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 $\psi_i = \phi_i\sigma_i$
- ϕ_i = space orbital, σ_i = spin function (α,β)
- Pauli Principle requires antisymmetry:

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

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
  - ϕ_i = optimized orbital
  - ε_i = orbital energy

HARTREE-FOCK METHOD

- Consider H_2:

- The 2-electron case can be written as
- $\Psi=\phi_1(1)\phi_1(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)](2^{-1/2})=\Phi\Sigma$
- Ψ=(space function) (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 <E> 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 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
  - $\Phi = [2(1+S)]^{-1} [\Phi_{ion} + \Phi_{cov}]$
  - S = overlap integral
  - So, HF wavefunction is equal mix of covalent & ionic contributions
  - Apparently OK ~ equilibrium geometry
  - Consider behavior as R --> ∞: S--> 0
  - $\Phi \text{-->} 1/2\ [\Phi_{ion} + \Phi_{cov}]$
  - $\langle E\rangle \text{-->} 1/4\langle\Phi_{ion}+\Phi_{cov}|H|\Phi_{ion}+\Phi_{cov}\rangle$

- 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->∞, many terms -> 0:
  - $\langle E \rangle_{R\to\infty} \to 1/2[(E_{H+} + E_{H-}) + 2E_H]$

- So, the HF wavefunction gives the wrong limit as H_2 dissociates, because ionic & covalent terms have equal weights.
- Must be OK ~ R_e, since HF often gives good geometries
- HF/CBS D_e~3.64 ev. Cf., D_e(expt)~4.75 ev

VALENCE BOND METHOD

- Alternative to MO, originally called Heitler-London theory
- *Presumes a* priori that bonds are covalent:
  - $\phi_1 = 1s_A(1)1s_B(2)$; $\phi_2 = 1s_A(2)1s_B(1)$
  - $\Psi_{VB} = [2(1+S_{12})]^{-1/2}[\phi_1 + \phi_2]$; $S_{12} = \langle\phi_1|\phi_2\rangle = S_{AB}^2$
- 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., $D_e(\text{expt}) \sim 4.75$ 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:
  - $\Psi_{VB,imp} = \Psi_{VB} + \gamma\Psi_{ion} = \Psi_{cov} + \gamma\Psi_{ion}$
  - where γ = variational parameter.
  - Expect $\gamma \sim 1$ ~$R=R_e$ & $\gamma \to 0$ 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)
  - $\Psi_{MO}=\phi_1(1)\phi_1(2)$: $\phi_1=1s_A + 1s_B$
- 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)
  - $\Psi_{MO,imp} = \Psi_{MO} + \lambda\Psi_{MO}^{*} = \phi_1(1)\phi_1(2) + \lambda\phi_2(1)\phi_2(2)$
  - where λ = variational parameter
  - $|\lambda| \sim 0$ at $R = R_e$
  - -> 1 as R-> ∞
- Can easily show that
  - $\Psi_{MO,imp} = \Psi_{VB,imp}$: $\gamma = (1+\lambda)/(1-\lambda)$
- $\Psi_{MO,imp}$ is simplest MCSCF wavefunction
  - Gives smooth dissociation to H + H
  - Called TCSCF (two configuration SCF)

H_2 RHF VS. UHF

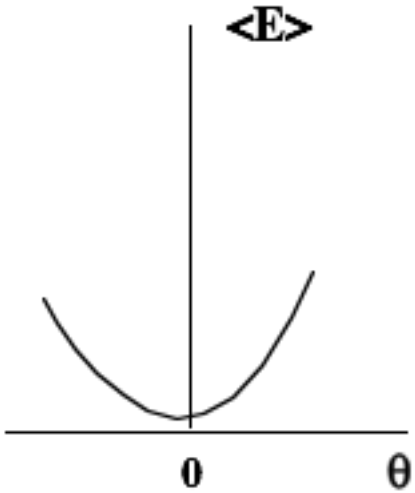
- Recall that
  - $\phi_1=[2(1+S)]^{-1/2}$ $(1s_A + 1s_B)$: bonding MO
  - $\phi_2=[2(1-S)]^{-1/2}$ $(1s_A - 1s_B)$: anti-bonding MO
- Ground state wavefunction is

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

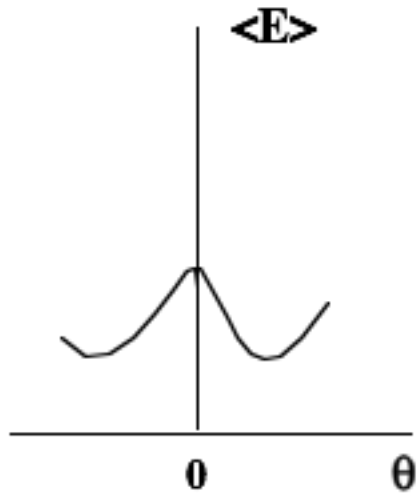
  - Ground state space function $\Phi=\phi_1(1)\phi_1(2)$
  - RHF since α,β electrons *restricted* to same MO

- Can introduce flexibility into the wavefunction by relaxing RHF restriction.
  - Define two new orbitals $\phi_1^{\alpha}, \phi_1^{\beta}$, so that
  - $\Phi_{UHF} = \phi_1^{\alpha}(1)\phi_1^{\beta}(2)$: 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:
  - $\phi_1^{\alpha} = \phi_1 \cos\theta + \phi_2 \sin\theta$ $\quad 0 \le \theta \le 45^{\circ}$
  - $\phi_1^{\beta} = \phi_1 \cos\theta - \phi_2 \sin\theta$ $\quad \theta = 0^{\circ}$: 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:



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->∞, θ-> 45°
  - 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.

Simplest way of going beyond simple RHF

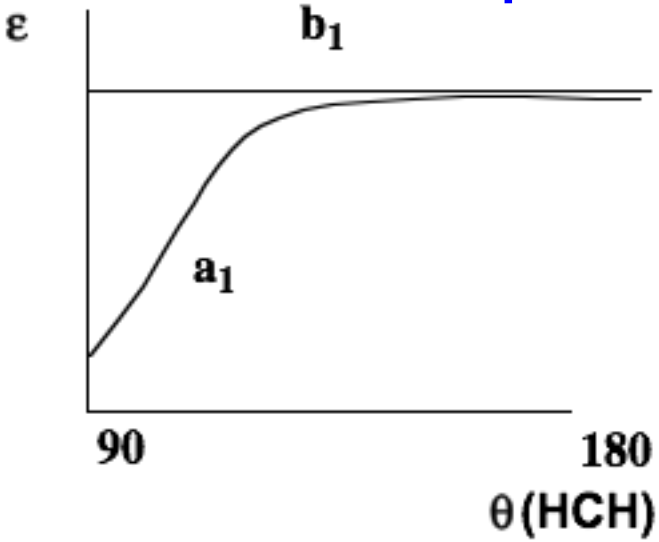
BUT: Beware spin contamination

MCSCF ACTIVE SPACES

- 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
- H_2: 2 electrons in 2 orbitals
- CH_2?

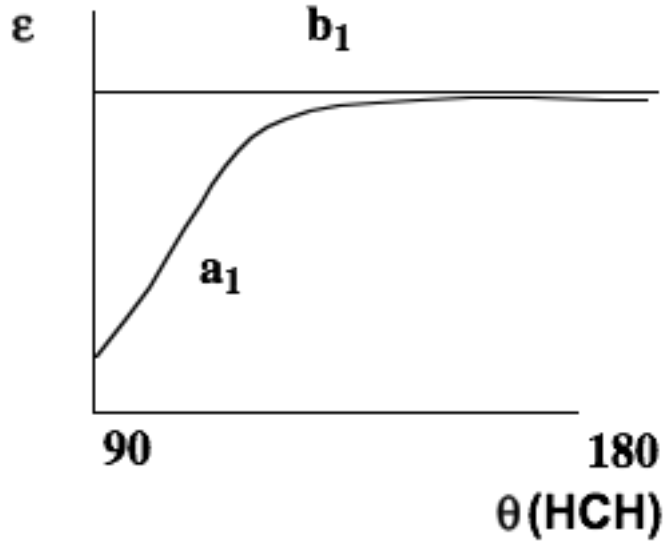
SINGLET CH_2

- 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-> 0 as θ-> 180˚
  - At θ=180˚, (a_1,b_1) become degenerate π orbital



- In CH_2, a_1=HOMO, b_1=LUMO
- At θ=90˚, N(a_1)~2, N(b_1)~0: HF OK
- At θ=180˚, (a_1,b_1) = degenerate π orbital, so

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

- There are 2 equally weighted configurations

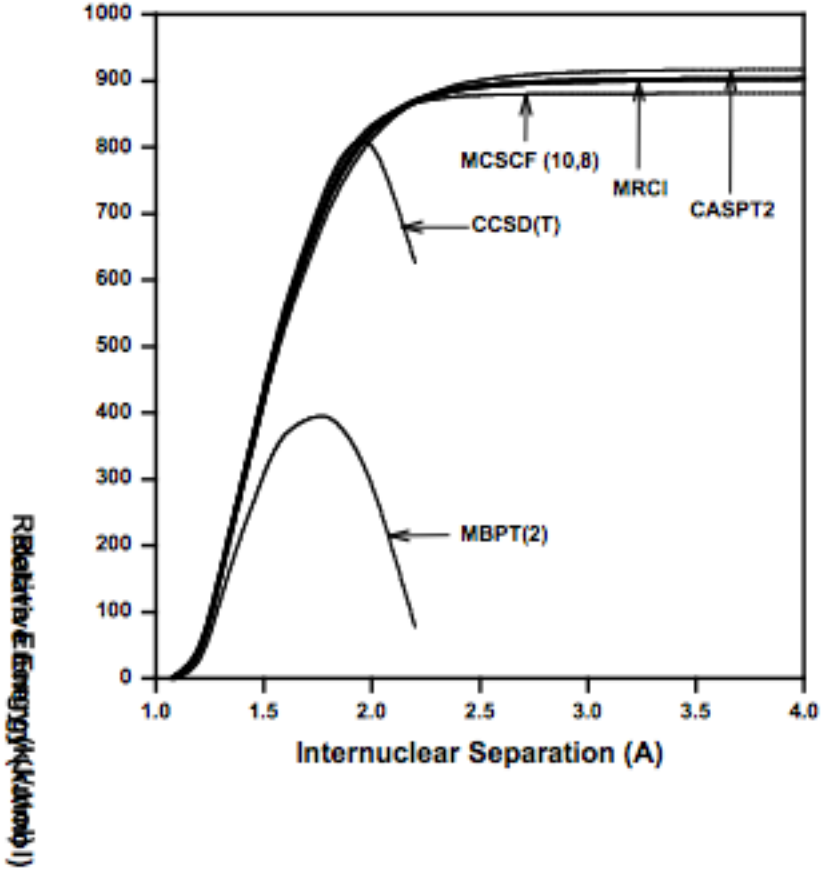
- Most general form of $^1CH_2$ wavefunction is

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

- This is a FORS or CASSCF wavefunction:
  - 2 active electrons in 2 active orbitals: (2,2)
  - At θ~90˚: C_1~1, C_2~0: NOON~2,0
  - At θ=180˚: $C_1=C_2=2^{-1/2}$: NOON~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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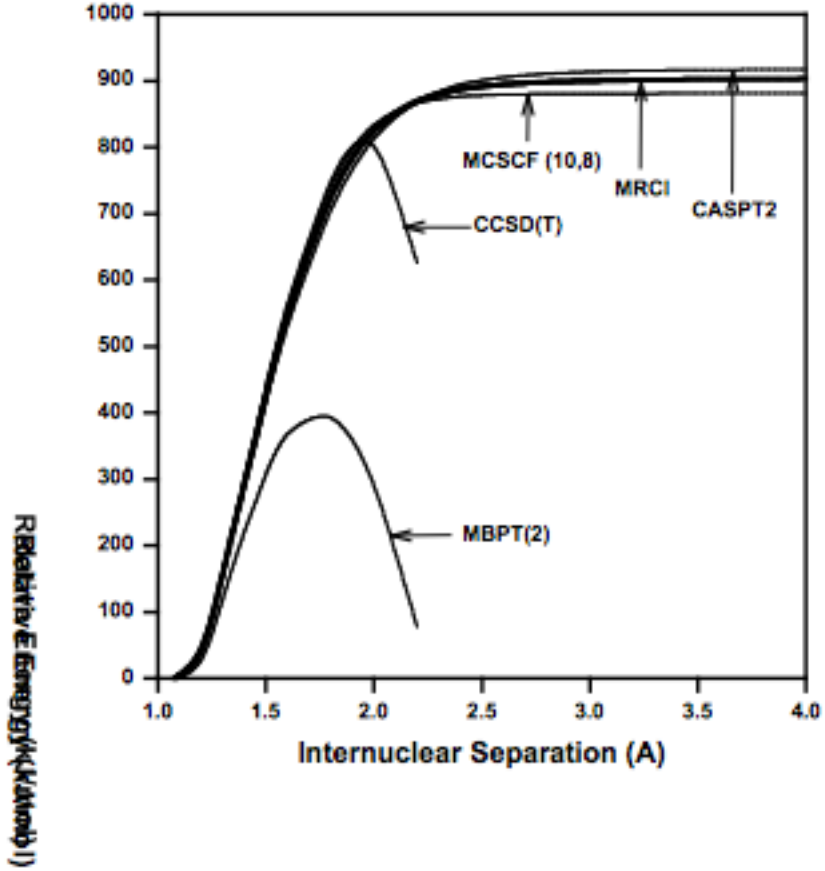
Internuclear Separation (A)
MCSCF (10,8)
MRCI
CASPT2
CCSD(T)
MBPT(2)

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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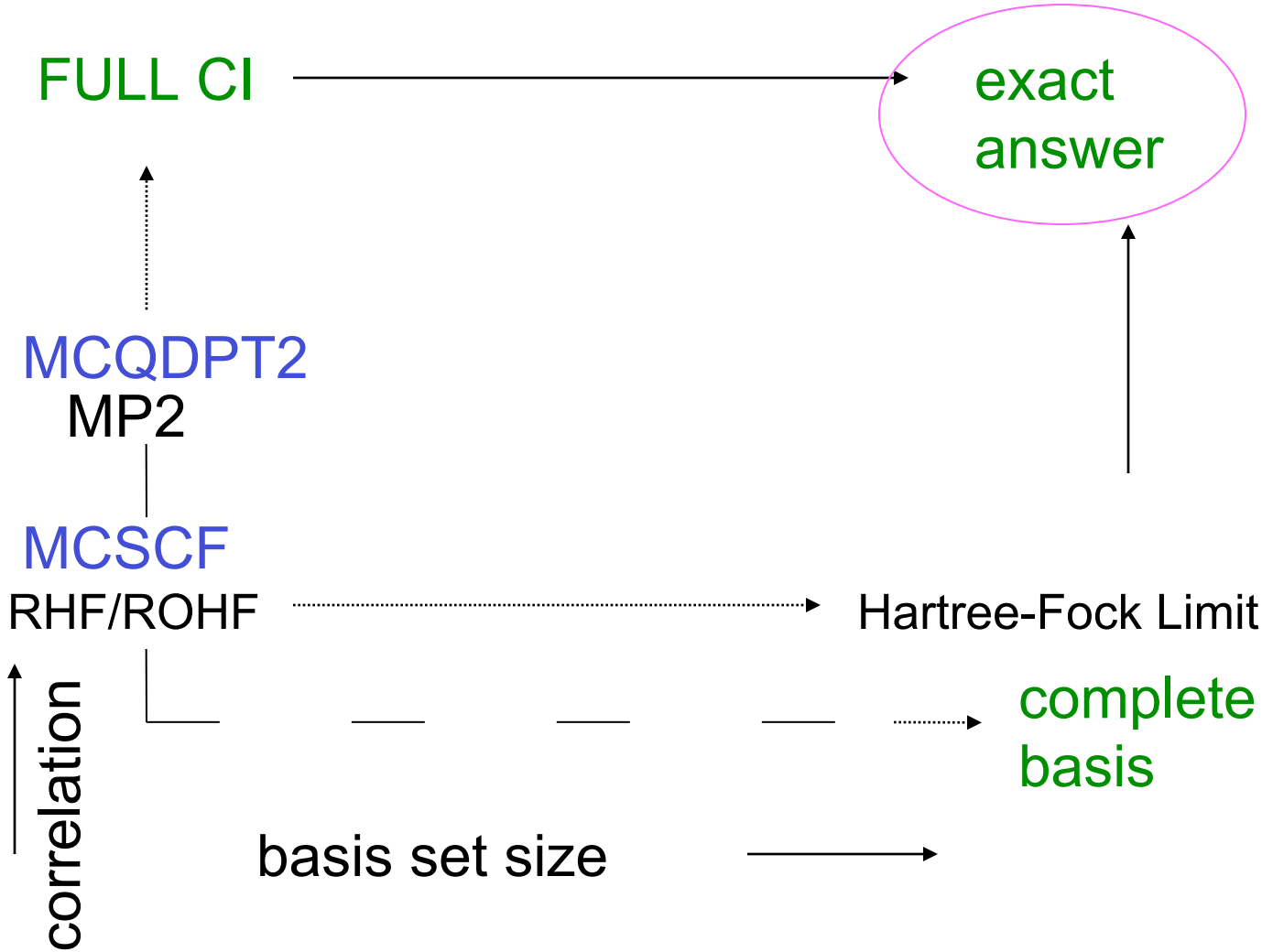
FULL CI
exact answer
MCQDPT2
MP2
MCSCF
RHF/ROHF
Hartree-Fock Limit
complete basis
correlation
basis set size