

Electronic Structure Methods

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References

- WFT
 - Szaboo & Ostlund “Modern Quantum Chemistry”
 - Helgaker, Jørgensen & Olsen “Molecular Electronic-Structure Theory”
- DFT
 - Dreizler & Gross “Density Functional Theory”
 - Koch & Holthausen “A Chemist's Guide to Density Functional Theory”

Notations

- Capital greek letters are N-electron wave functions Ψ Φ
- Caligraphic variables, τ , are N-electron variables
- Lower case greek letters are one-electron wave functions ϕ χ
- 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

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

$$\begin{aligned}\hat{H} &= \sum_i \left\{ \frac{1}{2} \nabla_i^2 + \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\} \\ &+ \sum_A \left\{ \frac{1}{2} \nabla_A^2 + \sum_{B>A} \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} \right\} \\ &+ \sum_{Ai} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}\end{aligned}$$

- The Born-Oppenheimer approximation

$$H = \sum_i \frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}) + \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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

$$\mathcal{E}_0 \leq E^{\text{HF}} = \langle \Psi_0(\mathbf{r}) | \hat{H} | \Psi_0(\mathbf{r}) \rangle$$

$$|\Psi_0(\mathbf{r})\rangle = |\phi_i^{\text{HF}}, \dots, \phi_k^{\text{HF}}\rangle$$

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

$$\Psi(\mathbf{r}) = |\phi_i, \dots, \phi_k\rangle$$

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = (N!)^{-1/2} \begin{vmatrix} \phi_i(\mathbf{r}_1) & \dots & \phi_k(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \phi_i(\mathbf{r}_N) & \dots & \phi_k(\mathbf{r}_N) \end{vmatrix}$$

Find minimum

- Variation of orbitals
- Orbitals are kept orthonormal
- Lagrangian multipliers ε

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

$$\mathcal{J}\phi_i(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_1)$$

$$\mathcal{K}\phi_i(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j(\mathbf{r}_1)$$

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 ϵ_i
- It is anti-symmetric
- Yields electron density

$$\rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

$$\Leftrightarrow \rho(\mathbf{r}) = \sum_i^N \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

HF wave function and Hamiltonian

- HF wave function is eigenfunction of the HF operator

$$H_0 \Psi_0(\mathbf{r}) = E_0 \Psi_0(\mathbf{r})$$

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

$$E_0 = \sum_i^N \varepsilon_i$$

$$h(i) = -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}) \quad \text{and} \quad v^{\text{HF}}(i) = \mathcal{J}(i) - \mathcal{K}(i)$$

Coulomb operator

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

$$\mathcal{J}\phi_i(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_1)$$

$$\mathcal{J}(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\mathcal{J}(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The Coulomb operator is local

Exchange operator

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

$$\mathcal{K}\phi_i(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j(\mathbf{r}_1)$$

- 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

- $\Psi_i^a = |\phi_1, \phi_2, \dots, \phi_{i-1}, \phi_a, \phi_{i+1}, \dots, \phi_N\rangle$

- $\langle \Psi_i^a | \hat{H} | \Psi \rangle = 0$

HF orbitals

$$v^{\text{HF}}(1)\phi_i(\mathbf{r}_1) = \sum_j^N \int d\mathbf{r}_2 \left[\frac{\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_1) - \frac{\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j(\mathbf{r}_1) \right]$$

- 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 $\chi_i(\mathbf{r})$

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

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

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

$$\mathbf{S}_{\mu\nu} = \langle \chi_{\mu}(\mathbf{r}) | \chi_{\nu}(\mathbf{r}) \rangle$$

The Fock matrix

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

$$\mathbf{F} = \mathbf{H} + \mathbf{G}$$

Kinetic part and external potential

$$\begin{aligned}\mathbf{H}_{\mu\nu} &= \mathbf{T}_{\mu\nu} + \mathbf{V}_{\mu\nu} \\ \mathbf{T}_{\mu\nu} &= -1/2 \langle \chi_\mu | \nabla^2 | \chi_\nu \rangle \\ \mathbf{V}_{\mu\nu} &= \langle \chi_\mu | v_{\text{ext}}(\mathbf{r}) | \chi_\nu \rangle\end{aligned}$$

The Fock matrix

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

$$\mathbf{F} = \mathbf{H} + \mathbf{G}$$

Electronic part

$$\mathbf{G}_{\mu\nu} = \sum_{\sigma\lambda} P_{\sigma\lambda} [\langle \mu\nu | \sigma\lambda \rangle - 1/2 \langle \mu\lambda | \nu\sigma \rangle]$$
$$P_{\sigma\lambda} = \sum_{ij}^N C_{\sigma i} C_{\lambda j}$$
$$\langle \mu\nu | \sigma\lambda \rangle = \int \frac{\chi_{\mu}(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \chi_{\sigma}(\mathbf{r}_2) \chi_{\lambda}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Self Consistent Field (SCF)

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

- Calculate integrals in the orbital basis
- Find transformation, X , to orthonormalize basis
- Use guess to calculate F' ($F'=X^T F X$)
- 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 $v^{\text{HF}}(i)$
- Static correlation
 - ◊ Energetically similar Slater determinant
 - ◊ A linear combination lowers the energy

Electron Correlation

H_2 in the dissociation limit

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

$$\begin{aligned} |\Psi_0\rangle &= \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\theta \\ &= [1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\ &\quad + 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2)]\theta \end{aligned}$$

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

Electron Correlation

H_2 in the dissociation limit

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

$$\begin{aligned} |\Psi_1\rangle &= \sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}_2)\theta \\ &= [1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\ &\quad - 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) - 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2)]\theta \end{aligned}$$

- Take a linear combination of both wave functions

Electron Correlation

H_2 in the dissociation limit

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

$$\begin{aligned} |\Psi_0\rangle - |\Psi_1\rangle &= [\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2) - \sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}_2)]\theta \\ &= [1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\ &\quad + 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2) \\ &\quad - 1s_L(\mathbf{r}_1)1s_L(\mathbf{r}_2) - 1s_R(\mathbf{r}_1)1s_R(\mathbf{r}_2) \\ &\quad + 1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2)]\theta \\ &= 2[1s_L(\mathbf{r}_1)1s_R(\mathbf{r}_2) + 1s_R(\mathbf{r}_1)1s_L(\mathbf{r}_2)]\theta \end{aligned}$$

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 $\Psi^{\text{HF}}(\mathbf{r})$
- Form all excited wave functions
 - singly $\Psi_i^a(\mathbf{r})$
 - doubly $\Psi_{ij}^{ab}(\mathbf{r})$
- Expand the wave function in basis of excited wave functions
- $$\Phi_0(\mathbf{r}) = c_0 \Psi^{\text{HF}}(\mathbf{r}) + \sum_{ia} c_i^a \Psi_i^a(\mathbf{r}) + \sum_{ijab} c_{ij}^{ab} \Psi_{ij}^{ab}(\mathbf{r}) \dots$$
- $$\Phi_0(\mathbf{r}) = c_0 \Psi_0(\mathbf{r}) + c_S \Psi_S(\mathbf{r}) + c_D \Psi_D(\mathbf{r}) + c_T \Psi_T(\mathbf{r}) \dots$$

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

- $\Phi_0 = N(c_0\Psi_0 + c_D\Psi_D + c_T\Psi_T \dots)$
- $\langle\Psi_0|\Phi_0\rangle = 1$

- Energy is then calculated

- $\hat{H}|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle \Leftrightarrow (\hat{H} - E_0)|\Phi_0\rangle = E_{corr}|\Phi_0\rangle$
- $\langle\Psi_0|(\hat{H} - E_0)|\Phi_0\rangle = E_{corr}$
- $E_{corr} = \langle\Psi_0|(\hat{H} - E_0)|N(c_0\Psi_0 + c_S\Psi_S + c_D\Psi_D + c_T\Psi_T \dots)\rangle$
- $E_{corr} = c_D\langle\Psi_0|\hat{H}|\Psi_D\rangle = \sum_{ijab} c_{ij}^{ab}\langle\Psi_0|\hat{H}|\Psi_{ij}^{ab}\rangle$

- 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

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

- 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 $\exp \hat{T}$
- $\exp \hat{T} = 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 \dots$
- $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots$
- 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

CCSD

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad \hat{T}|\Psi_0\rangle = \sum_{ia} t_i^a |\Psi_i^a\rangle + \sum_{ijab} t_{ij}^{ab} |\Psi_{ij}^{ab}\rangle$$

$$\exp \hat{T} = 1 + (\hat{T}_1 + \hat{T}_2) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2)^2 + \frac{1}{3!}(\hat{T}_1 + \hat{T}_2)^3 \dots$$

$$\begin{aligned} \exp \hat{T}|\Psi_0\rangle &= |\Psi_0\rangle + \sum_{ia} t_i^a |\Psi_i^a\rangle + \sum_{ijab} t_{ij}^{ab} |\Psi_{ij}^{ab}\rangle \\ &+ \frac{1}{2} \left(\sum_{ijab} t_i^a t_j^b |\Psi_{ij}^{ab}\rangle + 2 \sum_{ijkabc} t_{ij}^{ab} t_k^c |\Psi_{ijk}^{abc}\rangle \right. \\ &\left. + \sum_{ijklabcd} t_{ij}^{ab} t_{kl}^{cd} |\Psi_{ijkl}^{abcd}\rangle \right) \dots \end{aligned}$$

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 $t_{ij}^{ab} t_{klmn}^{cdef}$

$$t_{im}^{fb} t_{jkl n}^{acde} \quad t_{ij}^{ab} t_{kl}^{cd} t_{mn}^{ef} \quad t_i^f t_m^b t_n^e t_{jkl}^{acd}$$

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)

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

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

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

$$E(\lambda) = \varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2 \dots$$

$$|\Phi(\lambda)\rangle = |\Phi_0\rangle + \lambda|\Phi_1\rangle + \lambda^2|\Phi_2\rangle \dots$$

$$H_0|\Phi_0\rangle = \varepsilon_0|\Phi_0\rangle = E_0|\Psi_0\rangle$$

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

$$(H_0 - \varepsilon_0)|\Phi_2\rangle + (V - \varepsilon_1)|\Phi_0\rangle - \varepsilon_2|\Psi_0\rangle = 0$$

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:

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

$$|\Phi_1\rangle = \sum_{p \neq 0} \frac{\langle \Psi_p | V | \Psi_0 \rangle}{E_0 - E_p} |\Psi_p\rangle$$

$|\Psi_p\rangle$ 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
- $E_v[\rho(\mathbf{r})] = F_{\text{HK}}[\rho(\mathbf{r})] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$
- $F_{\text{HK}}[\rho(\mathbf{r})] = \langle \Psi[\rho(\mathbf{r})] | \hat{T} + \hat{W} | \Psi[\rho(\mathbf{r})] \rangle$

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
- $E_v[\rho(\mathbf{r})] \geq \mathcal{E}_0$ equality if $\rho(\mathbf{r}) = \rho_0(\mathbf{r})$
- There is a variational principle

Thomas-Fermi Model

- Kinetic energy

- $T_{\text{TF}}[\rho(\mathbf{r})] = 0.3(3\pi)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$

- Nuclear-electron and electron-electron energy

- $W_{\text{classic}} = -Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} + 1/2 \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$

- Non-classical energy

- $E_{\text{X}}[\rho(\mathbf{r})] = C_{\text{X}} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$

- $E_{\text{X}\alpha}[\rho(\mathbf{r})] = -\frac{9}{8} \left(\frac{3}{\pi}\right)^{1/3} \alpha \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$

Non-interacting reference system

- There is a non-interacting particle system
 - $\hat{f}^{\text{KS}} \phi_i^{\text{KS}} = [-1/2\nabla^2 + v_{\text{S},0}(\mathbf{r})]\phi_i^{\text{KS}} = \varepsilon_i \phi_i^{\text{KS}}$
- 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
 - $\int |\Phi^{\text{KS}}(\mathbf{r})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = \sum_i |\phi_i^{\text{KS}}(\mathbf{r}_1)|^2 = \rho_0(\mathbf{r}_1)$

KS energy definition

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

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

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

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

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

$$E_{\text{xc}}[\Phi^{\text{KS}}] = E_0 - T_{\text{S}} - W_{\text{ext}} - W_{\text{Coul}}$$

Correlation in HF and KS-DFT

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

HF

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

$$E_c^{\text{HF}} =$$

KS-DFT

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

$$E_c^{\text{KS}} =$$

$$T^{\text{HF}} = -\frac{1}{2} \sum_i \langle \phi_i^{\text{HF}} | \nabla^2 | \phi_i^{\text{HF}} \rangle \neq T = ?$$

$$T^{\text{KS}} = -\frac{1}{2} \sum_i \langle \phi_i^{\text{KS}} | \nabla^2 | \phi_i^{\text{KS}} \rangle \neq T = ?$$

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

$$E_c^{\text{HF}} = \Delta T^{\text{HF}}$$

KS-DFT

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$$E_c^{\text{KS}} = \Delta T^{\text{KS}}$$

$$W_{\text{coul}} = \int \rho_0 V_{\text{nuc}} dr + \int \rho_0(r_1) \rho_0(r_2) \frac{1}{r_{12}} dr_1 dr_2$$

$$W_{\text{coul}}^{\text{HF}} = \int \rho_0^{\text{HF}} V_{\text{nuc}} dr + \int \rho_0^{\text{HF}}(r_1) \rho_0^{\text{HF}}(r_2) \frac{1}{r_{12}} dr_1 dr_2$$

$$W_{\text{coul}}^{\text{KS}} = \int \rho_0^{\text{KS}} V_{\text{nuc}} dr + \int \rho_0^{\text{KS}}(r_1) \rho_0^{\text{KS}}(r_2) \frac{1}{r_{12}} dr_1 dr_2$$

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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

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

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KS-DFT

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

$$E_c^{\text{KS}} = \Delta T^{\text{KS}}$$

$$W_x^{\text{KS}} = \frac{1}{2} \sum_{ij} \langle \phi_i^{\text{KS}} \phi_j^{\text{KS}} | \phi_j^{\text{KS}} \phi_i^{\text{KS}} \rangle \neq W_{\text{ncl}} = ?$$

$$W_x^{\text{HF}} = \frac{1}{2} \sum_{ij} \langle \phi_i^{\text{HF}} \phi_j^{\text{HF}} | \phi_j^{\text{HF}} \phi_i^{\text{HF}} \rangle \neq W_{\text{ncl}} = ?$$

Correlation in HF and KS-DFT

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

HF

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

$$E_c^{\text{HF}} = \Delta T^{\text{HF}} + \Delta W_{\text{coul}}^{\text{HF}} + \Delta W_{\text{ncl}}^{\text{HF}}$$

KS-DFT

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

$$E_c^{\text{KS}} = \Delta T^{\text{KS}} + \Delta W_{\text{ncl}}^{\text{KS}}$$

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

Optimization

- Guess a density $\rho(\mathbf{r})$

- Calculate the potential

- ♦
$$v_S(\mathbf{r}) = \frac{\delta[W_{\text{ext}} + W_{\text{Coul}} + E_{\text{xc}}]}{\delta\rho(\mathbf{r})} = v_{\text{ext}}(\mathbf{r}) + v_{\text{Coul}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

- Calculate new density

- ♦
$$\varepsilon_i \phi_i(\mathbf{r}) = [-1/2\nabla^2 + v_S(\mathbf{r})]\phi_i(\mathbf{r})$$

- ♦
$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

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_{xc}

- Write xc functional in the form

$$\bullet E_{xc} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}$$

- $\varepsilon_{xc}(\rho(\mathbf{r}))$ is the exchange-correlation energy per particle
- Model $\varepsilon_{xc}(\rho(\mathbf{r}))$
- 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
 - ♦ $\epsilon_{xc} = \epsilon_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))$
- 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