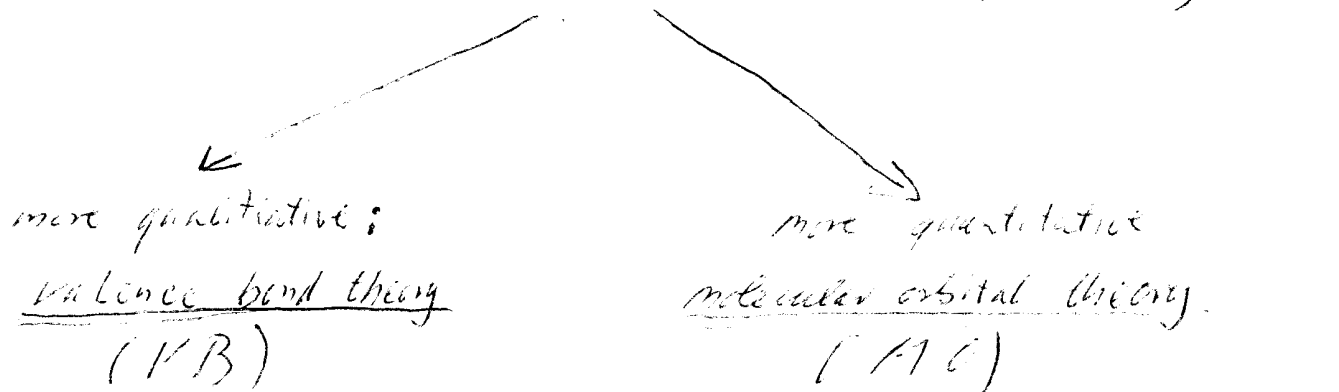


Molecular Structure

(1)

1. Introduction

- extend quantum mechanics from atoms to molecules
- focus on covalent bonds (ionic bonds just limiting case)

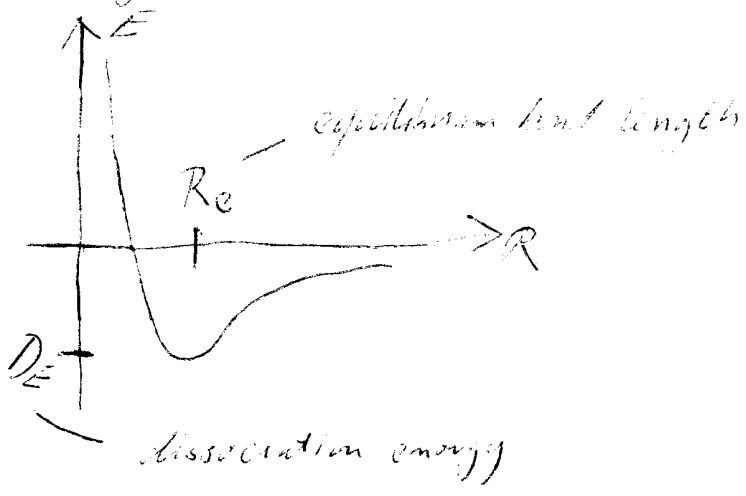


- shared e^- -pairs with wave function
- wavefunction of all e^- of all atoms involved in molecule
- σ -bonds
- π -bonds
- overlap of e^- -clouds
- promotion
- hybridization
- quantum chemistry

hydrogen \rightarrow diatomic molecules \rightarrow polyatomic molecules

Born - Oppenheimer approximation:

- distance of nuclei is stationary
⇒ molecular bonds are determined by electronic interactions (1000 stronger)
- good approximation for ground state
- bond length determined as vibrational problem



2. Valence bond theory

- language that you learned in your chemistry class

The hydrogen molecule H₂

$$\Psi = \Psi_{H1SA}(\vec{r}_1) \Psi_{H2SB}(\vec{r}_2) \pm \Psi_{H1SB}(\vec{r}_2) \Psi_{H2SA}(\vec{r}_1) =$$

$$= A(1) B(2) \pm A(2) B(1)$$

+ : e⁻ - clouds overlap!
⇒ bonding orbital

⇒ σ-bond : cylindrical symmetry
around internuclear axis

- : e⁻ - clouds do not overlap!
⇒ non-bonding orbital

e⁻ - spin pairing

Pauli - principle $\Psi(1,2) = -\Psi(2,1)$

$$\Psi(1,2) = [A(1)B(2) + A(2)B(1)] e^{\text{spin}}(1,2)$$

$$\Psi(2,1) = [A(2)B(1) + A(1)B(2)] e(2,1) =$$

$$= [A(1)B(2) + A(2)B(1)] e(2,1) =$$

⇒ $e(2,1) = -e(1,2)$ spin pairing

$$e(1,2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

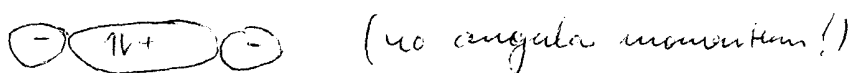
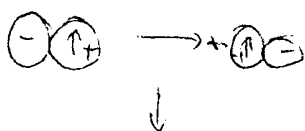
→ role of electron spin

- spins pair as atomic orbitals overlap (since they now occupy the same orbital)
- ψ_{H_2} can only be formed if electrons have opposed spins, achieving a wave function corresponding to low energy
- Pauli principle (wave functions of two electrons change sign when labels of electrons are interchanged)

How nuclear diatomic molecules (general case)

example: N_2 , nitrogen

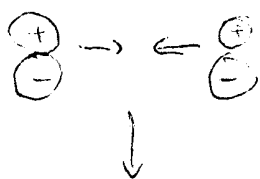
- electron configuration $2s^2 2p_x^1 2p_z^1 2p_y^1$ (Hund's rule)
- σ bond: spin pairing of $2 \times 2p_z^1$



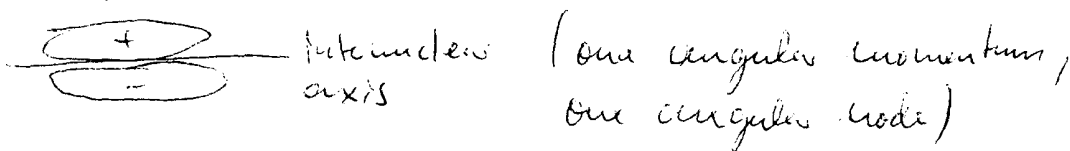
- remaining p orbitals → can not merge to σ bonds

π - bond formation

, π bond resembles a pair of electrons in a p orbital



N_2 : 2 π bonds! (with Lewis) $:N \equiv N:$



Polyatomic molecules

- σ bonds: spin pairing of electrons with cylindrical symmetry along the relevant nuclear axis
- π bonds: pairing of electrons which occupy AO of the appropriate symmetry

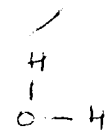
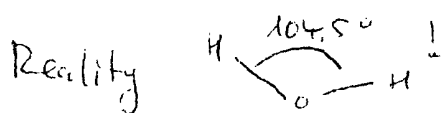
discrepancies

example H_2O : O configuration of ten valence electrons
 $2s^2 2p_x^2 2p_y^1 2p_z^1$

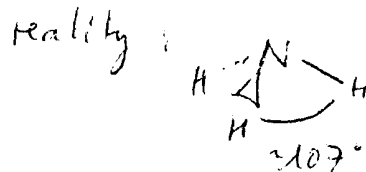
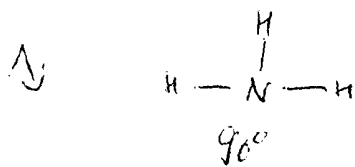
→ two unpaired 2p electrons → pair with a H's each

p_y and p_z : oriented to each other with 90°

→ H_2O : angular molecule



→ NH_3 : N configuration $2s^2 2p_x^1 2p_y^1 2p_z^1$



Promotion

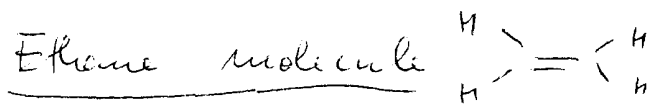
VB theory can not account for tetravalence of C:

$2s^2 2p_x^1 2p_y^1$ → divalency?

Solution: promotion to $2s^1 2p_x^1 2p_y^1 2p_z^1$

- promotion is no real process; however energy contribution to bonding!

- properties of hybrid orbitals - pronounced directional character
- increased bond strength \rightarrow
 - helps to repay promotion energy



- planar, HCH angles: 120°
- promotion: $\rightarrow 2s^1 2p^3$
- now using 3 \times sp^2 hybrid orbitals

$$h_1 = s + 2^{1/2} p_y \quad h_2 = s + \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y$$

$$h_3 = s - \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y$$

\rightarrow lie in plane, point to triangle corners

Superpositions in general: proportion in the mixture

is given by the square of the corresponding coefficient

$$h_1 : s \text{ to } p = 1:2$$

$$h_2 + h_3 : \text{total } p \text{ contribution, also } 2 \left(\pm \frac{3}{2} + \frac{1}{2} \right)$$

different signs \rightarrow result in different regions where constructive interference takes place

Structure of $H_2C=CH_2$:

3 sp^2 form σ bonds; CH_2 are in the same plane

to allow unhybridized p_z -Orbitals to form a π -bond

\rightarrow π -bond: no rotation possible

Ethyne $\text{HC}\equiv\text{CH}$

-8-

sp hybridized,

σ) bonds from $h_1 = s + p_z$, $h_2 = s - p_z$
along the C-C axis

4 electrons in $2p$ orbitals \rightarrow 2 π bonds,
perpendicular

General: hybridization of NAO \rightarrow formation
of N hybrid orbitals

more examples of hybridization schemes

Coordination number	arrangement	Composition
2	linear, Angular	sp, pd, sd sd
3	trigonal planar " pyramidal	sp^2, p^2d pd^2
6	octahedral	sp^3d^2

Molecular orbital theory

- electrons belong not to particular bonds but are treated as spreading throughout the entire molecule
- more fully developed than VB theory
- introduction by taking H atom as the fundamental species → developing the description of atoms; analogy: using H₂⁺, the simplest molecular species

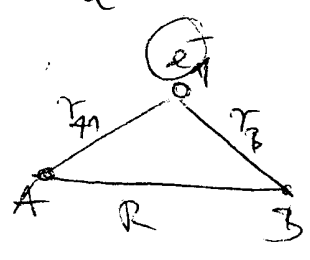
hydrogen molecule ion

The hydrogen molecule ion

The Hamiltonian of H₂⁺

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + V$$

$$V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R} \right)$$



attraction
nuclei-electron

repulsive
nucleus-nucleus

Solving Schrödinger eq. $H\psi = E\psi$

→ one electron wavefunction called MO (molecular orbitals)
MO ψ gives via $H\psi$ the e⁻ distribution in the molecule

- for H_2^+ -Ion: Schrödinger eq. can be solved - 2-
within the Born-Oppenheimer approxi-
mation

- Complicated wavefunctions, solutions can not be extended
to polyatomic systems \Rightarrow simpler procedure adopted

a) Linear combination of atomic orbitals

- 1 electron found in an AO belonging to
A AND in an AO belonging to B

- overall wavefunction: ~~from~~ results from
superposition of 2AO

$$\Psi_{\pm} = N(A \pm B) \quad A = \Psi_{1s_A} \quad B = \Psi_{1s_B}$$

technical term: LCAO, approximate MO

from LCAO is called LCAO-MO

\rightarrow σ orbital, (same definition as in VB-theory
is an MO, cylindrical symmetry along
internuclear axis)

Normalization of Ψ_{\pm} :

$\int \Psi \Psi^* d\tau$; find factor N

- substitute ~~into~~ LCAO ~~into~~ ~~the~~ integral
- atomic ~~orbitals~~ orbitals are ~~all~~ individually normalized

$$\Rightarrow = N^2 \left(\int A^2 d\tau + \int B^2 d\tau + 2 \int AB d\tau \right) = N^2 (1 + 1 + (2S))$$

$$S = \int AB d\tau$$

Normalization

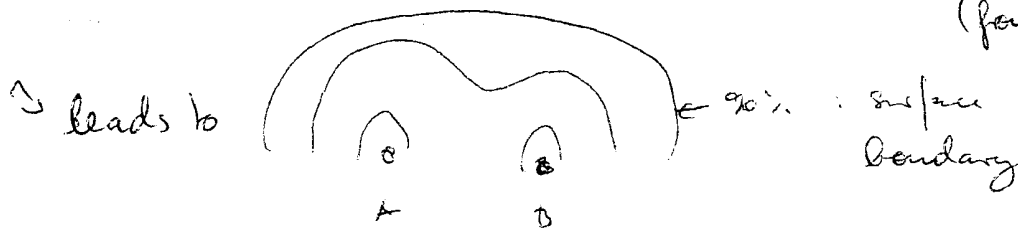
For the integral to be equal to 1, one requires:

$$N = \frac{1}{\{2(1+S)\}^{1/2}} \quad \left[\begin{array}{l} \text{Comment} \\ H_2^T: S \approx 0.55 \quad N = 0.56 \end{array} \right]$$

$$\text{Example: } A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}} \quad B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}}$$

and r_A and r_B are not independent!

$$r_B = (r_A^2 + R^2 - 2r_A R \cos \theta)^{1/2} \quad N^2 = 0.31 \quad (\text{from above})$$



b) Bonding orbitals

Basic interpretation: probability density is proportional to the square modulus of its wavefunction.

— probability density corresponding to the real wavefunction Ψ_+ in eq. 7 $\Psi_+^2 = N^2(A^2 + B^2 + 2AB)$

⇒ the total probability density proportional to

1) A^2 (electron would be confined to A - A_0)

2) B^2 (" " B - A_0)

3) $2AB$ (extra contribution to the density)

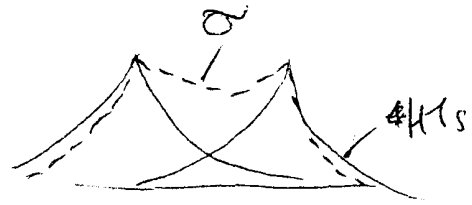
overlap density: crucial: advancement of the orbital

→ electrons accumulate where orbitals overlap and interfere constructively. (reflecting interaction with both nuclei)

- bonding orbital 1σ , σ of lowest energy

Calculation on H_2^+ : $R_e = 130 \text{ pm}$, $D_e = 177 \text{ eV}$
experimental 106 pm , 2.6 eV

Foll: justification p. 420

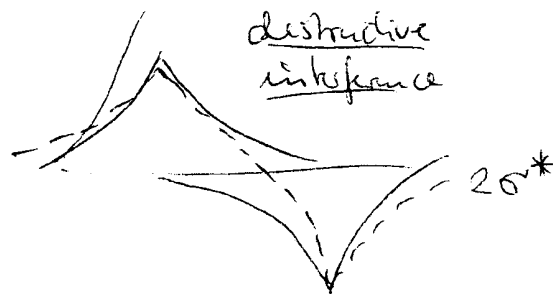


c) Antibonding orbitals

ψ_- corresponds to higher energy than ψ_+

also a σ orbital: 2σ antibonding orbital which raises the energy of a molecule

if occupied! (reduction in cohesion) often labelled as $2\sigma^*$ ('two sigma star')



- antibonding e^- : excluded from the inter-nuclear region
↳ pulls nuclei apart!

- $|E_- - E_{H1s}| > |E_+ - E_{H1s}|$ σ^* more antibonding than σ is bonding! presence of nuclei-repulsion!

molecular orbital energy level diagram

$2s^*$ —

$1s$ — — — $1s$

$1s$ $\uparrow\downarrow$

ground electronic configuration
of H_2 : accommodating
 e^- in the lowest
available orbital

Structure of diatomic molecules

- $1s$ - atom orbitals used for deduction of ground electronic configuration of many-electron atoms
- analogy: H_2^+ MO \rightarrow many-electron diatomic molecules

general procedure: - MO from LCAO

- electrons accommodated in the orbitals to achieve the lowest overall energy
- Pauli principle: no more than 2 electrons per orbital
- Hund's maximum multiplicity rule (parallel spin occupation of degenerate orbitals by electrons)

The hydrogen and helium molecules

- $2s$ and $2p_z$: distinctively different energies,
 may be ~~be~~ treated separately \rightarrow 4 σ orbitals
 fall into two sets: 1 consisting of 2 MO of the form:

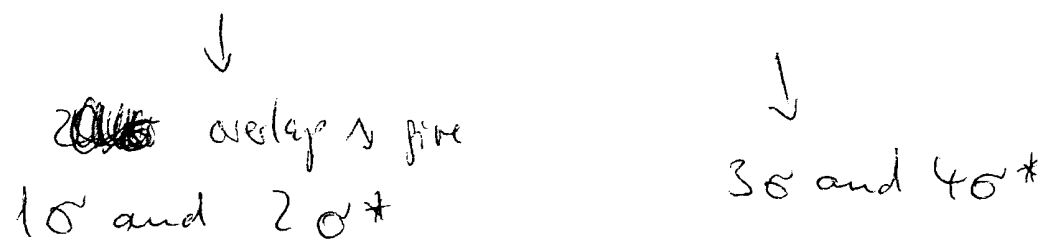
$$\psi = C_{A2s} \psi_{A2s} + C_B \psi_{B2s}$$

and another consisting of two orbitals of the form:

$$\psi = C_{A2p_z} \psi_{A2p_z} + C_{B2p_z} \psi_{B2p_z} \quad (14, 16b)$$

- A, B identical, $2s$ energies are the same \rightarrow
 coefficients are equal. same: $2p_z$ orbitals

$$\rightarrow \psi_{A2s} \pm \psi_{B2s} \quad \text{and} \quad \psi_{A2p_z} \pm \psi_{B2p_z}$$



Numbering follows increasing energy

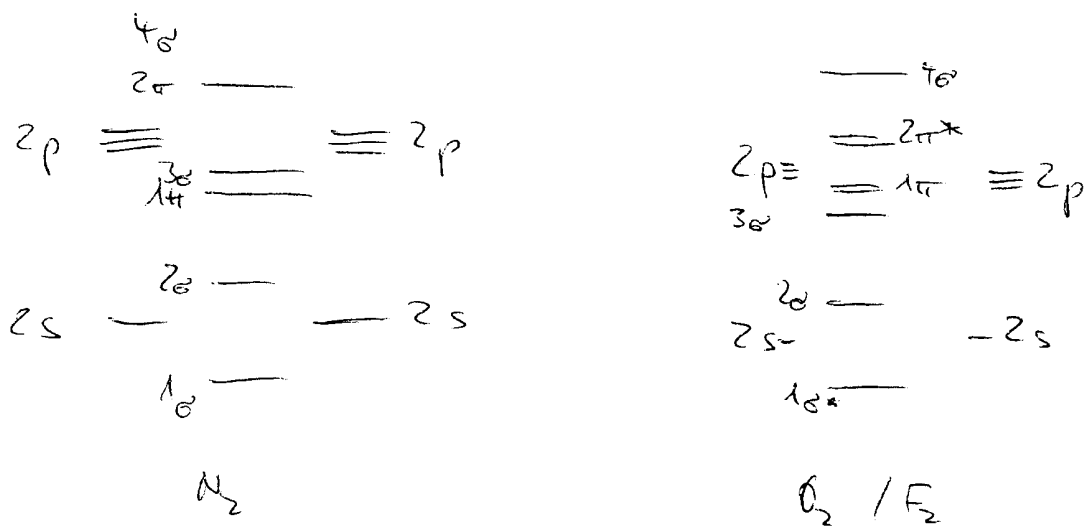
d) π - orbitals

- remaining $2p_x$ and $2p_y$ orbitals:
 overlap broadside-on

\rightarrow π - orbitals, 1 ~~aligned~~ unit of
 (def as before) orbital angular momentum

\rightarrow $2\pi_x$ and $2\pi_y$ bonding / antibonding orbitals
 π_x and π_y , π_x^* and π_y^* : degenerate

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



e) The overlap integral

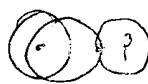
Attempt to build 2 atomic orbitals
 overlap: measured by the overlap integral S

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

pictured



small overlap



large overlap



zero overlap

$$S = 0.53 \text{ at } r_0 \text{ in } H_2^+$$

$$S = 0.2-0.3 \text{ for orbitals with } n=2$$

f) structure of diatomic molecules:

- 9 -

buildy-up principle, using the electrons from unbound atoms

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

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

→ $2\pi^*$ electrons occupy 2 orbitals, i.e. $2\pi_x^* 1 2\pi_y^*$

↳ 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: $\frac{1}{2}(8-6)=1$

low dissociation energy

Diatomic molecules:

-1-

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

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

Def trial wavefunction $\psi = C_A A + C_B B$ is real, not normalized
(because the coefficients can take arbitrary values)

(not normalized) $\int \psi^2 d\tau = 1$

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

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:

real wavefunction

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

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

The numerators:

-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, but can be combined into the parameters

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

\Rightarrow 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
(β = resonance integral)

\Rightarrow 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

Condition for \rightarrow 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:

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

→ 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)

↘ 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

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

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

↘ for a ratio of the coefficients ↘ need to find
individual values

attention: individual values can be found with ⁻⁴⁻ $\int \psi^2 dx = C_A^2 + C_B^2 + 2C_A C_B S = 1$ (normalized)

2 Simple Cases

complete solutions possible:

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:

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

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

B) diatomic molecule, $S = 0$ (different nuclei) ^{previously}

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

~~at~~ ~~to~~ ~~0~~ sorry!

Solutions can be expressed with ξ (eta)

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

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

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

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

- large energy difference in the AO: the MO 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
- solve the latter for energies \uparrow determinant
- use energies to find the coefficients of all AO for each MO
- \rightarrow greater ranges of shapes possible

Hückel approximation (E. Hückel 1931) - 6 -

- 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. Carbons) are treated identically \Rightarrow all α (Coulomb integrals) for AO that contribute to
- 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;

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

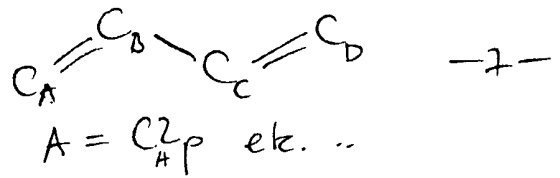
next:

- optimum ~~coefficients~~ coefficients / energies have to be found, solve the secular determinant

with $\alpha_A = \alpha_B = \alpha$

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

Eor 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:

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

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

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

- additional approximations 1) 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 ⁻⁸⁻
of molecular orbitals ~~without~~ (however!)

result of the Hückel-approximation:

ethene:

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

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:

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

Solutions: $x = 2.62$ and 0.38

-9-

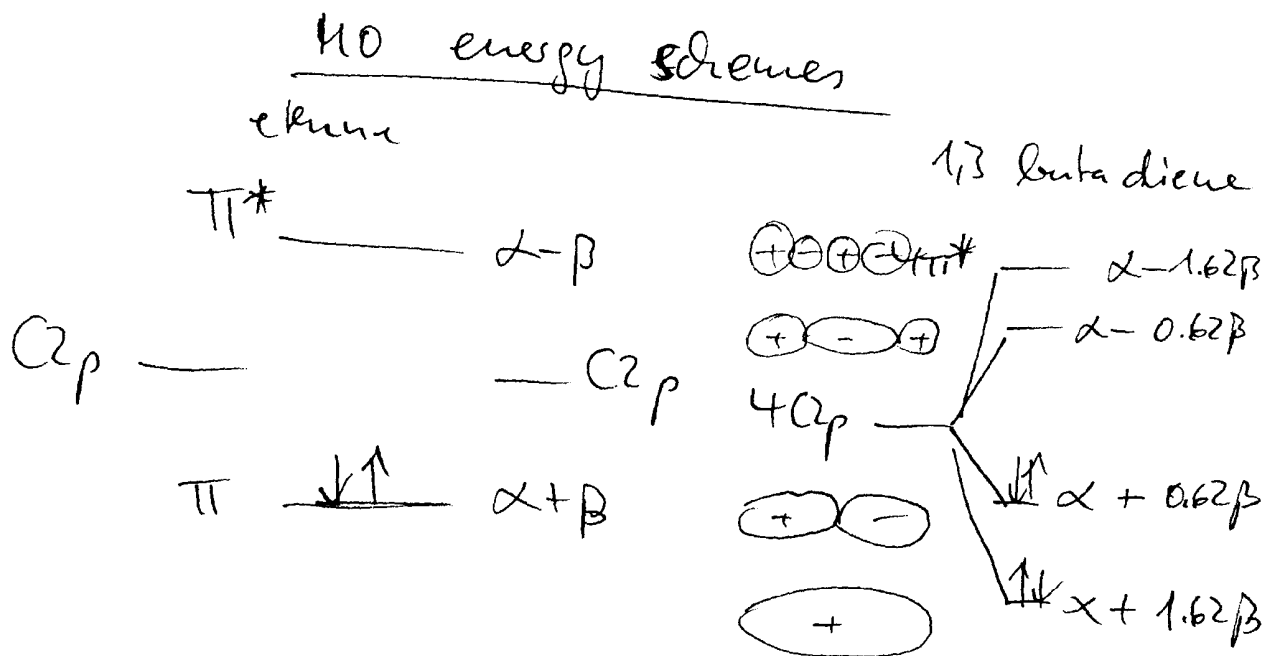
$$\downarrow E = \alpha + 1.62\beta \quad E = \alpha - 1.62\beta$$

(1 π) (3 π^*)

$$E = \alpha + 0.62\beta \quad E = \alpha - 0.62\beta$$

(2 π) (4 π^*)

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



Delocalisation energy # of electrons

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

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

energy of butadiene lies 0.48β lower than

two isolated π bonds $2(2\alpha - 2\beta)$!