

Going beyond simple Hückel...

Extended Hückel Theory (EHT)

- Created by Roald Hoffmann in the 60's
- Consider **valence** electrons (π and σ)
- **Core electrons** are still ignored
- The basis is not assumed to be orthonormal anymore: **we must calculate the overlap matrix S**
- The **atomic basis functions** are **Slater functions**
- It uses **Koopmans' theorem** for the diagonal elements

$$F_{ii} = -I_i \text{ where } I_i \text{ is the atomic ionization potential of the atom}$$

- Off-diagonal are

$$F_{ij} = -\frac{K}{2}(I_i + I_j)S_{ij} \text{ where } K = 1.75 \text{ is an empirical constant}$$

Generalized eigenvalue problem

How to solve a generalized eigenvalue problem $\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$?

This is simple: let's transform $\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}$ into $\mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}$

- ① Calculate the **orthogonalization matrix** \mathbf{X} such as $\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I}$
- ② Compute the Fock matrix in the **orthogonal basis** $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$
- ③ Compute the **eigenvectors** \mathbf{C}' and **eigenvalues** \mathbf{E} of \mathbf{F}'
- ④ **Back-transform the MOs** in original basis: $\mathbf{C} = \mathbf{X} \mathbf{C}'$

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \Rightarrow \mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{S}\mathbf{X}\mathbf{C}'\mathbf{E} \Rightarrow \underbrace{\mathbf{X}^\dagger \mathbf{F} \mathbf{X}}_{\mathbf{F}'} \mathbf{C}' = \underbrace{\mathbf{X}^\dagger \mathbf{S} \mathbf{X}}_{\mathbf{I}} \mathbf{C}'\mathbf{E} \Rightarrow \mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}$$

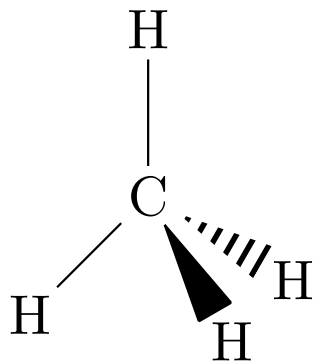
Different orthogonalizations

- ① **Symmetric orthogonalization** $\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger$
- ② **Canonical orthogonalization** (when you have linear dependencies) $\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$
- ③ **Gram-Schmidt orthogonalization** (numerically not super stable)

Methane in EHT

Slater basis set

$$\varphi_{nlm}(\mathbf{r}) = N \underbrace{r^{n-1} \exp(-\zeta r)}_{\text{radial}} \underbrace{Y_{\ell}^m(\theta, \phi)}_{\text{angular}}$$



Atomic orbitals (AO)

AO	Atom	Type	(n, ℓ, m)	ζ^1	IP (a.u.)
1	C	2s	(2, 0, 0)	1.625	0.7144
2	C	2p _z	(2, 1, 0)	1.625	0.3921
3	C	2p _x	(2, 1, ± 1)	1.625	0.3921
4	C	2p _y	(2, 1, ± 1)	1.625	0.3921
5	H	1s	(1, 0, 0)	1.200	0.5
6	H	1s	(1, 0, 0)	1.200	0.5
7	H	1s	(1, 0, 0)	1.200	0.5
8	H	1s	(1, 0, 0)	1.200	0.5

¹Exponents determined by Slater's rules

Methane in EHT (Take 2)

Overlap Matrix

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 & 0.5133 & 0.5133 & 0.5133 & 0.5133 \\ 0 & 1 & 0 & 0 & 0.4855 & -0.1618 & -0.1618 & -0.1618 \\ 0 & 0 & 1 & 0 & 0 & 0.4577 & -0.2289 & -0.2289 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0.3964 & -0.3964 \\ 0.5133 & 0.4855 & 0 & 0 & 1 & 0.1805 & 0.1805 & 0.1805 \\ 0.5133 & -0.1618 & 0.4577 & 0 & 0.1805 & 1 & 0.1805 & 0.1805 \\ 0.5133 & -0.1618 & -0.2289 & 0.3964 & 0.1805 & 0.1805 & 1 & 0.1805 \\ 0.5133 & -0.1618 & -0.2289 & -0.3964 & 0.1805 & 0.1805 & 0.1805 & 1 \end{pmatrix}$$

Fock Matrix

$$F = \begin{pmatrix} -0.7144 & 0 & 0 & 0 & -0.5454 & -0.5454 & -0.5454 & -0.5454 \\ 0 & -0.3921 & 0 & 0 & -0.3790 & 0.1263 & 0.1263 & 0.1263 \\ 0 & 0 & -0.3921 & 0 & 0 & -0.3573 & 0.1787 & 0.1787 \\ 0 & 0 & 0 & -0.3921 & 0 & 0 & -0.3094 & 0.3094 \\ -0.5454 & -0.3790 & 0 & 0 & -0.5 & -0.1579 & -0.1579 & -0.1579 \\ -0.5454 & 0.1263 & -0.3573 & 0 & -0.1579 & -0.5 & -0.1579 & -0.1579 \\ -0.5454 & 0.1263 & 0.1787 & -0.3094 & -0.1579 & -0.1579 & -0.5 & -0.1579 \\ -0.5454 & 0.1263 & 0.1787 & 0.3094 & -0.1579 & -0.1579 & -0.1579 & -0.5 \end{pmatrix}$$

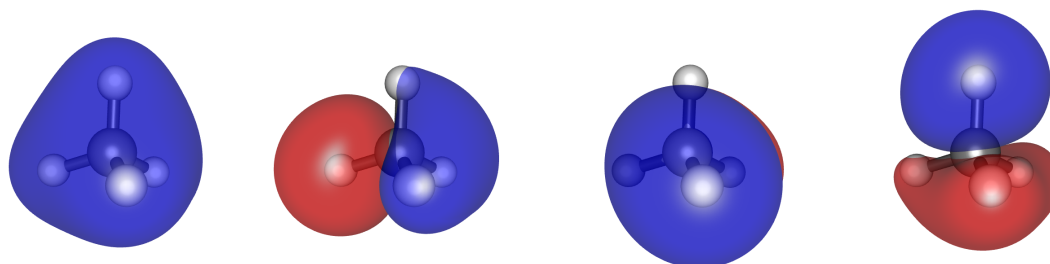
Methane in EHT (Take 3)

Eigenvalues = MO energies!

$$\mathbf{E} = (-0.8520 \quad -0.5488 \quad -0.5488 \quad -0.5488 \quad 0.2069 \quad 0.2069 \quad 0.2069 \quad 1.1898)$$

First four eigenvectors = Occupied MO!

$$\mathbf{C} = \begin{pmatrix} 0.6921 & 0 & 0 & 0 \\ 0 & 0.2727 & 0 & 0.6493 \\ 0 & 0.6493 & 0 & -0.2727 \\ 0 & 0 & 0.7042 & 0 \\ 0.3609 & 0.2381 & 0 & 0.5669 \\ 0.3609 & 0.4551 & 0 & -0.4134 \\ 0.3609 & -0.3466 & 0.5020 & -0.0767 \\ 0.3609 & -0.3466 & -0.5020 & -0.0767 \end{pmatrix}$$



EHT successes and pitfalls

EHT successes

- EHF is **non-iterative** \Rightarrow it can be used for large molecules
- Ok for **relative energies** of different geometrical configurations

EHT failures

- EHF restricted to **qualitative predictions** of conformation in molecules
- **Bad for geometries** due to poor off-diagonal elements
- **Potential energy surfaces (PES)** badly described (minima, transitions states, etc)
- **Do not take into account spin** (open-shell singlet and triplet states have same energy)
- Total energy (taken as sum of MO energies) **ill-defined**

Semi-Empirical Methods (SEM)

Come to the dark side, we have parameters...

- SEMs are based on Hartree-Fock theory but with (lots of) approximations
- They can be used for very large systems like proteins
- However, SEMs require parameters for each atom
- These parameters are atom-type dependent (like in classical force fields)
- There is a hierarchy of approximations:
ZDO, NDDO, INDO, CNDO
- MINDO models: MINDO/1, MINDO/2, MINDO/3
- NDDO models: MNDO, AM1, PM3, PM5
- If you really have to use SEMs, please consider PM6

Example with PM6: Stewart, J Mol Model 15 (2009) 765

