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

• Consider $H_2$:

• The 2-electron case can be written as

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

• $\Psi = \text{(space function)} \cdot \text{(spin function)}$
• Simplest MO for $H_2$ 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 $\langle E \rangle$ is
  \[ \langle E \rangle = \langle \Psi | H | \Psi \rangle = \langle \Phi | H | \Phi \rangle < \Sigma | \Sigma > \]
  - Since $H$ is spin-free
  - Main focus here is on space part:
    \[ \Phi = \phi_1(1)\phi_1(2) \]
    \[ = [2(1+S)]^{-1}[1s_A(1)+1s_B(1)][1s_A(2)+1s_B(2)] \]
- $\Phi = [2(1+S)]^{-1}[1s_A(1)1s_A(2)+1s_B(1)1s_B(2) + 1s_A(1)1s_B(2)+1S_A(2)1s_B(1)]$

**1st 2 terms = ionic, 2nd 2 terms = covalent**

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

- $S = \text{overlap integral}$

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

- Apparently OK ~ equilibrium geometry

- Consider behavior as $R \to \infty$: $S \to 0$

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

- $<E> \to 1/4<\Phi_{\text{ion}} + \Phi_{\text{cov}}|H|\Phi_{\text{ion}} + \Phi_{\text{cov}}>}$
• The Hamiltonian is

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

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

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

\[ \langle E \rangle_{R \to \infty} \to \frac{1}{2}[(E_{H+} + E_{H-}) + 2E_H] \]
• So, the HF wavefunction gives the wrong limit as $\text{H}_2$ dissociates, because ionic & covalent terms have equal weights.
• Must be OK $\sim R_e$, since HF often gives good geometries
• HF/CBS $D_e \sim 3.64$ ev. Cf., $D_e(\text{expt}) \sim 4.75$ ev
VALENCE BOND METHOD

- Alternative to MO, originally called Heitler-London theory
- *Presumes a priori* that bonds are covalent:
  - $\phi_1 = 1s_A(1)1s_B(2); \quad \phi_2 = 1s_A(2)1s_B(1)$
  - $\Psi_{VB} = [2(1+S_{12})]^{-1/2}[\phi_1 + \phi_2]; \quad S_{12} = \langle\phi_1|\phi_2\rangle = S_{AB}^2$
- Only covalent part, no ionic terms
- Apply linear variation theory in usual way:
  - Dissociation to correct limit H + H
  - $D_e \sim 3.78$ ev; cf., $D_e$ (expt) $\sim 4.75$ ev.
• So, the MO wavefunction gives the wrong limit as $H_2$ 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?
Could improve VB by adding ionic terms using variational approach:

\[ \Psi_{VB,imp} = \Psi_{VB} + \gamma \Psi_{ion} = \Psi_{cov} + \gamma \Psi_{ion} \]

- where \( \gamma \) = variational parameter.

- Expect \( \gamma \sim 1 \sim R = R_e \) & \( \gamma \to 0 \) 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)
  - $\Psi_{MO} = \phi_1(1)\phi_1(2): \quad \phi_1 = 1s_A + 1s_B$
- Antibonding orbital
  - $\Psi_{MO}^* = \phi_2(1)\phi_2(2): \quad \phi_2 = 1s_A - 1s_B$
  - 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

$$\Psi = | \phi_1 \bar{\phi}_1 |$$

- 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

- $\Phi_{UHF} = \phi_1^\alpha(1) \phi_1^\beta(2)$: 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:

  ![Diagram](image-url)

  RHF solution: stable
  RHF unstable: UHF

• 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

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

- Note that 1st 2 terms are just MCSCF wavefunction
- 3rd term corresponds to spin contamination
\( \Psi_{UHF} = \cos^2 \Theta | \phi_1 \phi_1 \rangle - \sin^2 \Theta | \phi_2 \phi_2 \rangle \\
- \sin \Theta \cos \Theta \{ | \phi_1 \phi_2 \rangle - | \phi_2 \phi_1 \rangle \} \)

- At \( \theta=0^\circ \), \( \Psi_{UHF} = \Psi_{RHF} = | \phi_1 \phi_1 \rangle \)
- At \( \theta=45^\circ \), \( \Psi_{UHF} = \frac{1}{2} | \phi_1 \phi_1 \rangle - \frac{1}{2} | \phi_2 \phi_2 \rangle - \frac{1}{2} \Psi \)
- So, UHF wavefunction correctly dissociates to \( H + H \), 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
BUT: Beware spin contamination
How many bonds \((m)\) am I going to break?

Could mean breaking bonds by excitation

How many electrons \((n)\) are involved?

Active space is \((n,m)\)

- \(n\) electrons in \(m\) orbitals
- Full CI within chosen active space: CASSCF/FORS

\(\text{H}_2\): 2 electrons in 2 orbitals

\(\text{CH}_2\)?
• Consider simple Walsh diagram

- In H₂O, a₁, b₁ both doubly occ lone pairs: HF OK
- b₁ = pure p HOMO, a₁ s character -> 0 as θ -> 180°
- At θ=180°, (a₁, b₁) become degenerate π orbital
- In CH$_2$, $a_1$=HOMO, $b_1$=LUMO
- At $\theta=90^\circ$, $N(a_1)$~2, $N(b_1)$~0: HF OK
- At $\theta=180^\circ$, ($a_1,b_1$) = degenerate $\pi$ orbital, so

$$\Psi = (2)^{-1/2} \{ |a_1 a_1^\dagger| - |b_1 b_1^\dagger| \}$$

- 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 $\text{N}_2$ dissociation:

- Breaking 3 bonds: $\sigma + 2\pi$
- **Minimum correct FORS/CASSCF=(6,6)**
  
  6 electrons in 6 orbitals "active space"

- $\text{N}_2$ 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
    - \( \sim \) 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 -> exact answer

MCQDPT2

MP2

MCSCF

RHF/ROHF

Hartree-Fock Limit

basis set size

correlation