AN INTRODUCTION TO MCSCF: PART 2

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ORBITAL APPROXIMATION

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

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

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

- Closed Shells:

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

ORBITAL APPROXIMATION

- For more complex species (one or more open shells) antisymmetric wavefunction is generally expressed as a linear combination of Slater determinants
- For example, consider simple excited state represented by excitation ϕ_i->ϕ_a out of closed shell:

$$\Psi = 2^{-1/2}[|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\ldots\ \phi_i\bar{\phi}_a\ldots\ \phi_N\bar{\phi}_N| \pm |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\ldots\ \phi_a\bar{\phi}_i\ldots\ \phi_N\bar{\phi}_N|]$$

- For more complex open shell species (e.g., low-spin open shells with multiple partially filled orbitals, such as s^1d^7 Fe) wavefunctions are linear combinations of several determinants.
- But, the coefficients on these determinants are determined by spin and symmetry, not by the Variational Principle

HARTREE-FOCK METHOD

- Optimization of the orbitals (minimization of the energy with respect to all orbitals), based on the Variational Principle) leads to Hartree-Fock equations (closed shells):

$$\hat{F}\phi_i = \varepsilon_i \phi_i$$

- For open shells, there are multiple Fock operators, one for each type of orbital occupancy; e.g. UHF: $\hat{F}_\alpha, \hat{F}_\beta$

LCAO METHOD

- Generally solve HF problem by LCAO expansion: expand ϕ_i as linear combination of basis functions (AOs), χ_μ:

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i}$$

- The $C_{\mu i}$ are expansion coefficients obtained via the Variational Principle
  - **FC = SC**ε
  - HFR matrix equation, *solved iteratively*

MCSCF METHOD

- Hartree-Fock (or DFT) is most common zeroth order wavefunction, but
- Many problems are not well represented by single configuration wavefunctions:
  - Diradicals (broadly defined)
  - Excited states
  - Transition states (frequently)
  - Unsaturated transition metals
  - High energy species
  - Generally, any system with <u>near degeneracies</u>

- In such cases, the correct zeroth order wavefunction is MCSCF:

$$\Phi = \sum_K A_K \Psi_K$$

- Φ is the MCSCF wavefunction
- Ψ_K is a configuration wavefunction
  - Can be a single determinant
  - Could be a linear combination of determinants in order to be spin-correct
  - Generally called configuration state function (CSF), meaning spin-correct, symmetry-correct configuration wavefunction

$$\Phi = \sum_K A_K \Psi_K$$

- Generally, two approaches to treating Φ in computer codes:
  - Expand in terms of CSFs
    - Most commonly GUGA (graphical unitary group approach)
    - Made feasible by Shavitt, Schaefer
  - Expand directly in terms of determinants
    - Generally faster code
    - More determinants to deal with
    - Each determinant not spin-correct, but easily dealt with
    - On balance, preferred method if code is well written
    - GAMESS code written by Joe Ivanic, ~ as fast as any code
  - Both available in GAMESS

$$\Phi = \sum_K A_K \Psi_K$$

- A_K are CI expansion coefficients
  - Determined variationally using linear variation theory

$$< E > = < \Phi \mid \hat{H} \mid \Phi > = \sum_{K,L} A_K A_L < \Psi_K \mid \hat{H} \mid \Psi_L >$$

$$\partial < E > / \partial A_K = 0, \cdots$$

$$HA = AE$$

- Solution of this (non-iterative) matrix eigenvalue equation yields
  - MCSCF energies E_M for each electronic state
  - CI coefficients A_{KM} corresponding to state M

MCSCF METHOD

- Solution of MCSCF problem requires two sets of iterations to solve for two sets of coefficients
  - For each set of CI coefficients A_K, solve for LCAO coefficients $C_{\mu i}$ (micro-iterations)
  - For given set of $C_{\mu i}$, solve CI equations for new A_K
  - Continue until self-consistency

MCSCF METHOD

- Most common implementation is FORS (fully optimized reaction space)/CASSCF (complete active space) SCF
  - Define active space in terms of orbitals and electrons
  - Perform full CI within active space
  - Very “chemical” approach
  - Can be computationally demanding
    - Ideal active space is full valence
    - Not always feasible; upper limit is (16,16)
  - Sometimes tricky to choose active space

- Two sets of coefficient optimizations
  - CI coefficients optimized by solving linear variation secular equation
  - Orbital optimization analogous to, but more complex than, simple HF solutions
    - Need to optimize mixing between sets of subspaces:core, active, virtual
      - Core-active
      - Active-virtual
      - Core-virtual
    - Cf., HF high-spin open shell: Fock operators for
      - Doubly occupied-singly occupied
      - Doubly occupied-virtual
      - Singly occupied virtual

- Orbital optimizations
  - As for HF, each subspace invariant to internal mixing
  - Only mixing between subspaces will change energy
  - **Exception**: if MCSCF is not FORS/ CASSCF (CI is not Full CI), must also optimize active-active mixing:
    - FORS simpler although more demanding computationally
    - Non-FORS less robust, more difficult to converge
  - Can think of optimization variables as rotation angles connecting orbitals in different subspaces (recall UHF)

- Orbital optimizations
  - Taylor expansion of orbital gradient
    - $g(x) = E'(x) = g(x_0) + g'(x_0)\cdot(x-x_0) + \cdots$
    - $g' = E''$ = orbital hessian - second derivative of energy wrt orbital rotations x. So, at optimal E
    - $E'(x) = 0 = E'(x_0) + E''(X_0)\cdot(x-x_0)$, ignoring higher order terms. Rearranging,
    - $x = x_0 - E'(x_0)/E''(x_0)$: Newton-Raphson equation
    - In many dimensions, x is vector
  - Completely analogous to geometry opt
  - Exact calc of orbital hessian (FULLNR=.T.)
    - Takes much more AO to MO 4-label integral transformation time (need 2 virtual indices as in [vo|vo], v = virtual, o = occupied
    - More memory required

- As in geom opt, alternative to FULLNR is approximate updating of orbital hessian
  - SOSCF=.T.: calc diagonal, guess off-diagonal
  - Takes more iterations, but less time.
  - Convergence less robust
  - Easily can do 750 basis functions on workstation
- Alternatives are
  - JACOBI: simple pairwise rotations, similar to SCFDM
  - FOCAS: uses only orbital gradients, not even diagonal hessian elements as in SOSCF. Each iteration is faster, but many more required
- Best strategy
  - Start with SOSCF
  - Use FULLNR as backup

CHOOSING ACTIVE SPACES

- Full valence active space
  - Occupied orbitals are usually easy: choose all of them.
  - Virtual orbitals not always easy:
    - # of orbitals wanted = minimal valence basis set
    - # of available virtuals generally much larger
    - Virtuals are generally more diffuse and not easy to identify, especially with
      - Large basis sets
      - Transition metals
      - High symmetry

- Strategies for full valence active space
  - MVOQ in $SCF
    - Since virtual MOs are typically diffuse, ease of identification is improved if they are made more compact
    - MVOQ = n removes n electrons from SCF calculation
    - Generates a cation with +n charge - pulls orbitals in
    - Easier to find correct virtuals for active space
    - Improved convergence

- Strategies for full valence active space
  - Localized orbitals (LMOs)
    - Specify LOCAL=BOYS or RUDNBERG in $CONTRL
    - Transforms orbitals to bonds, lone pairs
    - Easier to understand occupied FV space
    - Can use these to construct virtual part of FV active space
    - Disadvantage: LMOs destroy symmetry, so the size of the problem (# of determinants) increases
    - Partial solution: symmetry localized orbitals can be specified using SYMLOC=.T. in $LOCAL
      - Localizes orbitals only within each irrep
      - Sometimes not localized enough

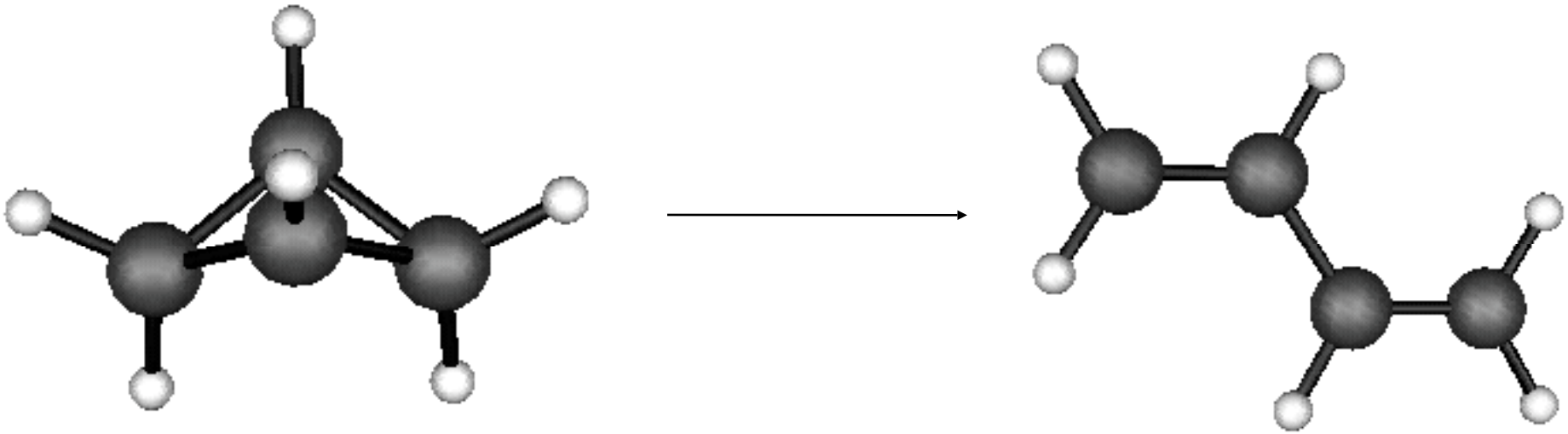
- Strategies for less than FV active space
  - Need to identify “chemically important” orbitals
    - Orbitals directly involved in the chemical process
    - Orbitals that may interact strongly with reacting orbitals
  - Examples
    - Recall H_2:
      - Active space includes H-H bonding orbital and H-H*
      - FORS(2,2): 2 electrons in 2 orbitals
    - Internal rotation in ethylene
      - FV active space is (12,12)
      - Minimum active space includes only CC $\sigma,\pi,\pi*,\sigma*$: (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

– More Examples

- Internal rotation in $H_2C{=}NH$
  - Start with analogous active space to ethylene: CN (4,4)
  - Recognize that N lone pair will interact with π system as internal rotation takes place
  - Add N lone pair to active space: (6,5), 6 electrons in 5 orbitals
  - Also correctly describes dissociation to H_2C + NH: NH fragment will be correctly described by $\sigma^2\pi_x^1\pi_y^1$
- Dissociation of $H_2C{=}O$ -> H_2C + O
  - Again, start with CO (4,4)
  - Recognize O has two lone pairs, one 2s, one 2p
  - Recognize that 2s lone pair has low energy & likely inactive
  - Including 2p lone pair [(6,5) active space] ensures three 2p orbitals are treated equally in dissociated oxygen
  - Isomerization to HCOH requires additional (4,4) from CH/OH

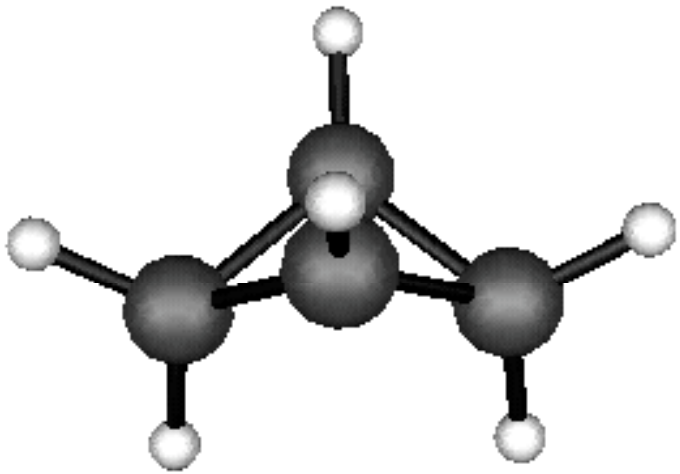
- Important to consider both reactant and product when choosing active space
  - Ensures number of active electrons & orbitals are same
  - Verifies reactant orbitals will be able to convert smoothly into product orbitals.
  - Transition state orbitals can help make this transition smooth

– Consider isomerization of bicyclobutane to 1,3-butadiene



- Superficially only need to break two bonds: FORS(4,4)
- But, to treat all peripheral bonds equally, need all of them in active space: FORS(10,10)

– Now, consider isoelectronic NO dimer, N_2O_2



- Replace two bridge CH groups with nitrogens
- Replace two peripheral CH_2 groups with oxygens
- Very high energy species: important HEDM compound
- First guess at good active space might be (10,10)
- *But*, one O lone pair on each O interacts strongly and *must* be included in active space for smooth PES
- Correct active space is (14,12)
- Pay attention to orbitals along reaction path!

MULTI-REFERENCE DYNAMIC CORRELATION

- Multi-reference CI: MRCI
  - CI from set of MCSCF configurations
  - Most commonly stops at singles and doubles
    - MR(SD)CI: Very demanding
    - ~ impossible to go past 14 electrons in 14 orbitals
- Multi-reference perturbation theory
  - Several flavors: CASPT2, MRMP2, GVVPT2
  - Mostly second order (except CASPT3)
  - More efficient than MRCI
  - Not usually as accurate as MRCI

MULTI-REFERENCE DYNAMIC CORRELATION

- MRCI, MRPT generally not size-consistent
  - +Q correction can make MRCI nearly size consistent
  - MRPT developers like to say the method is “not quite size-consistent”
  - Cf., GN methods are “slightly empirical”

STRATEGIES FOR INCONSISTENT ACTIVE SPACES

- Sometimes different parts of PES require different active spaces. Strategies
  - Optimize geometries, obtain frequencies with separate active spaces
  - Final MRPT or MRCI with composite active space
  - If composite active space is too large
    - Optimize geometries with separate active spaces
    - Use MRPT with separate active spaces to correlate all electrons

NATURAL ORBITAL ANALYSIS

- Complex wavefunctions like MCSCF are very useful, but qualitative interpretations are important
- Two useful tools are
  - Natural orbitals
  - Localized orbitals
- Natural orbitals introduced by Löwdin in 1955
  - Diagonalize the 1st order density matrix ρ
  - Simply the HF orbitals for HF theory

NATURAL ORBITAL ANALYSIS

- For fully variational methods (HF, MCSCF), 1st order density matrix is simply obtained from $\Psi\Psi^*$
- For other methods (MPn, CC, MRMP), must also calculate Hellmann-Feynman contribution: requires gradient of energy
- Eigenvectors of 1st order density matrix are natural orbitals
- Eigenvalues are natural orbital occupation numbers (NOON): λ_i

NATURAL ORBITAL ANALYSIS

- For RHF & ROHF, NOON are integers: 2,1,0
- For other methods,NOON are not integers
  - Deviation from 2 (occupied orbitals) or 0 (virtual orbitals) indicate importance of configurational mixing
  - For H_2, λ_1~2, $\lambda_2 \sim 0$ near R_e; $\lambda_1, \lambda_2 \sim 1$ near dissociation
- NOON are also good diagnostic for need for MCSCF zeroth order wavefunction
  - NOON for single reference assume non-physical values when such methods start to break down.
- Examples

Table 2. Natural orbital occupation numbers for the $^1A_1$ state of CH_2 as a function of bo each angle, the aug-cc-pVTZ/MBPT2 optimized bond length was used for all calculati optimum aug-cc-pVTZ/MBPT2 bond angle is 102.1 degrees.

Angle	Method	Principal Lone Pair NOON		non-Physical NOON
90.0	MRCI	1.896	0.077	---
	CASPT2	1.891	0.088	---
	CASSCF	1.912	0.085	---
	CCSD(T)	1.901	0.071	---
	MBPT2	1.961	0.015	-0.00003, 2.00001
102.1	MRCI	1.887	0.086	---
	CASPT2	1.885	0.094	---
	CASSCF	1.906	0.092	---
	CCSD(T)	1.894	0.077	---
	MBPT2	1.962	0.014	-0.00002, 2.00001
120.0	MRCI	1.862	0.112	---
	CASPT2	1.871	0.107	---
	CASSCF	1.894	0.105	---
	CCSD(T)	1.876	0.095	---
	MBPT2	1.961	0.015	-0.00003, 2.00000
150.0	MRCI	1.668	0.303	---
	CASPT2	1.771	0.203	---
	CASSCF	1.797	0.201	---
	CCSD(T)	1.772	0.196	---
	MBPT2	1.961	0.016	-0.00003, 2.00000
170.0	MRCI	1.104	0.865	---
	CASPT2	1.133	0.833	---
	CASSCF	1.154	0.846	---
	CCSD(T)	1.612	0.354	-0.00001
	MBPT2	1.960	0.016	-0.00003, 2.00000
180.0	MRCI	0.984	0.984	---
	CASPT2	0.982	0.982	---
	CASSCF	1.000	1.000	---
	CCSD(T)	1.572	0.394	-0.00001
	MBPT2	1.960	0.016	-0.00003, 2.00000

le 1. Natural Orbital Occupation Numbers for the N_2 Dissociation Curve

R (Å)		Natural Orbital Occupation Numbers σ	π	π*	σ*
1.078	MCSCF	1.983	1.945	0.061	0.018
	MRCI	1.964	1.924	0.071	0.021
	CASPT2	1.966	1.924	0.069	0.022
	MBPT2	1.963	1.930	0.061	0.022
	CCSD(T)	1.956	1.922	0.071	0.021
1.2	MCSCF	1.974	1.921	0.086	0.028
	MRCI	1.955	1.899	0.096	0.031
	CASPT2	1.956	1.900	0.094	0.032
	MBPT2	1.952	1.907	0.085	0.034
	CCSD(T)	1.951	1.898	0.095	0.031
1.4	MCSCF	1.951	1.862	0.145	0.052
	MRCI	1.932	1.837	0.158	0.057
	CASPT2	1.931	1.840	0.154	0.059
	MBPT2	1.918	1.847	0.149	0.066
	CCSD(T)	1.929	1.841	0.151	0.055
1.6	MCSCF	1.911	1.755	0.251	0.094
	MRCI	1.892	1.730	0.264	0.098
	CASPT2	1.887	1.732	0.260	0.103
	MBPT2	1.857	1.749	0.254	0.123
	CCSD(T)	1.895	1.735	0.255	0.091
1.8	MCSCF	1.825	1.558	0.446	0.179
	MRCI	1.817	1.545	0.446	0.174
	CASPT2	1.800	1.536	0.454	0.190
	MBPT2	1.761	1.601	0.414	0.212
	CCSD(T)	1.826	1.486	0.500	0.162
2.0	MCSCF	1.663	1.325	0.677	0.341
	MRCI	1.675	1.329	0.660	0.316
	CASPT2	1.640	1.308	0.681	0.350
	MBPT2	1.623	1.394	0.640	0.342
	CCSD(T)	1.563	1.174	0.811	0.425
2.2	MCSCF	1.480	1.176	0.825	0.522
	MRCI	1.502	1.182	0.807	0.487
	CASPT2	1.463	1.165	0.824	0.527
	MBPT2	1.442	1.128	0.939	0.519
	CCSD(T)	1.417	2.658	-.709	0.571
2.4	MCSCF	1.339	1.101	0.899	0.662
	MRCI	1.359	1.104	0.885	0.631
	CASPT2	1.326	1.094	0.896	0.665
	CCSD(T)	NONCONVERGENT			

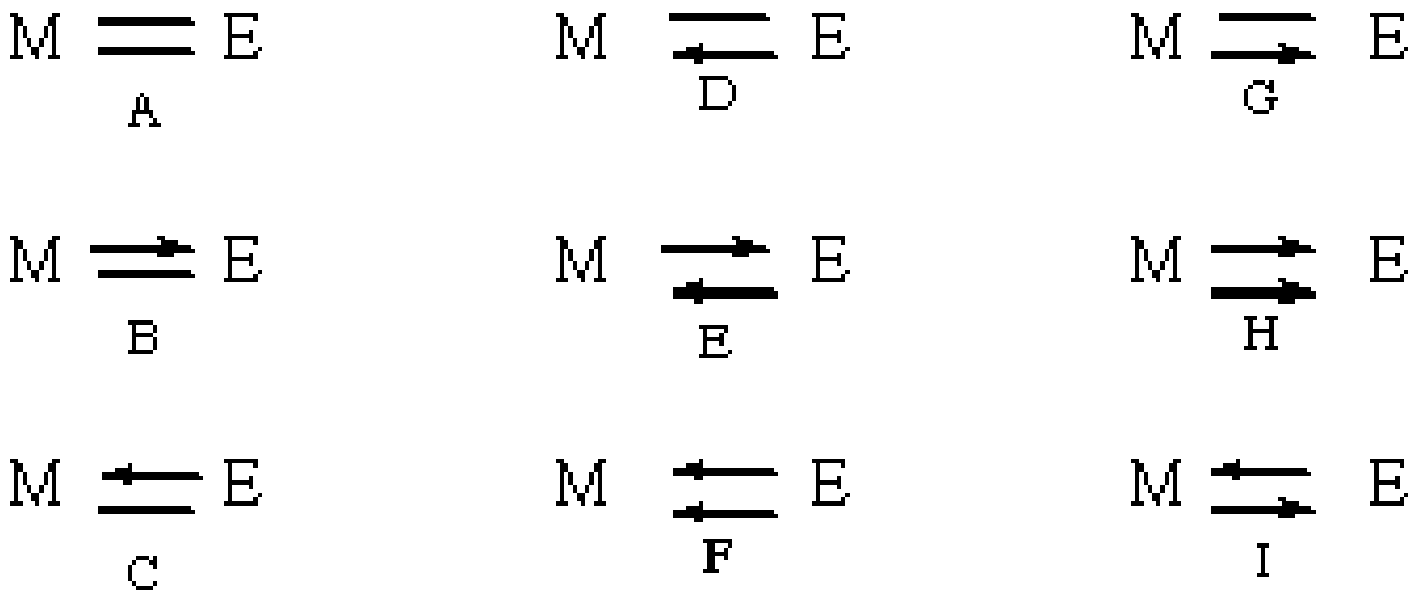
Table 1. Natural Orbital Occupation Numbers for the
ı Curve

R (Å)		Non-Physical NOON[a]
1.078	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00001
	CCSD(T)	2.00001(2)
1.2	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00001(2), -.00001
	CCSD(T)	2.00001(2)
1.4	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00001(2), -.00003, -.00076(2)
	CCSD(T)	2.00002, 2.00001
1.6	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00002(2), -.00018, -.00661(2)
	CCSD(T)	2.00002, 2.00001
1.8	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00002(2), -.00124, -.01806(2)
	CCSD(T)	2.00002, 2.00001
2.0	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.00027, 2.00002, -.00756, -.03766
	CCSD(T)	2.00001(2), -.00005(2), -.00004(2)
2.2	MCSCF	
	MRCI	
	CASPT2	
	MBPT2	2.02379, 2.00002, -.02571, -.07125

MCSCF/LMO/CI METHOD

- See Gordon&Cundari, Coord Chem Rev., *147*, 87-115 (1996)
  - Choose active space for particular bond type
  - Determine MCSCF LMOs within active space
    - These are atom-like in nature
  - Perform CI within LMO MCSCF space
  - Applied to analyze TM-MG double bonds
    - TM=transition metal (or Tom)
    - MG=main group (or Mark Gordon)

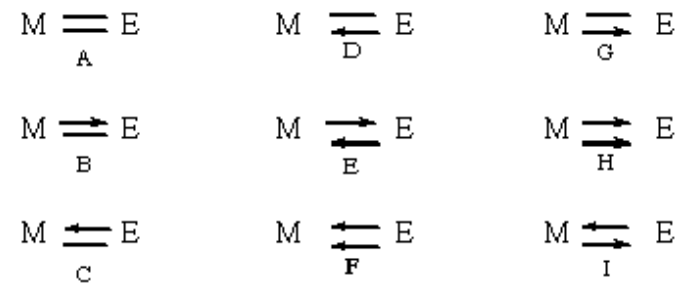
- Possible resonance contributors



  - Straight line = covalent structure, electrons shared
  - Arrow = ionic structure, both electrons on atom at base of arrow
  - Lower arrow = σ, upper arrow = π

Table 1. Percent contributors of covalent and ionic resonance structures in $H_2M{=}EH_2$ compounds. Nucleophilic structures are defined as those with M^+E^- ionicity, electrophilic means M^-E^+

	--- Ti ---		--- Zr ---		--- Nb ---		--- Ta ---	
	Si	C	Si	C	Si	C	Si	C
A	44.6	36.5	40.0	32.8	41.5	37.4	39.7	34.1
B	3.8	2.6	4.7	2.9	7.6	4.5	6.5	3.9
C	1.9	9.7	5.5	14.1	4.8	11.7	6.3	13.4
D	34.6	36.2	31.5	30.9	24.1	26.3	26.5	28.2
E	8.2	7.3	8.6	6.8	13.2	8.1	11.0	7.6
F	0.3	2.6	1.6	6.3	0.9	3.7	1.5	5.5
G	5.4	2.6	5.7	3.1	5.3	4.4	5.5	3.7
H	0.2	0.1	0.4	0.1	0.5	0.2	0.5	0.2
I	0.8	2.3	2.0	3.1	1.9	3.5	2.3	3.3
Neut.	53.6	46.1	50.6	42.7	56.0	49.0	53.0	45.0
Nucl.	36.8	48.5	38.6	51.4	29.8	41.7	35.3	47.1
Elec.	9.4	5.3	10.8	6.1	13.4	9.1	12.5	7.8



– This method 1st showed σ ylide structure

D is an important resonance contributor

NEW DEVELOPMENTS

- ORMAS (Joe Ivanic)
  - Occupation restricted multiple active spaces
  - Method for expanding size of MCSCF
    - Identify several smaller subspaces
- Eliminating deadwood from MCSCF, CI
  - Ruedenberg, Ivanic, Bytautas
  - Approaches exact Full CI
- Parallel MCSCF, CI

```
 $CONTRL SCFTYP=MCSCF RUNTYP=ENERGY NZVAR=3 COORD=ZMT $END
 $SYSTEM TIMLIM=5 MEMORY=300000 $END
 $BASIS GBASIS=STO NGAUSS=3  $END
 $DATA
        Methylene...1-A-1 state...MCSCF/STO-3G
        Cnv  2

        C
        H 1 rCH
        H 1 rCH 2 aHOH

        rCH=1.09
        aHOH=130.0
 $END
 $GUESS GUESS=MOREAD  NORB=7  $END
 $MCSCF CISTEP=GUGA  $END
 $DRT   NMCC=3 NDOC=1 NVAL=1  FORS=.T.  GROUP=C2V $END
--- RHF ORBITALS --- GENERATED AT 21:48:01 10-13-1999
        Methylene...1-A-1 state...MCSCF/STO-2G
E(RHF)=      -38.3704886597, E(NUC)=    6.1450312399,    8 ITERS
 $VEC
 1  1 9.93050334E-01 3.06416919E-02 0.00000000E+00 0.00000000E+00 7.13949414E-03
 1  2-7.56284556E-03-7.56284556E-03
 2  1-2.13664212E-01 6.49200772E-01 0.00000000E+00 0.00000000E+00 1.82338446E-01
 2  2 2.71289288E-01 2.71289288E-01
 3  1 0.00000000E+00 0.00000000E+00 5.42052798E-01 0.00000000E+00 0.00000000E+00
 3  2-4.66619722E-01 4.66619722E-01
 4  1 1.43219334E-01-6.53818237E-01 0.00000000E+00 0.00000000E+00 7.44709913E-01
 4  2 2.24175347E-01 2.24175347E-01
 5  1 0.00000000E+00 0.00000000E+00 0.00000000E+00 1.00000000E+00 0.00000000E+00
 5  2 0.00000000E+00 0.00000000E+00
 6  1 0.00000000E+00 0.00000000E+00 1.08196576E+00 0.00000000E+00 0.00000000E+00
 6  2 8.37855220E-01-8.37855220E-01
 7  1-1.69243066E-01 1.08779602E+00 0.00000000E+00 0.00000000E+00 8.71412547E-01
 7  2-9.04841898E-01-9.04841898E-01
```

```
! EXAM06.
!    1-A-1 CH2    MCSCF methylene geometry optimization.
!
!    At the initial geometry:
!    The initial energy is -37.187342653,
!    the FINAL E= -37.2562020559 after 14 iterations,
!    the RMS gradient is 0.0256396.
!
!    After 4 steps,
!    FINAL E= -37.2581791686, RMS gradient=0.0000013,
!    r(CH)=1.1243359, ang(HCH)=98.8171674
!
 $CONTRL SCFTYP=MCSCF RUNTYP=OPTIMIZE NZVAR=3 COORD=ZMT
$END
 $SYSTEM TIMLIM=5 MEMORY=300000 $END
 $BASIS GBASIS=STO NGAUSS=2  $END
 $DATA
        Methylene...1-A-1 state...MCSCF/STO-2G
        Cnv  2

        C
        H 1 rCH
        H 1 rCH 2 aHOH

        rCH=1.09
        aHOH=99.0
  $END
  $ZMAT  ZMAT(1)=1,1,2,   1,1,3,   2,2,1,3  $END
!
! Normally one starts a MCSCF run with converged SCF orbitals
$GUESS  GUESS=HUCKEL $END
!
! two active electrons in two active orbitals.
! must find at least two roots since ground state is 3-B-1
!
 $DET    NCORE=3 NACT=2 NELS=2 NSTATE=2 $END
```