References

• WFT
  – Szaboo & Ostlund “Modern Quantum Chemistry”
  – Helgaker, Jørgensen & Olsen “Molecular Electronic-Structure Theory”

• DFT
  – Dreizler & Gross “Density Functional Theory”
Notations

• Capital greek letters are N-electron wave functions $\Psi$ $\Phi$

• Caligraphic variables, $\tau$, are N-electron variables

• Lower case greek letters are one-electron wave functions $\phi$ $\chi$

• Bold variables, $\mathbf{r}$, are one-electron variables
What are they good for?

- Modelling of molecules
- Structure and energy
- Reaction path
- Properties of molecules
- TDHF, TDDFT
- QM/MM
- TST
- CPMD
Outline

- Introduction
- Hartree-Fock approximation (HF)
- Correlation
- Configuration Interaction (CI)
- Complete active space-SCF
- Multi-reference CI
- Coupled Cluster (CC)
- Perturbation Theory (PT)
- Density Functional Theory (DFT)
Schrödinger equation

• If we BELIEVE in quantum mechanics then

\[ \hat{H} |\Phi_0\rangle = \mathcal{E}_0 |\Phi_0\rangle \]

\[ \hat{H} = \sum_i \left\{ \frac{1}{2} \nabla_i^2 + \sum_{j > i} \frac{1}{\mathbf{r}_i - \mathbf{r}_j} \right\} \]
\[ + \sum_A \left\{ \frac{1}{2} \nabla_A^2 + \sum_{B > A} \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} \right\} \]
\[ + \sum_{A_i} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} \]

• The Born-Oppenheimer approximation

\[ H = \sum_i \frac{1}{2} \nabla_i^2 + \nu_{\text{ext}} (\mathbf{r}) + \sum_{j > i} \frac{1}{\mathbf{r}_i - \mathbf{r}_j} \]
HF Approximation

- General HF theory
  - Energy and wave function definition
  - Fock-, Coulomb- and Exchange operator
  - Local and non-local potential
  - Koopman's and Brillouin's theorem
- Roothaan equations
- Self-consistent field (SCF)
Definition of HF

- Energy is the expectation value of the exact non-relativistic electronic Hamiltonian
- Variational principle applies

\[ \mathcal{E}_0 \leq E_{\text{HF}} = \langle \Psi_0(r) | \hat{H} | \Psi_0(r) \rangle \]

\[ |\Psi_0(r)\rangle = |\phi_{i}^{\text{HF}}, \ldots, \phi_{k}^{\text{HF}}\rangle \]
Definition of HF

- The wave function is a single slater determinant
- It is composed of N orbitals (1e\(^{-}\)-wave function)
- N is the number of electrons

\[ \Psi(\mathbf{r}) = |\phi_i, \ldots, \phi_k\rangle \]

\[ \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = (N!)^{-1/2} \begin{vmatrix} \phi_i(\mathbf{r}_1) & \cdots & \phi_k(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \phi_i(\mathbf{r}_N) & \cdots & \phi_k(\mathbf{r}_N) \end{vmatrix} \]
Find minimum

- Variation of orbitals
- Orbitals are kept orthonormal
- Lagrangian multipliers $\varepsilon$

\[
f \phi_i(r) = \varepsilon_i \phi_i(r) \text{ with } f = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + \mathcal{J} - \mathcal{K}
\]

\[
\mathcal{J}\phi_i(r_1) = \sum_j \int dr_2 \frac{\phi_j^*(r_2)\phi_j(r_2)}{|r_1-r_2|} \phi_i(r_1)
\]

\[
\mathcal{K}\phi_i(r_1) = \sum_j \int dr_2 \frac{\phi_j^*(r_2)\phi_i(r_2)}{|r_1-r_2|} \phi_j(r_1)
\]
HF energy

\[ E^{\text{HF}} = \langle \Psi_0(\mathbf{r}) | \hat{H} | \Psi_0(\mathbf{r}) \rangle \]

\[ \langle \Psi_0(\mathbf{r}) | \hat{H} | \Psi_0(\mathbf{r}) \rangle = \sum_{i}^{N} \langle \phi_i | h | \phi_i \rangle + \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j | \phi_i \phi_j \rangle \]

\[ \langle \phi_i \phi_j | \phi_i \phi_j \rangle = \langle \phi_i \phi_i | \phi_j \phi_j \rangle - \langle \phi_i \phi_j | \phi_j \phi_i \rangle \]

\[ \langle \phi_i \phi_j | \phi_k \phi_l \rangle = \int \int \frac{\phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_k^*(\mathbf{r}_2) \phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \]
HF wave function

• Composed of N orbitals, often with lowest $\varepsilon_i$
• It is anti-symmetric
• Yields electron density

\[
\rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r}_2 \ldots d\mathbf{r}_N
\]

\[
\iff \rho(\mathbf{r}) = \sum_{i=1}^{N} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})
\]
HF wave function and Hamiltonian

- HF wave function is eigenfunction of the HF operator

\[ H_0 \Psi_0(r) = E_0 \Psi_0(r) \]

\[ H_0 = \sum_{i}^{N} f(i) = \sum_{i}^{N} [h(i) + v^{\text{HF}}(i)] \]

\[ E_0 = \sum_{i}^{N} \varepsilon_i \]

\[ h(i) = -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(r) \quad \text{and} \quad v^{\text{HF}}(i) = \mathcal{J}(i) - \mathcal{K}(i) \]
The Coulomb operator is local

\[ \mathcal{J} \phi_i(r_1) = \sum_j^N \int \, dr_2 \frac{\phi_j^*(r_2) \phi_j(r_2)}{|r_1 - r_2|} \phi_i(r_1) \]

\[ \mathcal{J}(r_1) = \sum_j^N \int \, dr_2 \frac{\phi_j^*(r_2) \phi_j(r_2)}{|r_1 - r_2|} \]

\[ \mathcal{J}(r_1) = \int \, dr_2 \frac{\rho(r_2)}{|r_1 - r_2|} \]

The Coulomb operator is local
Exchange operator

\[ f \phi_i(r) = \varepsilon_i \phi_i(r) \quad \text{with} \quad f = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + J - K \]

\[ \mathcal{K}\phi_i(r_1) = \sum_{j}^{N} \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j(\mathbf{r}_1) \]

- Exchange operator cannot be written as a function of \( r \)
- It is said to be non-local
HF orbitals

\[ f \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \]

- HF orbitals aren't unique
- \( \phi_i(\mathbf{r}) \) are called canonical HF orbitals
- Unitary transform of the occupied orbitals conserves the energy and density
- Unitary transform of the unoccupied orbitals conserves the energy and density
- Shapes of orbitals are somewhat arbitrary
HF orbitals

\[ f \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \]

- Canonical HF orbitals
  \[ \langle \phi_i(\mathbf{r})|\phi_j(\mathbf{r})\rangle = \delta_{ij} \]

  \[ \langle \phi_i|f|\phi_j \rangle = \langle \phi_i|h|\phi_j \rangle + \langle \phi_i\phi_j||\phi_i\phi_j \rangle = \varepsilon_i \delta_{ij} \]

- Brillouin's theorem
  \[ \Psi_i^a = |\phi_1, \phi_2, \ldots, \phi_{i-1}, \phi_a, \phi_{i+1}, \ldots, \phi_N \rangle \]

  \[ \langle \Psi_i^a|\hat{H}|\Psi \rangle = 0 \]
HF orbitals

\[ v^{HF}(1)\phi_i(r_1) = \sum_j^N \int d r_2 \left[ \frac{\phi_j^*(r_2)\phi_j(r_2)}{|r_1 - r_2|} \phi_i(r_1) - \frac{\phi_j^*(r_2)\phi_i(r_2)}{|r_1 - r_2|} \phi_j(r_1) \right] \]

- Orbitals “feel” all other occupied orbitals
- Occupied “feel” N-1 orbitals
- Unoccupied “feel” N orbital
- Koopman's theorem:
  - IP \( \approx -\varepsilon_i, \, 1 \leq i \leq N \) (occupied)
  - EA \( \approx -\varepsilon_i, \, N + 1 \leq i \) (unoccupied)
Summary

- HF is an independent particle model
- HF theory is a single slater determinant theory
- HF wave function is eigenfunction of the N-electron Fock operator
- The orbitals are solutions of the one-electron Fock operator
- HF wave function is a slater determinant of N independent particles
- HF potential is non-local
Summary

- HF orbitals are orthonormal
- HF wave function doesn't mix with singly excited wave functions (Brillouin's theorem)
- HF orbitals are defined up to a unitary transformation
- HF orbital energies are approximations to electron binding energies (Koopman's theorem)
Roothaan equations

- Introduction of M basis functions $\chi_i(r)$

$$\phi_i(r) = \sum_{\mu}^{M} C_{\mu i} \chi_\mu(r)$$

- Fock operator is expressed in basis set
- Yields a pseudo-eigenvalue matrix equation

$$\mathbf{F} \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{\varepsilon}$$

$$S_{\mu \nu} = \langle \chi_\mu(r) | \chi_\nu(r) \rangle$$
The Fock matrix

- Matrix elements are integrals of the operator
- Divide Fock matrix in two parts

\[
F = H + G
\]

Kinetic part and external potential

\[
H_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu}
\]

\[
T_{\mu\nu} = -\frac{1}{2} \langle \chi_\mu | \nabla^2 | \chi_\nu \rangle
\]

\[
V_{\mu\nu} = \langle \chi_\mu | v_{\text{ext}}(\mathbf{r}) | \chi_\nu \rangle
\]
The Fock matrix

- Matrix elements are integrals of the operator
- Divide Fock matrix in two parts

\[ F = H + G \]

Electronic part

\[ G_{\mu\nu} = \sum_{\mu,\nu} P_{\sigma\lambda} \left[ \langle \mu\nu | \sigma\lambda \rangle - \frac{1}{2} \langle \mu\lambda | \nu\sigma \rangle \right] \]

\[ P_{\sigma\lambda} = \sum_{i,j}^{N} C_{\sigma i} C_{\lambda j} \]

\[ \langle \mu\nu | \sigma\lambda \rangle = \int \frac{\chi_{\mu}(r_1)\chi_{\nu}(r_1)\chi_{\sigma}(r_2)\chi_{\lambda}(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 \]
Self Consistent Field (SCF)

\[ F \cdot C = S \cdot C \cdot \varepsilon \]

- Calculate integrals in the orbital basis
- Find transformation, \( X \), to orthonormalize basis
- Use guess to calculate \( F' \) (\( F'=X^TFX \))
- Solve eigenvalue equation and obtain new \( C' \)
- Calculate \( C=XC' \)
- Check difference between old and new \( C \)
  - Calculate new \( C' \) and then \( F' \) ...
  - Converged: Calculate energy and rest
Summary

• Introduction of a finite basis set (Roothaan equations)
• HF operator depends on its own solution
• Pseudo-eigenvalue equation
• Solution is found by SCF procedure
Electron Correlation

- HF is independent particle model
- Electrons of opposite spin don't interact
  - Wrong wave function, energies
- Dynamical correlation
  - Electrons get too “close”
  - Electrostatics are treated only on average \( \nu^{\text{HF}}(i) \)
- Static correlation
  - Energetically similar Slater determinant
  - A linear combination lowers the energy
Electron Correlation

$H_2$ in the dissociation limit

\[ \sigma_g = 1s_L + 1s_R \quad \sigma_u = 1s_L - 1s_R \quad \theta = \alpha_1 \beta_2 - \alpha_2 \beta_1 \]

\[ |\Psi_0\rangle = \sigma_g(r_1)\sigma_g(r_2)\theta \]
\[ = \left[ 1s_L(r_1)1s_L(r_2) + 1s_R(r_1)1s_R(r_2) \right. \]
\[ \quad + 1s_L(r_1)1s_R(r_2) + 1s_R(r_1)1s_L(r_2) \left. \right] \theta \]

- Ionic parts should have no contribution
- Only covalent parts should contribute
Electron Correlation

$H_2$ in the dissociation limit

$$\sigma_g = 1s_L + 1s_R \quad \sigma_u = 1s_L - 1s_R \quad \theta = \alpha_1\beta_2 - \alpha_2\beta_1$$

$$|\Psi_1\rangle = \sigma_u(r_1)\sigma_u(r_2)\theta$$

$$= \left[ 1s_L(r_1)1s_L(r_2) + 1s_R(r_1)1s_R(r_2) \\
- 1s_L(r_1)1s_R(r_2) - 1s_R(r_1)1s_L(r_2) \right] \theta$$

- Take a linear combination of both wave functions
Electron Correlation

$H_2$ in the dissociation limit

$$
\sigma_g = 1s_L + 1s_R \quad \sigma_u = 1s_L - 1s_R \quad \theta = \alpha_1 \beta_2 - \alpha_2 \beta_1
$$

$$
|\Psi_0\rangle - |\Psi_1\rangle = \left[ \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2) - \sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}_2) \right] \theta \\
= \left[ 1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\
+ 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2) \\
- 1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) - 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\
+ 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2) \right] \theta \\
= 2 \left[ 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2) \right] \theta
$$
Configuration Interaction

• HF is only an approximation
• Energies are reasonable for Atoms
• Energies are reasonable for Solids
• Energies are bad for dissociation curves
• Reason
  • Only single slater determinant
  • Correlation energy
    • $E_{\text{corr}} = \mathcal{E}_0 - E^{\text{HF}}$
Full CI

- Take HF wave function $\Psi^{\text{HF}}(r)$
- Form all excited wave functions
  - singly $\Psi^a_i(r)$
  - doubly $\Psi^a_i(r)$
- Expand the wave function in basis of excited wave functions

\[
\Phi_0(r) = c_0 \Psi^{\text{HF}}(r) + \sum_{i,a} c_i^a \Psi_i^a(r) + \sum_{i,j,a,b} c_{ij}^{ab} \Psi_{ij}^{ab}(r) \ldots
\]

\[
\Phi_0(r) = c_0 \Psi_0(r) + c_S \Psi_S(r) + c_D \Psi_D(r) + c_T \Psi_T(r) \ldots
\]
Full CI

• Determine coefficients by diagonalization of

\[
\begin{pmatrix}
\langle \Psi_0 | \hat{H} | \Psi_0 \rangle & 0 & \langle \Psi_0 | \hat{H} | \Psi_D \rangle & 0 \\
0 & \langle \Psi_S | \hat{H} | \Psi_S \rangle & \langle \Psi_S | \hat{H} | \Psi_D \rangle & \langle \Psi_S | \hat{H} | \Psi_T \rangle \\
\langle \Psi_D | \hat{H} | \Psi_0 \rangle & \langle \Psi_D | \hat{H} | \Psi_S \rangle & \langle \Psi_D | \hat{H} | \Psi_D \rangle & \langle \Psi_D | \hat{H} | \Psi_T \rangle \\
0 & \langle \Psi_T | \hat{H} | \Psi_S \rangle & \langle \Psi_T | \hat{H} | \Psi_D \rangle & \langle \Psi_T | \hat{H} | \Psi_T \rangle
\end{pmatrix}
\]

• Remember Brillouin's theorem

• Matrix elements of wave functions differing by more than 2 orbitals are zero
Full CI energy

• Intermediate normalization
  • $\Phi_0 = N(c_0 \Psi_0 + c_D \Psi_D + c_T \Psi_T \ldots)$
  • $\langle \Psi_0 | \Phi_0 \rangle = 1$

• Energy is then calculated
  • $\hat{H} | \Phi_0 \rangle = \varepsilon_0 | \Phi_0 \rangle \leftrightarrow (\hat{H} - E_0) | \Phi_0 \rangle = E_{corr} | \Phi_0 \rangle$
  • $\langle \Psi_0 | (\hat{H} - E_0) | \Phi_0 \rangle = E_{corr}$
  • $E_{corr} = \langle \Psi_0 | (\hat{H} - E_0) | N(c_0 \Psi_0 + c_S \Psi_S + c_D \Psi_D + c_T \Psi_T \ldots) \rangle$
  • $E_{corr} = c_D \langle \Psi_0 | \hat{H} | \Psi_D \rangle = \sum_{i,j,a,b} c_{ij}^{ab} \langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle$

• Energy is determined by doubly excited states
• Coefficients are determined by all states
Truncated CI

- FCI is usually too expensive
- Wave function is truncated
  - CIS \( \Phi_{CIS} = c_0 \Psi_0 + c_S \Psi_S \)
  - CISD \( \Phi_{CISD} = c_0 \Psi_0 + c_S \Psi_S + c_D \Psi_D \)
  - CISDT \( \Phi_{CISDT} = c_0 \Psi_0 + c_S \Psi_S + c_D \Psi_D + c_T \Psi_T \)
- Computationally feasible
- Not size-extensive
  - Energy of two infinitely separated identical systems is not equal to twice the energy of one system
Summary

- FCI gives exact energy in a given orbital basis
- Thus, it recovers all correlation energy
- It is too expensive for most systems

- Truncated CI recovers some correlation energy
- It is feasible for a lot of systems
- It is not size-extensive
- Error along the dissociation curve isn't constant
- Because it is a single reference method
Complete active space SCF

- FCI is too expensive
- Do FCI only for chemically interesting orbitals
- Choose core orbitals, which are kept fix
- Choose active occupied (n,m...) and virtuals (d,e...)
- Leave the rest untouched
- Make the linear combination
- Optimize both, expansion coefficients and orbitals, for the whole CASSCF wave function
CASSCF

\[
|\Phi_{\text{CASSCF}}\rangle = c_0 |\Psi_0\rangle + \sum_{nd} c_n^d |\Psi_n^d\rangle + \sum_{nmde} c_{nm}^{de} |\Psi_{nm}^{de}\rangle \ldots
\]

- Optimize the expansion coefficients and orbitals
- The orbitals are in general not the same as the HF orbitals
- We have a multi-reference wave function
CASSCF

- Chemical insight is needed
- Choose the number of electrons and the number of virtuals
- Then do a FCI in this “complete active space”
- But also vary the orbitals
Multi-reference CI

- Take an multi-reference wave function
- E.g. a CASSCF wave function
- For each determinant do a truncated CI calculation
- MRCI keeps error along the dissociation curve approximately constant
Coupled Cluster (CC)

• Take a reference wave function (HF)
• Excite wave function with $\exp \hat{T}$
  
  $$\exp \hat{T} = 1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 \ldots$$

• $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \ldots$

• Single excitation operator $\hat{T}_1 |\Psi_0\rangle = \sum_{ia} t_i^a |\psi_i^a\rangle$

• Double excitation operator $\hat{T}_2 |\Psi_0\rangle = \sum_{ijab} t_{ij}^{ab} |\psi_{ij}^{ab}\rangle$
Truncated CC

• If $\hat{T}$ is not truncated we recover FCI

• Truncation of $\hat{T}$ yields

  • CCS $\hat{T} = \hat{T}_1$

  • CCSD $\hat{T} = \hat{T}_1 + \hat{T}_2$

  • CCSDT $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$

• Truncated CC still yields **ALL** excited wave functions
\[
\hat{T} = \hat{T}_1 + \hat{T}_2 \quad \hat{T}\ket{\Psi_0} = \sum_{ia} t_i^a \ket{\Psi_i^a} + \sum_{ijab} t_{ij}^{ab} \ket{\Psi_{ij}^{ab}} \\
\exp \hat{T} = 1 + (\hat{T}_1 + \hat{T}_2) + \frac{1}{2} (\hat{T}_1 + \hat{T}_2)^2 + \frac{1}{3!} (\hat{T}_1 + \hat{T}_2)^3 \ldots \\
\exp \hat{T}\ket{\Psi_0} = \ket{\Psi_0} + \sum_{ia} t_i^a \ket{\Psi_i^a} + \sum_{ijab} t_{ij}^{ab} \ket{\Psi_{ij}^{ab}} \\
+ \frac{1}{2} (\sum_{ijab} t_i^a t_j^b \ket{\Psi_{ij}^{ab}} + 2 \sum_{ijkabc} t_{ij}^{ab} t_k^c \ket{\Psi_{ijk}^{abc}} \\
+ \sum_{ijklabcd} t_{ij}^{ab} t_{kl}^{cd} \ket{\Psi_{ijklabcd}^{abcd}}) \ldots
\]
Connected and Disconnected Clusters Amplitudes

- All excited wave functions enter the CC wave function
- For a given excited wave function $|\Psi_{ijklmn}^{abcdef}\rangle$
  - Connected amplitude $t_{ijklmn}^{abcdef}$
  - Disconnected amplitudes $t_{ij}^{ab} t_{klmn}^{cdef} t_{im}^{fb} t_{jkln}^{acde} t_{ij}^{ab} t_{kl}^{cd} t_{mn}^{ef} t_i t_m^{f} t_n^{e} t_{jkl}^{acd}$
Energy and Amplitudes

- Schrödinger equation \( \hat{H} \exp(\hat{T}) |\Psi_0\rangle = E \exp(\hat{T}) |\Psi_0\rangle \)

- Projected equation \( \exp(-\hat{T})\hat{H} \exp(\hat{T}) |\Psi_0\rangle = E |\Psi_0\rangle \)

- Energy equation \( \langle \Psi_0 | \exp(-\hat{T})\hat{H} \exp(\hat{T}) |\Psi_0\rangle = E \)

- Amplitude equations \( \langle \mu | \exp(-\hat{T})\hat{H} \exp(\hat{T}) |\Psi_0\rangle = 0 \)

  - \( \langle \mu \) is an excited wave functions with connected amplitude (e.g. singles and doubles for CCSD)
Summary

• Coupled cluster is an approximation to FCI

• It is in principle variational

• But in actual calculations the projected Hamiltonian is used → non-variational

• CC is size-extensive
Perturbation Theory (PT)

- Partitioning of Hamiltonian into two parts
  - Zeroth order Hamiltonian
  - Perturbation
- Solve zeroth order equations
  - Find wave function
  - Calculate energy
- Obtain solutions for exact Hamiltonian
- Choose Fock operator as zeroth order Hamiltonian
  \[ H_0 |\Psi_p\rangle = E_p |\Psi_p\rangle \]
Perturbation Theory (PT)

\[ \hat{H}(\lambda) = H_0 + \lambda V \]

\[ H_0 = \sum_i [h(i) + \nu_{\text{HF}}(i)] \quad V = \sum_i \sum_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \nu_{\text{HF}}(i) \]

\[ \hat{H}(\lambda) |\Phi(\lambda)\rangle = E(\lambda) |\Phi(\lambda)\rangle \]

\[ E(\lambda) = \varepsilon_0 + \lambda \varepsilon_1 + \lambda^2 \varepsilon_2 \ldots \]

\[ |\Phi(\lambda)\rangle = |\Phi_0\rangle + \lambda |\Phi_1\rangle + \lambda^2 |\Phi_2\rangle \ldots \]

\[ H_0 |\Phi_0\rangle = \varepsilon_0 |\Phi_0\rangle = E_0 |\Psi_0\rangle \]

\[ (H_0 - \varepsilon_0) |\Phi_1\rangle + (V - \varepsilon_1) |\Psi_0\rangle = 0 \]

\[ (H_0 - \varepsilon_0) |\Phi_2\rangle + (V - \varepsilon_1) |\Phi_0\rangle - \varepsilon_2 |\Psi_0\rangle = 0 \]
First order corrections

Energy:
\[ \langle \Psi_0 | (H_0 - \varepsilon_0) | \Phi_1 \rangle + \langle \Psi_0 | (V - \varepsilon_1) | \Psi_0 \rangle = 0 \]
\[ \varepsilon_1 = \langle \Psi_0 | V | \Psi_0 \rangle \]

Wave function:
\[ \langle \Psi_p | (H_0 - \varepsilon_0) | \Phi_1 \rangle + \langle \Psi_p | (V - \varepsilon_1) | \Psi_0 \rangle = 0 \]
\[ | \Phi_1 \rangle = \sum_{p \neq 0} \frac{\langle \Psi_p | V | \Psi_0 \rangle}{E_0 - E_p} | \Psi_p \rangle \]

\[ | \Psi_p \rangle \text{ are all excited wave functions of the HF solution} \]
Second order corrections

Energy:

\[ \langle \Psi_0 | (H_0 - \varepsilon_0) | \Phi_2 \rangle + \langle \Psi_0 | (V - \varepsilon_1) | \Phi_1 \rangle - \varepsilon_2 = 0 \]

\[ \varepsilon_2 = \langle \Psi_0 | V | \Phi_1 \rangle = \sum_{p \neq 0} \frac{|\langle \Psi_p | V | \Psi_0 \rangle|^2}{E_0 - E_p} \]

Wave function:

\[ \langle \Psi_p | (H_0 - \varepsilon_0) | \Phi_1 \rangle + \langle \Psi_p | (V - \varepsilon_1) | \Psi_0 \rangle = 0 \]

\[ |\Phi_2\rangle = \sum_{p \neq 0} \frac{\langle \Psi_p | V - \varepsilon_1 | \Phi_1 \rangle}{E_0 - E_p} |\Psi_p\rangle \]

|\Psi_p\rangle are all excited wave functions of the HF solution
Summary

- Choose a partitioning
- Solve the zeroth order
- Calculate the higher order corrections
- **NO OPTIMIZATION**
- Collapse if degeneracy occurs
- Wigners 2n+1 rule
- If HF is used as zeroth order, the first order energy is the HF energy
WFT vs. DFT

- WFT uses exact non-relativistic Hamiltonian
- It approximates the wave function
- Restricting the wave function (HF is single SD)

- DFT models Hamiltonian
- It doesn't approximate density (or wave function)

- WFT is an approximation
- DFT is a model
Density functional theory (DFT)

- Hohenberg-Kohn (HK) theorems
- Thomas-Fermi model
- Kohn-Sham (KS) theorems
- Correlation in HF and KS-DFT
- Approximations to $E_{xc}$
- Analogue of Koopman's theorem
1. HK theorem

- There is a one-to-one map between
  - The ground state wave function
  - The ground state density
  - The external potential

- \( \Psi(\mathbf{r}) \Leftrightarrow \rho(\mathbf{r}) \Leftrightarrow v(\mathbf{r}) \Rightarrow E \)

- There is an energy functional of the density

- \( E_v[\rho(\mathbf{r})] = F_{HK}[\rho(\mathbf{r})] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \)

- \( F_{HK}[\rho(\mathbf{r})] = \langle \Psi[\rho(\mathbf{r})]|\hat{T} + \hat{W}||\Psi[\rho(\mathbf{r})]\rangle \)
2. HK theorem

- The energy functional is such that
  - The global minimum is unique
  - The global minimum is attained at the ground state density
  - The ground state density yields the ground state energy
- \( E_v[\rho(r)] \geq \varepsilon_0 \) equality if \( \rho(r) = \rho_0(r) \)
- There is a variational principle
Thomas-Fermi Model

- Kinetic energy
  \[ T_{\text{TF}}[\rho(r)] = 0.3(3\pi)^{2/3} \int \rho^{5/3}(r) \, dr \]

- Nuclear-electron and electron-electron energy
  \[ W_{\text{class}} = -Z \int \frac{\rho(r)}{r} \, dr + \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 \]

- Non-classical energy
  \[ E_X[\rho(r)] = C_X \int \rho(r)^{4/3} \, dr \]
  \[ E_{X\alpha}[\rho(r)] = -\frac{9}{8} \left( \frac{3}{\pi} \right)^{1/3} \alpha \int \rho(r)^{4/3} \, dr \]
Non-interacting reference system

- There is a non-interacting particle system
  \[ \hat{f}^{\text{KS}} \phi_i^{\text{KS}} = [-1/2 \nabla^2 + \nu_{S,0}(\mathbf{r})] \phi_i^{\text{KS}} = \varepsilon_i \phi_i^{\text{KS}} \]

- The KS wave function minimizes the expectation value
  \[ \langle \Phi^{\text{KS}} | \hat{f}^{\text{KS}} | \Phi^{\text{KS}} \rangle \leq \langle \Phi | \hat{f}^{\text{KS}} | \Phi \rangle \]

- It shares the same density with the interacting system
  \[ \int |\Phi^{\text{KS}}(\mathbf{r})|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N = \sum_i |\phi_i^{\text{KS}}(\mathbf{r}_1)|^2 = \rho_0(\mathbf{r}_1) \]
KS energy definition

$$\Phi^{KS}(r) = \Phi^{KS}[\rho(r)](r)$$

$$E[\Phi^{KS}] = T_S[\Phi^{KS}] + W_{ext}[\Phi^{KS}] + W_{Coul}[\Phi^{KS}] + E_{xc}[\Phi^{KS}]$$

$$T_S[\Phi^{KS}] = \langle \Phi^{KS} \rangle - \frac{1}{2} \nabla^2 |\Phi^{KS}\rangle$$

$$W_{ext}[\Phi^{KS}] = \langle \Phi^{KS} | V_{ext}(r) | \Phi^{KS} \rangle$$

$$W_{Coul}[\Phi^{KS}] = \langle \Phi^{KS} | V_{Coul}(r) | \Phi^{KS} \rangle$$

$$E_{xc}[\Phi^{KS}] = E_0 - T_S - W_{ext} - W_{Coul}$$
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

**HF**

\[ E_{\text{HF}} = T_{\text{HF}} + W_{\text{HF}} + W_{x} \]

\[ E_{c_{\text{HF}}} = \]

**KS-DFT**

\[ E_{\text{KS}} = T_{\text{KS}} + W_{\text{KS}} + W_{x} \]

\[ E_{c_{\text{KS}}} = \]

\[ T_{\text{HF}} = -\frac{1}{2} \sum_{i} \langle \phi_{i}^{\text{HF}} | \nabla^{2} | \phi_{i}^{\text{HF}} \rangle \neq T = ? \]

\[ T_{\text{KS}} = -\frac{1}{2} \sum_{i} \langle \phi_{i}^{\text{KS}} | \nabla^{2} | \phi_{i}^{\text{KS}} \rangle \neq T = ? \]
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

**HF**

\[ E^{\text{HF}} = T^{\text{HF}} + W_{\text{coul}}^{\text{HF}} + W_x^{\text{HF}} \]

\[ E_c^{\text{HF}} = \Delta T^{\text{HF}} \]

**KS-DFT**

\[ E^{\text{KS}} = T^{\text{KS}} + W_{\text{coul}}^{\text{KS}} + W_x^{\text{KS}} \]

\[ E_c^{\text{KS}} = \Delta T^{\text{KS}} \]
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

**HF**

\[ E^{\text{HF}} = T^{\text{HF}} + W^{\text{HF}}_{\text{coul}} + W^{\text{HF}}_x \]

\[ E^{\text{HF}}_c = \Delta T^{\text{HF}} \]

**KS-DFT**

\[ E^{\text{KS}} = T^{\text{KS}} + W^{\text{KS}}_{\text{coul}} + W^{\text{KS}}_x \]

\[ E^{\text{KS}}_c = \Delta T^{\text{KS}} \]

\[ W_{\text{coul}} = \int \rho_0 V_{\text{nuc}} \text{d}r + \int \rho_0(r_1)\rho_0(r_2) \frac{1}{r_{12}} \text{d}r_1 \text{d}r_2 \]

\[ W^{\text{HF}} = \int \rho^{\text{HF}}_0 V_{\text{nuc}} \text{d}r + \int \rho^{\text{HF}}_0(r_1)\rho^{\text{HF}}_0(r_2) \frac{1}{r_{12}} \text{d}r_1 \text{d}r_2 \]

\[ W^{\text{KS}} = \int \rho^{\text{KS}}_0 V_{\text{nuc}} \text{d}r + \int \rho^{\text{KS}}_0(r_1)\rho^{\text{KS}}_0(r_2) \frac{1}{r_{12}} \text{d}r_1 \text{d}r_2 \]
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

\[
\begin{align*}
E^{\text{HF}} & = T^{\text{HF}} + W_{\text{coul}}^{\text{HF}} + W_x^{\text{HF}} \\
E^{\text{KS}} & = T^{\text{KS}} + W_{\text{coul}}^{\text{KS}} + W_x^{\text{KS}} \\
E_c^{\text{HF}} & = \Delta T^{\text{HF}} + \Delta W_{\text{coul}}^{\text{HF}} \\
E_c^{\text{KS}} & = \Delta T^{\text{KS}}
\end{align*}
\]
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

**HF**

\[ E_{\text{HF}} = T_{\text{HF}} + W_{\text{coul}}^{\text{HF}} + W_{x}^{\text{HF}} \]

\[ E_{c}^{\text{HF}} = \Delta T_{\text{HF}} + \Delta W_{\text{coul}}^{\text{HF}} \]

**KS-DFT**

\[ E_{\text{KS}} = T_{\text{KS}} + W_{\text{coul}}^{\text{KS}} + W_{x}^{\text{KS}} \]

\[ E_{c}^{\text{KS}} = \Delta T_{\text{KS}} \]

\[ W_{x}^{\text{KS}} = \frac{1}{2} \sum_{i,j} \langle \phi_{i}^{\text{KS}} \phi_{j}^{\text{KS}} | \phi_{j}^{\text{KS}} \phi_{i}^{\text{KS}} \rangle \neq W_{\text{ncl}} =? \]

\[ W_{x}^{\text{HF}} = \frac{1}{2} \sum_{i,j} \langle \phi_{i}^{\text{HF}} \phi_{j}^{\text{HF}} | \phi_{j}^{\text{HF}} \phi_{i}^{\text{HF}} \rangle \neq W_{\text{ncl}} =? \]
Correlation in HF and KS-DFT

\[ E = T + W = T + W_{\text{coul}} + W_{\text{ncl}} \]

**HF**

\[ E^{\text{HF}} = T^{\text{HF}} + W^{\text{HF}}_{\text{coul}} + W^{\text{HF}}_x \]

\[ E^{\text{HF}}_c = \Delta T^{\text{HF}} + \Delta W^{\text{HF}}_{\text{coul}} + \Delta W^{\text{HF}}_{\text{ncl}} \]

**KS-DFT**

\[ E^{\text{KS}} = T^{\text{KS}} + W^{\text{KS}}_{\text{coul}} + W^{\text{KS}}_x \]

\[ E^{\text{KS}}_c = \Delta T^{\text{KS}} + \Delta W^{\text{KS}}_{\text{ncl}} \]

Correlation in HF is not the same as in KS-DFT
Optimization

• Guess a density $\rho(r)$

• Calculate the potential
  \[ v_S(r) = \frac{\delta[W_{\text{ext}} + W_{\text{Coul}} + E_{\text{xc}}]}{\delta \rho(r)} = v_{\text{ext}}(r) + v_{\text{Coul}}(r) + v_{\text{xc}}(r) \]

• Calculate new density
  \[ \varepsilon_i \phi_i(r) = [-1/2 \nabla^2 + v_S(r)]\phi_i(r) \]
  \[ \rho(r) = \sum_i |\phi_i(r)|^2 \]
Orbitals in KS-DFT

- $f^{\text{HF}} \phi_i^{\text{HF}} = \varepsilon_i^{\text{HF}} \phi_i^{\text{HF}}$
- non-local potential
- Orbitals don't sum up to correct density
- $\varepsilon_i^{\text{HF}} \approx \text{IP}, \ i < N$
- $\varepsilon_i^{\text{HF}} \approx \text{EA}, \ i > N$
- $f^{\text{KS}} \phi_i^{\text{KS}} = \varepsilon_i^{\text{KS}} \phi_i^{\text{KS}}$
- local potential
- Orbitals sum up to correct density
- $\Delta \varepsilon^{\text{KS}} \approx \text{excitation energy}$

KS orbitals are at least as good as HF orbitals
Approximations to $E_{\text{xc}}$

- Write $\text{xc}$ functional in the form
  \[ E_{\text{xc}} = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r} \]

- $\varepsilon_{\text{xc}}(\rho(\mathbf{r}))$ is the exchange-correlation energy per particle

- Model $\varepsilon_{\text{xc}}(\rho(\mathbf{r}))$

- Split into exchange and correlation
Local Density Approximation (LDA)

- Model is the homogeneous electron gas
- Exchange part can be calculated analytically
- Correlation part is calculated from very accurate quantum Monte Carlo calculations
- Exchange is the Slater exchange
- Correlation was developed by Vosko, Wilk and Nusair
- It is called SVWN
Generalized Gradient Approx. (GGA)

- LDA doesn't take inhomogeneity into account
- Take also gradients of density
  - $\varepsilon_{xc} = \varepsilon_{xc}(\rho(r), \nabla \rho(r))$
- Named as first X then C
  - BLYP
  - BP86
  - BPW91
Hybrid Functionals

- Obtain better results by adding exact exchange
- The amount of exact exchange is determined empirically
- Most commonly used functional is the B3LYP functional
- It incorporates 20% exact exchange
- Error on the G2 data set is about 2 kcal/mol
Summary

- KS-DFT is a independent particle model
- It is in principle exact
- The exact functional is not known
- There is no sequence that converges to the exact energy
- Approximations have proven to be very good
Summary

- Solution is found by SCF-like procedure
- Correlation energy is not the same as in HF
- The potential is local
- Orbital energies approximate excitation energies (analogue of Koopman's theorem)
XC functionals

- LDA
- GGA
- Hybrids
- Meta-GGA
- Hyper-GGA
- Orbital-dependent functionals