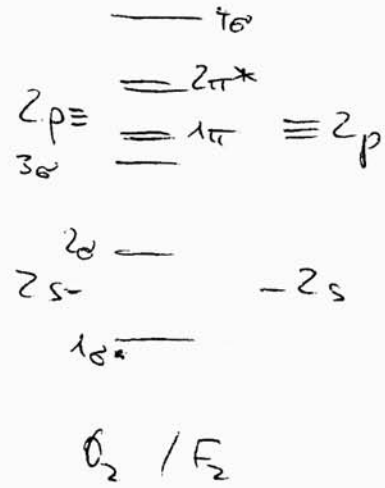
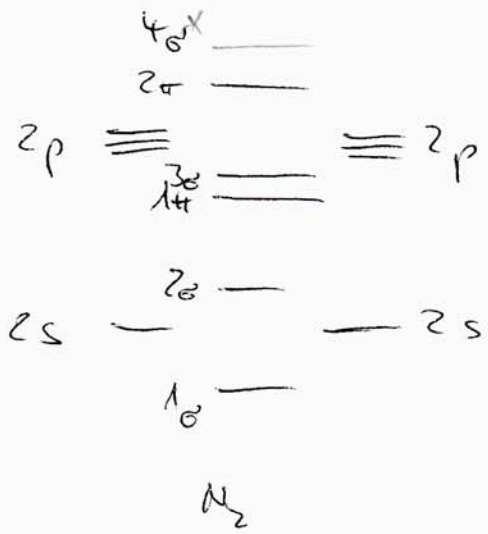


- Some cases: π orbitals are less strongly bonding than σ : maximum overlap occurs off-axis, switch occurs between N_2 and O_2 -8-



(from experiments: different order)

e) The overlap integral

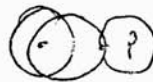
extent to which 2 atomic orbitals overlap: measured by the overlap integral S

$$S = \int \psi_A^* \psi_B d\tau$$

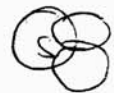
pictured



small overlap



large overlap



zero net overlap

follows

$\Rightarrow S = 0.58$ at r_0 in H_2^+

$\Rightarrow S = 0.2-0.3$ for orbitals with $n=2$

f) structure of diatomic molecules:

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building-up principle, using the electrons from unbound atoms \rightarrow

Δ ground state configuration of N_2 : $10 e^-$

$1\sigma^2 2\sigma^{*2} \uparrow \uparrow \pi^4 3\sigma^2$ \rightarrow bond order $\frac{1}{2}(8-2)=3$
high dissociation energy

- O_2 : $12 e^-$

$1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ bond order $\frac{1}{2}(8-4)=2$

\rightarrow $2\pi^*$ electrons occupy 2 orbitals, $1 2\pi_x^* 1 2\pi_y^*$

\rightarrow parallel spins, net spin angular momentum

$S=1$ triplet state! $O_2 = \text{paramagnetic!}$

confirmed by experiment (not predicted by valence bond theory!!)

- F_2 : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$: $14 e^-$

bond order: $\frac{1}{2}(\cancel{8} - 6) = 1$

low dissociation energy

\dagger

Heteronuclear diatomic molecules

- formed from atoms of different elements
e.g. CO, HF

- e electron pair not evenly shared
H-F bond: polar, having partial charges

- formalistic description:

electron in an orbital of the form:

$$\psi = c_A A + c_B B$$

proportion of atomic orbital A in the

bond: $|c_A|^2$, same applies for B

non polar bond: $|c_A|^2 = |c_B|^2$

pure ionic A^+B^- : $c_A = 0, c_B = 1$

- AO with lower energy makes larger contribution to bonding orbital, with higher energy: more to antibonding orbital

e.g. HF, general MO: $c_H \psi_H + c_F \psi_F = \psi$

$$\begin{array}{l} 0.78 \psi_H - 0.19 \psi_F \\ \hline \text{H} \quad \quad \quad - 13.4 \text{ eV} \end{array}$$

$$- 13.6 \text{ eV H } 1s \quad \text{-----}$$

$$\begin{array}{l} 0.18 \psi_H \quad \quad \quad \text{----- F } 2p - 18.6 \text{ eV} \\ + 0.98 \psi_F \quad \quad \quad \text{-----} \\ \hline \quad \quad \quad \quad \quad \quad - 18.8 \text{ eV} \end{array}$$

- Electronegativity: measures the attraction of electrons of bonding an atom (Pauling)

Distance molecules:

- More systematic way of discussing polarity
- Variational principle: energy calculated by use of an arbitrary wavefunction (trial wavefunction) is always higher than the true energy.

$$S = \int \psi_A^* \psi_B d\tau \quad \hat{=} \quad \underline{\text{overlap integral}}$$

trial wavefunction $\psi = C_A A + C_B B$ is real, not normalized

(because the coefficients can take arbitrary values)

expectation value - $E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$

search to minimize the value of E , by finding coefficients where $\frac{\partial E}{\partial C_A} = 0$ and $\frac{\partial E}{\partial C_B} = 0$

first denominator
trial wavefunction

$$\int \psi^2 d\tau = \int (C_A A + C_B B)^2 d\tau = C_A^2 \int A^2 d\tau + C_B^2 \int B^2 d\tau +$$

$$2 C_A C_B \int AB d\tau = C_A^2 + C_B^2 + 2 C_A C_B S$$

(because the individual A and B are normalized and the third is

The numerator:

-2-

$$\int \psi H \psi d\tau = \int (C_A A + C_B B) H (C_A A + C_B B) d\tau$$
$$= C_A^2 \int A H A d\tau + C_B^2 \int B H B d\tau + C_A C_B \int A H B d\tau + C_A C_B \int B H A d\tau$$

complicated integrals, that can be combined into two parameters

$$\alpha_A = \int A H A d\tau \quad \alpha_B = \int B H B d\tau \quad \beta = \int A H B d\tau = \int B H A d\tau$$

⇒ therefore,

$$\int \psi H \psi d\tau = C_A^2 \alpha_A + C_B^2 \alpha_B + 2 C_A C_B \beta$$

(α = Coulomb integral) later!
(β = resonance integral)

⇒ complete expression for E:

$$E = \frac{C_A^2 \alpha_A + C_B^2 \alpha_B + 2 C_A C_B \beta}{C_A^2 + C_B^2 + 2 C_A C_B S}$$

minimum found by differentiation

gradient zero → secular determinant

$$(\alpha_A - E)C_A + (\beta - ES)C_B = 0$$

$$(\beta - ES)C_A + (\alpha_B - E)C_B = 0$$

-3-

Secular
Equations

have a solution if the secular

determinant is zero:

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$

α called
Coulomb integral
(negative)

β : resonance
integral

↳ interpretation: electron energy

⇒ expands to a quadratic equation, two roots
give the energies of bonding and antibonding

MO (after variation principle: roots are best
energies for given basis set)

vanishes if orbitals
do not overlap,

↳ for a diatomic homonuclear molecule:

$$\alpha_A = \alpha_B = \alpha$$

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

Solutions are

$$= (\alpha - E)^2 - (\beta - ES)^2$$

$$\Rightarrow E_{\pm} = \frac{\alpha \mp \beta}{1 \pm S}$$

⇒ gives a ratio of the coefficients \Rightarrow need to find
individual values

attention: individual values can be found with $\int \psi^2 dx = 1$ (normalization)

2 Simple Cases

complete solutions possible:

the best wavefunction should be normalized

A) two equal nuclei: $\alpha_A = \alpha_B = \alpha$

$$E_+ = \frac{\alpha + \beta}{1 + S} \quad C_A = \frac{1}{(2(1+S))^{1/2}} \quad C_B = C_A$$

$$E_- = \frac{\alpha - \beta}{1 - S} \quad C_B = \frac{1}{(2(1-S))^{1/2}} \quad C_B = -C_A$$

orbitals have the form, now with normalization constant

bonding $\psi_+ = \frac{A+B}{(2(1+S))^{1/2}}$

anti-bonding $\psi_- = \frac{A-B}{2(1-S)^{1/2}}$

hetero nuclear

slid is a common approx. in elementary work

B) diatomic molecule, $S=0$ (different nuclei)

secular determinant is then:

$$\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

Solutions can be expressed with ξ (eta)

$$\xi = \frac{1}{2} \arctan \frac{2|\beta|}{\alpha_B - \alpha_A}$$

$$\Rightarrow E_+ = \alpha + \beta \tan \zeta \quad \psi_+ = A \cos \zeta + B \sin \zeta$$

$$E_- = \alpha - \beta \tan \zeta \quad \psi_- = -A \sin \zeta + B \cos \zeta$$

as difference $|\alpha_A - \alpha_B|$ increases ζ decreases

- large energy difference in the AO: the MOs differ only slightly from AO \Rightarrow bonding/antibonding effects are small.
- core and valence orbitals: difference in energy justifies to neglect the core orbitals to bonding (because β is so small)

Polyatomic Systems

- built in the same way, more AO to construct MO, spread over the whole molecule
- $\psi = \sum_i c_i \psi_i$
- find the coefficients: set up secular equations & determinant
- solve the latter for energies
- use energies to find the coefficients of all AO for each MO
- \rightarrow greater ranges of shapes possible

Hückel approximation (E. Hückel 1931) - 6 -

- conjugated molecules: alternation of single and double bonds
- π orbitals separately treated from σ
- σ form a rigid network determining the general shape of the molecule
- atoms of the same species (e.g. C atoms) are treated identically \Rightarrow all α (Coulomb integrals) for AO that contribute to π , set equal
- example ethene: >C=C< σ bonds taken as fixed, ~~the~~ focus on finding energies of the single π bond and its companion anti-bond

a) Ethene and frontier orbitals

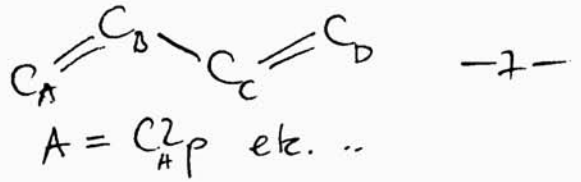
- LCAO ~~the~~ of $C2p$ orbitals (perpendicular to molecular plane) in ethene:

$$\psi = c_A A + c_B B \quad \left(\begin{array}{l} A = C2p \text{ of } A \\ B = \dots \end{array} \right)$$

next:

- optimum ~~coefficients~~ coefficients / energies have to be found, solve the secular determinant with $\alpha_A = \alpha_B = \alpha$
- $$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

For 1,3-butadiene



$$\psi = C_A A + C_B B + C_C C + C_D D \quad (\alpha_A = \alpha_B = \alpha_C = \alpha_D)$$

secular ~~equation~~ determinant:

$$0 = \begin{vmatrix}
 \alpha - E & \beta - ES_{AB} & \beta - ES_{AC} & \beta - ES_{AD} \\
 \beta - ES_{BA} & \alpha - E & \beta - ES_{BC} & \beta - ES_{BD} \\
 \beta - ES_{CA} & \beta - ES_{CB} & \alpha - E & \beta - ES_{CD} \\
 \beta - ES_{DA} & \beta - ES_{DB} & \beta - ES_{DC} & \alpha - E
 \end{vmatrix}$$

≠ Hückel-determinant: essentially the same
as in a homonuclear
diatomic molecule

butadiene: complicated! tedious calculation of
of resonance and overlap integrals

- additional approximations: all overlap-integrals
equal zero

2) all resonance integrals (β) between atoms
not neighbors: set to zero

3) all other resonance integrals: set to β

⇒ large simplifications, allows the calculation of molecular orbitals ~~without~~ (however!) -8-

result of the Hückel-approximation:

ethylene:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Solutions:
 $\alpha \pm \beta$
 β : negative

↓
 bonding π : $\alpha + \beta$

antibonding π^* : $\alpha - \beta$

- a promoted π electron has 2β more energy

than in the ground state

- result for 1,3 butadiene (see above!)

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

from the determinant results the eq:

$$x^2 - 3x + 1 = 0 \quad \text{with } x = (\alpha - E) / \beta$$

Solutions: $x = 2.62$ and 0.38

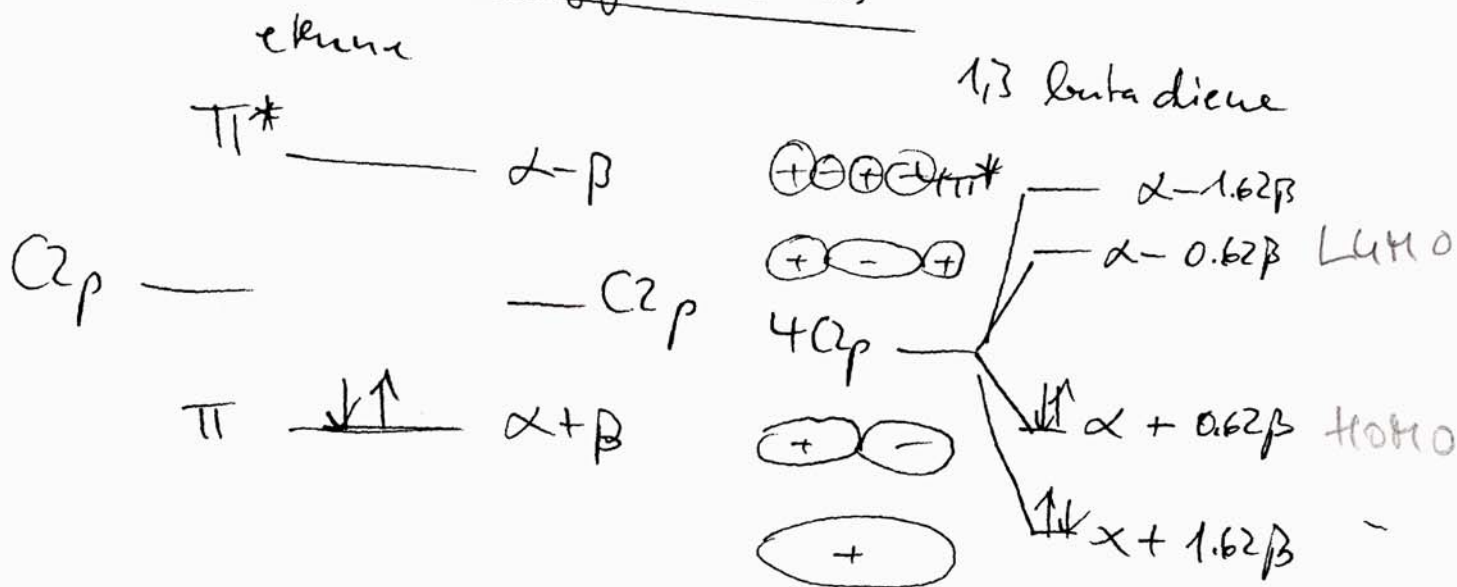
-9-

$$\Rightarrow E = \alpha + 1.62\beta \quad (1\pi) \quad E = \alpha - 1.62\beta \quad (3\pi^*)$$

$$E = \alpha + 0.62\beta \quad (2\pi) \quad E = \alpha - 0.62\beta \quad (4\pi^*)$$

4 p e⁻ of the C atoms are to be build in configuration of the ground state: $1\pi^2 2\pi^2$

MO energy schemes



Delocalisation energy # of electrons

- entire energy gain ethene: $2(\alpha + \beta) = 2\alpha + 2\beta$

- 1,3-butadiene: $2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta)$

energ of butadiene lies 0.48β lower than two isolated π bonds $2(2\alpha - 2\beta)$!

Extended Hückel theory

- R. Hoffmann 1963: \Rightarrow Hydrocarbons, Boron hydrides
- includes σ and π 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 wavefunction as a product of one-electron wavefunctions

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

N -electron closed-shell molecule,
electron 1 occupies orbital ψ_a with spin \uparrow
etc.

Pauli principle \rightarrow complex

\Rightarrow guessing wavefunction, optimization,
cycling, \Rightarrow until self consistent