

Density Functional Theory

LCAO approach: $\Psi_a = \sum_{i=1}^N c_{ia} \phi_i$ Ψ_a = one-electron molecular orbital

ϕ_i = atomic orbitals for N orbitals (Slater or Gaussian)

c_{ia} = orbital coefficients -- variational parameters

Variation Theorem: vary c_{ia} 's to find the lowest energy:

Hartree-Fock Equations:

$f_1 \Psi_a(1)\sigma(1) = \epsilon_a \Psi_a(1)\sigma(1)$ ϵ_a = one-electron orbital energy
for MO a, b, c, ...

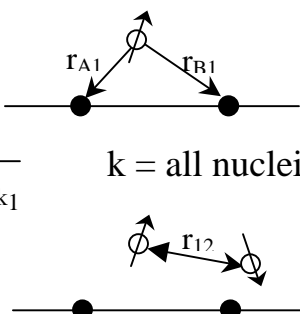
$f_1 = h_1 + \sum_{j=1}^{n/2} \{2J_j(1) - K_j(1)\}$ j = all the other filled orbitals
for electron 1, 2, 3, ...

core Hamiltonian:
$$h_1 = \frac{-\hbar^2}{2m} \nabla_1^2 - \sum_{k=1}^m \frac{Z_k e^2}{4\pi\epsilon_0 r_{k1}}$$
 k = all nuclei

HF electron-electron repulsion:

Coulomb operator: $J_j(1)$

Exchange operator: $K_j(1)$



Density Functional Theory:

$f_1 = h_1 + \sum_{j=1}^{n/2} \{2J_j(1) - V_j^{xc}(1)\}$ $E = E_T + E_V + E_J + E_{xc}$

kinetic + e-n attraction + Coulomb e-e repulsion + exchange-correlation energy

E_{xc} is taken as a function of the electron density: $\rho(r) = 2 \sum |\Psi(r)|^2$

Uniform Electron Gas (Quantum Monte Carlo Simulations)

Change electron density in one spot

Other electrons respond—motion correlated

difference density

"Wrap" this correlation around the nuclei

"Pure" DFT: BP, BLYP, EDF:

HF Coulomb

"Hybrid" B3LYP:

HF Coulomb and Exchange (exact)