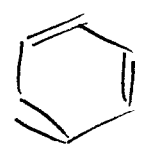Spreeding the π electrons over the whole molecule leads to a Stabilisation, compared to fixed, isolated π double bonds! $\Rightarrow$ delocalisation energy

$$(\triangleq 36 \, kJ/mol)$$

III

— another instance : benzene

Hückel approximation leads

to : $E = \alpha \pm 2\beta$, $\alpha \mp \beta$ and $\alpha \pm \beta$

$\Rightarrow$ delocalisation energy : $-150 \, kJ/mol$! (in terms
(π-Orbitals can take up all electrons!) of α and β?)

— Hückel method can also be formulated as
a matrix, secular determinant:

$$(H - ES)c = 0 \qquad S = \text{unit matrix}$$

Extended Hückel theory (R. Hoffmann)

— not confined to planar conjugated hydrocarbons ($\sigma + \pi$ orbitals!)
— does not ignore overlap, stores overlaps in matrix S
— diagonal elements of the H matrix (corresponding
to α of Hückel theory) set equal to the ionization
energy of the orbitals ($H: 13.6 \, eV$)
— off diagonal elements: assumed to be proportional to overlap

- population analysis; electron density concentration searched;
- draw-back of EHT: Cannot predict three-dimensional structures; linear H_2O then lower energy than angular...

Self - consistent field calculations

- sophisticated theories calculating shape and energies of MO and predict the structure/reactivity.

a) <u>Hartree - Fock equations</u> (respecting distributions of spins)

- many - electron ~~full~~ wavefunction as a product of one - electron wavefunctions

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

$e^- 1$ occupies MO Ψ_a with spin α, 2

- occupies MO Ψ_a with spin β etc.

To satisfy the Pauli principle: wavefunction has to change sign under the permutation of any pair of electrons by writing the wavefunction as a sum of all possible permutations with the appropriate sign;

$$\Psi = \Psi_{a,\alpha}(1) + \Psi_{a,\beta}(2) .. \Psi_{z,\beta}(N) - \Psi_{x,\beta}(1)... \Psi_{z,\beta}(N) \underset{L}{}$$

$N!$ terms in this sum; entire sum can be written as determinant;

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\chi a}(1) & \Psi_{a\beta}(1) & \cdots & \Psi_{z\beta}(1) \\ \Psi_{\chi a}(2) & \Psi_{a\beta}(2) & \cdots & \Psi_{z\beta}(2) \\ \vdots & & & \\ \Psi_{\chi a}(N) & & & \Psi_{z\beta}(N) \end{vmatrix} 3$$

Can also be written as:

$$\Psi = \left(\frac{1}{N!}\right)^{1/2} det \left| \Psi_{a\chi}(1) \; \Psi_{a\beta}(2) \cdots \Psi_{z\beta}(N) \right|$$

$\longrightarrow$ ~~contected~~ results in determinantal wave function is combined with variational principle, then; optimum wave functions <u>must satisfy</u> <u>the Hartree – Fock equations</u> :

$$\int_1 \Psi_{a,\sigma}(1) = \varepsilon \, \Psi_{a,\sigma}(1) \qquad \sigma = \text{either } \alpha \text{ or } \beta$$

$f_1 = $ Fock operator : $f_1 = h_1 + \sum_j (2 J_j(1) - K_j(1))$

with <u>$h_1 = $ Core hamiltonian</u> $h_1 = \frac{\hbar^2 \nabla_1^2}{2 m_e} - \sum_n \frac{Z_n e^2}{4\pi \varepsilon_0 r_{n1}}$

<u>$J = $ Coulomb operator</u>

$$J_j(1) \Psi_a(1) = \left\{ \int \Psi_j^*(2) \Psi_j \left(\frac{e^2}{4\pi \varepsilon_0 r_{12}} \right) d\tau_2 \right\} \Psi_a(1)$$

$K = $ exchange operator

$$K_j(1) \Psi_a(1) = \left\{ \int \Psi_j^*(2) \Psi_a(2) \left(\frac{e^2}{4\pi \varepsilon_0 r_{12}} \right) d\tau_2 \right\} \Psi_j(1)$$

① guess the initial form of the wave functions

② use them → Coulomb + exchange operators defined

→ Continuing: using newly found wave functions
~~until~~ until no change in energy and wavefunction
~~start~~ is obtained in the (cycle) ?
origin of the term 'self-consistent-field'
for this procedure

- difficulty: solving the H-F - equation
(initial point: linear combination of H atomic
orbitals)

<u>other</u> computational methods:

- <u>Semi empirical methods</u>: rely on spectroscopic
<u>data</u>, physical properties as ionization energies.

- ab initio methods: calculate <u>all</u>
integrals in the secular determinant

<u>Spectroscopy</u>

~~free rotational~~ <u>Pure rotation spectra</u>

- <u>Key</u> molecular parameter: <u>moment of inertia</u>

$$I = \sum_i m_i r_i^2$$

Some moments of inertia of molecules
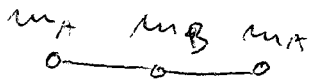
1) diatomics $I = \dfrac{m_A m_B}{m_A + m_B} = \mu R^2$

2) linear 3-atomic

$R \neq R'$ $I = m_A R^2 + m_c R'^2 - \dfrac{(m_A R - m_c R')}{m}$

$R = R'$ $I = 2 m_A R^2$

$\underset{\circ}{m_A} \quad \underset{\circ}{m_B} \quad \underset{\circ}{m_A}$

+ Symmetric rotors , + Spherical rotors

− initially : rigid rotors

Rotational energy levels

− obtained by solving the Schrödinger equation

− short cut : classical expression for the energy of a rotating body , expressing in angular momentum, then imposing the quantum mechanical properties of angular momentum into the equations

− classical expression : rotation about (axis a)

$$E_a = \frac{1}{2} I_a \omega_a^2 \quad \leftarrow \text{angular velocity}$$

rotation about three axes :

$$E = \frac{1}{2} I_a \omega_x^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$$

classical angular momentum $J_a = I_a \omega$

$$E = \frac{J_a^2}{2 I_a} + \frac{J_b^2}{2 I_b} + \frac{J_c^2}{2 I_c}$$

quantum mechanical properties of angular
momentum: $\left(E = \ell(\ell+1)\hbar^2 \right)$

Spherical rotors

— all three moments of inertia are equal to some
value $\overline{I}$ as in CH_4, SF_6 ;

$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$

replacement $\quad J^2 \longrightarrow J(J+1)\hbar^2$

$\searrow E_J = J(J+1)\dfrac{\hbar^2}{2I} \qquad J = 0, 1, 2 \ldots$

expressed in terms of B, the rotational constant

$$hcB = \frac{\hbar^2}{2I} \qquad \Downarrow \quad B = \frac{\hbar^2}{4\pi cI} \ [cm^{-1}]$$

expression for the energy :

$$E_J = hcB \, J(J+1) \qquad J = 0, 1, 2, \cdots$$

Symmetric rotors

— two moments of inertia equal, a third is different
— considering the principal axes : $I_{\parallel}$ and $I_{\perp}$ (two)

$\quad I_{\parallel} > I_{\perp}$ oblate (pancake-like) $\Big\}$ rotor
$\quad I_{\parallel} < I_{\perp}$ prolate (cigar-like)

$$E = \frac{J_b^2 + J_c^2}{2I_\perp} + \frac{J_a^2}{2I_\parallel} \quad \text{principal} \qquad \text{with } J^2 = J_a^2 + J_b^2 + J_c^2$$

$$E = \frac{J^2 - J_a^2}{2I_\perp} + \frac{J_a^2}{2I_\parallel} = \frac{J^2}{2I_\perp} + \left(\frac{1}{2I_\parallel} + \frac{1}{2I_\perp} \right) J_a^2$$

quantization: J^2 by $J(J+1)\hbar^2$ replaced

↑ angular momentum quantum number

~~Component of angular momentum about any axis is~~ ~~values $K\hbar$ $K = 0, \pm1, \pm2$~~

Component of angular momentum about any axis is restricted to $K\hbar$ with $K = 0, \pm1, \pm2 \ldots$

(K: principal axis M_J: reserved to a component of an externally defined axis)

J_Λ^2 replaced by $K^2 \hbar^2$

$\rightsquigarrow \quad F(J,K) = BJ(J+1) + (A-B)K^2 \quad J = 0,1,2\ldots$

$$K = 0, \pm1, \pm2 \ldots \pm J$$

$$A = \frac{\hbar}{2\pi c \, I_\parallel} \qquad B = \frac{\hbar}{4\pi I_\perp}$$

$K = 0$: energy levels depend only on $I_\perp$

$K \neq 0$: almost all angular momentum arises from rotation around the principal axis

sign of K: opposite senses of rotation

Linear rotors (CO_2, HCl, C_2H_2)

— only rotation $\perp$ to principal axis (internuclear)

$\searrow$ $K \equiv 0$, (zero angular momentum around the line)

and therefore: $F(J) = BJ(J+1)$ $\quad J = 0, 1, 2 \ldots$

Degeneracies

— Energy of a symmetric rotor : depends on J and K, each level except $K=0$: doubly degenerate.

— angular momentum : Component to an external axis, this is quantitized : $M_J \hbar$ with

$M_J = 0, \pm 1, \pm 2 \ldots \pm J$ $\searrow$ $2J+1$ values

$2J+1$ orientations have the same energy !

degeneracy : $2(2J+1)$ fold for $K \neq 0$

$\qquad\qquad 2J+1$ " " $K=0$

also linear rotor with $K=0$: $2J+1$ degeneracy

Spherical rotor : $(2J+1)^2$ $\searrow$ $J=10$ 441 states of the same energy !

— Stark effect :
degeneracy partly removed when an external electric field is applied to polar molecule
linear rotor in E :
$$E(J, M_J) = hcB(J(J+1)) + a(J, M_J) \mu^2 E^2$$

where $a(J, M_J) = \dfrac{J(J+1) - 3M_J^2}{2hcB J(J+1)(2J-1)(2J+3)}$ — 9 —

$\downarrow$ can be used to measure the dipole moment

Centrifugal distortion

— centrifugal forces distort the molecule

$\downarrow$ increase moment of inertia

empirical subtraction of energy

$$F(J) = hc\,B\,J(J+1) - D_J\,J^2(J+1)^2$$

$D_J =$ centrifugal distortion constant

$$= \frac{4B^3}{\tilde{\nu}^3} \leftarrow \text{vibrational wavenumber}$$

Rotational transitions

— selection rules : <u>must have a permanent</u>
dipole moment!

$$\Delta J = \pm 1 \qquad \Delta M_J = 0, \pm 1$$

$\downarrow$
absorption, emission

$\bigcirc$

Appearance of rotational spectra

- application of selection rules to the expression of a rigid symmetric or linear rotor, allowed $J \leftarrow J+1$ absorptions a

$$\hat{\nu}(J \leftarrow J+1) = 2B(J+1) \quad J = 0, 1, 2 \dots$$

- ~~with~~ accounting for centrifugal distortion:

$$\hat{\nu}(J \leftarrow J+1) = 2B(J+1) - \underbrace{4D_J(J+1)^3}_{\text{very small}}$$

- series of lines with separation of $2B$ with wavenumbers $2B, 4B, 6B \dots$

  $\rightarrow$ bond length of a linear rotor can be easily obtained

- <u>intensities</u>: pass through a maximum with increasing J before tailing off!

  reason: maximum in the population of energy levels!

  Boltzmann vs degeneracy $\left(N_J \propto N g_J \exp\left(\frac{-E_J}{kT}\right) \right)$

  $\curvearrowright J_{max} \approx \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$