

TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

Lecture 3 of 6



TEXAS A&M UNIVERSITY
Division of Research



Quantum Mechanics

Time-independent Schrödinger Equation

$$\hat{H}\psi = E\psi$$

\hat{H} Hamiltonian Operator

ψ Wavefunction (eigenfunction)

E Energy of the system (eigenvalue)



Quantum Mechanics

Approximations made in the Hamiltonian

- 1) Neglect relativistic effect
- 2) Neglect coupling of electronic states (adiabatic approximation)
- 3) Neglect coupling of the electronic and nuclear motion (Born-Oppenheimer approximation)



Quantum Mechanics – Many e⁻ Hamiltonian

$$\hat{H} = -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}$$

$$\hat{H} = \hat{T}_n + \hat{T}_e + V_{ne} + V_{ee} + V_{nn}$$

\hat{T}_n = Kinetic energy operator for the nuclei

\hat{T}_e = Kinetic energy operator for the electrons

V_{ne} = Coulombic attraction between the electrons and nuclei

V_{ee} = Coulombic repulsion between the electrons

V_{nn} = Coulombic repulsion between the nuclei



Quantum Mechanics

$$\hat{H} = \hat{T}_n + \hat{T}_e + V_{ne} + V_{ee} + V_{nn}$$

$$\hat{H} = \hat{H}_n + \hat{H}_e = \hat{H}_n + \hat{H}^o + \hat{H}^1 = (\hat{T}_n + V_{nn}) + (\hat{T}_e + V_{ne}) + (V_{ee})$$

$\psi^o =$ Slater Determinant

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \overline{\phi_1(1)} & \cdots & \phi_{N/2}(1) & \overline{\phi_{N/2}(1)} \\ \phi_1(2) & \overline{\phi_1(2)} & \cdots & \phi_{N/2}(2) & \overline{\phi_{N/2}(2)} \\ \vdots & \vdots & & \vdots & \vdots \\ \phi_1(N) & \overline{\phi_1(N)} & \cdots & \phi_{N/2}(N) & \overline{\phi_{N/2}(N)} \end{vmatrix}$$

Satisfies indistinguishability of the electrons and antisymmetry requirement of the wavefunction.



Hartree-Fock Theory

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

$$\hat{H}_e = \underbrace{\hat{T}_e + \hat{V}_{ne}}_{\text{Sum of } 1e^- \text{ interactions}} + \hat{V}_{ee} \leftarrow 2e^- \text{ interactions}$$

N = number of electrons

\hat{T}_e = Kinetic energy operator for the electrons

\hat{V}_{ne} = Coulombic attraction between the electrons and the nuclei

\hat{V}_{ee} = Coulombic repulsion between the electrons



Hartree-Fock Theory

Potential for electron 1 in atomic units: $V_1 = \sum_{i=2}^N \int \frac{|\chi_i|^2}{r_{1i}} dv_i - \frac{Z}{r_1}$

$1e^-$ Schrödinger equation:

$$\left[\frac{1}{2} \nabla_1^2 + V_1(r_1) \right] \chi_1(1) = \varepsilon_1 \chi_1(1) \quad \varepsilon_1 = \text{energy of the orbital for electron 1}$$



Hartree-Fock Theory

Hartree - Fock Eigenvalue Problem: $\hat{F}\chi_i = \varepsilon_i\chi_i \quad i = 1,2,3,\dots,N$

For a closed - shell system of N electrons and A nuclei:

$$\varepsilon_i = f_i = h_i + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})$$

$$h_i = \langle \chi_i | \frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{|R_A - r_1|} | \chi_i \rangle$$

Coulomb Integrals: $J_{ij} = \langle \chi_i(1)\chi_j(2) | \frac{1}{r_{ij}} | \chi_i(1)\chi_j(2) \rangle = \langle ij | ij \rangle$

Exchange Integrals: $K_{ij} = \langle \chi_i(1)\chi_j(2) | \frac{1}{r_{ij}} | \chi_j(1)\chi_i(2) \rangle = \langle ij | ji \rangle$

1 electron integrals

2 electron integrals



Hartree-Fock Theory

Hartree - Fock Eigenvalue Problem: $\hat{F}\chi_i = \varepsilon_i\chi_i \quad i = 1,2,3,\dots,N$

For a closed - shell system of N electrons and A nuclei:

$$\varepsilon_i = f_i = h_i + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})$$

$$E_{HF} = 2 \sum_{i=1}^{N/2} h_i + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) + V_{nuclei}$$

$$E_{HF} = 2 \sum_{i=1}^{N/2} \varepsilon_i - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) + V_{nuclei}$$

$E_{HF} \neq$ sum of orbital energies



Hartree-Fock Theory

$|F_{rs} - \varepsilon_i S_{rs}| = 0$ Secular equation with roots equal to ε_i

$FC = SC\varepsilon$ If $S=I$ then diagonalizing F solves for ε

F_{rs} - Fock Matrix
 S_{rs} - Overlap Matrix

Find a matrix X such that $X^+ SX = I$

Set $C = XC'$

$FXC' = SC'\varepsilon$

$X^+ FXC' = X^+ SC'\varepsilon$

$F'C' = C'\varepsilon$ Diagonalize F' to solve for ε

Transform the new C' back to C using

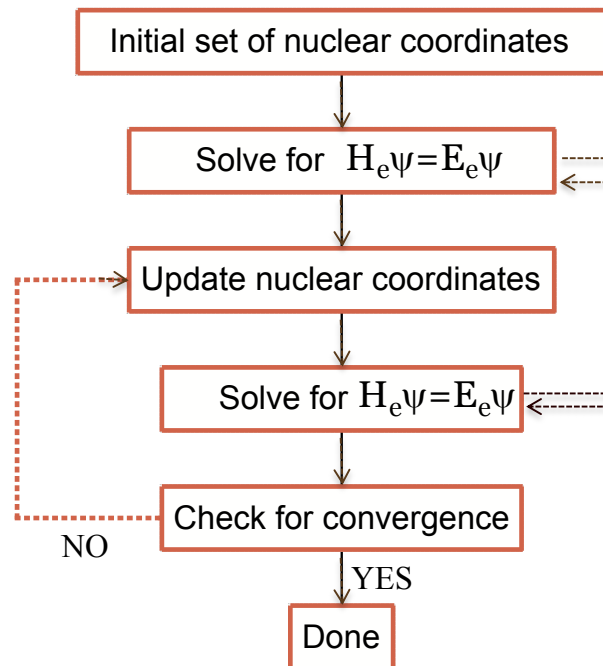
$C = XC'$ and compare with old C

Roothan equations:
Set of non-linear equations
Solved using matrix
methods and iteratively
(self consistent)

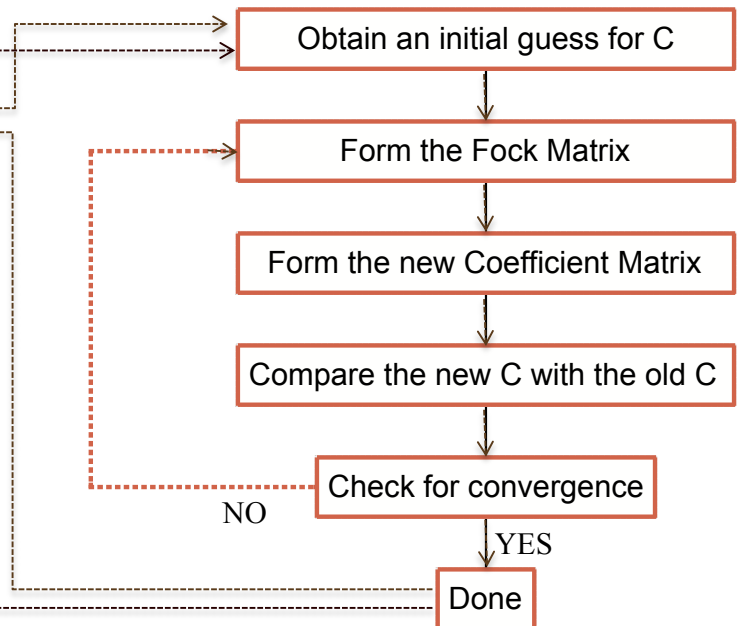


Geometry Optimization

Iterative Geometry Optimization Steps

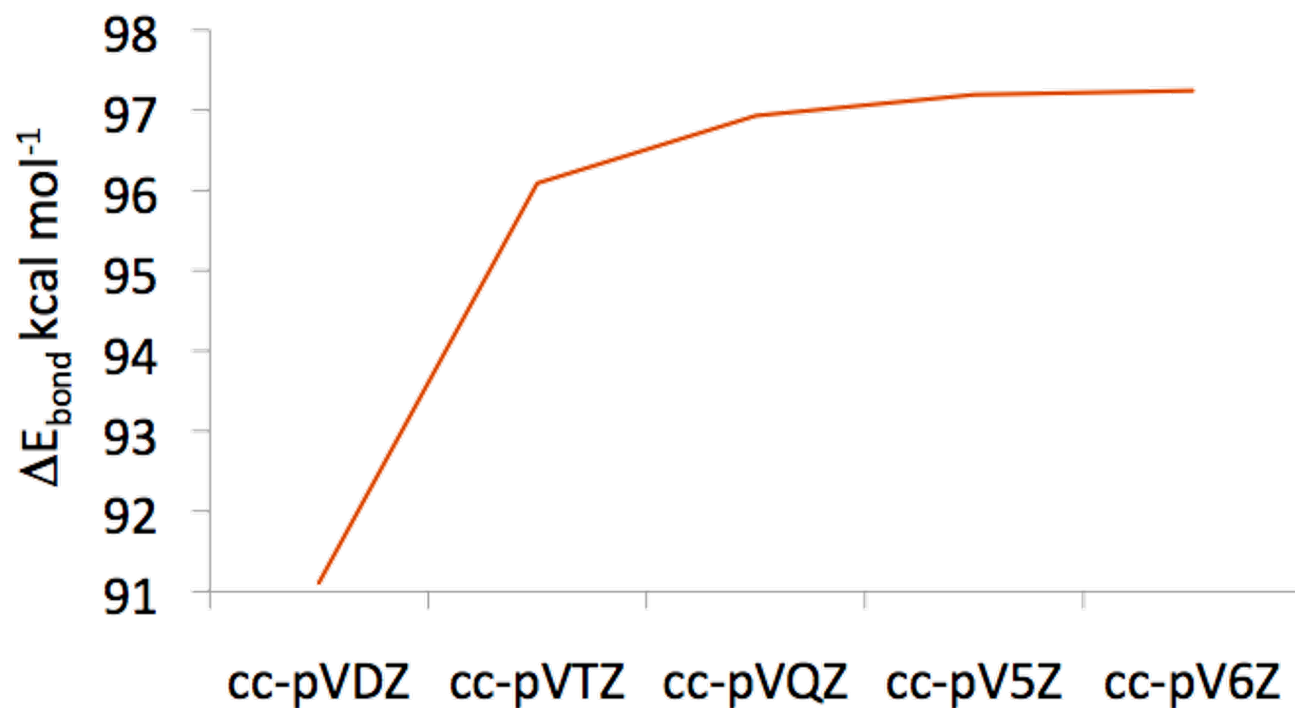


SCF (Self Consistent Field) iterative process to solve the non-linear Roothan Equations



Hartree-Fock Limit

Hydrogen Fluoride molecule Bond Energy (DE_{bond}) vs Basis set



Basis Set	DE_{bond}
cc-pVDZ	91.11
cc-pVTZ	96.09
cc-pVQZ	96.93
cc-pV5Z	97.19
cc-pV6z	97.24
Experimental	141.2



Hartree-Fock

Hartree-Fock Theory:

Variational ($E_{\text{HF}} \geq E_1$)

Size-Extensive ($E_{A \dots A} = E_A + E_A$)

Size-extensive:

$$2E_A = E_{A \dots A}$$

Where, E_A is the energy of molecule A and $E_{A \dots A}$ is the energy of two molecules of A separated by a large distance (ie non-interacting)

Size-intensive:

$$2E_A \neq E_{A \dots A}$$

Neglects instantaneous e^- correlation



Electron Correlation

- Electron Correlation – the motion of electrons are correlated
 - Coulomb hole – the probability of finding an electron of opposite spin near another electron is small $\uparrow\downarrow$
 - Fermi hole – the probability of finding an electron with the same spin near another electron is small $\uparrow\uparrow$
 - Hartree-Fock theory included electron correlation of electrons of the same spin (Fermi Hole) but does not include electron correlation of electrons of opposite spin.
- How to include electron correlation for electrons of the opposite spin (instantaneous e^- correlation)?
 - post-scf: Møller-Plesset Perturbation theory (MP x ($x=2, 3, 4, \dots$)), Configuration Interaction (CI), Coupled-Cluster (CC),
 - Density Functional Theory



Perturbation Theory

$$\hat{H} = \hat{H}_o + \lambda \hat{H}'$$

λ = Perturbation Parameter ranging from 0 to 1

$$\hat{H}\psi_o = (\hat{H}_o + \lambda \hat{H}')\psi_o = E_o\psi_o$$

Expand ψ_o and E_o as a Taylor series in powers of λ

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

$$E_o = E_o^{(0)} + \lambda E_o^{(1)} + \lambda^2 E_o^{(2)} + \dots \quad : \quad E_o^{(k)} = \left. \frac{1}{k!} \frac{d^k E_o}{d\lambda^k} \right|_{\lambda=0}$$

$k = 1, 2, 3, \dots$

$\psi_o^{(k)}$ and $E_o^{(k)}$ are the k^{th} order correction to the wavefunction and the energy



Møller-Plesset Perturbation Theory

Møller-Plesset Perturbation theory sets:

$$\hat{H}_o = \sum_{i=1}^N f_i \quad (\text{sum of } 1 e^- \text{ fock operators})$$

$$E_o(MP1) = E_o^{(0)} + E_o^{(1)} = \langle \psi_o^{(0)} | \hat{H}_o | \psi_o^{(0)} \rangle + \langle \psi_o^{(0)} | \hat{H}' | \psi_o^{(0)} \rangle = E_{HF}$$

To include dynamic electron correlation, we must go to 2nd order

$$E_o(MP2) = E_o^{(0)} + E_o^{(1)} + E_o^{(2)}$$

$$E_o(MP2) = \langle \psi_o^{(0)} | \hat{H}_o | \psi_o^{(0)} \rangle + \langle \psi_o^{(0)} | \hat{H}' | \psi_o^{(0)} \rangle + \sum_{m \neq 0} \frac{|\langle \psi_m^{(0)} | \hat{H}' | \psi_o^{(0)} \rangle|^2}{E_o^{(0)} - E_m^{(0)}}$$

$$E_o(MP2) = E_{HF} + \sum_{m \neq 0} \frac{|\langle \psi_m^{(0)} | \hat{H}' | \psi_o^{(0)} \rangle|^2}{E_o^{(0)} - E_m^{(0)}}$$

\hat{V}_{ee}



Møller-Plesset Perturbation Theory

$$E_o(MP3) = E_o^{(0)} + E_o^{(1)} + E_o^{(2)} + E_o^{(3)} = E_{HF} + E_o^{(2)} + E_o^{(3)}$$

$$E_o^{(3)} = \sum_{\substack{n \\ n \neq 0}} \sum_{\substack{m \\ m \neq 0}} \frac{\langle \psi_o^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{H}' | \psi_o^{(0)} \rangle}{(E_o^{(0)} - E_n^{(0)})(E_o^{(0)} - E_m^{(0)})} - E_o^{(1)} \sum_{\substack{n \\ n \neq 0}} \frac{|\langle \psi_o^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_o^{(0)} - E_n^{(0)}}$$

MP4 - includes singles, doubles, triples and quadruple excitations.

Triples are expensive and are often not computed by default: MP4(SDQ)

$$E_o(MP2) < E_o(MP1) = E_{HF}$$

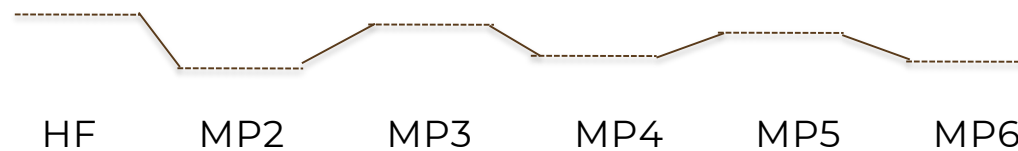
$$E_o(MP3) > E(MP2)$$

- MP is size-extensive but NOT variational
- Solved non-iteratively
- Core e⁻ not included in excitation by default in G16

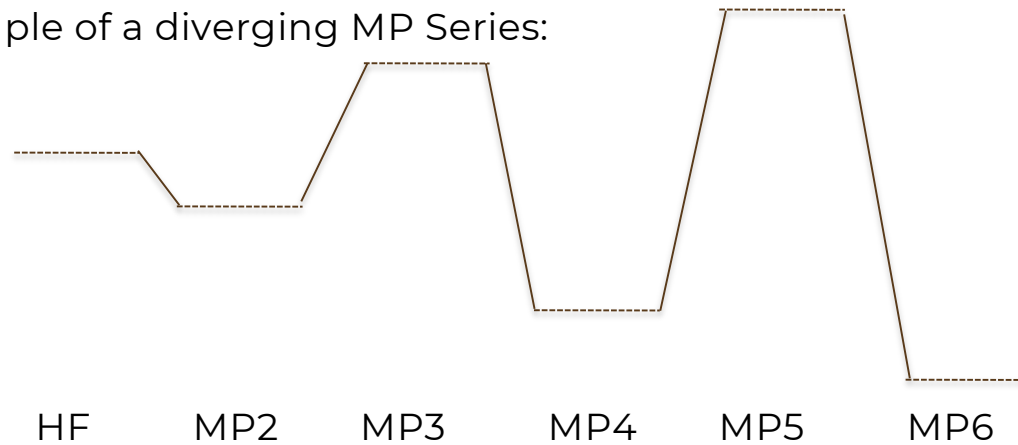


Møller-Plesset Perturbation Theory

Example of a converging MP Series:



Example of a diverging MP Series:



Configuration Interaction

$$|\psi_{CI}\rangle = |\hat{T}\psi_0\rangle$$

CSF (Configuration State Functions)

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

$$\psi_{CI} = \psi_0 + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a \psi_i^a + \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{vir}} c_{ij}^{ab} \psi_{ij}^{ab} + \dots$$

Truncated CI:

$$CIS: \hat{T} = \hat{T}_1$$

$$CID: \hat{T} = \hat{T}_2$$

$$CISD: \hat{T} = \hat{T}_1 + \hat{T}_2$$

$$CISDT: \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$$

- Full CI is variational and size-extensive
- Truncated CI is variational but size-intensive
- Solved iteratively
- Core e⁻ not included in excitation by default in G16



Quadratic Configuration Interaction (QCI)

- QCISD – Takes CISD and adds excitations to make it size-extensive at the cost of making it non-variational.
- QCISD(T) – QCISD with triple excitations added perturbatively.
- QCI is Size-extensive but non-variational.
- Solved iteratively.
- Core e⁻ not included in excitation by default in G16



Coupled Cluster

$$|\psi_{CC}\rangle = |e^{\hat{T}}\psi_0\rangle$$

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!}\hat{T}^k \quad ; \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_N$$

$$\hat{T}_1\psi_0 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \psi_i^a \quad ; \quad \hat{T}_2\psi_0 = \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{vir}} t_{ij}^{ab} \psi_{ij}^{ab} \quad ; \quad \text{etc.}$$

$t_i^a, t_{ij}^{ab}, \dots$ are the coupled - cluster amplitudes

$$\langle \psi_0 | \hat{H} e^{\hat{T}} | \psi_0 \rangle = E_{CC}$$

To solve for the coupled - cluster amplitudes :

$$\langle \psi_i^a | \hat{H} e^{\hat{T}} | \psi_0 \rangle = 0 \quad ; \quad \langle \psi_{ij}^{ab} | \hat{H} e^{\hat{T}} | \psi_0 \rangle = 0 \quad ; \quad \text{etc.}$$

Coupled sets of non - linear equations \therefore solve iteratively



Truncated Coupled-Cluster

Truncated CC:

$$CCD: \hat{T} = \hat{T}_2 \quad ; \quad e^{\hat{T}_2} = 1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{6}\hat{T}_2^3 + \dots$$

$$CCSD: \hat{T} = \hat{T}_1 + \hat{T}_2 \quad ; \quad e^{(\hat{T}_1 + \hat{T}_2)} = 1 + (\hat{T}_1 + \hat{T}_2) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2)^2 + \dots$$

$$CCSDT: \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \quad ; \quad e^{(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)} = 1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)^2 + \dots$$

CCSD(T): CCSD with perturbative Triples

- Truncated CC is size-extensive but non-variational
- Solved iteratively
- Core e⁻ not included in excitation by default in G16

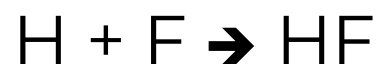


Ab initio Summary

- HF < MP2 < CISD < MP4(SDQ) ~ CCSD < MP4 < CCSD(T)
 - note: MP4 includes less e⁻ correlation but more triple excitations than CCSD(T)
 - Hartree-Fock does not include dynamic e⁻ correlation
 - PROS:
 - ✦ Hierarchy which includes more e⁻ correlation as you move up the hierarchy
 - CONS:
 - ✦ Computational cost for post-scf calculations is high.
 - ✦ The accuracy of post-scf (post-HF) levels of theory are highly dependent on the quality of the basis set



Hartree-Fock and Post-HF (Post-SCF)



Method	ΔE_{bond} (kcal mol ⁻¹)
HF/STO-3G	73.9
HF/6-311++G(3df,3pd)	97.9
MP2/6-311++G(3df,3pd)	144.9
MP3/6-311++G(3df,3pd)	137.9
MP4/6-311++G(3df,3pd)	141.8
QCISD/6-311++G(3df,3pd)	138.8
QCISD(T) /6-311++G(3df,3pd)	140.6
Experimental	141.2



Computational Cost

Level of Theory	Scaling
HF	N^3 iterative
Density Functional Theory	N^3 iterative
MP2	N^5 non-iterative
MP3, MP4(SDQ)	N^6 non-iterative
CISD, CCSD, QCISD	N^6 iterative
MP4(SDTQ)	N^7 non-iterative
MP5	N^8 non-iterative
CISDT, CCSDT, QCISDT	N^8 iterative
MP6	N^9 non-iterative
MP7	N^{10} non-iterative
CISDTQ, CCSDTQ, QCISDTQ	N^{10} iterative

$N \sim$ number of basis functions

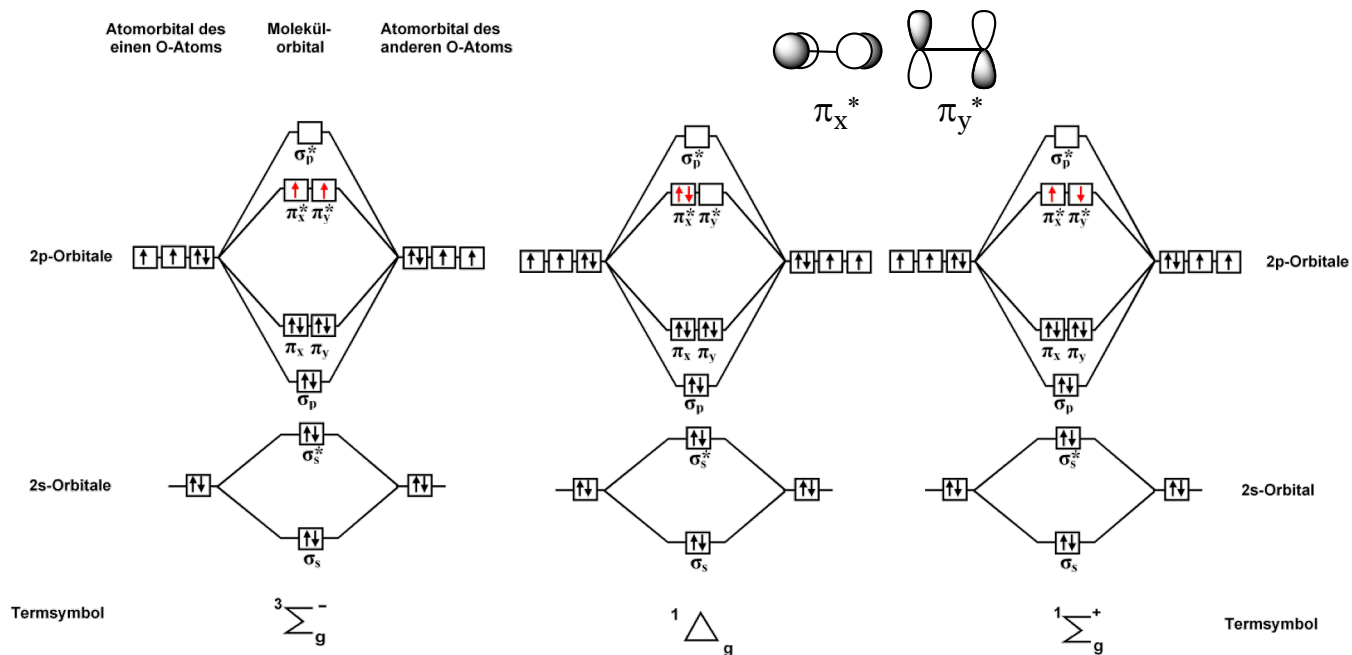


Single-reference vs. Multi-reference

- Single-reference
 - The molecular orbitals of a single wavefunction are optimized.
 - HF, DFT, MP_x, CCSD(T), CISD, etc
- Multi-reference
 - A linear combination of optimized wavefunctions with optimized wavefunction coefficient.
 - CASSCF (MCSCF), CAS-PT2, MRCI, RASSCF
 - $\Psi = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + \dots$
 - ✦ Φ_x are optimized wavefunctions and are generally referred to as Configuration State Functions (CSF).
 - ✦ c_i are optimized coefficients of the CSF's
- Test for MR Character
 - CCSD – T1 Diagnostic
 - ✦ T1 > 0.02 indicates that single reference methods will give poor results
 - ✦ D1 > 0.025 indicates that single reference methods will give poor results.



Multi-Reference Character



Triplett-Sauerstoff (stabil)

Singulett-Sauerstoff (kurzlebig, reaktiv)

$3 \Sigma_g^-$ CCSD/6-311G(d) T1 Diagnostic = 0.01383309

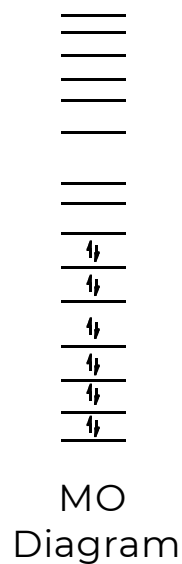
$1 \Delta_g$ CCSD/6-311G(d) T1 Diagnostic = 0.01367274

$1 \Sigma_g^+$ CCSD/6-311G(d) T1 Diagnostic = 0.02196049

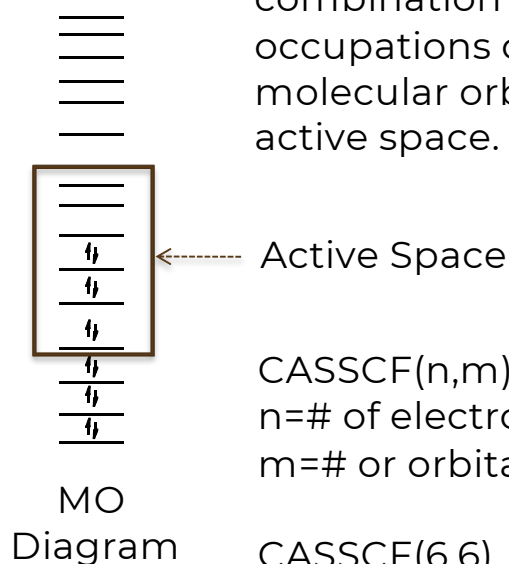


CASSCF

- Complete Active Space Self-Consistent Field (CASSCF)



Full CI would be a linear combination of all possible CSF for all possible occupations of the molecular orbitals.



CASSCF – Linear combination of all possible occupations of the molecular orbitals in the active space.

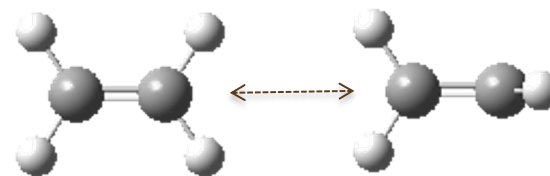
← Active Space

CASSCF(n,m)
n=# of electrons
m=# of orbitals

CASSCF(6,6)

Multi-Reference Character

- Internal rotation in ethylene

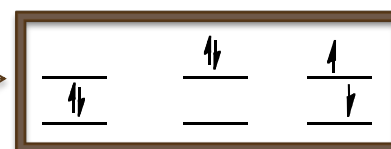


- FV active space is (12,12)
- Minimum active space includes only C-C $\sigma, \pi, \pi^*, \sigma^*$ (4,4)
- The two active spaces give ~same internal rotation barrier
- This active space cannot account for other processes, such as C-H bond cleavage

of CSF in an CASSCF(n,m) where m=n

n	# of CSF's
2	3
4	20
6	175
8	1,764
10	19,404
12	226,512
14	2,760,615

CSFs for CASSCF(2,2) →



Φ_1 Φ_2 Φ_3

$$\psi = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3$$

How to select your active space

- For each occupied bonding orbital select the corresponding virtual (unoccupied) antibonding orbital
- Use HF Natural orbitals to help pick out the important orbitals
 - Diagonal ρ matrix eigenvalues are occupation numbers which range from zero to two.
 - include orbitals that deviate from zero or two



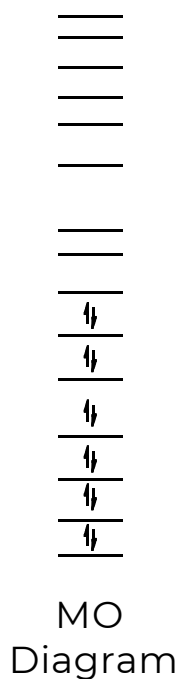
CAS-PT2

- CAS-PT2 – CASSCF + MP2 correction to the energy for **important** CSF's
- Determine the CSF coefficient cutoff.
- Check the CASSCF results of the systems/conformations that you are comparing to determine if the cutoff should be changed.

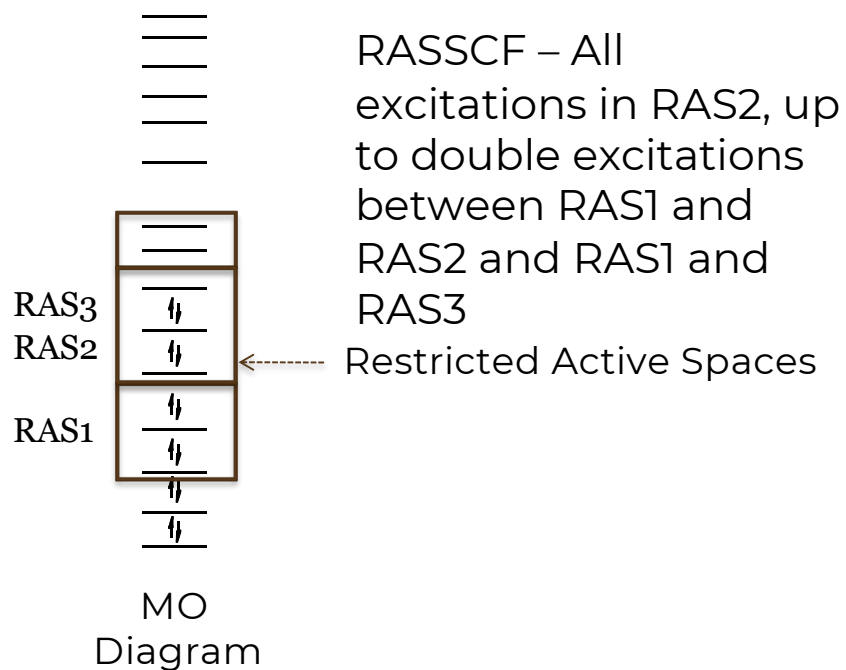


RASSCF

- Restricted Active Space Self-Consistent Field (RASSCF)

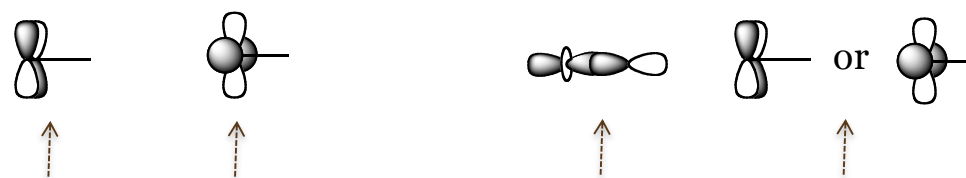


Full CI would be a linear combination of all possible CSF for all possible occupations of the molecular orbitals.



Multi-Reference Character

OsC $C_{\infty v}$



$3\Sigma^-$	3Δ
CCSD(T)	B3LYP
MP2	CASSCF(6,6) $\sigma\sigma\delta\delta\sigma^*\sigma^*$
CASSCF(10,10) $\pi\pi\sigma\sigma\delta\delta\sigma^*\sigma^*\pi^*\pi^*$	
CAS-PT2	
CAS-PT2(10,10)	

MRCI

- Multi-Reference Configuration Interaction
- Similar to CAS-PT2 but uses CISD to correct the energy of the CSF.
- Generally, which CSF's to include in the CISD correction are chosen via a cutoff or manually.



Variational and Size Extensive

Level of Theory	Variational	Size Extensive	Dynamic e-correlation
HF	yes	yes	No
Density Functional Theory	yes	yes	Yes
DFT Current Implementation	no	yes	Yes
MPx (x=2, 3, 4, etc)	no	yes	Yes
Coupled-Cluster (Truncated, CCD, CCSD, CCSD(T))	no	yes	Yes
Quadratic Configuration Interaction (QCID, QCISD, QCISD(T))	no	yes	Yes
Configuration Interaction (Truncated, CISD)	yes	no	Yes
Full CI	yes	yes	Yes
CASSCF	yes	Maybe yes	No
CASPT2	no	yes	yes
MRCI (Truncated)	Yes	No	yes

