

Introduction to Computational Quantum Chemistry

Lesson 04: Model Chemistries

Quick Review

For a hypothetical system with two interacting nucleus (A and B) and two electrons (e_i and e_j).

The total energy E_{tot} should represent all the interactions such as:

Nuclear Kinetic energy (T_N),

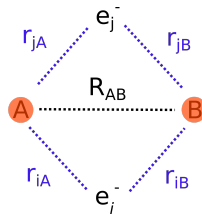
Electronic Kinetic Energy (T_e),

Nuclear-Nuclear Potential Energy (V_{NN})

Electron-Electron Potential Energy (V_{ee})

Nuclear-Electron Potential Energy (V_{Ne}).

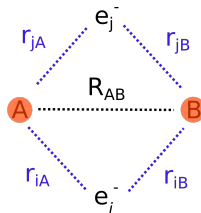
$$E_{tot} = T_N + T_e + V_{NN} + V_{ee} + V_{Ne} \quad (1)$$



Quick Review

invoking Born-Oppenheimer approximation making nuclear kinetic energy zero and nuclear potential energy constant, then we can have the total Electronic Energy from equation 1

$$E_e = T_e + V_{ee} + V_{Ne} \quad (2)$$



$$E_e = - \sum_i^e \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i>j}^{e^-} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_A \sum_i \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \quad (3)$$

Methods of Quantum Chemistry

- The assessment of *Electronic Energy* can be provided by various methods.
- *WaveFunction* Based:
 - Hartree-Fock (HF)
 - Møller-Plesset (MP)
 - Configuration Interaction (CI)
 - Coupled Cluster (CC)
- *Electron Density* Based
 - Density Functional Theory (DFT)

(I) WaveFunction Based Methods

Hartree Method

- distinguishable electrons
- wavefunction breaks Antisymmetry (Pauli principle)
- does not include Electron correlation
- case ${}_3\text{Li}$

$$\Psi_{Hartree} = 1s(1)\alpha 1s(2)\beta 2s(3)\alpha \quad (4)$$

Hartree-Fock Method

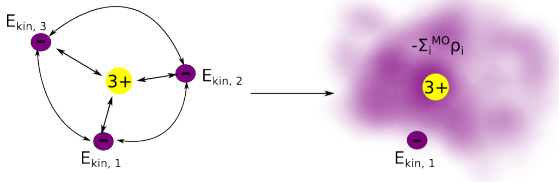
- indistinguishable electrons, antisymmetry is achieved by assuming that Ψ can be represented as single Slater determinant
- for example, Slater determinant for ${}_3\text{Li}$:
 - α electrons: without bars
 - β electrons: with bars

$$\Psi_{HF} = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ \overline{1s}(1) & \overline{1s}(2) & \overline{1s}(3) \\ 2s(1) & 2s(2) & 2s(3) \end{vmatrix} \quad (5)$$

- rows represent "Atomic Orbitals" while columns represent "individual electrons"
- to make the HF Method feasible, each atomic orbitals (Columns) in the Slater Determinant is approximated as a linear combination of basis sets (became known as Hartree-Fock-Roothaan SCF Procedure)

Self Consistent Field (SCF)

- every electron is optimized in time-averaged field of other electrons
- many-body problem \rightarrow One-body problem
- iterative optimization of basis functions coefficients until desired convergence is reached



HF-SCF Procedure, the Fock operator

- energy Operator (Fock Operator), depends only on coordinates of single electron
- for orbital ϕ_k :

$$\hat{F}(i)\phi_k(i) = \epsilon_k\phi_k(i), \quad (6)$$

where

$$\hat{F}(i) = -\frac{1}{2}\nabla_i^2 - \frac{Z_{Nu}}{r_{i-Nu}} + \sum_{j=1} (\hat{J}_j - \hat{K}_j) \quad (7)$$

- $\frac{1}{2}\nabla_i^2$ is kinetic energy operator
- $\frac{Z_{Nu}}{r_{i-Nu}}$ is attraction between electrons and nuclei
- \hat{J} is the **Coulombic** repulsion operator
- \hat{K} is the electronic **Exchange** operator

Coulombic Term, J

- local operator
- classical repulsion between electrons
- rate of interaction with other electrons

$$\hat{J}_j(1)\phi_i(1) = \left[\int \phi_j^*(2) \frac{1}{r_{ij}} \phi_j(2) d\tau(2) \right] \phi_i(1) \quad (8)$$

- basically this is a quantum mechanical version of Coulombic repulsion because we are looking at the 'probability' and not the exact location of the electrons

Exchange Term, K

- non-local operator
- only for electrons with same spin

$$\hat{K}_j(1)\phi_i(1) = \left[\int \phi_j^*(2) \frac{1}{r_{ij}} \phi_i(2) d\tau(2) \right] \phi_j(1) \quad (9)$$

- If ϕ_i and ϕ_j have opposite spin, then

$$\int \alpha \frac{1}{r_{ij}} \beta d\tau = 0$$

- If ϕ_i and ϕ_j have the same spin, then

$$\int \alpha \frac{1}{r_{ij}} \alpha d\tau \neq 0$$

- exchange energy, described *exactly*

HF Algorithm, A Psuedo EigenValue Method

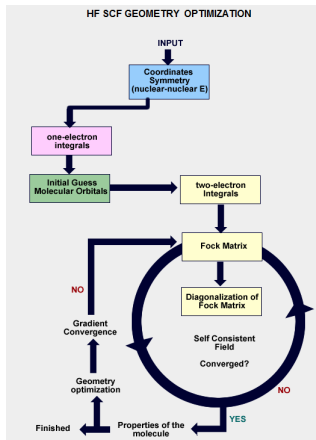
$$\hat{F}(i) = \hat{H}(1) + \sum_{j=1}^N (\hat{J}_j - \hat{K}_j) \quad (10)$$

$$\Psi = \sum_{v=1}^k c_{vi} \phi_v \quad (11)$$

$$\hat{F} \left[\sum_{v=1}^k C_{vi} \phi_v \right] = \varepsilon_i \left[\sum_{v=1}^k C_{vi} \phi_v \right] \quad (12)$$

$$\hat{F}C = \varepsilon SC \rightarrow F' = S^{-1/2} F S^{1/2} \rightarrow F' = C' \varepsilon C' \quad (13)$$

$$C' \rightarrow C_{vi} \quad (14)$$



Total Energy in HF method

- HF electronic energy is expressed as follows:

$$E_{HF} = \sum_{i=1}^N \left[2\epsilon_i - \sum_{j \geq i}^N (2J_{ij} - K_{ij}) \right] \quad (15)$$

- ϵ_i are the potential and kinetic energies of the electron
 - J_{ij} is the Coulomb integral
 - K_{ij} is the exchange integral
- the final HF energy:

$$E_{tot,0K} = E_{HF} + V_{NN} + ZPE \quad (16)$$

Advantages & Disadvantages of the HF method

- Advantages

- + very fast method (scaling with N^4)
- + good description of bond lengths (within 1% of experiment)
- + conformation energies predicted within 1-2 kcal/mol

- Disadvantages

- - doesn't treat electronic correlation
- - prediction of dissociation energies too high (closed-shell → two open-shell molecules)
- - too high dipole moments
- - vibrations about 10% too high (anharmonicity)
- - potential energy scans are meaningless

Post-Hartree Fock Methods

- designed for recovery of correlation energy which are computationally very demanding
- *Perturbative* approach (Møller-Plesset, MP)
- *Variational* approach (Configuration Interaction, CI)

Perturbation Theory

- system of mathematical methods where one knows exact solutions of simple problems and constructs conclusions to advanced ones
- the use of Taylor expansions (a powerful tool Math has to offer):

$$f_i(\lambda) = f_i|_{\lambda=0} + \left. \frac{\partial f_i}{\partial \lambda} \right|_{\lambda=0} \frac{\lambda}{1!} + \left. \frac{\partial^2 f_i}{\partial \lambda^2} \right|_{\lambda=0} \frac{\lambda^2}{2!} + \dots \quad (17)$$

- for specific accuracy a finite number of terms is used

Møller-Plesset Method

- method based on Rayleigh-Schrödinger perturbation theory
- adds a perturbation to the unperturbed Hamiltonian:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad (18)$$

- \hat{H}_0 is the HF Hamiltonian
- λ is a parameter which determines the size of perturbation

Perturbation OFF: $\lambda = 0 : \hat{H}\psi_i = E_i\psi_i$

Perturbation ON: $\lambda = 1 : \hat{H}\phi_i = W_i\phi_i$

Corrections to HF energies

- HF energy is the sum of zeroth- and first-order corrections
- electron correlation energy is sum of higher-order corrections

$$(\hat{H}_0 + \lambda \hat{H}')(\phi_i^0 + \lambda \phi_i^1 + \lambda^2 \phi_i^2 \dots) = W_i(\lambda)(\phi_i^0 + \lambda \phi_i^1 + \lambda^2 \phi_i^2 \dots) \quad (19)$$

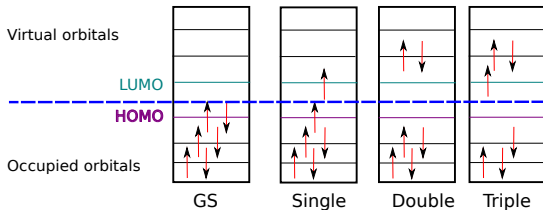
$$W_i(\lambda) = W_i^0 + W_i^1 + W_i^2 \dots \quad (20)$$

- first-order correction is calculated as:

$$W_i^1 = \phi_i \hat{H}' \phi_i \quad (21)$$

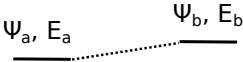
Calculating Correlation Energies

- exciting electrons from occupied orbitals to virtual ones
- MP2 (MP with 2nd order correction):
 - Two electron operator
 - Only double excitation contribute
- higher order corrections include higher order excitations



Interaction between Two Molecular Fragments

- strength of the interaction depends on square of the overlap
- is inversely dependent on the energy difference between the orbitals


$$W_a^2 = \frac{|\Psi_a \hat{H}' \Psi_b|^2}{E_a - E_b} \quad \text{and} \quad W_b^2 = \frac{|\Psi_b \hat{H}' \Psi_a|^2}{E_b - E_a} \quad (22)$$

Variational Theorem

- the energy of any “trial” wavefunction (W) is always an upper bound to the exact energy groundstate (E_{exact}).
- variation integral:

$$W \equiv \frac{\int \Psi_{CI}^* \hat{H} \Psi_{CI} d\tau}{\int \Psi_{CI}^* \Psi_{CI} d\tau} \geq E_{exact} \quad (23)$$

- Ψ_{CI} can be expanded as a linear combination of eigenfunctions Φ_i :

$$\Psi_{CI} = \sum_i c_i \Phi_i \quad (24)$$

Linear Variation Method

- variation integral expressed as sum of eigenfunctions Φ_i :

$$W = \frac{\sum_{ij} c_i c_j \int \Phi_i^* \hat{H} \Phi_j d\tau}{\sum_{ij} c_i c_j \int \Phi_i^* \Phi_j d\tau} \quad (25)$$

- substitution with:

- $H_{ij} = \int \Phi_i^* \hat{H} \Phi_j d\tau$... Interaction integral
- $S_{ij} = \int \Phi_i^* \Phi_j d\tau$... Overlap integral

$$W = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}} \quad (26)$$

Linear Variation Method

- differentiation with respect to c_i yields a non-trivial solution only if “secular determinant” equals to 0:

$$\begin{vmatrix} H_{11} - WS_{11} & H_{12} - WS_{12} & \dots & H_{1n} - WS_{1n} \\ \vdots & \vdots & \vdots & \vdots \\ H_{11} - WS_{21} & H_{22} - WS_{22} & \dots & H_{2n} - WS_{2n} \\ H_{n1} - WS_{n1} & H_{n2} - WS_{n2} & \dots & H_{nn} - WS_{nn} \end{vmatrix} = 0 \quad (27)$$

- if orthogonal basis system is used, then $S_{ij} = \delta_{ij}$

Configuration Interaction (CI)

- description using Slater determinant is approximate
- exact description using linear combination of Slater determinant for GS and excited states
- Full CI
 - all excitations calculated
 - only for tiny systems and small basis sets
 - size consistent
- Truncated CI
 - only selected excitations included
 - for larger systems
 - CIS, CISD, CID, CISDT...
 - Size Inconsistent

$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_S c_S \Psi_S + \sum_D c_D \Psi_D + \sum_T c_T \Psi_T + \dots \quad (28)$$



Matrix Elements

- Brillouin's theorem:
 - $\Psi_{HF} \hat{H} \Psi_S = 0$
- Slater-Condon rules:
 - if two Slater determinants differ more than two spatial molecular orbitals, then the matrix element is equal to zero

Structure of the CI matrix

CI matrix	Φ_{HF}	Φ_S	Φ_D	Φ_T	Φ_Q	Φ_5	...
Φ_{HF}	E_{HF}	0		0	0	0	0
Φ_S	0				0	0	0
Φ_D						0	0
Φ_T	0						0
Φ_Q	0	0					
Φ_5	0	0	0				
...	0	0	0	0			

Multiconfigurational SCF

- for cases with low-lying excited states and bond-breaking
- two levels of optimization:
 - molecular orbitals
 - configurational state functions
- CASSCF: Complete Active Space SCF
 - full CI for only selected orbitals
- RASSCF: Restricted Active Space SCF
 - selected (orbital) regions for:
 - smallest at full CI
 - larger at CISDT
 - largest at CISD ...

Coupled Cluster (CC) methods

- NOT variational methods
- cluster operators in form of exponential functions
- **solves** size-inconsistency of the **truncated CI**
- widely used
- CCSD(T): “The Gold Standard” of modern computations

Operators in Coupled Cluster

- single-particle excitation operator:

$$\hat{T}_1 \Phi_0 = \sum_{a=n+1}^b \sum_{i=1}^n t_i^a \Phi_i^a \quad (29)$$

- two-particle excitation operator:

$$\hat{T}_2 \Phi_0 = \sum_{b=a+1}^b \sum_{a=n+1}^{b-1} \sum_{j=i+1}^n \sum_{i=1}^{n-1} t_{ij}^{ab} \Phi_{ij}^{ab} \quad (30)$$

- where

- i, j - filled molecular orbitals
- a, b - virtual molecular orbitals
- t - probability of excitation

General Coupled Clusters

- “two-electron interactions” are dominant
- three or more electrons can interact simultaneously
- generalized excitation operator:

$$\hat{\tau}_{\mu} = \hat{\tau}_{ijk\dots}^{abc\dots} = \phi_a^* \phi_i \phi_b^* \phi_j \phi_c^* \phi_k \dots \quad (31)$$

- generalized CC wavefunction:

$$\Phi_{CC} = \left[\prod_{\mu} (1 + t_{\mu} \hat{\tau}_{\mu}) \right] \Phi_{HF} = e^{\hat{T}} \Phi_{HF} \quad (32)$$

- where

$$\hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu} \quad (33)$$

Truncated Coupled Cluster Methods

- truncation of excitation operator \hat{T} defines the method:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \dots$$

CCS	\hat{T}_1
CCSD	$\hat{T}_1 + \hat{T}_2$
CCSDT	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3$
CCSDTQ	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$
	\vdots

- NOTE: Truncated CC Methods are still **Size Consistent** as opposed to Truncated CIs

Energy in Coupled Cluster Methods

- Schrödinger equation:

$$\begin{aligned}\hat{H}e^{\hat{T}}\Phi_{HF} &= Ee^{\hat{T}}\Phi_{HF} \\ \Phi_{HF}\hat{H}e^{\hat{T}}\Phi_{HF} &= E\Phi_{HF}|e^{\hat{T}}\Phi_{HF}\end{aligned}$$

- power series expansion:

$$\begin{aligned}e^{\hat{T}}\Phi_{HF} &= (1 + \frac{\hat{T}}{1} + \frac{\hat{T}^2}{2} + \frac{\hat{T}^3}{6} \dots)\Phi_{HF}, \text{ then} \\ \Phi_{HF}|e^{\hat{T}}\Phi_{HF} &= \Phi_{HF}|\Phi_{HF} + \Phi_{HF}|\hat{T}\Phi_{HF} + \frac{1}{2}\Phi_{HF}|\hat{T}^2\Phi_{HF} + \dots\end{aligned}$$

- all but first term are equal to zero (orthogonal wavefunctions), thus

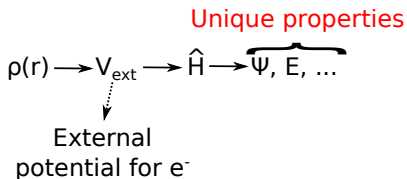
$$\Phi_{HF}\hat{H}e^{\hat{T}}\Phi_{HF} = E \tag{34}$$



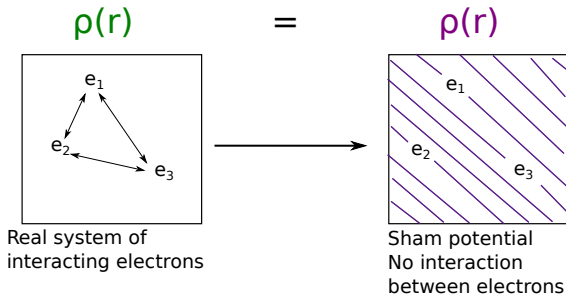
(II) Electron Density Based Method

Density Functional Theory (DFT)

- reversed workflow from *ab initio* methods
- potential of particles calculated from electron density
- energy as a **functional** of electron density ($E = F[\rho(\vec{r})]$)
- electron density is a function of 3 spatial coordinates only



Kohn-Sham (KS) Approach



- $E = F[\rho(\vec{r})]$

Energy Terms in DFT

- $E = F[\rho(\vec{r})]$
- $E = \hat{V}(\rho) + \hat{T}(\rho) + \hat{J}(\rho) + \hat{E}_{xc}(\rho)$
- $\hat{T}(\rho)$ Kinetic part from Kohn-Sham orbitals
- $\hat{E}_{xc}(\rho)$ Exchange-Correlation part most difficult
- NOTE: Flavors of DFT lies on the treatment of the Exchange-Correlation part

DFT Types

- LDA
 - Local Density Approximation
 - crudest model
 - space is divided into bins, where the electron density is calculated
- GGA Functional
 - Generalized Gradient Approximation
 - apart from the local density, the gradient of ρ is calculated
 - recovers some nonlocal interactions
 - examples: BLYP, PW91, PBE

DFT Types

- Hybrid Functionals

- including the exchange from HF calculation
- HF includes the exchange analytically
- B3LYP:
 - $E = 0.2E_{HF_{exchange}} + 0.8E_{Slater} + 0.72E_{B88} + 0.19E_{VWN3} + 0.81E_{LYP}$
- PBE0 - PBE with 25% of exact exchange

- Meta-GGA Functionals

- include higher-order derivatives of ρ
- M05 and M06L, TPSS
- Meta-Hybrid functionals include exact exchange from HF
- M06-2X, TPSSH

Time Dependent DFT (TDDFT)

- used for resolving response properties (UV/VIS...)
- solving the time-dependent Schrödinger equation:

$$\hat{H}(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t} \quad (35)$$

- where the Hamiltonian is a sum of kinetic, potential energy operators and, operator of external potential

Advantages and Disadvantages of DFT

- Advantages

- + provides treatment for Electronic Correlation
- + computational cheaper than Post Hartree-Fock methods thus practical for large systems
- + plenty of flavors to chose from in dealing with various molecular systems

- Disadvantages

- - basically the 'electron' literally see each other as a consequence of (J-K) not canceling each other as opposed to HF (Self Interaction Error)
- - fixed and not flexible, there's no systematic way to improve results such as tweaking basis sets and changing parameters

END