

- R. Hoffmann 1963  $\Rightarrow$  Hydrocarbons, Boron hydrides
- includes  $\sigma$  and  $\pi$  orbitals
- does not ignore overlap, calculates  $\Rightarrow$  matrix  $\hat{S}$
- still in use today

Self-consistent field calculations

- not only shapes and energies, but also structure and reactivity of molecules
- easy to formulate, difficult to implement
- Hartree-Fock equations:

Many-electron wave function as a product of one-electron wave functions

$$\Psi = \Psi_{a,\alpha}(1) \Psi_{a,\beta}(2) \dots \Psi_{z,\beta}(N) - \dots$$

N-electron closed-shell molecule,  
electron 1 occupies orbital  $\Psi_a$  with spin  $\alpha$ ,  
electron 2  $\Psi_a$  and spin  $\beta$  etc.

Pauli principle  $\rightarrow$  complex (permutations of pair of electrons)  
 $\Psi = \Psi_{a,\alpha}(1) \Psi_{a,\beta}(2) \dots \Psi_{z,\beta}(N) - \Psi_{a,\alpha}(2) \Psi_{a,\beta}(1) \dots \Psi_{z,\beta}(N) + \dots$   
 $\Rightarrow$  guessing wave function, optimization, cycling,  $\Rightarrow$  until self consistent

$\rightarrow$  N! terms in the sum

determinant :

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$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a,\alpha}(1) & \psi_{a,\beta}(1) & \dots & \psi_{z,\beta}(1) \\ \psi_{a,\alpha}(2) & \psi_{a,\beta}(2) & \dots & \psi_{z,\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{a,\alpha}(N) & \psi_{a,\beta}(N) & \dots & \psi_{z,\beta}(N) \end{vmatrix}$$

optimum wavefunctions

satisfy the Hartree-Fock equations

$$\int \hat{F}_1 \psi_{a,\sigma}(1) = \epsilon \psi_{a,\sigma}(1) \quad \sigma = \alpha \text{ or } \beta$$

$$\hat{F}_1 = \text{Fock operator} : h_1 + \sum_j \{ J_j(1) - K_j(1) \}$$

$$h_1 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \sum_n \frac{Z_n e^2}{4\pi\epsilon_0 r_{1n}} \quad \text{core Hamiltonian}$$

$J_j$ : Coulomb operator,  $K_j$ : exchange operator

further methods:

- semi-empirical: integrals from spectroscopic data
- ab initio: attempt to calculate all integrals in the secular determinant
- density functional theory: focus is electron density rather than the wavefunction; less demanding in computing but good description of experiments

# Molecular Symmetry

- symmetry of molecules
- symmetry ~~and~~ transformations of orbitals  
identify overlap integrals that vanish
- consider symmetry for LCAOS
- group ~~symmetry~~ theory

Symmetry elements:

- identity
- n-fold rotation
- reflection
- inversion
- n-fold improper rotation (rotation + reflection)

⇒ symmetry classification of molecules  
 rotation: Schoenflies system

immediate consequences:

• only molecules belonging to the groups

identity and mirror plane alone

$C_1$ ,  $C_{nv}$  and  $C_s$  may have a permanent electric dipole moment = polar molecules

• a molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation  $S_n$

two successive transformations:

- 1) rotation  $360^\circ/n$
- 2) reflection through a plane perpendicular to the axis of  $C_n$  rotation  
 ( $C_{nv}$  : have  $S_n$  axes)

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# Vanishing integrals and orbital overlap

symmetry characteristics of orbitals that belong to atoms in a molecule

⇒ character table

$$I = \int \psi_1 \psi_2 d\tau$$

$\psi_1$ : atomic orbital A

$\psi_2$ : atomic orbital B

$I$ : overlap integral

The value of  $I$  is independent of the orientation of the molecule.

⇒  $I$  is invariant under any symmetry operation of the molecule (group theory expression)

⇒ The integral is nonzero only if the integrand itself the product  $\psi_1 \psi_2$  is unchanged by any symmetry operation.

⇒ only orbitals of the same symmetry species may ~~not~~ have nonzero overlap!

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⇒ considers this in construction of LCAOs ⇒ symmetry-adapted linear combinations (SALCs)

same applies to selection rules:

$$\mu_{z,fi} = -e \int \psi_f^* z \psi_i d\tau$$

unchanged by any symmetry operation

transitions  
initial state  $|i\rangle$   
with wavefct.  $\psi_i$   
and final state  
 $|f\rangle$  with wavefct.  $\psi_f$

gives the electric transition dipole moment with respect to an axis  $z$ , or the  $z$ -component → IR / Raman / activity

# Spectroscopy

can be concluded for specific vibrations etc. or electron.

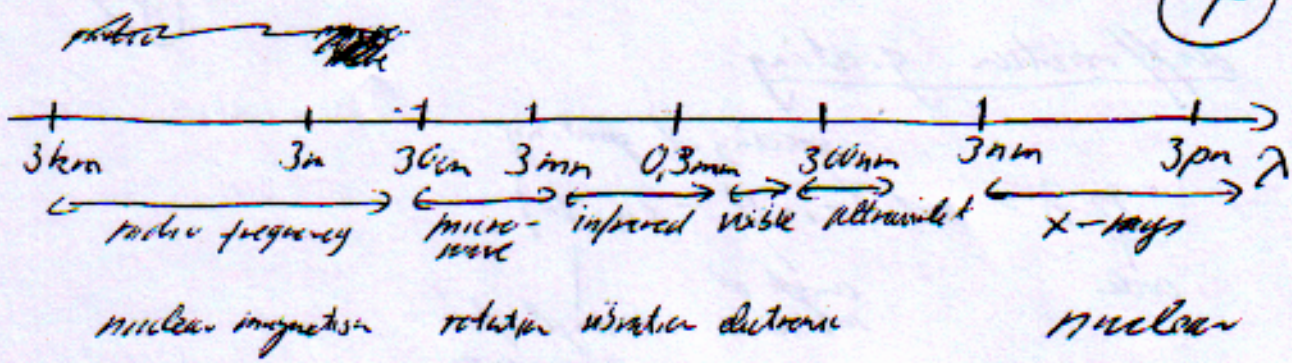
transitions

spectral lines: absorption, emission, or scattering of photons when the energy of a molecule changes

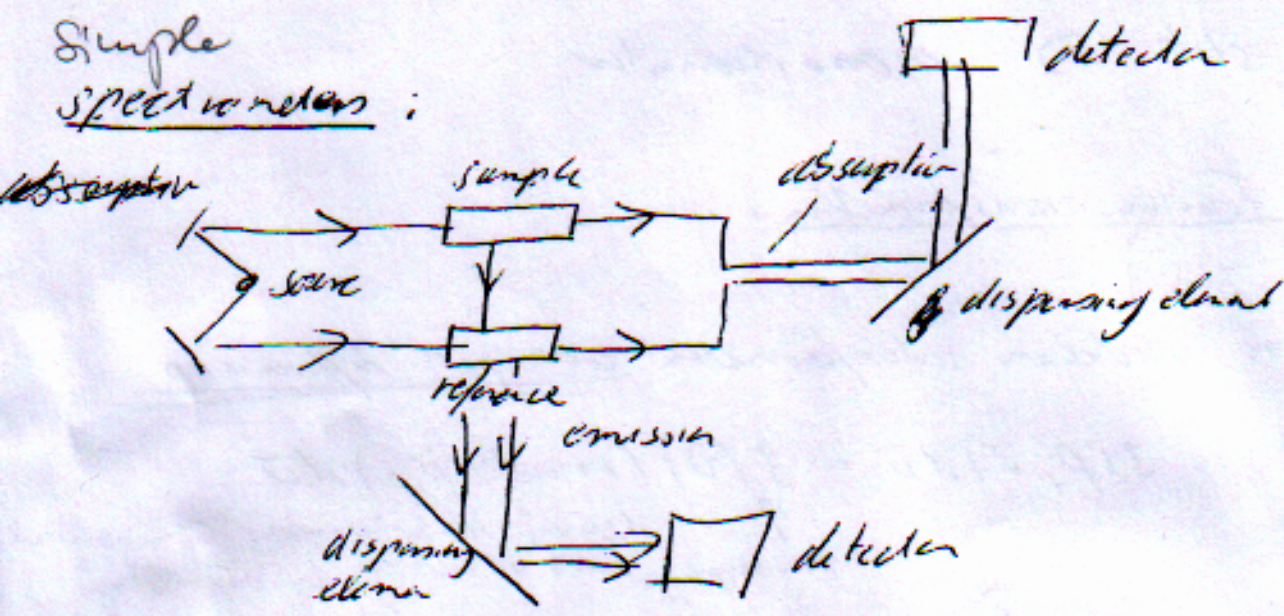
frequency  $\nu$ , wavelength  $\lambda$ , wavenumber  $\tilde{\nu}$

$$\lambda = \frac{c}{\nu} \quad \tilde{\nu} = \frac{\nu}{c}$$

emission — spectroscopy  
absorption —



Simple speedometers:



Source:

- lamps: tungsten, quartz-tungsten-halogen
- gas discharge lamps: Xenon, Mercury, Deuterium
- Lasers: + OPOs, tapered fibers, Ti:Sapphire-lasers

dispersive element:

separates radiation into different frequencies

# diffraction grating

$$n\lambda = d(\sin\theta - \sin\phi)$$

↑ ↑ ↑  
ord. angle of incidence angle of emergence

, spacing of grating

+ slit  $\Rightarrow$  monochromator

## or Fourier transformation:

use Michelson interferometer with path difference p

$$J(p, \tilde{\nu}) d\tilde{\nu} = J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$$

↑ ↑  
from single converts wavenumber component into variation in intensity

intensity  $\Rightarrow$   $I(p) = \int_{-\infty}^{\infty} J(p, \tilde{\nu}) d\tilde{\nu} = \int_{-\infty}^{\infty} J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$

↑  
sum from all wavenumbers present

$$\Rightarrow \boxed{J(\tilde{\nu}) = \frac{1}{2} \int_0^{\infty} \{ I(p) - \frac{1}{2} I(0) \} \cos 2\pi \tilde{\nu} p dp}$$

↑

spectrum we require, obtained by Fourier transform

## Detectors:

- photomultiplier (PMT): tube or photo diode
- charge-coupled device (CCD)
- mercury-cadmium-telluride (MCT) - detector



# Raman Spectroscopy

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molecular energy levels are explored by examining the frequencies present in the radiation scattered by molecules

Stokes radiation: laser

1 in  $10^7$  of the incident photons collide with molecules, give up some of their energy, and emerge with a lower energy

Anti-Stokes radiation:

incident photons collect energy from molecules  $\Rightarrow$  higher frequency radiation

Rayleigh radiation:

radiation without change of frequency  
notch filter absorbs this radiation

Intensities of spectral lines

$$T = \frac{J}{J_0}$$

transmitted  
incident

Beer - Lambert law

$$J = J_0 10^{-\epsilon c_j l}$$

$\epsilon$ : molar absorption coefficient (extinction coefficient)  
 $l$ : length of sample (thickness  $d$  also)  
 $c_j$ : molar concentration

also common: absorbance  $A = \lg \frac{I_0}{I}$  or  $A = -\lg T$

Absorption intensities: ( $\rightarrow$  Einstein)

$$\Rightarrow A = \epsilon \cdot c_j \cdot l$$

$$= \epsilon \cdot c \cdot d$$

stimulated absorption  $w = B \rho$

$w$ : rate of change of probability of the molecule being found in the upper state

$B$ : Einstein coefficient

$\rho d\nu$ : energy density of radiation in the frequency range  $\nu$  to  $\nu + d\nu$

$$= \frac{8\pi h \nu^3}{c^3} \frac{w_{\text{act}}}{e^{-1}}$$

Planck - Distr.)

stimulated emission:  $w' = B' \rho$  - Einstein coeff. of stimulated emission

+ spontaneous emission:

total rate of transition from the upper to the lower state:

$$w' = A + B' \rho$$

Einstein coeff. of spontaneous emission

$$B = B'$$

$$A = \left( \frac{8\pi h \nu^3}{c^3} \right) B$$