Chapter 3. Orbitals and Bonding

- What to master
  - Assigning Electrons to Atomic Orbitals
  - Constructing Bonding and Antibonding Molecular Orbitals with Simple MO Theory
  - Understanding Sigma and Pi Bonds
  - Identifying the Hybridization of Atoms in Molecules
  - Understanding and Using Resonance
  - Recognizing Energy Levels of Molecular Orbitals

Chapter 3. Orbitals and Bonding

- Atomic orbitals (AOs): 📖 62 Figure 3.1
  - orbital: the space occupied by electrons; principal (*n*), angular (*l*), magnetic (*m*) & spin (*s*) quantum numbers
    - 1*s*, 2*s*, 2p_x, 2p_y, 2p_z, 3*s*, 3p_x, 3p_y, 3p_z, 3d_{xy}, 3d_{xz}, 3d_{yz}, 3$d_{x^2-y^2}$, 3d_{z^2}
  - the more the nodes, the higher the energy level
- Electron configuration: 📖 64 Figure 3.2
  - distribution of electrons among orbitals: aufbau principle, Pauli exclusion principle & Hund's rule
  - ground state vs excited state

Molecular Orbitals (I)

- Molecular orbitals (MOs)
  - the LCAO approximation: e.g., H_2 📖 66 Figure 3.3
  - energy level diagram of H_2: 📖 66 Figure 3.4
  - shape of a sigma (σ) bond: cylindrical; symmetrical around the internuclear axis, 📖 67 Figure 3.5
  - How about a He_2 molecule? Is it stable enough to exist?

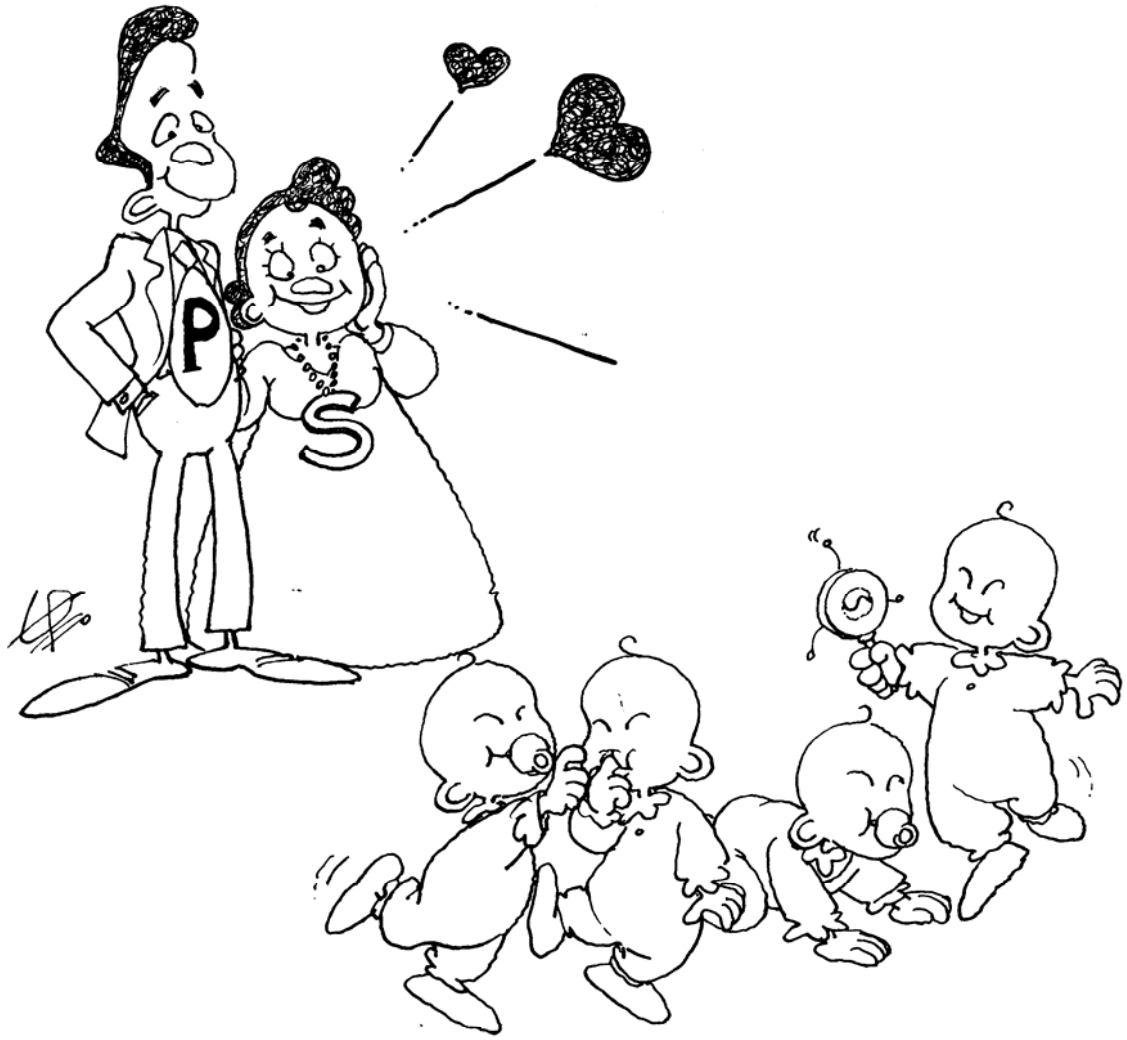
Molecular Orbitals (II)

- Valence bond theory (VBT)
  - assumption for complex molecules: MOs localized between two bonded atoms
  - Summary: 📖 68 bottom
    - 2 MOs from 2 AOs of 2 atoms (No. of MOs = No. of AOs)
    - one combination: bonding (σ) MO, the other: antibonding (σ^*) MO
    - the same rules for electron assignment to MOs as to AOs
    - $E_{dis} \approx$ No. of electrons x ΔE
    - $\Delta E \propto$ degree of overlap of the AOs (too close, too unstable)

Bonding & Hybridization (I)

- Single bonds & *sp³* hybridization
  - experimental data for CH_4: the same bond length & angle
    - hybridization of *s* & 3 *p*: 4 ***sp³*** (to fit the data), 📖 69 Fig. 3.6 (cf.)
    - σ bonds for CH_4: 📖 70 Figure 3.7
  - other compounds: CH_3-CH_3, NH_3, CH_3-OH; 📖 71 Figure 3.8
    - σ bonding for a C-C bond: 📖 70 middle

SP^3 Hybridization



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Hybridization (II)

- Double bonds & sp^2 hybridization
  - experimental data for $CH_2=CH_2$: planar, 📖 72 Figure 3.9
    - hybridization of *s* & 2 *p*: 3 ***sp²*** & the rest 1 *p*
  - pi(π) bond from the *p*-*p* overlap: 📖 73 Figure 3.10
    - energy level of π and π^*: 📖 74 Figure 3.11 (ΔE_π = 64, ΔE_σ = 81)
    - difficult rotation around a double bond: 📖 74 Figure 3.12
    - other molecules with ***sp²***: CH_2NH, CH_2O; 📖 75 Figure 3.13

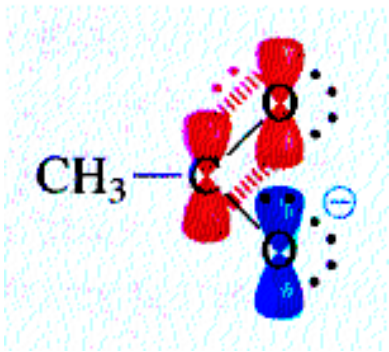
Hybridization (III)

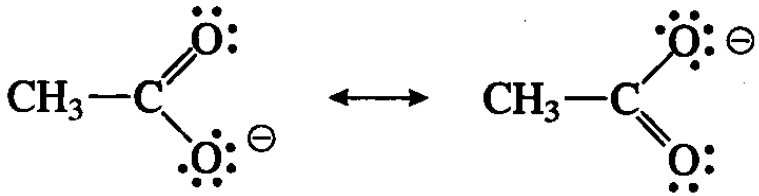
- Triple bonds & *sp* hybridization
  - experimental data for HC≡CH: linear, 📖 76 Figure 3.14
    - hybridization of *s* & 1 *p*: 2 ***sp*** & the rest 2 *p*
    - perpendicular pi(π) bonds
    - others with an ***sp*** orbital: HCN, 📖 76, Problem 3.7

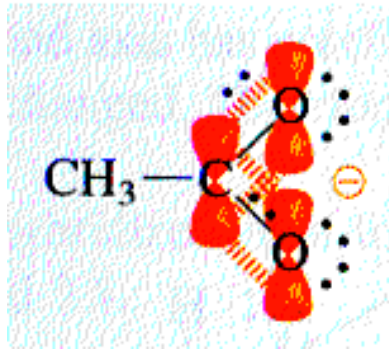
Practice makes perfect: Problems 3.8 & 3.9, 📖 77

Resonance (I)

- Delocalized MOs (= resonance)
  - conjugated parallel *p* orbitals: carboxylate; 📖 79 Figure 3.15
  - resonance stabilization: MO theory
  - *practice*: 📖 79 Practice 3.1 & 📖 80 Practice 3.2

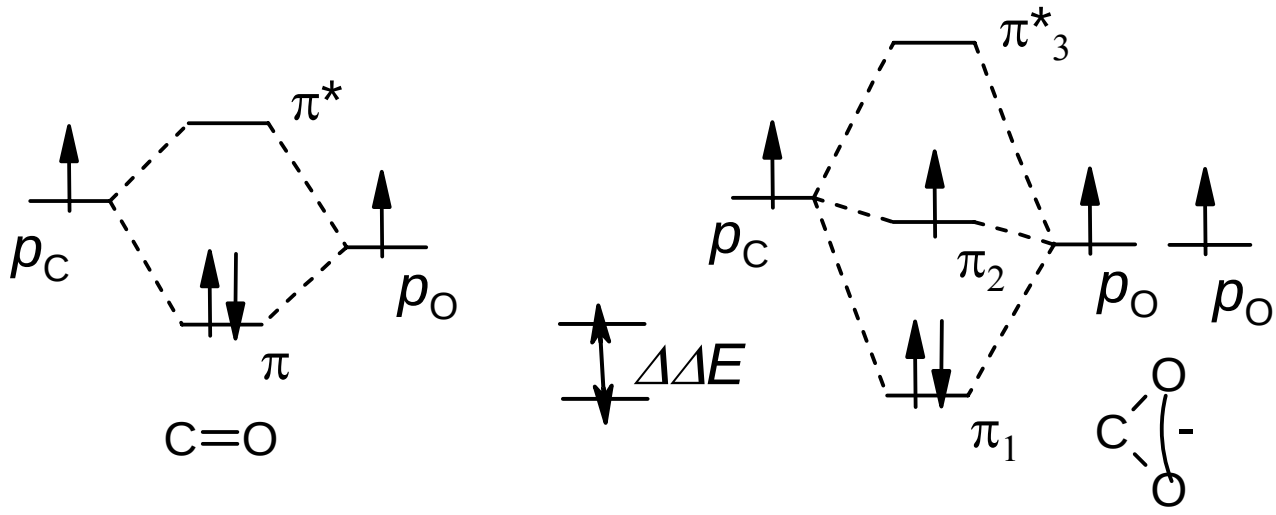






Resonance by MO Theory

- Further stabilization by conjugation



Resonance (II)

- Rules for applying resonance structures

1. Move only π & nonbonding e^- : 📖 82 Problem 3.12
2. The same No. of e^- and charge: 📖 83 Problem 3.13
3. Relative stability by octet rule & charge: 📖 84 Practice 3.5
   - more bonding, fewer charge, closer unlike charge, farther like chare & negative charge on more electronegative atom
4. Real structure ≈ the most stable one (resonance structure)
5. The more the important resonances, the more stable: 📖 85, Problem 3. 14 & 3.15

Resonance (III)

- Types of resonance interactions
  1. unshared electrons: carboxylate, enolate, carboxylic acid
     - curved double-headed arrow: 📖 86 Figure 3.16
  2. one electron: allyl radical
     - curved single-headed arrow: 📖 87 Figure 3.17
  3. empty *p* orbitals (no e^-): allyl cation; 📖 87 Figure 3.18
  4. atoms of different electronegativities: 📖 88 Figure 3.19
  5. cyclic conjugation: benzene, 📖 89 Figure 3.20

Resonance (IV)

- Combinations of the resonance types

  - the anion of phenol: phenoxide, 📖 90 Figure 3.21 (1&5)
  - conjugated C=C with C=O: 📖 92 Figure 3.22 (3&4)
  - *practice*: 📖 92 Practice 3.6 & 📖 93 Problem 3.17

Resonance (V)

- Properties predicted from resonance structures
  - naphthalene: 📖 94 Focus On
    - bond length: cf. C-C 1.54 Å, C=C 1.34 Å
    - stability: relatively unstable to benzene (identical, 1.40 Å)
  - bond energy: C-H; ethane vs propene
    - smaller E_{dis} of propene: resonance stabilized radical

Energy Levels of MOs

- Relative levels of orbital energies: $\sigma < \pi < n < \pi^* < \sigma^*$
  - ethane: 📖 95 Figure 3.23 (only σ MOs)
  - ethylene: 📖 96 Figure 3.24 (σ & π MOs)
  - formaldehyde: 📖 96 Figure 3.25 (σ & π MOs and n AOs)
  - *practice*: 📖 97 Problem 3.18

공부하는 방법

"그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이, 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다.

이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다." - 퇴계 이황 (금장태 著)