The Standard Models:
Multi-Configuration SCF

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Multiconfigurational Wave Functions

Multiconfigurational Self-Consistent Field; generalization of the Hartree-Fock wave function to system dominated by more than one electronic configuration.

MCSCF method is crucial when degeneracy or near-degeneracy occur between different electronic configurations.

- Describe bond breakings
- Excited state
- Transition metal
- Open-shell system

MCSCF Concept

- Introduce as small number of (active) orbitals: ≈10–20 with occupation numbers η allowed to vary.

- Active orbitals with **occupations:** $0 \ll \eta \ll 2$

- **Select configurations** (many-particle basis states) to include.

- **OPTIMISE** the orbitals and the CI coefficients

- Simplify general MCSCF ansatz by including all configurations generated by allocating all **active electrons** to these **active orbitals**

- MCSCF optimization based on this simplification is coined as *complete active space self-consistent field* — or simply **CASSCF**

Select MCSCF Configuration Spaces

In this approach partion the MO space into three subspace containing the ***inactive, active*** and ***virtual*** orbitals.

Introduce a **small number of orbitals** (active orbitals), where the occupation are allowed to vary.

The active orbitals are those which (for some geometry) has **occupation numbers** significantly **larger than 0 and smaller than 2**.
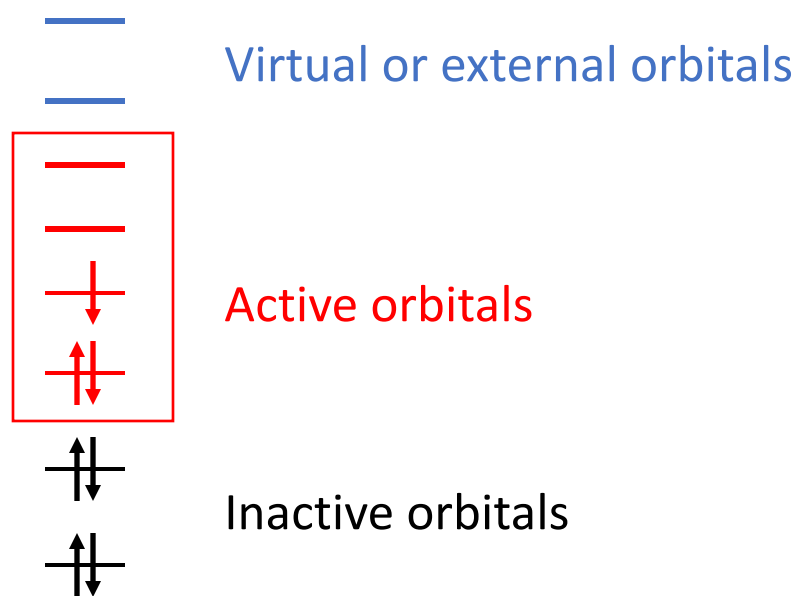
Virtual or external orbitals

Active orbitals

Inactive orbitals

MCSCF Purpose

- MCSCF **does not describe** the short-range correlation contributions that arise as $r_{12} \to 0$, that is **dynamical correlation**.

- MCSCF aims at including **non-dynamical correlation** that arises from

  ✓ configurational near-degeneracies and/or

  ✓ gross deficiencies in the RHF wave function

- Includes near-degenerate orbitals to account for **static correlation**

- **Will in general not describe the complete correlation energy!**

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Multi-reference Problem

Some molecules are not well-described by a single Slater determinant,

e.g. O_3

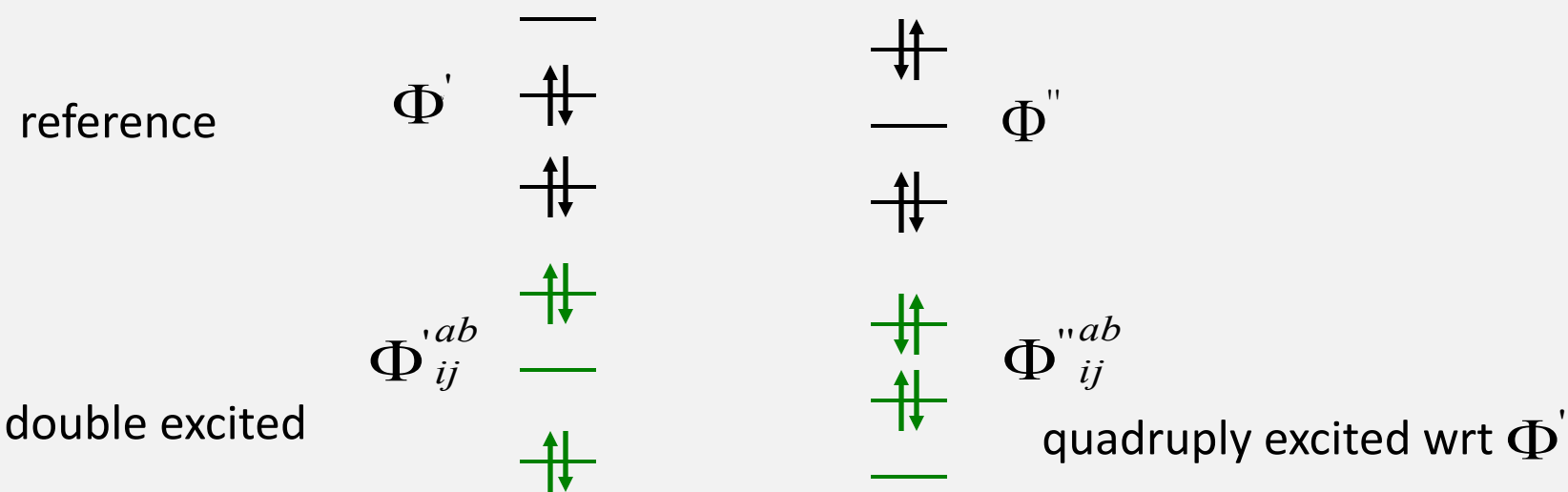
zwitterionic

biradical

Φ'

Φ''
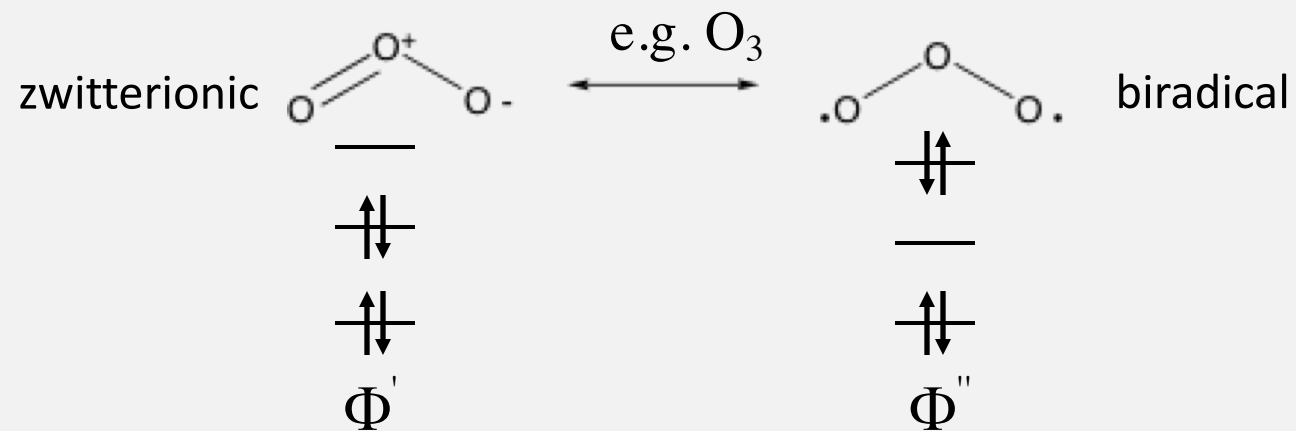
Both determinants are important for a qualitative description!
Both determinants should be used as reference in the truncated scheme!

$$\Phi_{MCSCF} = c'\Phi' + c''\Phi''$$

$$\Phi'' = \sum_{i>j,a>b} c'^{ab}_{ij} \Phi'^{ab}_{ij}$$
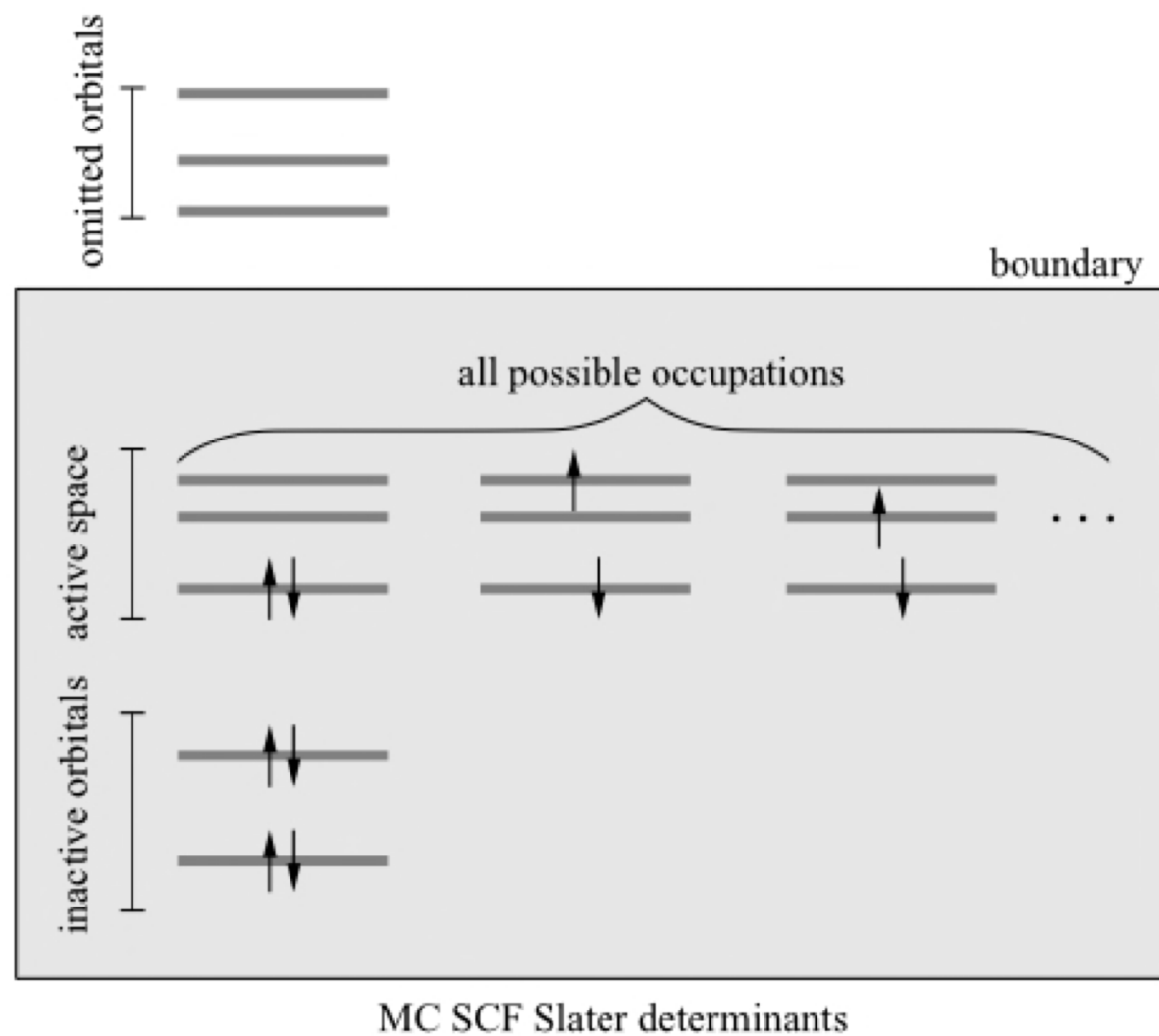
Multi Reference Configuration Interaction (MRCI)

reference Φ' $\qquad$ Φ''

double excited Φ'^{ab}_{ij} $\qquad$ Φ''^{ab}_{ij} quadruply excited wrt Φ'

$$\Phi_{MR-CISD} = c'\Phi' + c''\Phi'' + \sum_{ia} c'^{a}_{i}\Phi'^{a}_{i} + \sum_{ia} c''^{a}_{i}\Phi''^{a}_{i}$$

$$+ \sum_{i>j\,a>b} c'^{ab}_{ij}\Phi'^{ab}_{ij} + \sum_{i>j\,a>b} c''^{ab}_{ij}\Phi''^{ab}_{ij}$$

MR-CISD includes higher than double excitation wrt to Hartree-Fock!!

Complete Active Space (CAS) SCF method

MC SCF Slater determinants

Complete Active Space (CAS) SCF method

In **CASSCF** distributing the *active electrons* in all possible ways among the active orbitals: a full CI in the active space.

We still have to choose the active orbitals, but then configuration generation is automatic.

Number of configurations generated in an [n,m]-CASSCF wave function

$$CSFs = \frac{M!(M+1)!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}+1\right)!\left(M-\frac{N}{2}\right)!\left(M-\frac{N}{2}+1\right)!}$$

N number of electrons
M number of basis

n=m	Number of CSFs
2	3
4	20
6	175
8	1764
10	19404
12	226512
14	2760615

Selection of MCSCF Configuration Spaces

Usually, the greatest difficulty faced in setting up an MCSCF calculation is the selection of configuration space. (**not yet Black Box**)

Even for rather small system, it is often impossible to generate an MCSCF configuration space sufficiently flexible to describe the physical process and also to be computational tractable.

Ad hoc choices of configurations
(very useful when you already know the answer. . .)

More systematic approaches, e.g., all configurations required for proper dissociation.
Easy for diatomics, but dissociation to what in a polyatomic?

CASSCF – active orbital spaces

- Sometimes simple and intuitive like for H_2: $(\sigma_g, \sigma_u)^2 \longrightarrow CAS(2,2)$

- Ground state of N_2 requires 2p orbitals: $(\sigma_g, \pi_u, \pi_g, \sigma_u)^6 \longrightarrow CAS(6,6)$

- Picking CAS for main-group dimers can be straightforward... but does not necessarily have to be the case.

- **Transition metal** dimers are far from trivial!

- In general, including the full valence space is not an option (too many e-/o) Simple guidelines:

  - ✓ Breaking a C-H or C-C bond in a hydrocarbon $\longrightarrow$ include $(\sigma, \sigma*)^2$

  - ✓ Spectroscopy/reaction of aromatic/conjugated π-systems $\longrightarrow$ include $(\pi, \pi*)$

Choosing the Active Orbitals

The Choice of active orbitals requires an insight into electronic structure, which often rather obvious.

1) For each occupied orbital, there will typically be one corresponding virtual orbital. This leads naturally to [n,m]-CASSCF wave functions, where n and m are identical or nearly so.

2) Should include all orbitals where the occupation number changes significantly during a process (like a reaction, excitation, ionization), or where the occupation number differs significantly from two or zero.

3) Active orbital space will be different on different parts of an energy surface.

4) The orbital energies from an UHF calculation may be used for selecting the important orbitals.

Choosing the Active Orbitals

5) In the optimal case, an energy gap occurs between active orbitals, inactive and also external orbitals.

6) The natural orbitals of a UHF wave function will have partial occupation numbers, and useful to divide occupied orbitals into inactive and active.

7) running a preliminary MP2 or CISD calculation prior to the MCSCF to include some electron correlation, and obtain orbitals with non-integer occupation numbers.

8) If the underlying RHF wavefunction is poor, the MP2 correction may also give poor results, and selecting the active MCSCF orbitals based on MP2 occupation number may again lead to erroneous results.

Restricted Active Space (RAS) SCF model

RASSCF introduce several active spaces and restrict the number of electrons in each subspace in some way.

Employs five orbital subspaces instead of three:

1. Inactive orbital space

2. RAS 1 space: upper limit on the allowed number of holes.

3. RAS 2 space: no constrain on the occupation

4. RAS 3 space: upper limit on the allowed number of electrons.

5. External orbital space
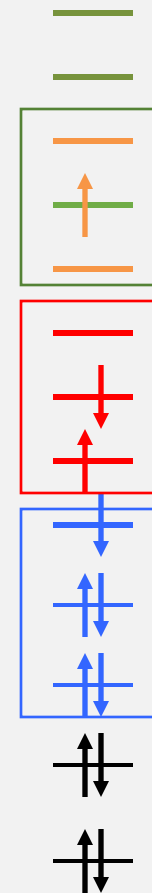
Restricted Active Space (RAS) SCF model

- Closed Shell SCF (RAS1, RAS2, RAS3 empty).

- CASSCF (RAS1 and RAS3 empty).

- SDTQ...CI with a closed shell reference function (RAS2 empty).

- Multireference SDCI with a CASSCF reference (max two holes in RAS1 and max two electrons in RAS3).

The RAS concept complicates the orbital optimization.
It is necessary to introduce orbital rotations between the three RAS spaces, which may lead to convergence problems.

Multiconfigurational Wave Functions

In MCSCF theory, the wave function is written as a linear combination of the determinants or CSFs, whose expansion coefficients are optimized simultaneously with the MOs according to the variation principle.

$$\Psi = \sum_m \Phi_m C_m \qquad \left| T, \mathbf{C} \right\rangle = \exp(-\hat{T}) \sum_m C_m \left| m \right\rangle$$

C_m are the configuration expansion coefficients

$\exp(-\hat{T})$ carries out orbital rotation in the same way as for HF wave functions

$$E_{MC} = \min_{T,C} \frac{\left\langle T, C \left| \hat{H} \right| T, C \right\rangle}{\left\langle T, C \middle| T, C \right\rangle}$$

This model allows for a highly flexible description of the electronic system.

Optimization of MCSCF Wave Functions

The Wave Function

or

$$\Psi = \sum_m \Phi_m C_m$$

$$\left|0'\right\rangle = \sum_m \left|m'\right\rangle C_m$$

The optimization problem

Determine the MOs and the MC coefficients using the variational principle

$$E = \frac{\left\langle 0'\left|\hat{H}\right|0'\right\rangle}{\left\langle 0'\middle|0'\right\rangle}$$

Optimization of MCSCF Wave Functions

Hamiltonian (Second Quantization)

$$\hat{H} = \sum_{ij} h_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl} g_{ijkl} (\hat{E}_{ij} \hat{E}_{kl} - \delta_{kj} \hat{E}_{il})$$

$$h_{ij} = \int \phi_i^*(x) \hat{h}(x) \phi_j(x) \, dx$$

$$g_{ijkl} = \int \int \phi_i^*(x_1) \phi_j(x_1) \hat{G}(x_1, x_2) \phi_k^*(x_2) \phi_l(x_2) \, dx_1 dx_2$$

are the one- and two-electron integrals.

"Excitation or generator operator" define as:

$$\hat{E}_{ij} = \hat{a}_{i\alpha}^+ \hat{a}_{j\alpha} + \hat{a}_{i\beta}^+ \hat{a}_{j\beta}$$

Optimization of MCSCF Wave Functions

Contribution from one-electron operator

One-electron operator:
$$\hat{h} = \sum_{ij} h_{ij} \hat{E}_{ij}$$

Matrix elements:
$$\langle m | \hat{h} | n \rangle = \sum_{ij} h_{ij} \langle m | \hat{E}_{ij} | n \rangle = \sum_{ij} h_{ij} D_{ij}^{mn}$$

D_{ij}^{mn} is the one-electron coupling coefficients or density matrix.

Contribution from two-electron operator

Two-electron operator:
$$\hat{g} = \tfrac{1}{2} \sum_{ijkl} g_{ijkl} (\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il})$$

Matrix elements:
$$\langle m | \hat{g} | n \rangle = \sum_{ijkl} g_{ijkl} \langle m | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | n \rangle = \sum_{ijkl} g_{ijkl} P_{ijkl}^{mn}$$

P_{ijkl}^{mn} is the two-electron coupling coefficients or density matrix.

Optimization of MCSCF Wave Functions

Total MCSCF energy

$$E = \left\langle 0 \left| \hat{H} \right| 0 \right\rangle = \sum_{ij} h_{ij} D_{ij} + \sum_{ijkl} g_{ijkl} P_{ijkl} + h_{nuc}$$

- One- and two-electron integrals h_{ij} and g_{ijkl} contain the information about the molecular orbitals (the **MO coefficients**).

- The density matrices **D** and **P** contain the information about the **CI coefficients**.

- **Energy depends** on **MOs and CI coefficients**, so these parameters to be varied.

Optimization of MCSCF Wave Functions

Parameterization:

In the classical MCSCF method we :

1. Take a **finite CI expansion** with the **fixed molecular orbital** for their construction.

2. **Calculate** the **coefficients for CSFs** by the variational method (the molecular orbitals do not change)

3. **Vary** the **MO coefficients** at the **fixed CI coefficients** to obtain the best MOs.

4. Return to point 1 until self-consistency is achieved.

Exponential Parameterization (Unitary MCSCF method):

We need two mathematical facts to present the unitary MCSCF method.

First : if $\hat{A}$ is a anti-Hermitian operator, i.e. $\hat{A}^+ = -\hat{A}$ then $\hat{U} = \exp(i\hat{A})$ is a unitary operator satisfy $\hat{U}^+\hat{U} = \hat{U}\hat{U}^+ = 1$

Second: this is the commutator expansion.

$$e^{-\hat{A}}\hat{H}e^{\hat{A}} = \hat{H} + [\hat{H},\hat{A}] + \frac{1}{2!}[[\hat{H},\hat{A}],\hat{A}] + \frac{1}{3!}[[\hat{H},\hat{A}],\hat{A}],\hat{A}] + \dots$$

MOs are orthonormal and we wish to preserve it.

Optimization of MCSCF Wave Functions

We introduce two new operators:

1) $$\hat{T} = \sum_{ij} T_{ij} \hat{a}_i^+ \hat{a}_j$$

Where T is an anti-Hermitian operator, $\hat{T}^+ = -\hat{T}$

$\hat{a}_i^+ \, and \, \hat{a}_j$ are the creation and annihilation operator, respectively.

MOs are orthonormal and we wish to preserve it therefore used unitary transformation.

We rewrite the above equation for spin-orbital:

$$\hat{T} = \sum_{ij} T_{ij} \hat{E}_{ij}$$
$$\hat{E}_{ij} = \hat{a}_{i\alpha}^+ \hat{a}_{j\alpha} + \hat{a}_{i\beta}^+ \hat{a}_{j\beta}$$

Optimization of MCSCF Wave Functions

Exponential Parameterization (Unitary MCSCF method):

The variational parameters for the CI part of the wave function could be CI coefficient C_m in the MCSCF wave function.

$$|0\rangle = \sum_m C_m |m\rangle$$

The variational of CI coefficient are made with restriction that total wave function remains normalized. $\sum_m |C_m|^2 = 1$

The problem can be solved by the complementary space $|K\rangle$ which is orthogonal to MCSCF state $|0\rangle$: $\langle 0|K\rangle = 0$

2) $\hat{S} = \sum_{K \neq 0} S_{K0} (|K\rangle\langle 0| - |0\rangle\langle K|)$ S_{K0} are variational parameters $\hat{S}^+ = -\hat{S}$

Variation describe by unitary rotation between the MCSCF state and the complementary space

unitary transformation of $|0\rangle$: $|0'\rangle = e^{\hat{S}} |0\rangle$

$|0'\rangle$ remains normalized.

Optimization of MCSCF Wave Functions

$$\left|0'\right\rangle = e^{\hat{T}} e^{\hat{S}} \left|0\right\rangle$$

- Transformation of both orbital and configuration space

- Wave function is normalized

- The parameters T and S can vary freely

- The order of operators is not arbitrary

The energy function

$$E(T,S) = \left\langle 0 \right| e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} \left| 0 \right\rangle$$

Optimization of MCSCF Wave Functions

Expand through second order in **T** and **S**

$$E = \left\langle 0' \left| \hat{H} \right| 0' \right\rangle = \left\langle 0 \left| e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} \right| 0 \right\rangle$$

$$E^{(2)}(T, S) = \left\langle 0 \left| \hat{H} \right| 0 \right\rangle = \left\langle 0 \left| [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] \right| 0 \right\rangle$$

$$+ \left\langle 0 \left| \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] \right| 0 \right\rangle$$

The optimal energy

Vary **T** and **S** such that the energy becomes

$$\frac{\partial E}{\partial T_{ij}} = 0 \qquad \frac{\partial E}{\partial S_{K0}} = 0$$

Solutions

1. The Newton Raphson method
2. Approximate /Quasi Newton methods

The Newton-Raphson method in general

Try to find a stationary point for a function E($\mathbf{p}$), where $\mathbf{p}$ is a set of parameters that can be freely varied.

Taylor expansion of the E=E($\mathbf{p}$) around a point $\mathbf{p_0}$:

We arbitrarily can put $\mathbf{p_0}$ = 0.

$$E(\mathbf{p}) = E(0) + \sum_i \left(\frac{\partial E}{\partial p_i}\right)_0 p_i + \frac{1}{2}\sum_{ij} p_i \left(\frac{\partial^2 E}{\partial p_i \partial p_j}\right)_0 p_j + \cdots$$

$$= E(0) + \mathbf{g}^+\mathbf{p} + \frac{1}{2}\mathbf{p}^+\mathbf{H}\mathbf{p} + \cdots$$

$\mathbf{g}$ is the gradient vector and $\mathbf{H}$ is the Hessian matrix

The Newton-Raphson method in general

An approximation to the stationary point is found by finding the stationary point energy truncated at the second order of $E^{(2)}$.

$$E(\mathbf{p}) \approx E^{(2)} = E(0) + \sum_i \left(\frac{\partial E}{\partial p_i} \right)_0 p_i + \frac{1}{2} \sum_{ij} p_i \left(\frac{\partial^2 E}{\partial p_i \partial p_j} \right)_0 p_j$$

$$\frac{\partial E^{(2)}}{\partial p_i} = 0 \rightarrow \mathbf{g} + \mathbf{H}\mathbf{p} = \mathbf{0} \quad (\mathbf{p} = -\mathbf{H}^{-1}\mathbf{g})$$

For this p, a new **g** and **H** is constructed, and continue until convergence.

MCSCF gradient and Hessian

Expand the exponential operators to second order

$$E^{(2)}(T, S) = \langle 0 | \hat{H} + [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] | 0 \rangle$$

First term is the zeroth order energy E(**0**,**0**).

Orbital gradient

Second term gives the first derivative with respect to T_{ij}.

$$\langle 0 | [\hat{H}, \hat{T}] | 0 \rangle = \sum_{i>j} T_{ij} \langle 0 | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle \qquad \hat{T} = \sum_{i>j} T_{ij}(\hat{E}_{ij} - \hat{E}_{ji}) = \sum_{i>j} T_{ij} \hat{E}_{ij}^-$$

$$\frac{\partial E}{\partial T_{ij}} = g_{ij}^o \qquad\qquad g_{ij}^o = \langle 0 | [\hat{H}, \hat{E}_{ij}^-] | 0 \rangle$$

The stationary requirement $g_{ij}^o = 0$ is the Extended Brillouin Theorem.

MCSCF gradient and Hessian

Expand the exponential operators to second order

$$E^{(2)}(T, S) = \left\langle 0 \middle| \hat{H} + [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] \middle| 0 \right\rangle$$

The CI gradient

Third term gives the first derivative with respect to S_{K0}.

$$\left\langle 0 \middle| [\hat{H}, \hat{S}] \middle| 0 \right\rangle = \sum_{K \neq 0} S_{K0} \left(\left\langle 0 \middle| \hat{H} \middle| K \right\rangle + \left\langle K \middle| \hat{H} \middle| 0 \right\rangle \right)$$

$$\frac{\partial E}{\partial S_K} = g_K^c \qquad\qquad g_K^c = 2 \left\langle K \middle| \hat{H} \middle| 0 \right\rangle$$

MCSCF gradient and Hessian

Expand the exponential operators to second order

$$E^{(2)}(T, S) = \langle 0 | \hat{H} + [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}| 0 \rangle$$

Second derivatives

The Hessian matrix is divided into three parts:

$$\mathbf{H} = \begin{pmatrix} \mathbf{H^{cc}} & \mathbf{H^{co}} \\ \mathbf{H^{oc}} & \mathbf{H^{oo}} \end{pmatrix}$$

Orbital-orbital part (oo)

Configuration-configuration part (cc)

CI coupling part (co)

MCSCF gradient and Hessian

Expand the exponential operators to second order

$$E^{(2)}(T, S) = \left\langle 0 \right| \hat{H} + [\hat{H}, \hat{T}] + [\hat{H}, \hat{S}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{S}], \hat{S}] + [[\hat{H}, \hat{T}], \hat{S}] \left| 0 \right\rangle$$

The Hessian part

cc block
$$H_{KL}^{(cc)} = 2\left(\left\langle K \right| \hat{H} \left| L \right\rangle - \delta_{KL} \left\langle 0 \right| \hat{H} \left| 0 \right\rangle \right)$$

oo block
$$H_{ij,kl}^{(oo)} = \left\langle 0 \right| \hat{E}_{ij}^- \hat{E}_{kl}^- \hat{H} \left| 0 \right\rangle + \left\langle 0 \right| \hat{H} \hat{E}_{ij}^- \hat{E}_{kl}^- \left| 0 \right\rangle - 2\left\langle 0 \right| \hat{E}_{ij}^- \hat{H} \hat{E}_{kl}^- \left| 0 \right\rangle$$

coupling block
$$H_{K,ij}^{(co)} = H_{ij,K}^{(oc)} = 2\left\langle K \right| [\hat{H}, \hat{E}_{ij}^- \left| 0 \right\rangle$$

MCSCF gradient and Hessian

Newton-Raphson equations in matrix form

$$\mathbf{g} + \mathbf{Hp} = \mathbf{0}$$

$$\mathbf{Hp} = \mathbf{-g}$$

$$\begin{pmatrix} \mathbf{H^{cc}} & \mathbf{H^{co}} \\ \mathbf{H^{oc}} & \mathbf{H^{oo}} \end{pmatrix} \begin{pmatrix} \mathbf{S} \\ \mathbf{T} \end{pmatrix} = -\begin{pmatrix} \mathbf{g^c} \\ \mathbf{g^o} \end{pmatrix}$$

Number of elements in **H** for medium scale calculation

- Assume: 200 orbitals, 20 occupied orbitals, 10^6 Slater determinates
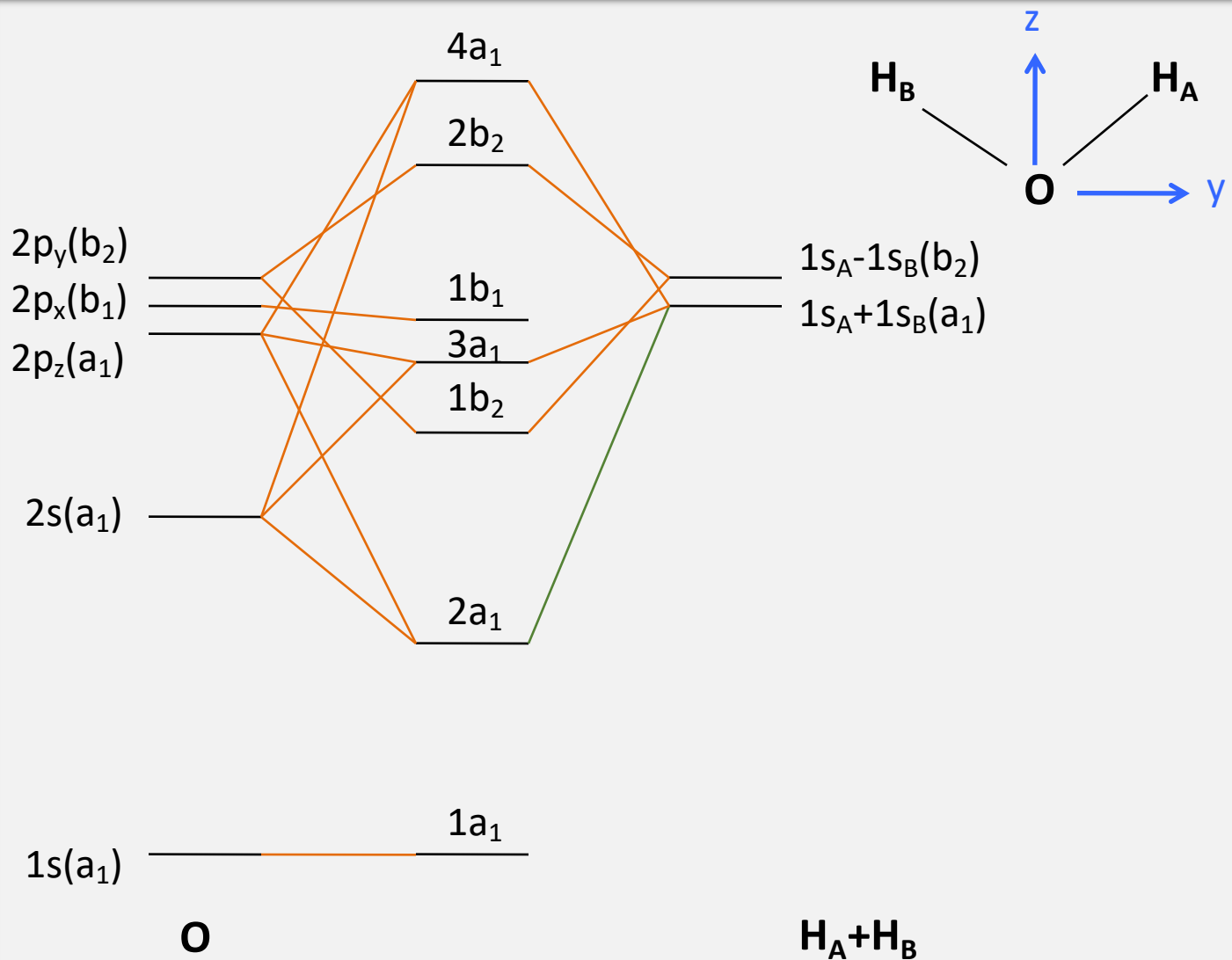- Number of orbital rotations: $20 \times 200 = 4000$

$\mathbf{H^{oo}}$: $4000 \times 4000 = 16 \times 10^6$ – not problematic
$\mathbf{H^{oc}}$: $4000 \times 10^6 = 4 \times 10^9$ – difficult to store
$\mathbf{H^{cc}}$: $10^6 \times 10^6 = 10^{12}$ – difficult to store

NOT POSSIBLE TO EXPLICITLY CONSTRUCT THE HESSIAN MATRIX

MCSCF Calculation for Dissociation of H_2O

Dissociation of H_2O into atomic fragments: O (^{3}P) and H (^{2}S).

Configuration in equilibrium region: **$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$**

Active spaces (A_1, A_2, B_1, B_2) :

(2,0,0,2): $3a_1$, $1b_2$, $4a_1$, $2b_2$ MOs needed to describe the breaking of the two OH bonds, four electron in four active orbitals.
This active space is confirmed by the FCI occupation numbers.

(2,0,1,2): insert the $2p_x$ lone-pair orbital (B_1) to have all degenerate 2p orbitals in active space, to ensure the symmetry-correct dissociation of the water.

(3,0,1,2): *valence active space,* 2s orbital excepted to interact quite strongly with 2p.
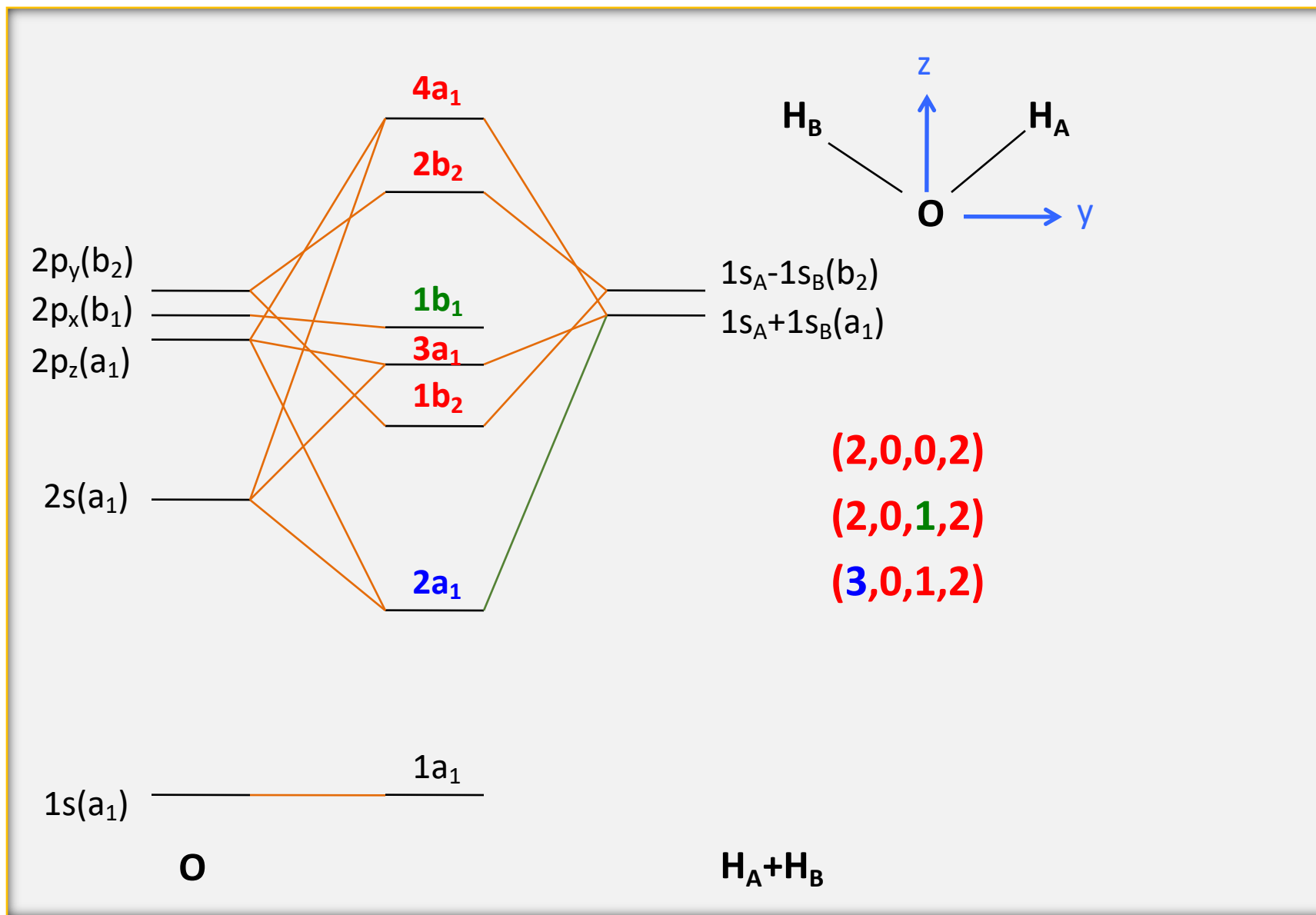
The Electronic Ground State of the Water Molecule

	$R=R_{ref}$	$R=2R_{ref}$	$R=2.5R_{ref}$	$R=8R_{ref}$
W_{HF}	0.941	0.589	0.337	0.000
[a]$\eta(1a_1)$	**1.9999**	**1.9999**	**1.9999**	**1.9999**
[b]$\eta(1a_1)$	2.0000	2.0000	2.0000	2.0000
$\eta(2a_1)$	**1.9837**	**1.9801**	**1.9806**	**1.9810**
$\eta(2a_1)$	1.9991	1.9990	1.9998	2.0000
$\eta(3a_1)$	**1.9836**	**1.5538**	**1.2270**	**1.0000**
$\eta(3a_1)$	1.9780	1.5162	1.2053	1.0000
$\eta(4a_1)$	**0.0278**	**0.4434**	**0.7680**	**0.9949**
$\eta(4a_1)$	0.0235	0.4866	0.7948	1.0000
$\eta(1b_1)$	**1.9714**	**1.9739**	**1.9758**	**1.9765**
$\eta(1b_1)$	1.9994	1.9995	1.9999	2.0000
$\eta(1b_2)$	**1.9609**	**1.6242**	**1.2995**	**1.0000**
$\eta(1b_2)$	1.9768	1.5840	1.2715	1.0000
$\eta(2b_2)$	**0.0290**	**0.3689**	**0.6957**	**0.9949**
$\eta(2b_2)$	0.0232	0.4147	0.7286	1.0000

cc-pVDZ natural orbital occupation numbers of the [a]FCI and [b]CASSCF (3,0,1,2) wavefunction

Potential energy curve of the valence CAS (3,0,1,2) and FCI wave function, and the difference between CAS and FCI energies.
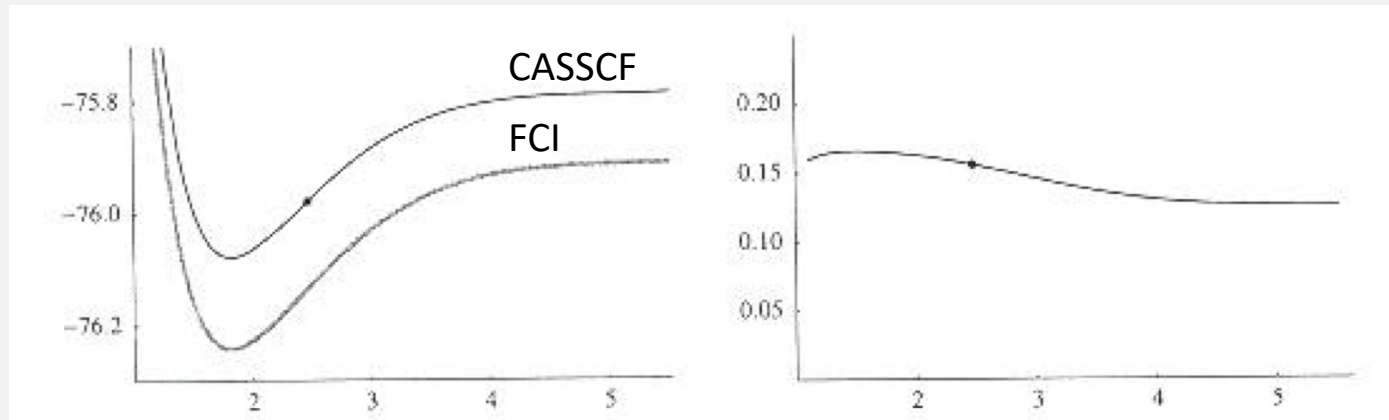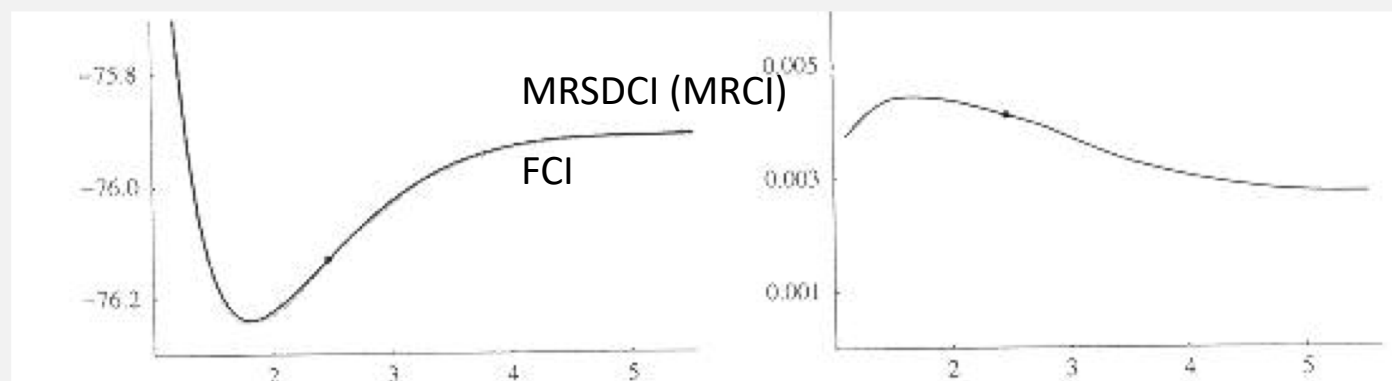

at **R_{ref}** about **25%** of correlation energy recover **(not consider dynamic correlation)**

at **$2R_{ref}$,** about **63%** of correlation energy recover, **(consider static correlation)**

the CAS error decreases somewhat at large distance, since there are fewer electrons to correlate in dissociation limit.

Multi-reference single and double CI (MRSDCI) potential energy curve.

	R=R_{ref}		R=2R_{ref}	
	E-E_{FCI}	W	E-E_{FCI}	W
RHF	0.217822	0.941	0.363954	0.589
CAS(3,0,1,2)	0.164025	0.962	0.133568	0.967
MRSDCI	0.004425	-	0.003208	-

MRSDCI error is about 40 times smaller than CAS.

CAS weight is almost constant across the surface.

By combining the truncated CI with MR, we get wave function which provide accurate approximation to FCI in all internuclear distances.

INTERESTING CHALLENGE FOR THE MCSCF TECHNIQUE

Multi-reference CI (MRCI):

Multi-reference CI method including all single and double excitations with respect to a given set of reference states.

$$\Phi_{MR-CISD} = c'\Phi' + c''\Phi'' + \sum_{ia} c_i'^a \Phi_i'^a + \sum_{ia} c_i''^a \Phi_i''^a$$

$$+ \sum_{i>j\,a>b} c_{ij}'^{ab} \Phi_{ij}'^{ab} + \sum_{i>j\,a>b} c_{ij}''^{ab} \Phi_{ij}''^{ab}$$

Accurate results can normally be obtained at least for the excitation energies.

Several difficulties connected with it:

1. large near-degeneracy effects of the excited states in the wave function: MCSCF treatment is necessary.

2. Different electronic states have in many cases differently shaped orbitals: error of using common set cannot recover by MRCI.

3. A well optimized wave function is important for the calculation of transition properties: specific calculation of orbitals more important than extensive inclusion of correlation.

4. Cannot easily extended to large system: MRCI expansion becomes excessively large.

Calculations on states that are not the lowest of their spin and spatial symmetry are more difficult …

MCSCF Theory for Several Electronic States

Important area application of the MCSCF theory is the simultaneously study of several electronic states

1. **Separate optimization of the individual states**
2. **State averaging MCSCF theory**

In order to compute excitation energies, transition moments, relative PES etc. it is required that all states involved are orthogonal.

Two possibilities:
1. choose state-selective MOs and orthonormalize the final wave function before computing properties
2. choose one set of MOs for all states

State Averaging MCSCF Theory

Simultaneous optimization all the electronic states in a common orbital basis.

Accomplish by introducing an energy function to which each electronic state contributes with a weight factor.

Orbital not optimized separately for each state, but are instead determined to minimize an average energy of all states.

The method provides directly a set of orthogonal, noninteracting electronic state.

$$|I\rangle = \sum_i C_{Ii}|i\rangle$$

$$\langle I|J\rangle = \delta_{IJ}$$

To achieve this goal

$$E_{av} = \sum_I^M w_I E_I$$

w_I Fixed numerical parameters, chosen based on physical consideration.

The only change is the replacement of the single state density matrices with average matrices.

$$E_{av} = \sum_{ij} h_{ij} \tilde{D}_{ij} + \sum_{ijkl} g_{ijkl} \tilde{P}_{ijkl}$$

$$\begin{cases} \tilde{D}_{ij} = \sum_{I}^{M} w_I D_{ij}^{I} \\ \tilde{P}_{ijkl} = \sum_{I}^{M} w_I P_{ijkl}^{I} \end{cases}$$

At least we have one set of orbitals and M CI wave function.

It is then possible the to identify the root of interest and start an MCSCF calculations for that specific root.

The average orbitals are the good starting orbitals.

If doing MCSCF calculations for the specific root
two things will be happen:

If we are lucky, root will stay in the same position relative to the other roots.
We have a set of orbitals optimized specifically for this root and a wave function with optimized CI coefficients.

If we are unlucky, *A root flipping* happen

The optimization of the orbitals for an excited state leads to a reordering of the solutions. for example we are looking for the third root. Follow the MCSCF we notice that the energy of third root drops more than that of second root.

MOs optimized
for X state

MOs optimized
for A state

46
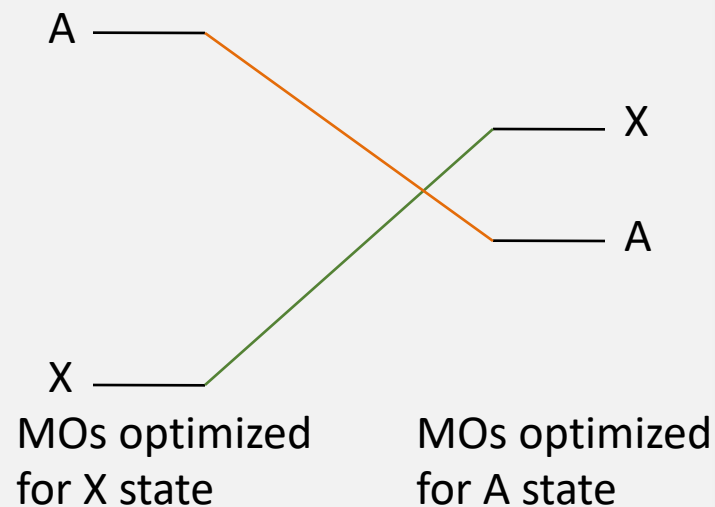
Final Comments

• In the MCSCF and CI methods it is *up to us* to decide which set of determinants we consider sufficient for the description of the system.

• In the MCSCF unlike CI the molecular orbital coefficients are not fixed and modified in such a way as to have the total energy as low as possible.

• MCSCF model allows for a highly flexible description of the electronic system where both one-electron functions (the MOs) and the N-electron function (the configurations) may adapt to the physical situation.

• the "black box" situation of HF and post-Hf applications has not yet been reached for the MCSCF theory.

• A development toward more automatic procedures are necessary if the MCSCF method is going to be widely used in chemistry.