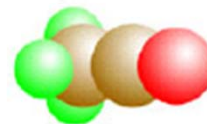


Quantum Mechanics - 4

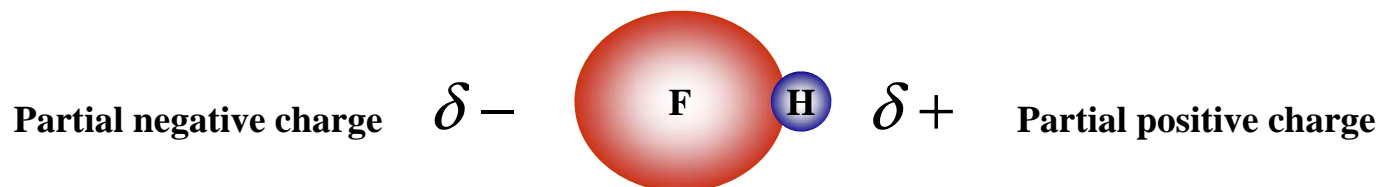
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강정원

Heteronuclear Diatomic Molecules

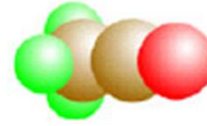


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- Molecules formed from two different atoms
 - CO , HCl, ...
 - Electron distribution is not evenly shared
 - Electron pair to be found closer to one atom than the other → energetically favorable
- Polar bond
 - A covalent bond electron pair is evenly shared



Polar bonds



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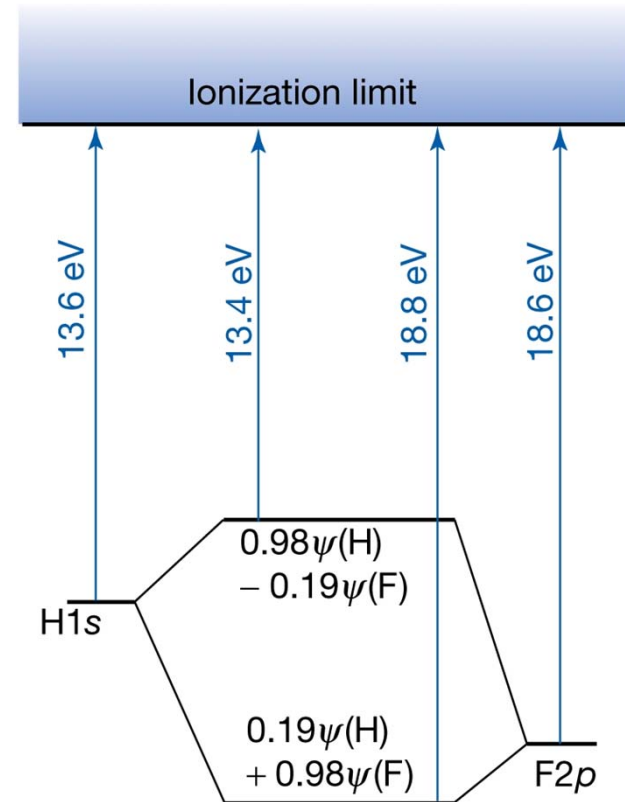
- A polar bond consists of two electrons in an orbital

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

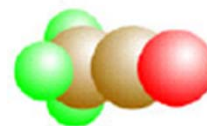
- nonpolar bond $|c_A| = |c_B|$
- polar bond $|c_A| \neq |c_B|$
- ionic bond $|c_A| = 0, |c_B| = 1$

- Contribution to total orbital

- lower energy makes large contribution to **bonding orbital**
- higher energy makes large contribution to **antibonding orbital**



Electronegativity



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- Power of an atom to attract to electron to itself

- Pauling electronegativity

$$|\chi_A - \chi_B| = 0.102 \left\{ D(A-B) - \frac{1}{2} [D(A-A) + D(B-B)] \right\}^{1/2}$$

- Mulliken electronegativity scale

- I : ionization energy
- E_{ea} : electron affinity

$$\chi_M = \frac{1}{2} (I + E_{ea})$$

- Relation

$$\chi_p = 1.35 \chi_M - 1.37$$

Element	Electro - negativity
H	2.2
C	2.6
N	3.0
O	3.4
F	4.0
Cl	3.2
Cs	0.79



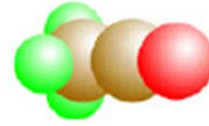
The Variation Principle



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- More systematic way of discussing bond polarity
- **“Variation Principle”**
 - If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than true energy
- Arbitrary wave function → trial wave function
- Varying coefficient of trial wavefunction until the lowest energy is reached → the best value
- Optimum MO can be built from basis set (the given set of atomic orbitals)

Secular Equation



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

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

Minimum energy condition

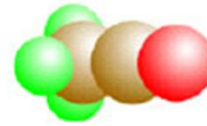
$$\frac{\partial E}{\partial c_A} = 0, \frac{\partial E}{\partial c_B} = 0$$

$$\begin{aligned} \int \psi^* \psi d\tau &= \int (c_A A + c_B B)^2 d\tau \\ &= c_A^2 \int A^2 d\tau + c_B^2 \int B^2 d\tau + 2c_A c_B \int AB d\tau = c_A^2 + c_B^2 + 2c_A c_B S \end{aligned}$$

$$\begin{aligned} \int \psi^* H \psi d\tau &= \int (c_A A + c_B B) H (c_A A + c_B B) d\tau \\ &= c_A^2 \int A H A d\tau + c_B^2 \int B H B d\tau + c_A c_B \int A H B d\tau + c_A c_B \int B H A d\tau \end{aligned}$$

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

Secular Equation



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$$E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S} \quad \frac{\partial E}{\partial c_A} = 0, \frac{\partial E}{\partial c_B} = 0$$

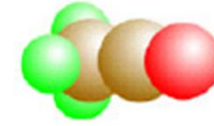
$$(\alpha_A - E)c_A - (\beta - ES)c_B = 0$$

$$(\beta - ES)c_A - (\alpha_B - E)c_B = 0$$

- To solve secular equation, we need to know E of the orbital
- E can be found from the solution of secular determinant

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

Procedure



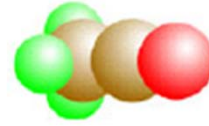
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$$\begin{vmatrix} (\alpha_A - E) & (\beta - ES) \\ (\beta - ES) & (\alpha_B - E) \end{vmatrix} = 0 \quad \Rightarrow \quad \text{Find } E$$

$$\begin{aligned} (\alpha_A - E)c_A - (\beta - ES)c_B &= 0 \\ (\beta - ES)c_A - (\alpha_B - E)c_B &= 0 \end{aligned} \quad \Rightarrow \quad c_A, c_B$$

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

Small Quiz

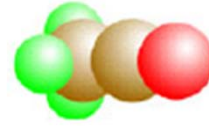


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- Find Solution for diatomic molecule when

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

Simple case



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

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

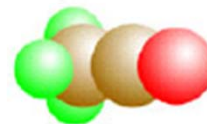
$$E_+ = \frac{\alpha + \beta}{1 + S} \quad c_A = \frac{1}{\{2(1+S)\}^{1/2}} \quad c_B = c_A$$

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

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

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

Molecular Orbital for Polyatomic Systems



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- The similar method as in diatomic molecules

- Use more atomic orbitals to construct MO

$$\psi = \sum_i c_i \psi_i$$

- Setup secular equation \rightarrow secular determinant \rightarrow solve E \rightarrow find coefficients \rightarrow MO

- Main difference

- Bond length and bond angle
- The shape of molecule can be predicted varying positions of atoms \rightarrow conformation with the lowest energy

The Hückel Approximation

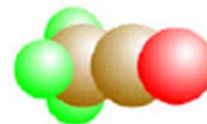


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- Conjugated molecules
 - Approximation suggested by Hückel (1931)
 - Alteration of single and double bond
 - π bond are considered separately from σ bond

 - σ bonds form a rigid framework for the shape of molecules
 - concentrate on π orbital

Ethene



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- π orbital : LCAO of the $C2p$ orbitals

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

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

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

Hückel approximations



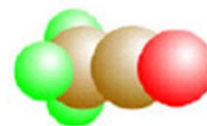
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- All overlap integrals are set equal to 0
- All resonance integral between non-neighbors are set to zero
- All remaining resonance integrals are set equal (β)

- All diagonal elements : $\alpha - E$
- Off-diagonal elements between neighboring atoms : β
- All other elements : 0

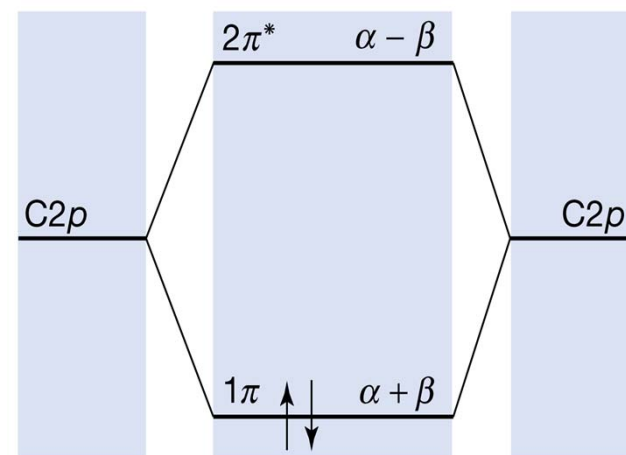
$$\begin{vmatrix} \alpha - E & \beta \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad E_{\pm} = \alpha \pm \beta$$

Frontier Orbitals

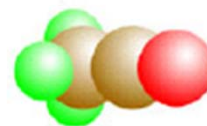


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- Two orbitals
 - Bonding orbital : 1π
 - Antibonding orbital : $2\pi^*$
- ground state : $1\pi^2$
- Frontier orbitals
 - Highest Occupied Molecular Orbital (HOMO) : 1π
 - Lowest Unoccupied Molecular Orbital (LUMO) $2\pi^*$



Homework



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- Perform energy minimization for
 - Benzene
 - Ethanol
 - Water
 - Acetaldehyde
- Draw electrostatic potential surface (eplot diagram)