

Diatomic molecules:

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- 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)

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 $\frac{\partial E}{\partial C_B} = 0$

Proof:

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 numerals:

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

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

$$C_A C_B \int B H A d\tau$$

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,

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

$\left(\begin{array}{l} \alpha = \text{Coulomb integral} \\ \beta = \text{resonance integral} \end{array} \right)$

\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

gradient zero \rightarrow ~~secular determinant~~

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

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

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

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

↳ gives a ratio of the coefficients ↳ need to find individual values

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

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}

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

~~...~~ sorry!

Solutions can be expressed with ξ (relax)

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

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

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

as distance $|\alpha_A - \alpha_B|$ increases δ 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
- $\psi = \sum_i c_i \phi_i$
- 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 -

- 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
- example ethene: >C=C< σ bonds taken as fixed, ~~the~~ focus on finding energies of the single π bond and its companion anti-bond

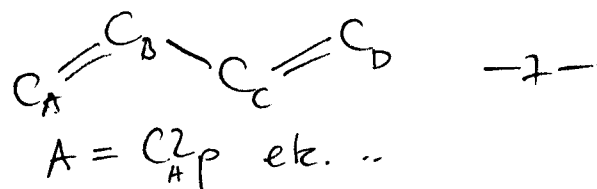
a) Ethene and frontier orbitals

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

Ex 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:

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

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

butadiene: complicated! tedious calculations 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:

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:

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

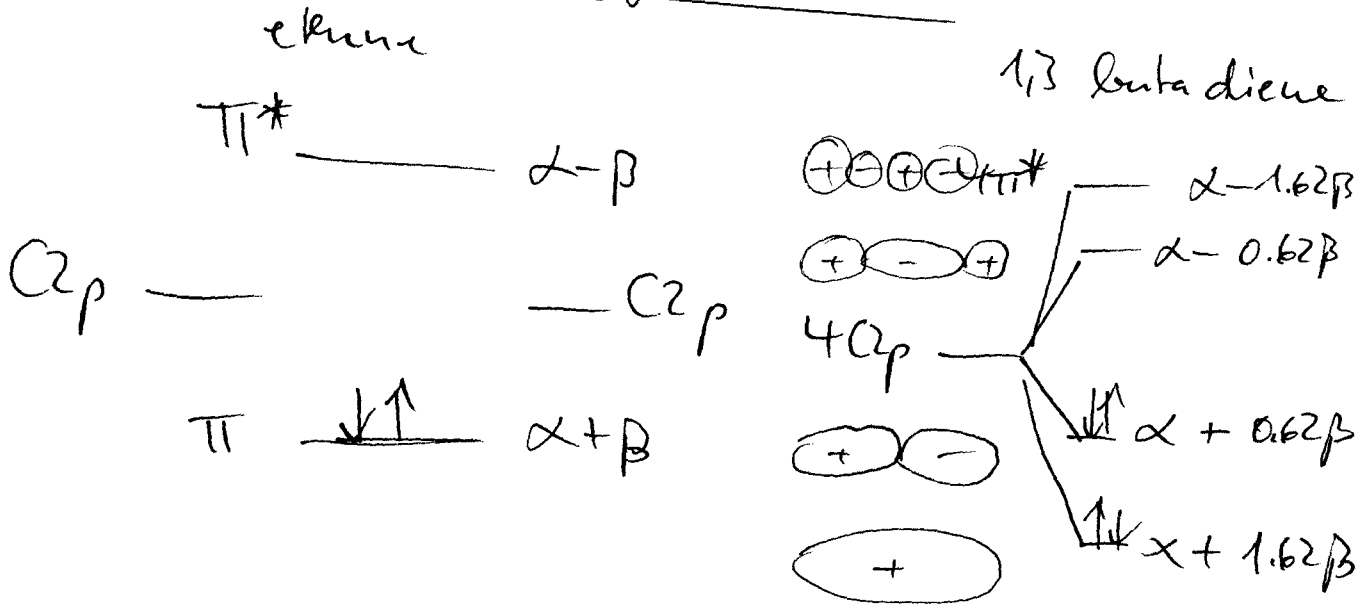
Solutions: $x = 2.62$ and 0.38

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

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

4p 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 ethen: $2(\alpha + \beta) = 2\alpha + 2\beta$

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 $2(2\alpha - 2\beta)$!