CHM 673
Lecture 16: Density Functional Theory

Electron correlation

Electron correlation can be recovered in post-Hartree-Fock calculations employing:

- Variational principle: Configuration Interaction methods (CISD, QCISD(T), etc)

- Perturbation theory: Moller-Plesset perturbation theory (MP2, MP4, etc)

- Coupled-cluster ansatz (CCSD, CCSD(T), CCSDT etc)

- Density Matrix Renormalization Group (DMRG) theory

- Quantum Monte-Carlo (QMC)

or using Kohn-Sham Density Functional Theory (DFT)

Density Functional Theory (DFT)

Main object of DFT: electron density n(r)

Density of 1 electron: $n(r) = |\Psi(r)|^2$

N electrons: $n(r) = N \int |\Psi(r_1, r_2, r_3, ..., r_N)|^2 dr_2 dr_3, ..., dr_N$

Density depends on 3 coordinates while the wave function depends on 4N coordinates

The goal of DFT is to find a functional connecting electronic density and energy   E = E[n(r)]

Does electron density contain sufficient information to uniquely define the electronic energy?

- $\int n(r) dr = N$

- Cusps of density define positions of nuclei
- Heights of cusps define nuclear charges

Hohenberg-Kohn theorems

1ˢᵗ Hohenberg-Kohn theorem (1964):
The ground state energy is completely determined by electronic density

$$n(r) <---> E_{gs}$$

(but the connection is unknown)

Recall the electronic Hamiltonian: $\hat{H} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$

In DFT language, the V_{Ne} is referred to as the external potential V_{ext} – this is a potential exerted to electrons by nuclei. V_{ext} might also include other external fields such as electromagnetic field.

For a given number of electrons, the external potential defines the Hamiltonian

Then the Hohenberg-Kohn theorem can be reformulated as follows:
V_{ext} → H → E_{gs} <---> n(r)
The ground state electronic density uniquely defines the external potential

1st Hohenberg-Kohn theorem

The ground state electronic density uniquely defines the external potential

V_{ext} <---> n(r)

Proof by contradiction:

Assume there exist 2 different external potentials $V_{ext,1}$ and $V_{ext,2}$ that result in the same density n(r)

$$\hat{V}_{ext,1} \rightarrow \hat{H}_1 \rightarrow \Psi_1 \quad \xrightarrow{\hspace{2cm}} E_1$$

$$\hat{V}_{ext,2} \rightarrow \hat{H}_2 \rightarrow \Psi_2 \quad n(r)$$

$$\xrightarrow{\hspace{2cm}} E_2$$

Ψ_1 and Ψ_2 are different lowest energy wave functions

Use Ψ_2 as an approximate wavefunction for H_1 and recall the variational principle:

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle > E_1$$

$$\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle > E_1$$

$$E_2 + \langle \Psi_2 | \hat{V}_{ext,1} - \hat{V}_{ext,2} | \Psi_2 \rangle > E_1$$

1st Hohenberg-Kohn theorem

$$\hat{V}_{ext,1} \rightarrow \hat{H}_1 \rightarrow \Psi_1 \quad \longrightarrow \quad E_1$$
$$\hat{V}_{ext,2} \rightarrow \hat{H}_2 \rightarrow \Psi_2 \quad \longrightarrow \quad E_2$$

$n(r)$

Ψ_1 and Ψ_2 are different lowest energy wave functions

$$n_1(r) = n_2(r) = n(r) = N \int |\Psi_1|^2 dr = N \int |\Psi_2|^2 dr$$

Then $\quad E_2 + \langle \Psi_2 | \hat{V}_{ext,1} - \hat{V}_{ext,2} | \Psi_2 \rangle > E_1 \quad$ can be rewritten as

$$E_2 + \int n(r)(\hat{V}_{ext,1} - \hat{V}_{ext,2}) dr > E_1$$

Starting from the other side (using Ψ_1 as an approximate wavefunction for H_2) we get:

$$E_1 + \int n(r)(\hat{V}_{ext,2} - \hat{V}_{ext,1}) dr > E_2$$

together: $\quad E_1 + E_2 > E_1 + E_2$

Thus, there cannot be two different V_{ext} that yield the same ground state electron density

2nd Hohenberg-Kohn theorem: variational principle

If the ground state energy E0 is the functional if the ground state density, so must be its individual components:

$$E_0[n_0] = T[n_0] + E_{ee}[n_0] + E_{Ne}[n_0]$$

$$E_0[n_0] = T[n_0] + E_{ee}[n_0] + \int n_0(r)\hat{V}_{Ne}dr$$

$\underbrace{\phantom{T[n_0] + E_{ee}[n_0]}}$ universally valid $\qquad$ $\underbrace{\phantom{\int n_0(r)\hat{V}_{Ne}dr}}$ system-dependent

$$F_{HK}[n] = T[n] + E_{ee}[n] = \langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle$$

universal Hohenberg-Kohn functional

There is a single F_{HK} that is exact for all problems! Holy grail of DFT is to find F_{HK}

The universal functional F_{HK} delivers the ground state energy of the system if and only if the input density is the true ground state density n_0

Orbital-free DFT

$$E[n] = T[n] + E_{ee}[n] + E_{ne}[n]$$

what do we know about these functionals?

Kinetic energy functional $T[n] = ?$

Electron-nuclear attraction

$$E_{ne}[n(r)] = -\Sigma_A^{nuclei} \int \frac{Z_A}{|r - R_A|} n(r) dr$$

Electron-electron interactions: Coulomb

$$J[n(r)] = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr'$$

exchange $K[n] = ?$

Orbital-free DFT

Consider a uniform electron gas (UEG)

Kinetic energy (Thomas & Fermi, 1927):

$$T_{TF}[n(r)] = c_F \int n^{\frac{5}{3}}(r) dr$$

$$C_F = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$$

Exchange energy (Dirac, 1929):

$$K_D[n(r)] = -c_X \int n^{\frac{4}{3}}(r) dr$$

$$C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$$

Thomas-Fermi-Dirac theory:

$$E_{TFD}[n] = T_{TF}[n] + E_{ne}[n] + J[n] + K_D[n]$$

Exact for UEG, but does not predict bonding in molecules!

Orbital-free DFT

Why Thomas-Fermi-Dirac theory does not work?

$$T_{TF}[n]$$ underestimates kinetic energy by ~10%

Ne atom: E_{kin} = 128.9 a.u.
                $E_{exchange}$ = - 12.1 a.u.
                E_{corr} = - 0.4 a.u.

Kinetic density functional is the biggest problem!

Orbital-free DFT

How to improve Thomas-Fermi-Dirac theory?

Let's do a Taylor expansion of T[n]. Effectively, we will include terms depending on the derivatives (or gradient) of the density:

$$T[n] = T_{TF}[n] + T_2[n] + T_4[n] + T_6[n] + ...$$

$$T_{TF}[n(r)] = c_F \int n^{\frac{5}{3}}(r) dr \qquad \text{underestimation by ~10\%}$$

$$T_2[n] = \frac{1}{9} \int \frac{|\nabla n(r)|^2}{8n(r)} dr \qquad \text{underestimation by ~1\%}$$

Weizsacker term, exact for 1 and 2 electrons

$T_4[n]$ overestimation by >1%

$T_6[n]$ divergence

Orbital-free DFT

A similar Taylor expansion for exchange term K[n] :

$$K[n] = K_D[n] + K_2[n] + K_4[n] + K_6[n] + \ldots$$

$$K_D[n(r)] = -c_X \int n^{\frac{4}{3}}(r)dr$$

$$K_2[n] = -\frac{5}{216}(3\pi^5)^{-\frac{1}{3}} \int \frac{|\nabla n(r)|^2}{n^{\frac{4}{3}}(r)}dr$$

Thomas-Fermi-Dirac model with gradient terms is improved (bonding is allowed) but the accuracy is still low.

However, if such a functional (depending only on density and its derivatives) could be derived, the field of computational chemistry were revolutionized

Kohn-Sham DFT

Solution: Kohn & Sham approach

Represent kinetic energy as two terms:
>	one will be exact through orbitals (Slater Determinant term, T_{SD}),
>	second – small correction

Price:
- back to orbitals (from 3 to 4N coordinates)
- correlation functional reappears as a separate term E_{xc}

Kohn-Sham functional: $E_{KS}[n] = T_{SD}[n] + E_{ne}[n] + J[n] + E_{xc}[n]$

where E_{xc} is defined as: $E_{xc}[n] = \underbrace{(T[n] - T_{SD}[n])}_{\text{kinetic correlation energy}} + \underbrace{(E_{ee}[n] + J[n])}_{\text{potential correlation \& exchange energies}}$

Kohn-Sham DFT

Kohn-Sham functional: $\qquad E_{KS}[n] = T_{SD}[n] + E_{ne}[n] + J[n] + \boxed{E_{xc}[n]}$

compare with Hartree-Fock energy: $\qquad E_{HF}[\{\chi\}] = T + E_{ne} + J \boxed{-\ K}$

Using variational principle, Kohn-Sham functional results in a self-consistent problem

$$\hat{f}^{KS}\chi_i = \varepsilon_i \chi_i$$

with $\qquad \hat{f}^{KS}(x_1) = \hat{h}(x_1) + \Sigma_j \hat{J}_j(x_1) + V_{xc}(x_1)$

exchange-correlation potential $\qquad V_{xc} = \dfrac{\delta E_{xc}}{\delta n}$

Kohn-Sham theory is exact if V_{xc} is known