Chapter 15. Computational Chemistry

Hartree-Fock theory

$$\Psi(1,2,...N) = \hat{P}_{ij}\left[\chi(1)\chi(2)...\chi(N)\right]$$

where $\hat{P}_{ij}$ is the projection operator to antisymmetrize the Hartree wavefunction. χ is the molecular spin-orbital with its spatial part as LCAO:

$$\psi(i) = \sum_\alpha c_\alpha \phi_\alpha^{AO}$$

A set of coupled linear equations can be set up for the expansion coefficients $\{c_\alpha\}$, which is called the Hartree-Fock (HF) equations.

The HF equations can be solved iteratively, yielding the MOs and their energies.

HF is an approximation, because it ignores electron-electron correlation.

Post-HF treatments:

Moller-Plesset (MP) perturbation theory

Configuration interaction (CI) method.

Density functional theory

DFT is based on the premise that the energy is a functional of electron density:

$$E = E[\rho]$$

where

$$\rho = \sum_i \left| \psi_i^{MO} \right|^2$$

DFT accounts for electron-electron correlation via the exchange-correlation functional. As a result, it is usually more accurate than HF.

These methods are implemented in Gaussian.

Capabilities:

1. Geometry
2. Electrostatics
3. Reaction energy
4. Transition state and barrier height
5. Potential energy surface
6. Reaction mechanism
7. Reaction dynamics