

Lecture 13: Extensions of HMO Theory

Filipp Furche

Chem 150/250 Fall 2023

11/06/2023



UCI IRVINE

<http://ffgroup.chem.uci.edu>

Heteroatoms

- Change α , β for heteroatoms X and C-X bonds:

$$\alpha_X = \alpha + h\beta, \quad \beta_{CX} = k\beta$$

- Dimensionless “heteroatom parameters” h, k depend on oxidation state and hybridization.
- Example: $h = 0.5, k = 0.8$ for N in pyridine, but $h = 1.5, k = 1.0$ in pyrrole
- Qualitative heteroatom effect on π charges, bond orders, resonance energies: “Alchemical” perturbation theory for deviations from C parameters
- Also used for inorganic aromatic systems

Extended Hückel Theory (EHT)

- All-electron theory, originally restricted to valence electrons
- Minimal basis of Slater-type basis functions (STOs)
- Use complete overlap matrix (no CNDO)
- One-electron EHT Hamiltonian matrix:
 - ▶ Diagonal elements $H_{\mu\mu}$: Experimental (valence) IPs of atoms
 - ▶ Offdiagonal elements: Wolfsberg-Helmholtz approximation

$$H_{\mu\nu} = K \frac{H_{\mu\mu} + H_{\nu\nu}}{2} S_{\mu\nu},$$

where $K = 1.75$ (Wolfsberg-Helmholtz constant)

- Solve generalized eigenvalue problem

$$\mathbf{HC} = \mathbf{SC}\epsilon,$$

where $\epsilon_{ij} = \epsilon_i \delta_{ij}$ is diagonal

Other Semiempirical Electronic Structure Theories

- Pariser-Parr-Pople method: Adds nearest neighbor two-electron interaction potential (“Hubbard U”)

$$U_{\mu\nu\kappa\lambda} = U\delta_{\mu\nu}\delta_{\kappa\lambda}$$

to Hückel Hamiltonian

- CNDO/2, ZINDO, Fenske-Hall, MNDO, DFTB: EHT-like theories including some electron interaction effects at mean-field level

When to Use Hückel Theory

- Use Hückel theory for
 - ▶ qualitative analysis, e.g., size-dependent behavior
 - ▶ analysis of more advanced calculations (ab-initio calculation of α, β)
 - ▶ generation of initial MOs for self-consistent field calculations
- Avoid Hückel theory for
 - ▶ polar and ionic bonds
 - ▶ small-gap and transition metal compounds
 - ▶ excited states, electronic properties
 - ▶ quantitative calculations