Density Functional Theory

Shiv Upadhyay

University of Pittsburgh

October 12, 2018

Hartree-Fock reminder

Molecular electronic Hamiltonian

$$H = T + V_{ee} + V_{en}$$

Hartree-Fock reminder

Molecular electronic Hamiltonian

$$H = T + V_{ee} + V_{en}$$

Make the approximation that the electrons interact with the *mean field* of the other electrons

Hartree-Fock reminder

Molecular electronic Hamiltonian

$$H = T + V_{ee} + V_{en}$$

Make the approximation that the electrons interact with the
mean field of the other electrons

$$H = T + V_{ee} + V_{en}$$

Hartree-Fock reminder

Molecular electronic Hamiltonian

$$H = T + V_{ee} + V_{en}$$

Make the approximation that the electrons interact with the *mean field* of the other electrons

$$H = T + V_{ee} + V_{en}$$

$$F = H^{\text{core}} + G$$

$$G_{\lambda\sigma} = \sum_{\lambda\sigma} P_{\lambda\sigma}[2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)]$$

Why do we need DFT???

HF neglects *electron correlation*

Why do we need DFT???

HF neglects *electron correlation*

Electron correlation can be static (multiple near equal energy configurations) and dynamics electron/electron reactions.

$$E_{\text{corr}} = E_{\text{HF}} - E_{\text{TRUE}} \tag{1}$$

Why do we need DFT???

HF neglects *electron correlation*

Electron correlation can be static (multiple near equal energy configurations) and dynamics electron/electron reactions.
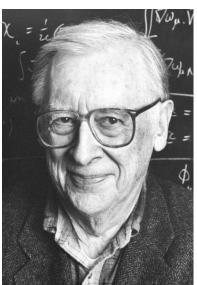
$$E_{\text{corr}} = E_{\text{HF}} - E_{\text{TRUE}} \qquad (1)$$

This happens because in reality the electrons don't interact with the mean field of the electrons; they interact with all the other electrons.

1998 Nobel Prize