AN INTRODUCTION TO MCSCF
ORBITAL APPROXIMATION

\[ \Psi_{hp} = \psi_1(1)\psi_2(2)\ldots\psi_N(N) \]

- Hartree product (hp) expressed as a product of spinorbitals \( \psi_i = \phi_i \sigma_i \)
- \( \phi_i = \) space orbital, \( \sigma_i = \) spin function \((\alpha, \beta)\)
- Pauli Principle requires antisymmetry:

\[ \Psi = \hat{A}\Psi_{hp} = |\psi_1(1)\psi_2(2)\ldots\psi_N(N)| \]
• For more complex species (one or more open shells) antisymmetric wavefunction is generally expressed as a linear combination of Slater determinants

• Optimization of the orbitals (minimization of the energy with respect to all orbitals), based on the Variational Principle) leads to:
HARTREE-FOCK METHOD

- Optimization of orbitals leads to
  - $F \phi_i = \varepsilon_i \phi_i$
  - $F = $ Fock operator $= h_i + \sum_i (2J_i - K_i)$ for closed shells
  - $\phi_i = $ optimized orbital
  - $\varepsilon_i = $ orbital energy
HARTREE-FOCK METHOD

- Closed Shells: Restricted Hartree-Fock (RHF)

\[ \Psi = |\phi_1 \]

- Consider \( H_2 \):

\[ \Psi = |\phi_1 \]

- The 2-electron case can be written more simply

\[ \Psi = \phi_1(1)\phi_1(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)](2^{-1/2}) = \Phi \Sigma \]

- \( \Psi \) = (space function) (spin function)
Simplest MO for H₂ is minimal basis set:

\[ \phi_1 = [2(1+S)]^{-1/2} (1s_A + 1s_B) \]

- \(1s_A, 1s_B\) = AOs on \(H_A, H_B\), respectively

Expectation value of energy \(<E>\) is

\[ <E> = <\Psi|H|\Psi> = <\Phi|H|\Phi> <\Sigma|\Sigma> \]

- Since H is spin-free,
- Main focus is on space part:
  - \(\Phi = \phi_1(1)\phi_1(2)\)
  - \[ = [2(1+S)]^{-1}[1s_A(1)+1s_B(1)][1s_A(2)+1s_B(2)] \]
\[ \Phi = [2(1+S)]^{-1}[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] \]

- First 2 terms = ionic, second 2 terms = covalent

- \[ \Phi = [2(1+S)]^{-1} [\Phi_{\text{ion}} + \Phi_{\text{cov}}] \]

- So, HF wavefunction is equal mix of covalent & ionic contributions

- Apparently OK ~ equilibrium geometry

- Consider behavior as R --> \( \infty \): S --> 0

- \[ \Phi --> 1/2 [\Phi_{\text{ion}} + \Phi_{\text{cov}}] \]

- \[ \langle E \rangle --> 1/4 \langle \Phi_{\text{ion}} + \Phi_{\text{cov}} | H | \Phi_{\text{ion}} + \Phi_{\text{cov}} \rangle \]
• The Hamiltonian is

\[ H = H_1^{(0)} + H_2^{(0)} + \frac{1}{r_{12}} \]

\[ H_1^{(0)} = -(\frac{1}{2})\nabla_1^2 - \frac{Z_A}{r_{A1}} - \frac{Z_B}{r_{B1}} \]

• Plugging in & recognizing that as \( R \rightarrow \infty \), many terms \( \rightarrow 0 \):

\[ \langle E \rangle_{R \rightarrow \infty} \rightarrow \frac{1}{2}[(E_{H+} + E_{H-}) + 2E_H] \]
• So, the HF wavefunction gives the wrong limit as $H_2$ dissociates, because ionic & covalent terms have equal weights.
• Must be OK $\sim R_e$, since HF often gives good geometries
• $HF/MBS \ D_e \sim 3.64 \ ev$. Cf., $D_e(expt) \sim 4.75 \ ev$
VALENCE BOND METHOD

- Alternative to MO, originally called Heitler-London theory
- Presumes a priori that bonds are covalent:
  - \( \phi_1 = 1s_A(1)1s_B(2); \quad \phi_2 = 1s_A(2)1s_B(1) \)
  - \( \Psi_{VB} = [2(1+S_{12})]^{-1/2}[\phi_1 + \phi_2]; \quad S_{12} = \langle \phi_1 | \phi_2 \rangle = S_{AB} \)
- Apply linear variation theory in usual way:
  - Dissociation to correct limit H + H
  - \( D_e \sim 3.78 \text{ ev}; \text{ cf.}, \quad D_e(\text{expt}) \sim 4.75 \text{ ev.} \)
So, the MO wavefunction gives the wrong limit as \( \text{H}_2 \) dissociates, whereas VB gives correct limit.

- Both MO and VB give poor \( D_e \)
- MO incorporates too much ionic character
- VB completely ignores ionic character
- Both are inflexible

- How can these methods be improved?
IMPROVING VB AND MO

• Could improve VB by adding ionic terms using variational approach:
  \[ \Psi_{\text{VB,imp}} = \Psi_{\text{VB}} + \gamma \Psi_{\text{ion}} = \Psi_{\text{cov}} + \gamma \Psi_{\text{ion}} \]
  where \( \gamma \) = variational parameter.
  Expect \( \gamma \approx 1 \) \( \sim R = R_e \) & \( \gamma \to 0 \) as \( R \to \infty \)

• Generalized valence bond (GVB) method: W.A. Goddard III

• Since MO method over-emphasizes ionic character, want to do something similar, but in reverse
IMPROVING VB AND MO

• Improve MO by allowing electrons to stay away from each other: decrease importance of ionic terms. Recall (ignoring normalization)
  \[ \Psi_{\text{MO}} = \phi_1(1)\phi_1(2): \phi_1 = 1s_A + 1s_B \]

• Antibonding orbital
  \[ \Psi_{\text{MO}^*} = \phi_2(1)\phi_2(2): \phi_2 = 1s_A - 1s_B \]
  - Keeps electrons away from each other.
So, we write (ignoring normalization)

\[ \Psi_{\text{MO,imp}} = \Psi_{\text{MO}} + \lambda \Psi_{\text{MO}}^* = \phi_1(1)\phi_1(2) + \lambda \phi_2(1)\phi_2(2) \]

- where \( \lambda \) = variational parameter
- \( |\lambda| \sim 0 \) at \( R = R_e \)
- \( \rightarrow 1 \) as \( R \rightarrow \infty \)

Can easily show that

\[ \Psi_{\text{MO,imp}} = \Psi_{\text{VB,imp}} : \gamma = (1+\lambda)/(1-\lambda) \]

\( \Psi_{\text{MO,imp}} \) is simplest MCSCF wavefunction

- Gives smooth dissociation to \( H + H \)
- Called TCSCF (two configuration SCF)
H₂ RHF VS. UHF

- Recall that
  - $\phi_1 = [2(1+S)]^{-1/2} (1s_A + 1s_B)$: bonding MO
  - $\phi_2 = [2(1-S)]^{-1/2} (1s_A - 1s_B)$: anti-bonding MO

- Ground state wavefunction is
  \[ \Psi = |\phi_1 \phi_1| \]
  - Ground state space function $\Phi = \phi_1(1)\phi_1(2)$
  - RHF since $\alpha, \beta$ electrons restricted to same MO
• Can introduce flexibility into the wavefunction by relaxing RHF restriction.

  - Define two new orbitals $\phi_1^\alpha, \phi_1^\beta$, so that

  - $\Phi_{\text{UHF}} = \phi_1^\alpha(1) \phi_1^\beta(2)$: Unrestricted HF/UHF, different orbitals for different spins: DODS

• Can expand these 2 UHF orbitals in terms of 2 known linearly independent functions. Take these to be $\phi_1, \phi_2$:

  - $\phi_1^\alpha = \phi_1 \cos \theta + \phi_2 \sin \theta \quad 0 \leq \theta \leq 45^\circ$

  - $\phi_1^\beta = \phi_1 \cos \theta - \phi_2 \sin \theta \quad \theta = 0^\circ$: RHF solution
• Can expand $\phi_1^\alpha, \phi_1^\beta$ in terms of $1s_A, 1s_B$

• Then derive $\langle E(\theta) \rangle$, $d\langle E(\theta) \rangle/d\theta$, $d^2\langle E(\theta) \rangle/d\theta^2$
  
  – Details in Szabo & Ostlund; 2 possibilities:

• Corresponds to Pople RHF/UHF stability test
As H-H bond in H$_2$ is stretched,

- Optimal value of $\theta$ must become nonzero, since
- We know RHF solution is incorrect at asymptote
- As $R \to \infty$, $\theta \to 45^\circ$
- Can express UHF wavefunction as

$$
\Psi_{UHF} = \cos^2 \Theta \left| \phi_1 \bar{\phi}_1 \right| - \sin^2 \Theta \left| \phi_2 \bar{\phi}_2 \right|
$$

$$
- \sin \Theta \cos \Theta \left\{ \left| \phi_1 \bar{\phi}_2 \right| - \left| \phi_2 \bar{\phi}_1 \right| \right\}
$$

- Note that 1$^{st}$ 2 terms are just MCSCF wavefunction
- 3$^{rd}$ term corresponds to spin contamination
\[ \Psi_{UHF} = \cos^2 \Theta \mid \phi_1 \bar{\phi}_1 \mid - \sin^2 \Theta \mid \phi_2 \bar{\phi}_2 \mid - \sin \Theta \cos \Theta \{ \mid \phi_1 \bar{\phi}_2 \mid - \mid \phi_2 \bar{\phi}_1 \mid \} \]

- At \( \theta=0^\circ \), \( \Psi_{UHF} = \Psi_{RHF} = \mid \phi_1 \bar{\phi}_1 \mid \)
- At \( \theta=45^\circ \), \( \Psi_{UHF} = \frac{1}{2} \mid \phi_1 \bar{\phi}_1 \mid - \frac{1}{2} \mid \phi_2 \bar{\phi}_2 \mid - \frac{1}{2^3} \Psi \)
- So, UHF wavefunction correctly dissociates to \( \text{H} + \text{H} \), but wavefunction is 50-50 mixture of singlet and triplet
- UHF therefore gives non-integer natural orbital occupation numbers.

Simplest way of going beyond simple RHF
MCSCF ACTIVE SPACES

- How many bonds (m) am I going to break?
- How many electrons (n) are involved?
- Active space is (n,m)
  - n electrons in m orbitals
  - Full CI within chosen active space: CASSCF/FORS
- H₂: 2 electrons in 2 orbitals
- H₂=CH₂?
Consider simple Walsh diagram

- $\varepsilon_{orbital\ energy}$
- $\varepsilon = \text{orbital energy}$

In $\text{H}_2\text{O}$, $a_1$, $b_1$ both doubly occ lone pairs: HF OK
- $b_1 = \text{pure p HOMO, } a_1$ s character $\rightarrow$ 0 as $\theta \rightarrow 180^\circ$
- At $\theta = 180^\circ$, ($a_1$, $b_1$) become degenerate $\pi$ orbital
- In \( \text{CH}_2 \), \( a_1 = \text{HOMO} \), \( b_1 = \text{LUMO} \)
- At \( \theta = 90^\circ \), \( N(a_1) \sim 2 \), \( N(b_1) \sim 0 \): HF OK
- At \( \theta = 180^\circ \), \((a_1, b_1) = \) degenerate \( \pi \) orbital, so

\[
\Psi = (2)^{-1/2} \{ |a_1 \bar{a}_1| - |b_1 \bar{b}_1| \}
\]
- There are 2 equally weighted configurations
Most general form of $^1\text{CH}_2$ wavefunction is

$$\Psi = C_1 |a_1 \bar{a}_1| + C_2 |b_1 \bar{b}_1|$$

This is a FORS or CASSCF wavefunction:
- 2 active electrons in 2 active orbitals: (2,2)
- At $\theta \sim 90^\circ$: $C_1 \sim 1$, $C_2 \sim 0$: NOON $\sim 2,0$
- At $\theta = 180^\circ$: $C_1 = C_2 = 2^{-1/2}$: NOON $\sim 1,1$
Now consider $N_2$ dissociation:

- Breaking 3 bonds: $\sigma + 2\pi$
- Minimum correct FORS/CASSCF=(6,6)

6 electrons in 6 orbitals “active space”

- $N_2$ used as benchmark for new methods designed for bond-breaking
  - Head-Gordon
  - Piecuch
  - Krylov
MCSCF

- Scales exponentially within active space
  - Full CI within active space: size consistent
- Necessary for
  - Diradicals
  - Unsaturated transition metals
  - Excited states
  - Often transition states
- CASSCF accounts for near-degeneracies
- Still need to correct for rest of electron correlation: “dynamic correlation”
MULTI-REFERENCE METHODS

- **Multi-reference CI: MRCI**
  - CI from set of MCSCF configurations
  - SOCI in GAMESS
  - Most commonly stops at singles and doubles
    - MR(SD)CI: NOT size-consistent
    - Very demanding
    - ~ impossible to go past 14 electrons in 14 orbitals

- **Multi-reference perturbation theory (MBPT)**
  - More efficient than MRCI
  - Not usually as accurate as MRCI
  
Size-consistency depends on implementation
FULL CI

MCQDPT2

MP2

MCSCF

RHF/ROHF

correlation

basis set size

Hartree-Fock Limit

complete basis

exact answer

basis set size