Multireference Methods

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Quantum Chemical Methods

Figure: From Sergey A. Varganov
What is still missing?

- Bond breaking
  - Including transition states

- Excited states
  - Interactions with light

- Diradicals
  - Degenerate orbital pictures
We need multiple determinants
Separate correlation

- Dynamic correlation
  - Short range cusp conditions
  - Perturbation theories are very efficient
  - Requires large basis sets

- Static correlation
  - Degeneracies in orbitals or determinants
  - “chemical intuition”

- Full CI does both
  - Much too expensive
What is the Lewis structure of ozone?
What are the molecular orbitals?

- Each oxygen supplies 1s, 2s and 3 2p orbitals
- Hartree-Fock will only fill the first 12 orbitals
- The HOMO energy is -0.4810 a.u.
- The LUMO energy is -0.0299 a.u.
Ozone

- Distribute 4 electrons in the 3 $\pi$ orbitals
  - Full CI = CISD
Ozone

- Multi-configurational Self Consistent Field
  - Improve the energy by minimizing the orbitals
  - Variational

- Fully Optimized Reaction Space (FORS)
  - Complete Active Space Self Consistent Field (CAS)
  - Full CI within a “chosen” orbital space

- MCSCF does not imply CASSCF
Ozone

- CASSCF(4,3) determinants

0.864
-0.240
-0.240
-0.295
-0.159
0.159
What about the orbitals?

- Hartree-Fock orbitals have little physical meaning
  - DFT orbitals even less
  - Orbital energies may be helpful

- Determinants define electron configurations
  - Where are electrons?

- Natural orbitals have populations
  - Diagonalize the density matrix
  - $\mathbf{U}$ are orbitals and $\mathbf{n}$ are electron occupations

\[
\psi = \sum_k A_k \psi_k
\]

\[
\mathbf{P} = \psi^*\psi
\]

\[
\mathbf{PU} = \mathbf{nU}
\]
Ozone
Active space

1. RHF/UHF

2. Localize

3. *Valence Virtual Orbitals*
   - Similar options in some QC codes

4. Chemical Intuition required to make the CAS
Diels-Alder reaction

How many orbitals would we need?
- 6 $\pi$ orbitals
Smooth surfaces

- Partly intuition

- The active space and orbitals must be stable
  - Rotation within the active space: OK
  - Rotation between active and core: NO
Connecting to Spectroscopy

- **UV Absorption**
  - Higher roots of the CI matrix
    - Orbitals are optimized for the average of multiple states
  - Full valence not needed
  - Difference of two density matrices helps understand the transition
Urcail excited states

Figure 1. SA-CASSCF/cc-pVTZ dipole moments and excited-state density difference for (a) the ground state, (b) the $n-\pi^*$ excited state, and (c) the $\pi-\pi^*$ excited state. Red regions represent depletion of the ground-state density upon excitation, and blue regions represent enhanced density.

Figure: *J. Phys. Chem. A* 2011, 115, 4574
Implications for PES

Figure: http://ccmaol1.chim.unisi.it/comp-photochem/lecture3.html
Other methods

- **Restricted Active Space (RAS)**
  - Four orbital spaces: core, RAS I, II and III
  - RAS I has a minimum number of electrons
  - RAS II is the active space
  - RAS III has a maximum number of electrons
  - In Molcas

- **Occupationally Restricted Multiple Active Spaces (ORMAS)**
  - Define multiple active spaces with min and max occupations
  - In GAMESS

- Both methods extrapolate to Full CI
Dynamic correlation

- CASSCF has no dynamic correlation
  - Similar to Hartree-Fock

- MR-CISD
  - Very accurate for excitation energies
  - Still not size-consistent

- Alternatives to MR-CI expansions
  - Good for potential energy surfaces
  - MRPT, CASPT, MCQDPT
  - MRCC: Multiple types
References

http://esqc.ups-tlse.fr/11/lectures/MCMRM-1x2.pdf