | σ'_v | |
|-------------------|---|-------|------------|-------------|-----------|
| $(0,0,0)\psi_i$ | 1 | 1 | 1 | 1 | A_1 |
| μ_x | 1 | -1 | 1 | -1 | B_1 |
| $(1,0,0)\psi_f^*$ | 1 | 1 | 1 | 1 | A_1 |
| $(\mu_{fi})_x$ | 1 | -1 | 1 | -1 | B_1 |
| A_1 | 1 | 1 | 1 | 1 | A_1 |
| | 1 | -1 | 1 | -1 | $a_1 = 0$ |

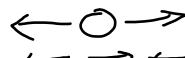
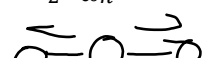
But $(\mu_{fi})_z \neq 0$, the mode is IR active

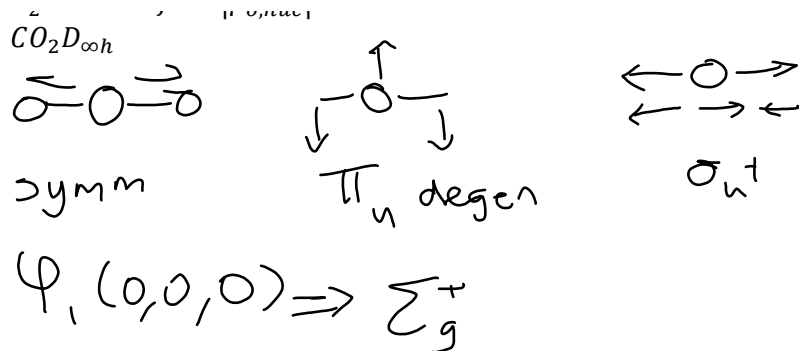
All modes for H_2O are active

A_1 modes after $|\vec{\mu}_{o,nuc}|$

B_2 modes after $|\vec{\mu}_{o,nuc}|$

$CO_2 D_{\infty h}$





$$\psi_1(0,0,0) \Rightarrow \Sigma_g^+$$

$$\psi_f^*(1,0,0) \Rightarrow \Sigma_g^+$$

$$\mu_z: \Sigma_g^+ \otimes \Sigma_u^+ \otimes \Sigma_g^+ = \Sigma_u^+ \neq \Sigma_g^+$$

Therefore forbidden

$$\mu_x, \mu_y: \Sigma_g^+ \otimes \Pi_u \otimes \Sigma_g^+ = \Pi_u \neq \Sigma_g^+$$

Bend

$$x, y, (\Pi_u \otimes \Pi_u) \otimes \Sigma_g^+ = (\Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g) \otimes \Sigma_g^+ = \text{overall 1 term has nonzero } \Sigma_g^+$$

$$\mu_z: (\Pi_u \otimes \Sigma_u^+) \otimes \Sigma_g^+ = \Pi_g \otimes \Sigma_g^+$$

$$\mu_x, \mu_y: (\Pi_u \otimes \Pi_u) \otimes \Sigma_g^+ = (\Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g) \otimes \Sigma_g^+$$

There is a $\Sigma_g^+ \otimes \Sigma_g^+$ term

This is IR active to \perp components of $\vec{\mu}$

Asymmetric stretch

$$\mu_z \Sigma_z^+ \otimes \Sigma_u^+ \otimes \Sigma_g^+ \Rightarrow \Sigma_g^+$$

IR active for parallel transitions

For fundamental transitions for linear molecules

| | | |
|----------------|------------------|------------------------------------|
| μ_z | "parallel bands" | P and R Branch $\Delta J = \pm 1$ |
| μ_x, μ_y | "perp band" | PQR branches $\Delta J = 0, \pm 1$ |

Rotational States

Tuesday, March 29, 2016 10:46 AM

Rotational of atoms \rightarrow no $\vec{\mu}$, no I

1) Rotations of diatomic molecules

Define:

Space Fixed Frame (SFF) as moving at constant \vec{v} wrt CM

The origin in this new frame is at the location of the center of mass

The axis in $x'y'z'$ frame is determined by using θ, ϕ in the Space Fixed Frame (SFF),

This choice of co-ordinate separates the CM motion from rotation

For a free molecule, no potential energy

The Hamiltonian is purely kinetic

$$\hat{H} = \hat{T}_A + \hat{T}_B = -\frac{\hbar^2}{2m_a}\nabla_a^2 - \frac{\hbar^2}{2m_b}\nabla_b^2$$

Instead of R_A, R_b

$$R = r_a - r_b$$

$$r_{cm} = \frac{m_a r_a + m_b r_b}{m_a + m_b}$$

$$m = m_a + m_b$$

$$\mu = \frac{m_a m_b}{M}$$

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{cm}^2 - \frac{\hbar^2}{2\mu}\nabla_{rel}^2$$

$$\nabla_{rel}^2 = \partial_x^2 + \partial_y^2 + \partial_z^2 = \partial_R^2 + \frac{2}{R}\partial_r - \frac{L^2}{R^2\hbar^2}$$

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

For a rigid rotor

$$R = |\vec{R}| = \text{constant}$$

$$\nabla^2 = -\frac{L^2}{R^2\hbar^2}$$

$$H_{\text{rigid rotor}} = -\frac{\hbar^2}{2\mu}\nabla_{rel}^2 = \frac{L^2}{2\mu R^2}$$

HW

$$B_e = \frac{1}{2} \frac{\hbar^2}{\mu r_e^2}$$

$$B = \frac{\hbar^2}{2\mu r}$$

$$\tilde{B} = \frac{B}{hc}$$

Polyatomics

Tuesday, March 29, 2016 10:49 AM

Rotationals of Polyatomic molecules

$$\hat{H} = \hat{T}_n = \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2$$

Define the moment of inertia tensor

$$I_{ij} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix}$$

$$L_i = I_{ij} \omega_j$$

$$I_{xx} = \sum_{\alpha} m_{\alpha} (y_{\alpha}^2 + z_{\alpha}^2)$$

$$I_{yy} = \sum_{\alpha} m_{\alpha} (z_{\alpha}^2 + x_{\alpha}^2)$$

$$I_{xy} = I_{yx} = - \sum_{\alpha} m_{\alpha} x_{\alpha} y_{\alpha}$$

symmetric matrix \rightarrow 6 components

We can re-orient the axes xyz to make I diagonal

This is the principal axis system

$$I_{ij} \rightarrow I' = \begin{bmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{bmatrix}$$

Convention is that $I_c \geq I_b \geq I_a$

Using this new frame,

$$\hat{T}_{rot} = \frac{1}{2} \sum_{i=1}^3 I_i \Omega_i^2 = \sum_i \frac{L_i^2}{2I_i}$$

$$\hat{H}_{rot} = \frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c}$$

Define 3 rotational constraints

$$A = \frac{h}{8\pi I_a}$$

$$H_{rot} = \frac{1}{\hbar^2} (AL_a^2 + BL_b^2 + CL_c^2)$$

Example BF_3

$$r_{cm} = \frac{1}{m} \sum m_{\alpha} r_{\alpha}$$

$$m = \sum m_{\alpha}$$

Axis out of plane of the molecule

$$r_{bf} = 1.30A$$

$$I_c = 3m_F (r_{BF})^2 = 3 * 19u (1.30A)^2 = 1.6 * 10^{-38} gcm^2$$

$$I_b = 2 \times (r_{BF} \cos(30^\circ))^2 m_F$$



$$= \frac{3}{2} m_F r_{BF}^2$$

$$I_a = m_F r_{BF}^2 + 2 \times m_F (r_{BF} \sin(30^\circ))^2 = \frac{3}{2} m_F r_{BF}^2$$

$$I_a = I_b = \frac{1}{2} I_c$$

This is a special consequence of the high symmetry of molecule

Relation of I_{ij} to symmetry

The c_n principal axis coincides with one of a,b,c

The reflection plane contains 2 of a,b,c

If principal rotation axis has $n \geq 3$ then 2

I_a, I_b, I_c are equal

Spectroscopy

Tuesday, March 29, 2016 10:47 AM

Define rotation constant

$$B_e(\text{Hz}) = \frac{h}{8\pi^2 I_e},$$

$$I = \mu R_e^2$$

$$\tilde{B}_e(\text{cm}^{-1}) = \frac{h}{8\pi^2 I_e c}$$

$$H_{\text{rig}} = \frac{1}{2} L^2$$

$$E_{\text{rot}} = h B_e (J(J+1)) = hc \tilde{B}$$

$$\Delta E_{\text{rot}} = 2h B_e (J+1)$$

Spectroscopic Structure Determination

Measure B (from the spectrum)

→ know masses, $I_e \rightarrow R_e^2$, can obtain *geometric info from the spectrum*

Selection Rules

Dipole transitions

$$\Delta J = \pm 1, \quad \text{total angular momentum}$$

$$\Delta m = 0, \pm 1, \quad \text{component angular momentum}$$

$$\vec{\mu}_o \neq 0$$

Molecules must have permanent dipole moment

The spectrum is a series of equally spaced lines ($2B_e h$)

Typically $h B_e \sim 2 \text{cm}^{-1}, 60 \text{GHz}$

This formula gives a good amount of rotational line spacing, but what about intensity

The effect of thermal population

Causes a distribution in the states of the

Molecules

Intensity is proportional to the distribution of the population

$$I_{\text{absorp.}(J(J+1))} \propto N(J)$$

$$\propto g_J e^{-\frac{E_{\text{rot}}}{k_b T}}$$

$$\propto \alpha(2J+1) e^{-\frac{E_{\text{rot}}}{k_b T}}$$

1) This is pure rotational spectrum

→ *can combine*

This is with vibrations → *rovibrational spectrum*

2) Molecules rotors are not ideally rigid

a. Known as centrifugal distortions

b. Centrifugal distortion R_e depends on J

3) Nuclear Spin Statistics

Special Cases

Tuesday, March 29, 2016 10:50 AM

The 5 types of Rigid rotor

A. linear molecule (including diatomic)

Here $I_a = 0$

$$I_b = I_c = I$$

$$H_{rot} = \frac{1}{2I} (L_b^2 + L_c^2) = \frac{L^2}{2I}$$

Eg HCN, CO_2

Linear

2 quantum numbers J, M

$$J = 0, 1, 2, \dots, \infty$$

$$M = -J, -J + 1, \dots, +J$$

Since $E = E_J$, has a degeneracy of $g = 2J + 1$

B. Spherical Top

Any time we have more than 1 C_n ($n \geq 3$) axis

$$I_a = I_b = I_c = I$$

$\text{CH}_4, \text{SF}_6, \text{C}_{60}$

$$\hat{H}_{rot} = \frac{L_a^2 + L_b^2 + L_c^2}{2I} = \frac{L^2}{2I}$$

$$E_{rot} = hBJ(J + 1)$$

All too symmetric to be polar, ie we have a dipole moment $\vec{\mu}_0$, ie we can not really observe

3 quantum numbers, J, M, K

$$J = 0, \dots, \infty$$

$$K, M = -J, -J + 1, \dots, J$$

$E = E_J$, degeneracies of $g = (2J + 1)^2$

C. Symmetric Top

a. Prolate

$$I_a < I_b = I_c$$

Eg $\text{CH}_3\text{CN}, \text{NH}_3, \dots$

$$\begin{aligned} \hat{H}_{rot} &= \frac{L_a^2}{2I_a} + \frac{L_b^2 + L_c^2}{2I_c}, \quad \text{note } L^2 = L_a^2 + L_b^2 + L_c^2 \\ &= \frac{L_a^2}{2I_a} + \frac{L^2 - L_a^2}{2I_b} = \frac{L^2}{2I_b} + \frac{L_a^2}{2} \left(\frac{1}{I_a} - \frac{1}{I_b} \right) \end{aligned}$$

a. Oblate

$$I_a = I_b < I_c$$

$$\hat{H} = \frac{L_a^2 + L_b^2}{2I_a} + \frac{L_c^2}{2I_c}$$

$$= \frac{L^2 - L_c^2}{2I_a} + \frac{L_c^2}{2I_c}$$

$$= \frac{L^2}{2I_a} + \frac{L_c^2}{2} \left(\frac{1}{I_c} - \frac{1}{I_a} \right)$$

Eg $\text{C}_6\text{H}_6, \text{BF}_3 \dots$

$$E_{rot} = E_{JK} = \frac{J(J + 1)\hbar^2}{2I_a} + K^2\hbar^2 \left(\frac{1}{2I_c} - \frac{1}{2I_a} \right)$$

3 quantum numbers J,K,M

$$E = E(J, K)$$

$$K = 0, \quad E = E(J) \Rightarrow 2J + 1 \text{ (M values)} = g$$

$$K \neq 0, \quad E = E(J, K^2) \text{ values of } k = \pm 1, \pm 2 \dots$$

$$g = 2(2J + 1)$$

D. Asymmetric

a. Asymmetric Top

General Case

$$I_a \neq I_b \neq I_c$$

Eg H_2O

$$\text{General } \hat{H}_{rot} = \frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c}$$

Asymmetric tops

3 quantum numbers J,M,K

$k \neq \text{projection of } \vec{L} \text{ along any axis}$

E are still independent of M

No simple expression for $E(J,K)$

Asymmetry splits $\pm K$ degeneracies of symmetric tops

Symmetry

Tuesday, March 29, 2016 10:56 AM

Correlation diagram

index levels

order of levels

\Rightarrow *not quantitative energy levels*

1) Consideration

$C_{\infty v}, D_{\infty v}$ – linear motors

O_h, T_d, I_h , spherical top

$\left\{ \begin{array}{l} C_n \text{ axis } n \geq 3 \\ S_4 \text{ axis} \end{array} \right\} \Rightarrow \text{symmetric top}$

Dipole Transtions

Tuesday, March 29, 2016 10:57 AM

1) Electric Dipole Transition Among Rotational States

For pure rotational spectra of the molecule must be polar (gross selection rule)

Nonpolar molecules may have very weak pure rotational spectra

eg O₂ = M1 (magnetic dipole transition) is triplet has spin

$$\vec{\mu} = \vec{\mu}_{el} + \vec{\mu}_{nuc} = -e \sum_i r_i + Z_1 e \vec{R} + Z_2 e \vec{R}_2$$

$$\vec{\mu}_{fi} = \iint \psi_f^* \vec{\mu} \psi_i d\tau_{nuc} d\tau_{el}$$

$$\psi = \psi_{el} \otimes \psi_{nuc} = \psi(\vec{r}; \vec{R}) \chi(\vec{R})$$

$$\begin{aligned} \vec{\mu}_{fi} &= \iint \psi_f^* \chi_f^* (\vec{\mu}_{el} + \vec{\mu}_{nuc}) \psi_i \chi_i d\tau_{el} d\tau_{nuc} \\ &= \int d\tau_{nuc} \chi_f^* \left(\int d\tau_{el} \psi_f^* \vec{\mu}_{el} \psi_i \right) \chi_i + \int d\tau_{nuc} \chi_f^* \vec{\mu}_{nuc} \left(\int \psi_f^* \psi_i \right) \chi_i \\ &= \int d\tau_{nuc} (\chi_f^* [\mu_{el}^{fi}] \chi_i) + \int d\tau_{nuc} \left(\chi_f^* \vec{\mu}_{nuc} \left(\int d\tau_{el} \psi_f^* \psi_i \right) \chi_i \right) \end{aligned}$$

Case 1. Within some electronic state $\psi_f = \psi_i$

$$\langle \vec{\mu}_{el} \rangle = \int \psi_i^* \vec{\mu}_{el} \psi_i = 0 \text{ if molecule is inversion symmetric}$$

$\vec{\mu}_{el}$ is odd under inversion

$$\int \chi_f \langle \mu_{el} \rangle \chi_i \approx 0 \text{ even for less symmetric molecules}$$

$$\begin{aligned} \vec{\mu}_{el} &= \mu_{el}(\vec{R}) \\ &\approx \vec{\mu}_{el}(\vec{R}_{eq}) \end{aligned}$$

$$\mu_{fi} = \int \chi_f^* \vec{\mu}_{nuc} \chi_i d\tau$$

Case 2. Electronic transition

$$\int \psi_f^* \psi_i d\tau = 0$$

$$\vec{\mu}_{fi} = \int \chi_f^* \vec{\mu}_{el}^{fi} \chi_f d\tau_{nuc}$$

$$\vec{\mu}_{el} = \int d\tau_{el} \psi_f^* \vec{\mu}_{el} \psi_i$$

Special cases

Tuesday, March 29, 2016 10:57 AM

1. Diatomic and Linear Mols

$$\psi_{v,J,M} = \chi_v(q) Y_{J,M}(\theta, \phi) (\psi_{el})$$
$$q = R - R_e$$

For ground vibrational and electronic state

$$\vec{\mu}_{fi} = \int \psi_{v,J,M}^* \vec{\mu}_{nuc} \psi_{v,J,M}^i$$

$$\vec{\mu}_{nuc} = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z}$$
$$= \mu_{nuc} (\sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z})$$

$$\vec{\mu}_{fi}^{comp} = \mu_{nuc} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta Y_{J',M'}^*(\theta, \phi) \begin{bmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{bmatrix} Y_{J,M}(\theta, \phi)$$

For $\mu_{fi} \neq 0$

Need μ_{nuc}

$$\Delta J = \pm 1$$

$$\Delta M = 0, \pm 1$$

2. Symmetric and Asymmetric tops

Symmetric $\mu_{nuc} \neq 0$

$$\Delta J = 0, \pm 1$$

$$\Delta M = 0, \pm 1$$

$$\Delta K = 0$$

Transition frequency

$$\nu_{J+1,K} \leftarrow \nu_{J,K} 2B(J+1)$$

Asymmetric

$\vec{\mu}$ has components along a, b, c

$$\Delta J = 0, \pm 1, \quad \Delta M = 0, \pm 1$$

$$\mu_a \neq 0$$

$$\Delta k_a = 0, \pm 2, \pm 4, \dots$$

$$\Delta k_c = \pm 1, \pm 3$$

$$\mu_b \neq 0$$

$$\Delta k_a = \pm 1, \pm 3$$

$$\Delta k_c = \pm 1, \pm 3$$

$$\mu_c \neq 0$$

$$\Delta k_a = \pm 1, \pm 3$$

$$\Delta k_c = 0, \pm 2, \pm 4$$

Stein felt book molecules and radiation

Hertzberg books multivolume 2 ish

Symmetry of Degenerate Normal Mode

Tuesday, March 29, 2016 11:18 AM

Eg. The E modes of NH_3 $\Gamma^{vib} = 2A_1 \oplus 2E$



$$\begin{aligned} v_3 = 0, & \quad (0,0) A_1 \\ v_3 = 1, & \quad (0,1), (1,0) E \\ v_3 = 2, & \quad (2,0), (0,2), (1,1) \end{aligned}$$

C_{3v}

Character of $\Psi_{v_3=2}$ is not simply $E \otimes E$ but one can show

$$\chi_v^{(R)} = \frac{1}{2} [\chi(R)\chi_{v-1}(R) + \chi(R^v)]: \text{This is for } E \text{ normal modes}$$

$$\chi_2(R) = \frac{1}{2} [\chi(R)\chi_1(R) + \chi(R^2)]$$

$$\chi_2(E) = (\chi(E)^2 + \chi(E^2)) = \frac{1}{2}(4 + 2) = 3$$

$$\chi_2(C_3) = \frac{1}{2} (\chi(C_3)^2 + \chi(C_3^2))$$

$$= \frac{1}{2} ((-1)^2 + (-1)) = 0$$

$$\chi_2(\sigma_v) = \frac{1}{2} (\chi(\sigma_v)^2 + \chi(\sigma_v^2)) = \frac{1}{2} (\chi(\sigma_v)^2 + \chi(E)) = +1$$

$$\frac{1}{2}(0^2 + 2) = +1$$

$$\psi_{vib} = \chi_{v_1}(Q_1)\chi_{v_2}(Q_2)\chi_{v_3}(Q_3)\chi_{v_4}(Q)$$

$$= |v_1, v_2, v_3, v_4\rangle$$

$$= |0,0,2,0\rangle$$

$$A_1 \oplus E$$

$$1 + 2 = 3 \text{ fold}$$

Vibrational and Rovibrational Spectra in Polyatomic

Tuesday, March 29, 2016 11:39 AM

Main vibrational transitions follow $\Delta v = 1$ selection rule

Anharmonicity allow overtones

$$\Delta v = 2, 3, 4, \dots$$

Some low energy vibrational levels may be thermally populated

- Known as hot bands

Can get absorption at differences of fundamental absorptions (anharmonic)

$$CO_2 = \tilde{E}(0,0,1) - \tilde{E}(1,0,0) = cm^{-1}, CO_2 \text{ laser}$$

Combination Bands

$$\Delta v_i = 1 \dots$$

$$\Delta v_j = 1 \dots$$

Anharmonicity, can also shift energies slightly

Rotational Structure

Linear molecules para, perp

Nonlinear molecules is more complicated

Eg Symmetric top

Parallel band

μ along principle axis of rotation

$$\Rightarrow \Delta K = 0, \Delta J = 0, \pm 1$$

3 branches PQR

$$P_k^Q(J), Q_k^Q(J), R_K^Q(J)$$

Perpendicular bands

$\vec{\mu} \perp \text{principal axis}$

$$\Rightarrow \Delta k = \pm 1, 6 \text{ bands}$$

$$P_k^{(R)}(J) Q_k^{(R)}(J) R_k^{(R)}(J)$$

Further rotation - vibration coupling

-Coriolis force, fictitious force

- Leads to further splitting

Raman Spectroscopy

Tuesday, March 29, 2016 11:54 AM

E brick wilson molecular vibration

VIII A brief Look at Raman

-previously: single photon absorbed or emitted

-Raman: 2 photons are involved

-irradiate and measure another

A type of light scattering

1. Rayleigh Scattering
 - a. Elastic scattering
 - b. $E_{\text{photon}}, \lambda$ remains the same
 - c. Direction can change
 - i. Scattering distribution depends on λ
2. Raman Scattering
 - a. The scattered photon has a different energy than incident
 - b. $h\nu_{\text{initial}} = h\nu_{\text{scattered}} \pm h\nu_{\text{molecule}}$
 - i. Rovibrational energy of a molecule

If the scattered photon has lost energy, then it is (red shifted), this is a Stokes shifted

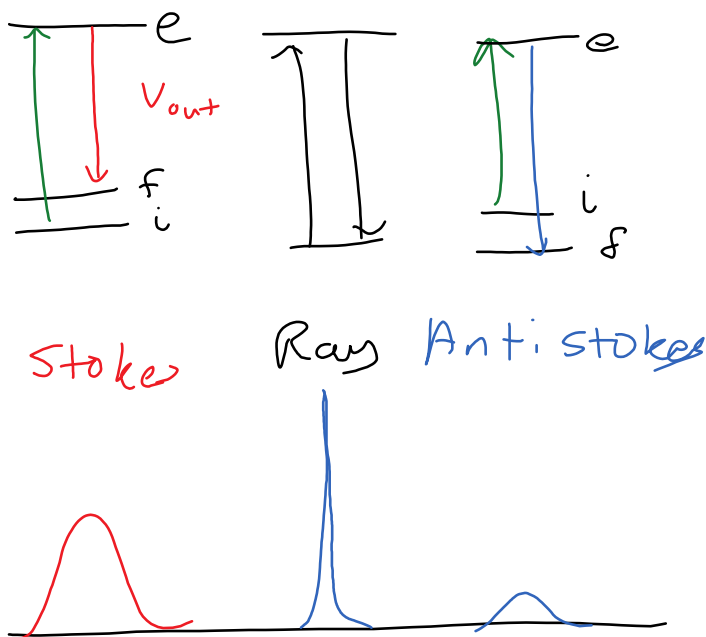
If the photon has gained energy, then it is (blue shifted), then it is anti Stokes

The blue shift requires the molecule to be in a higher excited state

The Raman Shift

$$\Delta\nu = |\nu - \nu_{\text{inc}}|$$

3. Scattering Process



But intensity of Raman Scattering light depends on the λ_{inc}

- Enabled by tunable lasers

4. Dielectric Polarizability
 - Necessary for RS

- \vec{E} field induces a $\vec{\mu}$

- $\mu_j = \sum_i \alpha_{ji} E_i$

α is a 2nd rank tensor

α_{ij} has a principal axis system

- Here α_{ij} 3×3 matrix

- Rovibrational Raman

- $\left(\frac{\partial \alpha_{ij}}{\partial Q_i} \right)_0 \neq 0$

- Raman Active

Dielectric Polarizability

Thursday, March 31, 2016 11:13 AM

Vibrational Raman

For Vibrational Raman active mode $\left(\frac{\partial \alpha_{ij}}{\partial Q_\alpha}\right) \neq 0$

Rotational Symmetry

-need lower than spherical symmetry

This is due to high symmetry of the Inertia tensor of the molecule
 α remains unchanged

Transition probability Selection Rule

$$(\alpha_{\rho,\sigma})_{i,f} = \langle i|\alpha|f\rangle = \left\langle i \left| \frac{1}{\hbar} \sum_n \left(\frac{(\mu_\rho|n\rangle\langle n|\mu_\sigma)}{\omega - \omega_{ni}} - \frac{(\mu_\sigma|n\rangle\langle n|\mu_\rho)}{\omega + \omega_{nf}} \right) \right| f \right\rangle$$

Intensities vary with incident wavelength but not the position of the shift

In BO approximation

$$|i\rangle = |\psi_g(\vec{r}; \vec{Q})| \chi_o^g(Q) \rangle = |g, o\rangle$$

$$|f\rangle = |\psi_g\rangle | \chi_{v''}^g(Q) \rangle = |g, v''\rangle$$

$$|n\rangle = |\psi^{el}\rangle | \chi_{v'}^{el}(Q) \rangle = |e, v'\rangle$$

α_{if} is composed terms like $\langle i|\mu_e|n\rangle\langle n|\mu_\sigma|f\rangle$

Taylor expand μ

$$\mu_e = \mu_e^o + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu_\rho}{\partial Q_i} \right) Q_i$$

$$\langle g, o | \mu | e, v \rangle = \mu_e^o \langle \chi_o^g(Q) | \chi_{v'}^{el}(Q) \rangle + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu}{\partial Q_i} \right)_0 \langle g | Q_i | e \rangle$$

An overlap of vibrational wavefunction

Franck Condon Factor

Non-zero because vibrational states differing in electronic are not necessarily orthogonal

$\sum_{i=1}^{3N-6} \left(\frac{\partial \mu}{\partial Q_i} \right)_0 \langle g | Q_i | e \rangle$ together with $\langle n | \mu | f \rangle$, we get α_{if} consisting of product $Q_i Q_j$ (bilinear) all possibilities include $x^2, y^2, z^2, xy, xz, yz$

For nonzero only if

Raman active

$\Gamma_{(i)} \otimes \Gamma_{(\alpha)} \otimes \Gamma_{(f)}$ contains A_1

Use the character table and normal symmetries

For centrosymmetric molecule CO_2

- Mutual exclusion (from \hat{i})
 - o Each normal mode is either, IR active or Raman Active
 - o Centro symmetry for center of inversion

Off resonance Raman (*NRS*)

Thursday, March 31, 2016 11:38 AM

- $|n\rangle$ is a *virtual state*
 - Not a real excited state
- Signal is weak
 - Need a lot of sample
 - $\Delta J = 0, \pm 2$
 - $\Delta v = \pm 1$ (*weak*)

Resonance Raman Scattering (PRS)

- $|n\rangle$ is a *real electronic excited state*
- λ_{inc} is resonant with any electronic state
- fluorescence is a possibility
- Some lives are dramatically enhanced
- Much more sensitive
 - I_2 in solvents
- High intensity of light
 - $(\vec{E}) \rightarrow$ *larger signals and overtone anharmonicity*

- 1) Use a laser (focus)
 - Tunable diode laser
- 2) Surface may enhance \vec{E} field
 - a. Sers, surface enhanced
- 3) Silicon Photodetectors

Electronic Transition

Thursday, March 31, 2016 11:55 AM

UV/vis from an electronic transition

A. Atomic Spectra

- a. Flame emission/discharge tubes
 - i. Show line spectra characteristic

1. Hydrogen atom

$$-\frac{\hbar^2}{2\mu} \nabla^2 \Phi = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \Phi = E\Phi$$

$$\Phi_{n,l,m_l,m_s} = R_{nl}(r)Y_{l,m_l}(\theta, \phi)x\left\{\begin{matrix} \alpha \\ \beta \end{matrix}\right\}$$

$R_{nl}(r)$ is a radial wavefunction

a) Energy spectrum

$$a. E_n = \frac{-Z^2 e^2}{4\pi\epsilon_0 2\alpha_0 n^2} = -\frac{Z^2}{n^2} (13.6 \text{ eV})$$

Here α_0 is the bohr radius $= 0.529 \text{ \AA} = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$

b) Angular wavefunction

$$L^2 |Y_{l,m_l}\rangle = \hbar^2 (l(l+1)) |l, m_l\rangle$$

$$L_z |l, m_l\rangle = m_l \hbar |l, m_l\rangle$$

$$c) S^2 |\alpha\rangle = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 |\alpha\rangle$$

$$S^2 |\beta\rangle = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 |\beta\rangle$$

$$S_z |\alpha\rangle = \frac{1}{2} \hbar |\alpha\rangle, \quad m_s = \pm \frac{1}{2}$$

$$S_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle$$

$$d) g_n = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

e) Selection Rule (El-electric dipole moment)

$$a. \text{ Electronic electric dipole moment} = \hat{\mu} = q\hat{r} = -e r (\sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z})$$

$$b. \vec{\mu}_{if} = \langle n, l, m_l, m_s | \vec{\mu} | n', l', m'_l, m'_s \rangle = -e \int_0^\infty r R^* R' r^2 dr \iint_{(0,0)}^{(\pi, 2\pi)} Y^*(\theta, \phi) Y'(\theta, \phi) \begin{pmatrix} \sin \theta \cos \phi \\ \cos \theta \cos \phi \\ \cos \theta \end{pmatrix} d\theta d\phi \int S^* S' ds$$

c. The integrals yields selection rules

$$i. \delta_{m_s, m'_s} \Rightarrow \Delta m_s = 0$$

$$ii. \int d\phi e^{-im_l \phi} \begin{pmatrix} \cos \phi \\ \sin \phi \\ 1 \end{pmatrix} e^{im'_l \phi}$$

$$iii. \theta \text{ int}, \quad \Delta l = \pm 1$$

any Δn is possible

f) Transition Frequency

$$g) \tilde{\nu} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$h) R_H = \text{Rydberg} = \frac{2\pi^2 \mu e^4}{(2\pi\epsilon_0)^2 \hbar^3 c} = 109,737 \text{ cm}^{-1}$$

- 1) Lyman series UV $n_1 = 1, n_2 = 2, 3, 4$
- 2) Balmer series $n_1 = 2, n_2 = 3, 4, 5 \dots$
- 3) Pasichinen series, etc

| 1 | Δl | Δm_l | Δm_s | Δn |
|-----------|------------|-------------------|--------------|------------|
| <i>E1</i> | ± 1 | $0, \pm 1$ | 0 | Any |
| <i>M2</i> | 0 | $0, \pm 1$ | $0, \pm 1/2$ | 0 |
| <i>E2</i> | $0, \pm 2$ | $0, \pm 1, \pm 2$ | 0 | any |

Tuesday, April 5, 2016 11:10 AM

$$\text{a. } \left(-\frac{\hbar^2}{2\mu} \sum_{i=1}^N \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^n \frac{ze^2}{r_e} + \sum_{(i,j)>1}^N \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} \right) \Phi = E\Phi$$

$$\text{ii. } \Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \dots & \psi_3(1) \\ \dots & \dots & \dots \\ \psi_1(N) & \dots & \psi_N(N) \end{vmatrix}$$

$$q(s, L) = (2L+1)(2s+1)$$

$$\vec{J} = \sum_{i=1}^N \vec{J}_i$$

Real atoms are always intermediate between Russel Saunders and JJ coupling

c) Atomic "terms"

- Well define energy levels \rightarrow line spectra
- In the absence of $e-e$ interactions levels depend only on m and n
- $e-e$ interaction

A term specifies L and S

It is not a single state but a manifold of states

To a first order approximation, differences in terms of energies yield the spectrum

d) Term symbol

- In the absence of external field fields (\vec{E}, \vec{B}) m_l and m_s states are still degenerate
- Each manifold of a term is labelled by L^{2S+1}
 - S if $L = 0$
 - P if $L = 1$

e) H atom

- $1e^- \Rightarrow l = L = 0, 1, 2, 3$
 S, P, D, F, G, H

f) $(letter)_{j=L \pm S}^{2 \text{ for doublet}}$

- Subscript j technically defines a level different j values for same L, S are part of same term
- Eg. $1s \frac{1}{2}^2$ ground state
- $2p \frac{3}{2}^2 \frac{1}{2}^2$
- Terms indicate L and S
- Spectroscopic lines corresponds
- This is generalized for molecules, where a term can include degrees of freedom e^-, vib^l, rot^l
Note: Spin orbital interaction split interaction splits levels in the sample terms

| Names | $2s+1$ | S | |
|-------|--------|-----|---------|
| | 1 | 0 | Singlet |
| | 2 | 1/2 | Doublet |
| | 3 | 1 | Triplet |
| | 4 | 3/2 | Quartet |

Multi electron atoms

Example, carbon atoms

Carbon is $1s^2 2s^2 2p^2$ filled sub shells $L = 0, S = 0$

We only are concerned with the valence levels since every filled sub level has approximately 0 contribution to angular momentum

terms ?

$S^1, P^1, D^1, S^3, P^3, D^3$,

this is naive since pauli exclusion principle excludes

P^1, S^3, D^3

There are 15 possible configuration consistent with pauli

$$M_e \quad \begin{array}{ccc} 1 & 1 & \\ \hline +1 & 0 & -1 \\ \hline & 1 & \\ \hline \end{array}$$

$$m_L = \sum_{i=1}^N m_{l_i}$$

$$m_S = \sum_{i=1}^N m_{s_i}$$

In fact only $S^1(1), D^1(5), P^3(9) = 1 + 5 + 9 = 15$

Can determine possible terms using matrix m_L, m_S

eg $S_{L=0}^3 \Rightarrow m_L=0$

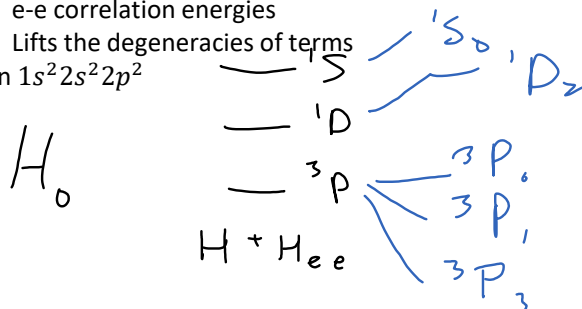
~~m_L — m_S — Pauli:~~

e) Terms and energies

a. e-e correlation energies

b. Lifts the degeneracies of terms

f) When $1s^2 2s^2 2p^2$



Hund's Rule

1) States with largest S is the lowest energy

a. Higher $S \Rightarrow$ higher energy

b. For states with the same S ,

c. Highest $L \Rightarrow$ lowest energy

Because corresponding orbitals avoid each in space, reduce e-e repulsion

d. Spin-orbit coupling

$$i. H_{so} \cong \sum_{i=1}^N \lambda_i(r) \vec{l}_i \cdot \vec{s}_i \approx \lambda_{so} \vec{L} \cdot \vec{S}$$

$$\vec{J} = \vec{L} + \vec{S} = \left\{ \begin{array}{c} L + S \\ \dots \\ 0 \\ \dots \\ -L - S \end{array} \right\} \text{ are possible } J \text{ values}$$

Hund's Third Rule

states with the same L and S

Less than $\frac{1}{2}$ filled smallest J is lowest energy

more than $\frac{1}{2}$ filled largest J is lowest energy

Lande Rule

$$E_{J+1} - E_J = \lambda(J + 1)$$

Stuff

Thursday, April 7, 2016 11:08 AM

Gotriatian Diagram

- Columns resolve difference terms
- Allowed transition shwon as arrows -> spectrum

Selection Rules

$$\Delta J = 0, \pm 1$$

$$\Delta L = \pm 1$$

$$\Delta S = 0$$

Hyperfine Structure

- Splitting at high resolution
- Due to nuclear spin
- Coupling between nuclear spin and electron spin
 - \vec{I}_{nuc} for nucleus and \vec{L} and S for e^-
 - Absent for $I=0$
- B electronic Spectra of Diatomics
- $A - A$ for $D_{\infty h}$
- $A - B$ for $C_{\infty v}$

| Σ | Π | Δ | Φ |
|----------|-------|----------|--------|
| S | P | D | F |
| 0 | 1 | 2 | 3 |

$\frac{+}{-}$ reflection

$\frac{u}{g}$ inversion

$|m_l|$ compound of orbital along z internuclear axis

MO electronic states

$V(r, R)$ is no longer spherical but has symmetry of molecule

$\Rightarrow l, j$ are not good quantum numbers

ψ_{mo} = wavefunction for e^- in the molecule \cong LCAO, the tight binding approximation

Σ_i atomic orbital states = $\Sigma_i c_i \chi_i$

Symmetry adapted, so ψ belongs for one of the irreducible reps

Notation

σ^* - antibonding σ_{mo}

- nodal plane

| AOs | | S | P | F |
|---------|--|----------|-------|---|
| l | | 0 | 1 | 2 |
| MO | | σ | π | d |
| $ m_l $ | | 0 | 1 | 2 |

| | | |
|------------|---------------|--------------|
| σ | \rightarrow | σ_g |
| σ^* | \rightarrow | σ_u^* |
| π | \rightarrow | π_u |
| π^* | \rightarrow | π_g |

Molecular Term Symbols

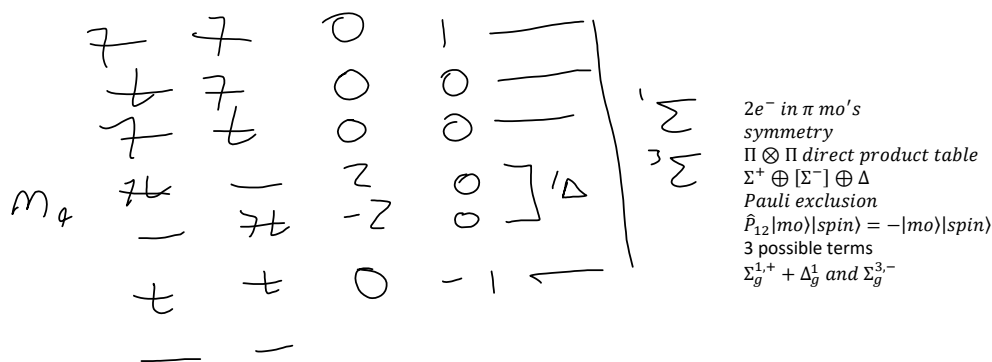
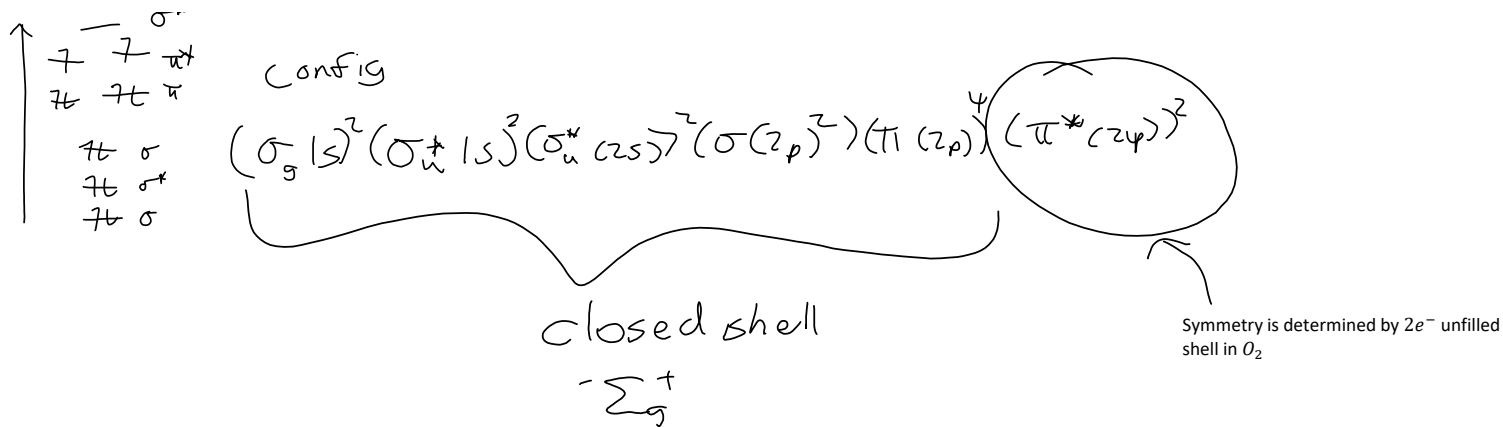
- Analogous to atom
- $m_l = \vec{L}$ component along bond
 - $= \Sigma_i m_{li}$
- $|m_l| = 0, 1, 2, \dots$
- $\Lambda = \Sigma, \Pi, \Delta, \Phi$
- S = total spin
- symbol
 - Σ^{2s+1}, etc
- Closed Shells
 - $\Sigma_g^{1,+}$ or $\Sigma^{1,+}$
- Degeneracy
 - $g = 2s + 1, \Lambda = 0$
 - $= 2(2S + 1), \Lambda \neq 0$

Open Shell configuration need to consider pauli exclusion

Ground State of O_2

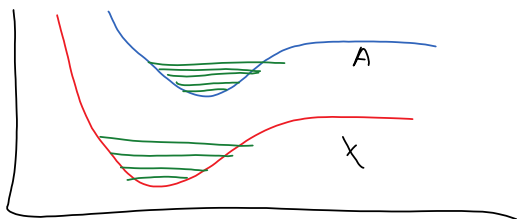
↑ σ^*
↑ π^*
↑ π config

ψ 



$$\Phi_{\Sigma_g^3} = [\Pi_{+1}^+ \Pi_{-1}^-(2) - \Pi_{+1}^-(2) \Pi_{-1}^+(1)] \Rightarrow \left\{ \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \alpha(2)\beta(1)) \right\} \text{ symmetric triplet}$$

$$\Phi_{\Sigma_g^{1,+}} = [\dots - \dots] \left\{ \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \right\}$$



Selection Rules
 E | electric dipole $\langle f | \vec{\mu} | i \rangle$
 $\Gamma_i \otimes \Gamma_\mu \otimes \Gamma_f$ must contain Σ_g^+, Σ^+

$D_{\infty h}$
 $x, y, \quad \pi_u$
 $z, \quad \Sigma_u^+$
 Must have $u \rightarrow \{f\}$
 Change in parity

Dependence on ψ
 $\psi_\phi = e^{im_l \phi}$
 $\int_0^{2\pi} d\phi \rightarrow \delta_{m_l, m_l'} (z \text{ comp})$
 $\Delta l = 0, \quad \text{parallel involving } \mu_z$
 $\Delta l = \pm 1, \quad \text{perp transition } \mu_{x,y}$

Rovibrational Structure of Electronic Spectra
 Generalization of atomic terms
 Spectroscopic terms energies
 $E = E_{elec} + E_{vib} + E_{rot}$
 $h\nu = \Delta E$

$$(E'_{el} - E''_{el}) + (E'_{vib} - E''_{vib}(v'')) + (E'_{rv}(J') - E''_{rv}(J''))$$

Frank - Condon Principle

Transition dipole matrix element is proportional

$$\langle f | \mu | i \rangle \propto \langle v'' | v' \rangle$$

$\Delta v = 0, \pm 1, \pm 2, \dots$, *vibronic transition*

Rotational structure

$$v_R = v_o + 2B' + (3B' - B'')J + (B' + b'')J^2$$

Transition

Tuesday, June 14, 2016 10:10 AM

$$\rho(v)dv \equiv \frac{8\pi v^2}{c^3} \cdot \frac{h\nu}{e^{kT}-1} dv$$
$$dP = \frac{c}{4\pi} \rho(v) dA d\Omega dv \cos \theta$$
$$\frac{d}{dt} P_{12} = B_{12} \rho(v), \quad \text{this correspondns to energy used to pump states from 1 to 2, decrease fock number by 1}$$
$$\frac{d}{dt} P_{21} = B_{21} \rho(v), \quad \text{the induced emission of photons, results in increase of fock number by 1}$$
$$\frac{d}{dt} P_{21}^{spon} = A_{21}, \quad \text{this induced spontaneous emission is due to ground state flucuationas field}$$
$$N_l(E_l) = N \frac{g_l}{Z} e^{-\frac{E_l}{kT}}$$
$$Z = \sum_l g_l e^{-\frac{E_l}{kT}}$$
$$\sum_l N_l = N,$$
$$N_2 [B_{21} \rho(v) + A_{21}] = B_{12} N_1 \rho(v)$$
$$\frac{N_2}{N_1} = \left(\frac{g_2}{g_1} \right) e^{\frac{h\nu}{kT}}, \quad E_2 - E_1 = h\nu$$
$$\rho(v) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{g_1}{g_2} \frac{B_{12}}{B_{21}} e^{\frac{h\nu}{kT}} - 1}$$
$$B_{12} = \frac{g_2}{g_1} B_{21}$$
$$A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21}$$

There are 4 spectral densities
 $W_v,$ radiant energy
 $P_v,$ radiant power
 $\rho_v,$ spectral densities
 $L_v,$ radiance

$$\sigma_{ik} = n r_{ij}^2 \text{ for } |i\rangle \text{ to } |k\rangle$$

$$P_{ik} = I_o \cdot \Delta v \cdot \int \alpha_{ij}(\omega) d\omega$$

$$P_{ik} = \frac{\hbar \omega}{c} I_o B_{ik} \left(N_l - \frac{g_l}{g_k} N_k \right) \Delta V$$

$$B_{ik} = \frac{c}{\hbar \omega} \int \sigma_{ik}(\omega) d\omega$$

$$\kappa_i = \frac{N_i e^2}{2 \epsilon_0 m} \sum_k \frac{\omega f_{ik} \gamma_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \, ,$$

$$n_i' = 1 + \frac{N_i e^2}{2 \epsilon_0 m} \frac{(\omega_{ik}^2 - \omega^2) f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \, ,$$

In [geometry](#), a **solid angle** (symbol: **Ω**) is the two-dimensional angle in three-dimensional space that an object [subtends](#) at a point. It is a measure of how large the object appears to an observer looking from that point. In the [International System of Units](#) (SI), a solid angle is expressed in a [dimensionless unit](#) called a [steradian](#) (symbol: sr).

From <https://en.wikipedia.org/wiki/Solid_angle>

$$d\Omega = \sin \theta \, d\theta d\varphi$$

Transition Equations

Thursday, June 16, 2016 9:34 AM

Table 2.2 Relations between the transition matrix element D_{ik} and the Einstein coefficients A_{ik} , B_{ik} , the oscillator strength f_{ik} , the absorption cross section σ_{ik} , and the line strength S_{ik} . The numerical values are obtained, when λ [m], B_{ik} [$\text{m}^3\text{s}^{-2}\text{J}^{-1}$], D_{ik} [As m], m_c [kg]

| | | |
|--|---|---|
| $A_{ki} = \frac{1}{g_k} \frac{16\pi^3 \nu^3}{3\epsilon_0 \hbar c^3} D_{ik} ^2$ $= \frac{2\pi \hbar \nu^2 e^2}{m \cdot \epsilon_0 \cdot c^3} f_{ik}$ $= \frac{2.82 \times 10^{46}}{g_k \cdot \lambda^3} D_{ik} ^2 \text{ s}^{-1}$ | $B_{ik}^{(v)} = \frac{1}{g_i} \frac{2\pi^2}{3\epsilon_0 \hbar^2} D_{ik} ^2$ $= \frac{e^2 f_{ik}}{4m\epsilon_0 \hbar \nu_{ik}}$ $= 6 \times 10^{31} \lambda^3 \frac{g_i}{g_k} A_{ki}$ | $B_{ik}^{(\omega)} = \frac{1}{g_i} \frac{\pi}{3\epsilon_0 \hbar^2} D_{ik} ^2$ $= \frac{\pi e^2 f_{ik}}{2m\epsilon_0 \hbar \omega_{ik}}$ $= \frac{g_k}{g_i} B_{ki}$ |
| $f_{ik} = \frac{1}{g_i} \frac{8\pi^2 m_e \nu}{e^2 \hbar} D_{ik} ^2$ $= \frac{g_k}{g_i} \cdot 4.5 \times 10^4 \lambda^2 A_{ki}$ | $S_{ik} = D_{ik} ^2$ $= (7.8 \times 10^{-21} g_i \lambda) f_{ik}$ | $\sigma_{ik} = \frac{1}{\Delta \nu} \frac{2\pi^2 \nu}{3\epsilon_0 \hbar g_i} \cdot S_{ik}$ |
| $\alpha_{ik} = \sigma_{ik} \cdot N_i = \frac{2\omega}{c} \kappa$ | $A_{ik} = \frac{8\pi \hbar \nu^3}{c^3} B_{ik}^{(v)}$ | $B_{ik}^{(v)} = \frac{c}{\hbar \nu} \int_0^\infty \sigma_{ik}(\nu) d\nu$ |

$$\alpha(\omega) = \left[N_i - \frac{g_i}{g_k} N_k \right] \sigma_{ik}(\omega)$$

$$B_{ik} = \frac{c}{\hbar \omega} \int \sigma_{ik}(\omega) d\omega = \frac{c \bar{\sigma}_{ik}}{\hbar \omega} \int_0^\infty g(\omega - \omega_o) d\omega, \text{ for about a single frequency}$$

$$P_{ik} = B_{ik} \cdot q = \frac{c}{\hbar \omega \cdot \Delta \omega} \int q(\omega) \cdot \sigma_{ik}(\omega) d\omega$$

$$S_{ik} = \sum_{m_i, m_k} |D_{m_i, m_k}|^2 = |D_{ik}|^2$$

Coherence

Thursday, June 16, 2016 9:48 AM

$$\Delta s_c \approx c \Delta t = \frac{c}{\Delta \omega} = \frac{c}{2\pi \Delta \nu}$$

If the path difference gets to large, the wave will no longer be coherent temporally at detection
Lower Spectral widths results in larger coherent lengths or times

$$\theta \cong \frac{\lambda}{b} \approx \frac{d}{r}$$

$$d\Omega = \frac{\lambda^2}{b^2} \approx \theta^2$$


Larger divergence angle (spread) for larger wavelengths

$$\Delta p_x \Delta x \geq \hbar$$

$$\Delta p_y \Delta y \geq \hbar$$

$$\Delta p_z \Delta z \geq \hbar$$

$$\Delta p_x \Delta x \Delta p_y \Delta y \Delta p_z \Delta z \geq \hbar^3 = V_{ph}$$

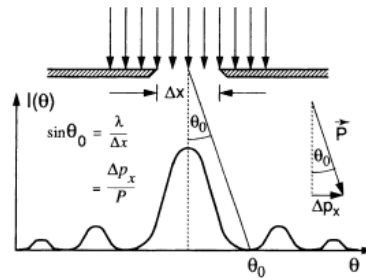
V_{ph} is the volume of the elementary cell in phase space

The minimum uncertainty of the x and y direction with z as the propagation axis

$$\Delta p_x = \Delta p_y = \frac{|p|\lambda}{2\pi b} = \frac{\hbar \omega}{c} \lambda \frac{1}{2\pi b} = \frac{\hbar \omega}{c} \frac{d}{2\pi r}$$

Natural broadening due to quantum mechanics

$$\Delta p_z = \frac{\hbar}{c} \Delta \omega, \text{ spread mostly caused by the uncertainty in the frequency}$$



Quantitative description of Coherence

Coherence Function and the Degree of Coherence

Temporal and Spatial coherence, concerned with the correlation between optical fields at P_0 at various times or at the same time at different points

$$E(r, t) = A_0 e^{i(\omega t - \vec{k} \cdot \vec{r})} + c.c.$$

$$E(P, t) = k_1 E_1 \left(S_1, t - \frac{r_1}{c} \right) + k_2 E_2 \left(S_2, t - \frac{r_2}{c} \right)$$

$$\frac{r_1}{c} = t_1, \quad \frac{r_2}{c} = t_2$$

k_1 and k_2 are complex and depend on the distance from the source to the location P

$$I_p = \epsilon_0 c \langle E \cdot E^* \rangle = |k_1|^2 \langle E_1 E_1^* \rangle + |k_2|^2 \langle E_2 E_2^* \rangle + 2 \text{Re} \{ k_1 k_2^* \langle E_1(t + \tau) E_2^*(t) \rangle \}$$

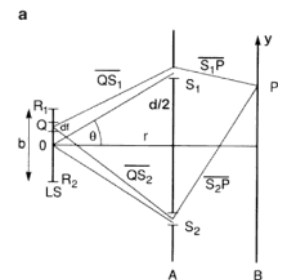
$$I_p = \epsilon_0 c [|k_1|^2 I_{S1} + |k_2|^2 I_{S2} + 2 |k_1| |k_2| \text{Re} \{ \Gamma_{12}(\tau) \}]$$

$$\Gamma_{11}(\tau) = \langle E_1(t + \tau) E_1^*(t) \rangle$$

$$\Gamma_{22}(\tau) = \langle E_2(t + \tau) E_2^*(t) \rangle$$

$\tau = 0$ is the self coherence functions

$$\Gamma_{11}(\tau = 0) = \frac{I_1}{\epsilon_0 c}, \quad \Gamma_{22}(\tau = 0) = \frac{I_2}{\epsilon_0 c}$$



$$\gamma_{12}(\tau) = \frac{\Gamma_{12}(\tau)}{\sqrt{\Gamma_{11}(0)\Gamma_{22}(0)}} = \frac{\langle E_1(t+\tau)E_2(t) \rangle}{\sqrt{\langle |E_1(t)|^2 \rangle \langle |E_2(t)|^2 \rangle}}$$

$$I_p = I_1 + I_2 + 2\sqrt{I_1 I_2} \Re\{\gamma_{12}(\tau)\}$$

$$\gamma_{12}(\tau) = |\gamma_{12}(\tau)| e^{i\phi_{12}(\tau)}$$

$\phi_{12}(\tau) = \phi_1(\tau) - \phi_2(\tau)$ is the phase of the fields E_1 and E_2

$\gamma_{12}(\tau)$ is a measure of degree of coherence

$|\gamma_{12}(\tau)| = 1$ describes interference of two completely coherent waves

$0 < |\gamma_{12}(\tau)| < 1$ describes partial coherence and thus

For γ_{11}

$$\gamma_{11}(\tau) = \frac{\langle E(t+\tau)E^*(t) \rangle}{|E(t)|^2} = \left\langle e^{i(\phi(t+\tau) - \phi(t))} \right\rangle$$

$$\gamma_{11}(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \cos(\Delta\phi) + i \sin \Delta\phi \, dt$$

Monochromatic waves have infinite coherent length, $\Delta\omega = 0 \Rightarrow \Delta s_c = \infty$

$$\phi(t) = \omega t - \vec{k} \cdot \vec{r}, \Delta\phi = \phi(t+\tau) - \phi(t) = \omega\tau$$

For a wave with large spectral width, $\Delta\omega \Rightarrow \tau > \frac{\Delta s_c}{c} = \frac{1}{\Delta\omega}$, the phase fluctuate between 0 and 2π

Resulting in an average of 0

$$\Delta s_c = c\Delta t = \frac{c}{\Delta\omega}$$

$\Delta\phi(t) \approx \Delta\omega\tau$, for large $\Delta\omega$, this leads to $\Delta\phi$ ranging from 0 to 2π

For γ_{12}

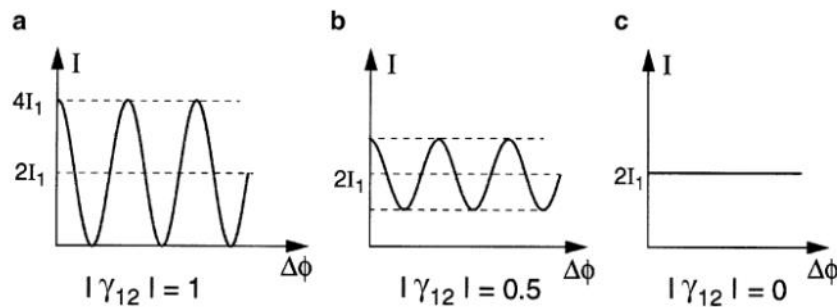


Figure 2.35 Interference pattern $I(\Delta\phi)$ of two-beam interference for different degrees of coherence

For quasi monochromatic planewaves of different paths, both same frequency

$$\phi_{12}(\tau) = \vec{k} \cdot (\vec{r}_2 - \vec{r}_1)$$

$$I_p = I_1 + I_2 + 2\sqrt{I_1 I_2} |\gamma_{12}(\tau)| \cos \phi_{12}(\tau)$$

Coherence of Atomic Systems

Thursday, June 16, 2016 12:40 PM

Wave functions are in phase at the excitation time

For a pulse laser duration of Δt , it has a spectral bandwidth of $\Delta\omega \cong \frac{1}{\Delta t}$

$|a\rangle$ and $|b\rangle$ can be excited if their energy separation ΔE is smaller than $\hbar\Delta\omega$ ie the bandwidth of the laser

An ensemble of atoms is coherently excited if the wave functions of the atoms have the same phase for all atoms

This phase relation may change with differing frequencies with the time dependent part of the excited states

Phase diffusions refers to the wave functions oscillating at different frequencies (due to differing energies) as well as relaxation processes for different atoms

Density Matrix

$$\psi(r, t) = \psi_a + \psi_b = a(t)u_a e^{-\frac{iE_a t}{\hbar}} + b(t)u_b e^{-i\left(\frac{E_b}{\hbar}\right)t - \phi}$$

$$\begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} \text{ or } (\psi_a, \psi_b)$$

$$\tilde{\rho} = |\psi\rangle\langle\psi| = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} (\psi_a, \psi_b) = \begin{pmatrix} |\psi_a|^2 & \psi_a^* \psi_b \\ \psi_a \psi_b^* & |\psi_b|^2 \end{pmatrix} = \begin{pmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{pmatrix}$$

$$|\psi_a|^2 = |a(t)|^2 = \rho_{aa}$$

$$|\psi_b|^2 = |b(t)|^2 = \rho_{bb}$$

$$\psi_a^* \psi_b = a(t) e^{i\frac{E_a t}{\hbar}} b(t) e^{-i\frac{E_b t}{\hbar} + i\phi} = ab e^{i\left(\frac{E_a - E_b}{\hbar}\right)t + \phi} = \rho_{ab}$$

$$\psi_a \psi_b^* = ab e^{-i\left(\frac{E_a - E_b}{\hbar}\right)t + \phi} = \rho_{ba}$$

$$u_a = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{and} \quad u_b = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

If ϕ , the phase of the atomic wave functions are random for different atoms in the ensemble,

The nondiagonal elements average and thus the incoherent density matrix is thus

$$\tilde{\rho}_{incoh} = \begin{pmatrix} |a(t)|^2 & 0 \\ 0 & |b(t)|^2 \end{pmatrix}$$

The dipole atomic moment matrix is defined to be

$$D = -e\langle\vec{\psi}|r|\vec{\psi}\rangle$$

$$D = -D_{ab}(a^* b e^{-i\omega_{ba}t} + a b^* e^{i\omega_{ba}t}) = D_{ab}(\rho_{ab} + \rho_{ba})$$

Coherent Relaxation of Excited States

$$i\hbar\dot{\tilde{\rho}} = [H, \tilde{\rho}]$$

$$H = H_0 + H_1(t) + H_R$$

$$H_0 = \begin{bmatrix} E_a & 0 \\ 0 & E_b \end{bmatrix}$$

$$H_1(t) = -\mu E(t) = \begin{bmatrix} 0 & -D_{ab}E_0(t) \\ -D_{ba}E_0(t) & 0 \end{bmatrix} \cos(\omega t)$$

$$H_R = \hbar \begin{bmatrix} \gamma_a & \gamma_\varphi^a \\ \gamma_\varphi^b & \gamma_b \end{bmatrix}$$

$$i\hbar\rho_{bb}\gamma_b = [H_R, \tilde{\rho}]_{bb}$$

$$T_b = \frac{1}{\gamma_b} = \frac{i\hbar\rho_{bb}}{[H_R, \tilde{\rho}]_{bb}}$$

a

a

a

Widths and Profiles of Spectral Lines

Friday, June 17, 2016 10:52 AM

$$I(\nu) = \nu_o$$

$$\text{Full Width Half Max: FWHM: } \delta\nu = |\nu_2 - \nu_1| \text{ where } I(\nu_2) = I(\nu_1) = \frac{I(\nu_o)}{2}$$

$$\delta\lambda = -\left(\frac{c}{\nu^2}\right)\delta\nu = |\lambda_1 - \lambda|$$

$$\left|\frac{\delta\nu}{\nu}\right| = \left|\frac{\delta\omega}{\omega}\right| = \left|\frac{\delta\lambda}{\lambda}\right|$$

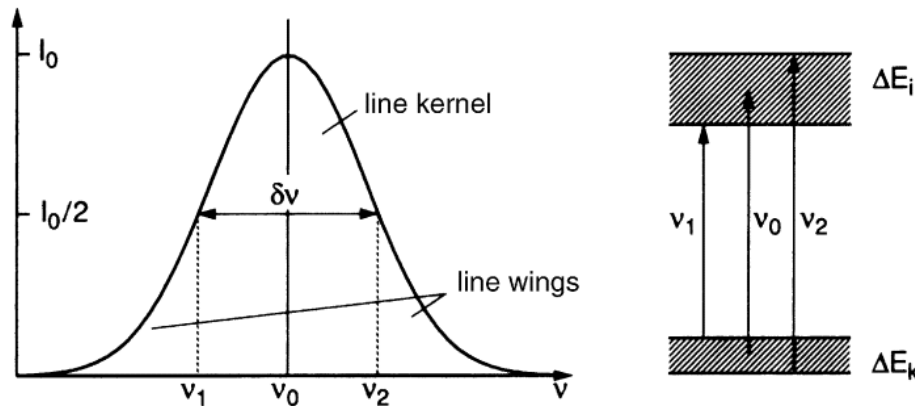


Figure 3.1 Line profile, halfwidth, kernel, and wings of a spectral line

Classical description of natural linewidth

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0$$

$$x(t) = x_0 e^{-\frac{\gamma}{2}t} \left[\cos \omega t + \frac{\gamma}{2\omega} \sin \omega t \right]$$

$$\omega = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$$

Since γ is small for atoms

$$x(t) = x_0 e^{-\frac{\gamma}{2}t} \cos \omega t$$

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t) e^{-i\omega t} dt = \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{i(\omega - \omega_0) + \frac{\gamma}{2}} + \frac{1}{i(\omega + \omega_0) + \frac{\gamma}{2}} \right)$$

$$\begin{aligned} I(\omega - \omega_0) &\propto A(\omega) A^*(\omega) = \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{i(\omega - \omega_0) + \frac{\gamma}{2}} + \frac{1}{i(\omega + \omega_0) + \frac{\gamma}{2}} \right) \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{-i(\omega - \omega_0) + \frac{\gamma}{2}} + \frac{1}{-i(\omega + \omega_0) + \frac{\gamma}{2}} \right) \\ &= \frac{x_0^2}{8\pi} \left(\frac{1}{(\omega - \omega_0) + \frac{\gamma}{2}} + \frac{1}{(\omega + \omega_0) + \frac{\gamma}{2}} \right) \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{(\omega - \omega_0) + \frac{\gamma}{2}} + \frac{1}{(\omega + \omega_0) + \frac{\gamma}{2}} \right) \\ &= \frac{x_0^2}{8\pi} \left(\frac{1}{\left((\omega - \omega_0) + \frac{\gamma}{2} \right)^2} + \frac{2}{(\omega^2 - \omega_0^2) + \frac{\gamma^2}{4} + \gamma\omega} \right) \end{aligned}$$

$$\approx \frac{x_0^2}{8\pi} \left(\frac{1}{(\omega - \omega_0)^2 + \frac{\gamma^2}{4} + \gamma(\omega - \omega_0)} + \frac{2}{(\omega^2 - \omega_0^2) + \frac{\gamma^2}{4} + \gamma\omega} \right) ??$$

Anyways

$$I(\omega - \omega_0) = \frac{C}{(\omega - \omega_0)^2 + \frac{\gamma^2}{4}}$$

The normalized lorentian profile

$$L(\omega - \omega_0) = \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$\delta\omega_n = \gamma \quad \text{or}$$

$$I(\omega - \omega_0) = I_0 L(\omega - \omega_0) = I_0 \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$I(\omega_0) = \frac{2I_0}{\pi\gamma}, |k\rangle \leftrightarrow |i\rangle$$

In literature, often $I(\omega) = I_0 g(\omega - \omega_{ik})$ with $I_0 = I(\omega_0)$

$$g(\omega - \omega_{ik}) = \frac{\Gamma^2}{(\omega_{ik} - \omega)^2 + \Gamma^2}, \text{ as opposed to } L(\omega - \omega_0)$$

With Γ describing the spread of the function

$$(\omega_{ik} - \omega)^2 = \Gamma^2$$

$$(\omega_{ik} - \omega) = \pm \Gamma$$

$$\omega_{\pm} = \omega_{ik} \pm \Gamma$$

$$\delta\omega = |\omega_+ - \omega_-| = (\omega_{ik} + \Gamma) - (\omega_{ik} - \Gamma) = 2\Gamma = \text{FWHM}$$

Lifetime of Excited State

$$\delta\omega_n = \frac{A_i}{2\pi} = \frac{1}{2\pi\tau_i}, \quad \delta\omega_n = A_i = \frac{1}{\tau_i}$$

$$\frac{dW_{ik}}{dt} = N_i A_{ik} \hbar \omega_{ik}$$

$$\Delta E = \sqrt{\Delta E_i^2 + \Delta E_k^2} \Rightarrow \delta\omega_n = \sqrt{\frac{1}{\tau_i^2} + \frac{1}{\tau_k^2}}$$

Natural Linewidth of Absorbing Transitions

$$dI = -\alpha I dz$$

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega) \left[N_i - \frac{g_i}{g_k} N_k \right]$$

$$I = I_0 e^{-\alpha(\omega)z} = I_0 e^{-\sigma_{ik} N_i z}$$

$$\alpha(\omega) = \frac{Ne^2}{4\epsilon_0 mc} \frac{\gamma}{(\omega_0 - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$n' = 1 + \frac{Ne^2}{4\epsilon_0 m \omega_0} \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}$$

Doppler Width

Friday, June 17, 2016 1:33 PM

$$\mathbf{v} = \{v_x, v_y, v_z\}$$

$$\omega_e = \omega_0 + \vec{k}_{\text{photon}} \cdot \vec{v}_{\text{molecule}}$$

$$\omega'_a = \omega - \vec{k} \cdot \vec{v}$$

$$\omega_a = \omega_0 \left(1 + \frac{v_z}{c}\right)$$

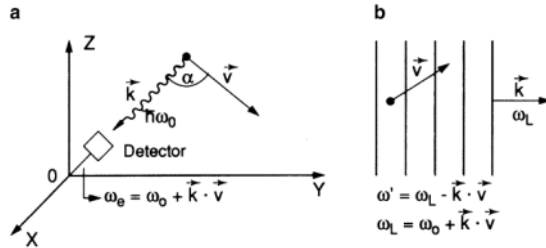


Figure 3.5 a Doppler shift of a monochromatic emission line and b absorption line

At thermal equilibrium

v_p is the spread of the distribution

$$v_p^2 = \frac{2kT}{m}$$

$$n_i(v_z)dv_z = \frac{N_i}{v_p\sqrt{\pi}} e^{-\left(\frac{v_z}{v_p}\right)^2} dv_z$$

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}} e^{-\left(\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right)^2} d\omega$$

$$I(\omega) = I_0 e^{-\left(\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right)^2}$$

$$\delta\omega_D = 2\sqrt{\ln 2} \frac{\omega_0 v_p}{c}$$

$$I(\omega) = I_0 e^{-\frac{(\omega-\omega_0)^2}{0.36\delta\omega_D^2}}$$

At room temperature,

$$\delta\omega_D = 2\sqrt{\ln 2} \frac{\omega_0 v_p}{c} = \frac{\omega_0}{c} \sqrt{\frac{8kT \ln 2}{m}}$$

$$\delta\omega_D = \frac{2\omega_0}{c} \sqrt{\frac{2RT \ln 2}{M}}$$

Larger masses result in small spread

$$L(\omega - \omega') = \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}} e^{-\left(\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right)^2} d\omega$$

$$I(\omega) = I_0 \int n(\omega') L(\omega - \omega') d\omega'$$

$$I(\omega) = \frac{\gamma N_i c}{2v_p \pi^{\frac{3}{2}} \omega_0} \int_0^\infty \frac{e^{-\left(\left[\frac{c}{v_p}\right] \frac{(\omega_0 - \omega')}{\omega_0}\right)^2}}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2} d\omega'$$

This is a voight profile

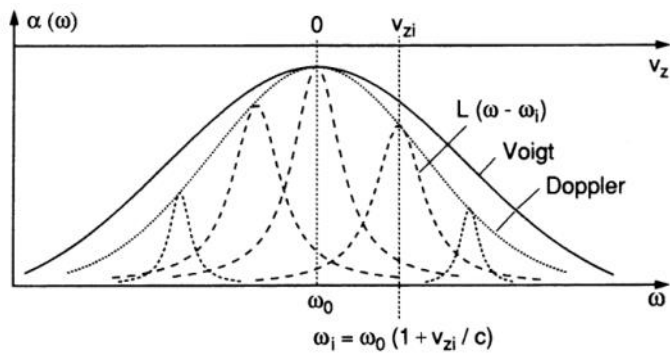


Figure 3.8 Voigt profile as a convolution of Lorentzian line shapes $L(\omega_0 - \omega_i)$ of molecules with different velocity components v_{zi} and central absorption frequencies $\omega_i = \omega_0(1 + v_{zi}/c)$

ΔE

a
Aa

a

Collisional Broadening of Spectral Lines

Friday, June 17, 2016 4:24 PM

When atoms/molecules approach each other, the various energy levels are shifted up and down depending on the wavefunction

Positive energy shifts indicate repulsion
Negative energy shifts indicate attraction

R_c is the collision radius

$$\tau_c \approx \frac{R_c}{v}$$

$$\omega_{ik} = \frac{|E_i(R) - E_k(R)|}{\hbar}$$

The transition is short compared to collision time so that ΔR is relatively small during the transition
The mean value of R depends on the pressure and temperature

$$\omega_{ik}(R_m)$$

A

Must consider collision distance

The probability that the distance between A and B lies in the range R and $R + dR$

$$N(R)dR = N_0 4\pi R^2 e^{-\frac{V(R)}{kT}} dR$$

Collisional Broadening causes shifts in energy

$$I(\omega)d\omega = C$$

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^6}$$

Anyways, the result is that that during collision, the energy levels are shifted and broadened

$$\frac{dI(\omega, T)}{dT} = \frac{V_i(R)}{kT^2} I(\omega, T)$$

There are elastic collisions that result in quenching of the intensity of fluorescence's

The probability for depopulation of E_i

$$A_i = A_i^{rad} + A_i^{col} \text{ with } A^{col} = N_B \sigma_i v$$

$$N(R)dR = N_0 4\pi R^2 e^{-\frac{V(R)}{kT}} dR$$

This basically shows that for small distances between the atoms, the probability is low

$$v = \sqrt{\frac{8kT}{\pi\mu}}, \quad \mu = \frac{M_A M_M}{M_A + M_B}, \quad p_B = N_B kT$$

$$A_i = \frac{1}{\tau_{sp}} + ap_B, \quad a = 2\sigma_{ik} \sqrt{\frac{2}{\pi\mu kT}}$$

$$\delta\omega = \delta\omega_m + \delta\omega_{col} = \gamma_n + \gamma_{col} = \gamma_n + ap_B$$

Elastic collision, when no energy is lost. Amplitude does not change
A

$$I(\omega) = C^* \frac{1}{(\omega - \omega_0 - \Delta\omega)^2 + \left(\frac{\gamma_n + \gamma_{col}}{2}\right)^2}$$

Relations Between Interaction Potential, Line Broadening and Shifts

Friday, June 17, 2016 6:17 PM

$$V_i(R) = \frac{C_i}{R^n}$$

$$\hbar\Delta\omega(R) = \frac{(C_i - C_k)}{R^n}$$

σ_s and σ_b

$$V_i(R) = \frac{C_i}{R^n}, \quad V_k(R) = \frac{C_k}{R^n}$$

$$\hbar\Delta\omega(R) = \frac{C_i - C_k}{R^n}, \text{ the shift due to collision}$$

Line broadening from phase shift from the frequency shift

Quenching of collisions which shorten the effective lifetime of the excited level

$$\Delta\phi(R_0) = \int_{-\infty}^{\infty} \Delta\omega dt = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{C_i - C_k}{[R_0^2 + \bar{v}^2(t - t_0)^2]^{\frac{n}{2}}} dt = \alpha_n \frac{C_i - C_k}{v R_0^{n-1}}$$

a

a

New table
New desktop
New mobile work station
New tablet
New monitor
New fans

$$\Delta E \Delta t > \frac{\hbar}{2}$$
$$\hbar \Delta \omega \Delta t > \frac{\hbar}{2}$$
$$2\pi \Delta \nu \Delta t > \frac{1}{2}$$
$$\Delta \nu \Delta t > \frac{1}{4\pi}$$