AN INTRODUCTION TO MCSCF: PART 2
**ORBITAL APPROXIMATION**

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

- 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:

\[ \Psi = \hat{A}\Psi_{hp} = |\psi_1(1)\psi_2(2)...\psi_N(N)| \]

- Closed Shells:

\[ \Psi' = |\phi_1\phi_1\phi_2\phi_2...\phi_N\phi_N| \]
• 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 $\phi_i \rightarrow \phi_a$ out of closed shell:

$$\Psi = 2^{-1/2} [ \phi_1 \phi_1 \phi_2 \phi_2 \cdots \phi_i \phi_a \cdots \phi_N \phi_N \mid \pm \mid \phi_1 \phi_1 \phi_2 \phi_2 \cdots \phi_i \phi_a \cdots \phi_N \phi_N \mid]$$
• For more complex open shell species (e.g., low-spin open shells with multiple partially filled orbitals, such as s\(^1\)d\(^7\) 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):

\[ \hat{F}\phi_i = \epsilon_i \phi_i \]

- 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 $\phi_i$ as linear combination of basis functions (AOs), $\chi_\mu$:

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

• The $C_{\mu i}$ are expansion coefficients obtained via the Variational Principle
  – $FC = SC_\varepsilon$
  – 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 near degeneracies
In such cases, the correct zeroth order wavefunction is MCSCF:

$$\Phi = \sum_k A_k \Psi_k$$

- $\Phi$ is the MCSCF wavefunction
- $\Psi_k$ 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
Generally, two approaches to treating $\Phi$ 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
  - Can be faster code
  - More determinants to deal with
  - Each determinant not spin-correct, but easily dealt with
  - Not as robust: GUGA code is generally preferred
  - Some applications only available for determinant code

- Both available in GAMESS

$$\Phi = \sum_{x} A_{x} \Psi_{x}$$
\[ \Phi = \sum_k A_k \Psi_k \]

- \( A_k \) are CI expansion coefficients
  - Determined variationally using linear variation theory

\[ \langle E \rangle = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{k,l} A_k A_l \langle \Psi_k | \hat{H} | \Psi_l \rangle \]

\[ \partial \langle E \rangle / \partial A_k = 0, \ldots \]

\[ HA = AE \]

- Solution of this (non-iterative) matrix eigenvalue equation yields
  - MCSCF energies \( E_M \) for each electronic state
  - CI coefficients \( A_{KM} \) corresponding to state \( M \)
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 \( \sim (16,16) \)
  - 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, especially diffuse functions
      – Transition metals
      – High symmetry
• Strategies for full valence active space
  – MVOQ in $\text{SCF}$
    • Since virtual MOs are typically diffuse, ease of identification is improved if they are made more compact
    • $\text{MVOQ} = n$ 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 H₂:
      – Active space includes H-H bonding orbital and H-H*
      – FORS(2,2): 2 electrons in 2 orbitals
    • Internal rotation in ethylene
      – Full Valence 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$_2$C=NH**
  - Start with analogous active space to ethylene: CN (4,4)
  - Recognize that N lone pair will interact with $\pi$ 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$_2$C + NH: NH fragment will be correctly described by $\sigma^2\pi_x^1\pi_y^1$

- **Dissociation of H$_2$C=O -> H$_2$C + 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, $\text{N}_2\text{O}_2$
• 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
    • ~ very difficult to go past 16 electrons in 16 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
  – Can “blow up” if perturbation is too big
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 “nearly size-consistent”
    Not really true
  - 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
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 $\rho$
- 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 non-Hellmann-Feynman contribution: requires gradient of energy

- Eigenvectors of 1st order density matrix are natural orbitals

- Eigenvalues are natural orbital occupation numbers (NOON): $\lambda_i$
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$_2$, $\lambda_1 \sim 2$, $\lambda_2 \sim 0$ 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 bond angle, the aug-cc-pVTZ/MBPT2 optimized bond length was used for all calculations. The optimum aug-cc-pVTZ/MBPT2 bond angle is 102.1 degrees.

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</table>
MCSCF/LMO/CI METHOD

  – 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 $\text{H}_2\text{M}=\text{EH}_2$ compounds. Nucleophilic structures are defined as those with $\text{M}^+\text{E}^-$ ionicity, electrophilic means $\text{M}^-\text{E}^+$.

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<th>Zr</th>
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<th>Ta</th>
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<td>12.5</td>
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</table>

This method 1st to show $\sigma$ ylide structure D is an important resonance contributor
STEPS TO RUN CASSCF

• RUN HF TO GET STARTING ORBITALS
  – Grab $vec$ group from .dat & insert in input file
• Set up MCSCF input file
$$CONTRL \textbf{SCFTYP}=\textbf{MCSCF} \ \textbf{RUNTYP}=\textbf{ENERGY} \ \textbf{MULT}=1 \ \$END$$

$$BASIS \ \textbf{GBASIS}=\textbf{N31} \ \textbf{NGAUSS}=6 \ \textbf{NDFUNC}=1 \ \$END$$

$$GUESS \ \textbf{GUESS}=\textbf{MOREAD} \ \textbf{NORB}=4 \ \$END$$

$DATA$

RHF/6-31G(d) H2

DNH  2

HYDROGEN  1.0  .0000000000  .0000000000  .3650000000

$END$


RHF/6-31G(d) H2

E(RHF)= -1.1268278242, E(NUC)= 0.7249003414, 7 ITERS

$VEC$

1 1 3.28562555E-01 2.69295789E-01 3.28562555E-01 2.69295789E-01
2 1 1.20677971E-01 1.74055284E+00-1.20677971E-01-1.74055284E+00
3 1 7.61861020E-01-6.85623406E-01 7.61861020E-01-6.85623406E-01
4 1-1.13103226E+00 1.35731210E+00 1.13103226E+00-1.35731210E+00

$END$

$DRT \ \textbf{NMCC}=0 \ \textbf{NDOC}=1 \ \textbf{NVAL}=1 \ \textbf{FORS}=\textbf{.T.} \ \textbf{GROUP}=\textbf{D2H} \ \$END$

$MCSCF \ \textbf{CISTEP}=\textbf{GUGA} \ \textbf{FORS}=\textbf{.T.} \ \$END$
H$_2$ LOG FILE
$CONTRL SCFTYP=MCSCF RUNTPY=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
    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
$END
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
“ALTERNATIVES” TO MCSCF

• SINGLE REFERENCE METHODS
  – Spin-Flip: Anna Krylov
  – Completely renormalized CCSD(T): Piecuch
    • Adds a denominator to CCSD(T) that permits correct single bond breaking
    • Potentially huge impact: Treats diradicals correctly
    • Open or closed shells
    • CCTYP=CR-CCL in GAMESS
RECENT DEVELOPMENTS

- ORMAS (Joe Ivanic)
  - Occupation restricted multiple active spaces
  - Method for expanding size of MCSCF
    - Identify several smaller subspaces
    - Also ORMAS-PT2

- Eliminating deadwood from MCSCF, CI
  - Ruedenberg, Ivanic, Bytautas
  - Extrapolate to complete basis set
  - Interpolate to exact Full CI
  - Allows full CI on much larger systems

- Parallel MCSCF, CI