AN INTRODUCTION TO MCSCF: PART 2
\( \Psi_{hp} = \psi_1(1)\psi_2(2)\ldots\psi_N(N) \)

- Hartree product (hp) expressed as a product of spinorbitals \( \psi_i = \phi_i\sigma_i \)
- \( \phi_i = \text{space orbital, } \sigma_i = \text{spin function } (\alpha, \beta) \)
- Pauli Principle requires antisymmetry:

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

- Closed Shells:

\[
\Psi = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\ldots\phi_N\bar{\phi}_N |
\]
• 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:

$$\Psi = 2^{-1/2} \left[ | \phi_1 \phi_1 \phi_2 \phi_2 \cdots \phi_i \phi_a \cdots \phi_N \phi_N | \pm | \phi_1 \phi_1 \phi_2 \phi_2 \cdots \phi_a \phi_i \cdots \phi_N \phi_N | \right]$$
• 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):

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

• 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 $\phi_i$ 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
  
  – $FC = SC\epsilon$
  – HFR matrix equation, solved iteratively
• 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
\[ \Phi = \sum_{K} A_K \Psi_K \]

- 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
    - 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 such code
- Both available in GAMESS
\[ \Phi = \sum_{K} A_K \Psi_K \]

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

\[ <E> = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{K,L} A_K A_L \langle \Psi_K | \hat{H} | \Psi_L \rangle \]

\[ \frac{\partial <E>}{\partial A_K} = 0, \ldots \]

\[ HA = AE \]

- Solution of this (non-iterative) matrix eigenvalue equation yields
  - MCSCF energies \( E_M \) for each electronic state
  - CI coefficients \( A_{KM} \) corresponding to state \( M \)
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
    • \( g(x) = E'(x) = g(x_0) + g'(x_0) \cdot (x-x_0) + \cdots \)
    • \( g' = E'' = \text{orbital hessian} \) - 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 \([vo|vo]\), \( v = \text{virtual}, o = \text{occupied} \))
    • 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$_2$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, N₂O₂
• 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
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
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): $\lambda_i$. 
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$_2$, $\lambda_1 \sim 2$, $\lambda_2 \sim 0$ 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. At each 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 = $\sigma$, upper arrow = $\pi$
Table 1. Percent contributors of covalent and ionic resonance structures in H₂M=EH₂ compounds. Nucleophilic structures are defined as those with M\(^+\)E\(^-\) ionicity, electrophilic means M\(^-\)E\(^+\).

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Zr</th>
<th>Nb</th>
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<td>37.4</td>
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<td>8.1</td>
<td>8.1</td>
<td>7.6</td>
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<tr>
<td>I</td>
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<td>0.9</td>
<td>0.9</td>
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<td>35.3</td>
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<td>Elec.</td>
<td>9.4</td>
<td>10.8</td>
<td>13.4</td>
<td>12.5</td>
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</table>

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
  Cn 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 1.00000000E+00 0.00000000E+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