

AN INTRODUCTION TO MCSCF

ORBITAL APPROXIMATION

$$\Psi_{\text{hp}} = \psi_1(1)\psi_2(2)\dots\psi_N(N)$$

- Hartree product (hp) expressed as a product of spinorbitals $\psi_i = \phi_i \sigma_i$
- ϕ_i = space orbital, σ_i = spin function (α, β)
- Pauli Principle requires antisymmetry:

$$\Psi = \hat{A}\Psi_{\text{hp}} = |\psi_1(1)\psi_2(2)\dots\psi_N(N)|$$

ORBITAL APPROXIMATION

- 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)

$$\Psi = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_N \bar{\phi}_N|$$

- Consider H_2 : $\Psi = |\phi_1 \bar{\phi}_1|$
- The 2-electron case can be written more simply
- $\Psi = \phi_1(1)\phi_1(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)](2^{-1/2}) = \Phi\Sigma$
- $\Psi = (\text{space function}) (\text{spin function})$

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

- $\Phi = [2(1+S)]^{-1} [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)]$
- 1st 2 terms = ionic, 2nd 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 $R \rightarrow \infty$: $S \rightarrow 0$
 - $\Phi \rightarrow 1/2 [\Phi_{\text{ion}} + \Phi_{\text{cov}}]$
 - $\langle E \rangle \rightarrow 1/4 \langle \Phi_{\text{ion}} + \Phi_{\text{cov}} | H | \Phi_{\text{ion}} + \Phi_{\text{cov}} \rangle$

- The Hamiltonian is

$$H = H_1^{(0)} + H_2^{(0)} + 1 / r_{12}$$

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

- Plugging in & recognizing that as $R \rightarrow \infty$, many terms $\rightarrow 0$:

$$- \langle E \rangle_{R \rightarrow \infty} \rightarrow 1/2[(E_{H+} + E_{H-}) + 2E_H]$$

- 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., $D_e(\text{expt}) \sim 4.75$ ev

VALENCE BOND METHOD

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

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 γ = variational parameter.
 - Expect $\gamma \sim 1$ $\sim R=R_e$ & $\gamma \rightarrow 0$ as $R \rightarrow \infty$
- 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)
 - $\Psi_{MO} = \phi_1(1)\phi_1(2): \phi_1 = 1s_A + 1s_B$
- Antibonding orbital
 - $\Psi_{MO}^* = \phi_2(1)\phi_2(2): \phi_2 = 1s_A - 1s_B$
 - 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 λ = variational parameter
 - $|\lambda| \sim 0$ at $R = R_e$
 - $\lambda \rightarrow 1$ 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 $\text{H} + \text{H}$
 - Called TCSCF (two configuration SCF)
 - Also called GVB (Generalized Valence Bond)

RHF VS. UHF

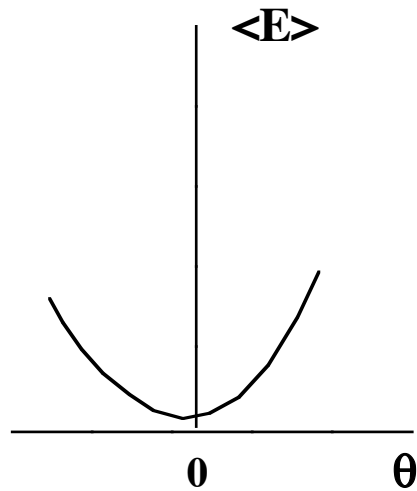
- Recall that
 - $\phi_1 = [2(1+S)]^{-1/2} (1s_A + 1s_B)$: bonding MO
 - $\phi_2 = [2(1-S)]^{-1/2} (1s_A - 1s_B)$: anti-bonding MO
- Ground state wavefunction is

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

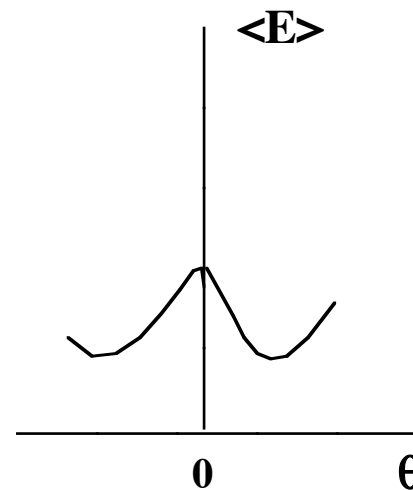
- Ground state space function $\Phi = \phi_1(1)\phi_1(2)$
- RHF since α, β electrons *restricted* to same MO

- 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 ϕ_1, ϕ_2 :
 - $\phi_1^\alpha = \phi_1 \cos\theta + \phi_2 \sin\theta$ $0 \leq \theta \leq 45^\circ$
 - $\phi_1^\beta = \phi_1 \cos\theta - \phi_2 \sin\theta$ $\theta = 0^\circ$: 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:



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

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

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

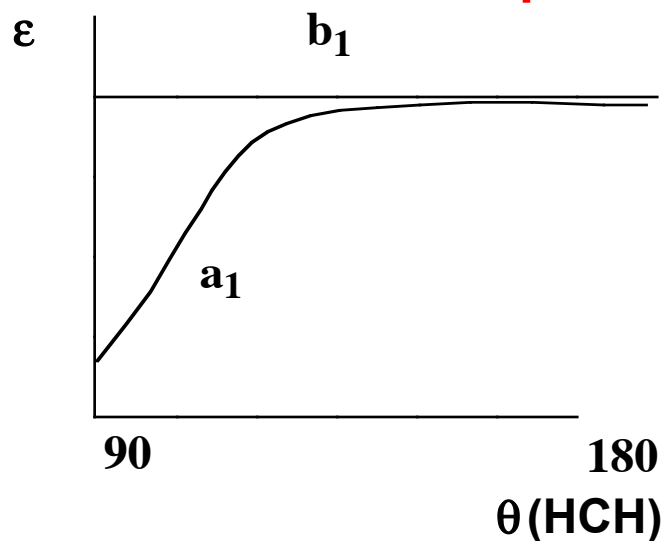
- Note that 1st 2 terms are just MCSCF wavefunction
- 3rd term corresponds to spin contamination

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

- At $\theta=0^\circ$, $\Psi_{UHF} = \Psi_{RHF} = |\phi_1 \bar{\phi}_1|$
- At $\theta=45^\circ$, $\Psi_{UHF} = 1/2 |\phi_1 \bar{\phi}_1| - 1/2 |\phi_2 \bar{\phi}_2| - 1/2 {}^3\Psi$
- 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.

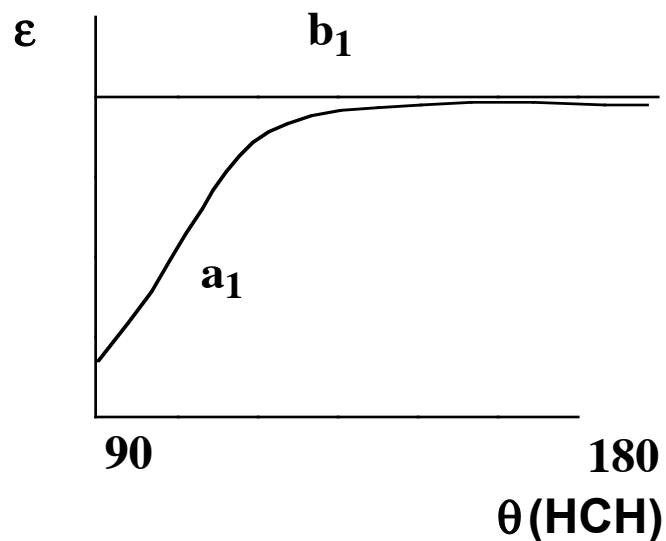
SINGLET CH_2

- Consider simple Walsh diagram



ϵ = orbital energy

- In H_2O , a_1 , b_1 both doubly occ lone pairs: HF OK
- b_1 = pure p HOMO, a_1 s character $\rightarrow 0$ as $\theta \rightarrow 180^\circ$
- At $\theta = 180^\circ$, (a_1, b_1) become degenerate π orbital



- In 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 $\theta = 180^\circ$, $(a_1, b_1) = \text{degenerate } \pi \text{ orbital}$, so

$$\Psi = (2)^{-1/2} \{ |a_1 \bar{a}_1| - |b_1 \bar{b}_1| \}$$

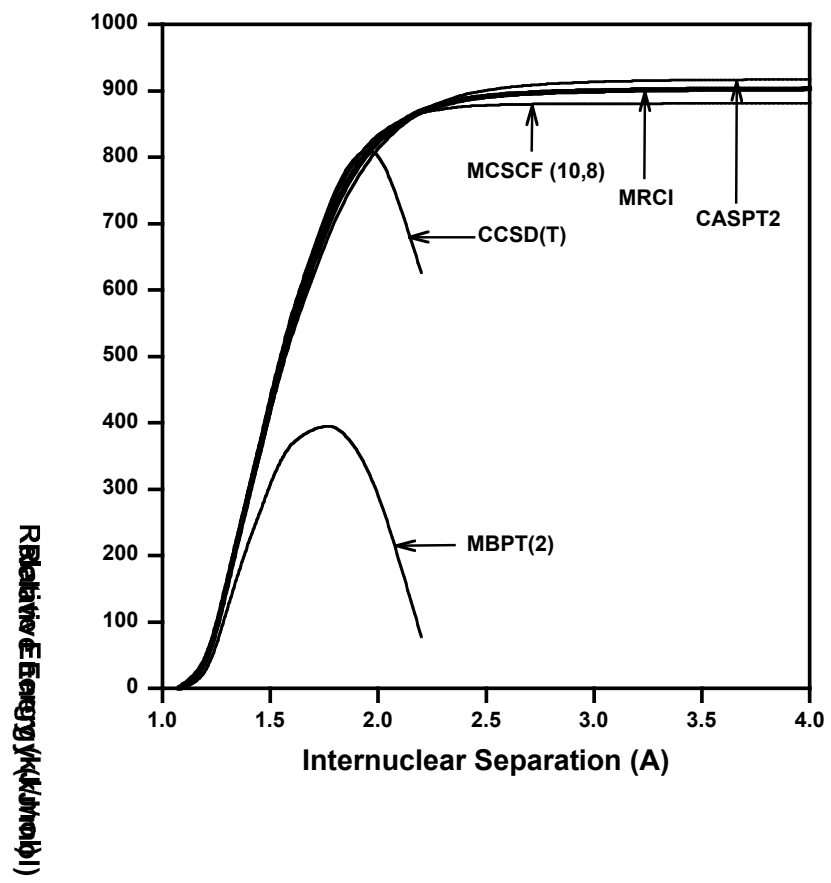
- There are 2 equally weighted configurations

- 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)
 - 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**
 - More efficient than MRCI
 - Not usually as accurate as MRCI
 - Size consistency depends on implementation

