

# Multiconfigurational and multireference methods

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# Contents of the lectures

## Wednesday, Sept. 11

- Molecular orbitals for H<sub>2</sub> using RHF and UHF
- Introduction to the MCSCF method
- The CASSCF method
- Examples of some simple CASSCF calculations
- Excited states

## Thursday, Sept. 12

- RASSCF, optimization, CASSI/RASSI

## Friday, Sept. 13

- Adding dynamic correlation

# A reminder - HF and CI

## Hartree-Fock

- Minimize the energy of one Slater determinant or a symmetry/spin-defined combination of Slater determinants
- The individual unoccupied orbitals have a limited meaning

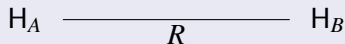
## CI: Configuration Interaction

- Expand wave function as a linear combination of Slater determinants  $|0\rangle = \sum_I C_I |SD_I\rangle$
- The orbitals are fixed
- The parameters  $C_I$  are chosen to minimize the energy
- Leads to eigenvalue problem  $HC = EC, H_{IJ} = \langle SD_I | \hat{H} | SD_J \rangle$
- If all determinants of a given basis is included, the Schrödinger equation projected on the basis is solved - full CI (FCI)

# Molecular Orbitals for H<sub>2</sub>

RHF

The molecule



Groundstate in a minimal basis: ( $1s_A, 1s_B$ )

- MOs defined by symmetry:
  - $1\sigma_g = N_g(1s_A + 1s_B)$        $1\sigma_u = N_u(1s_A - 1s_B)$ .
  - $N_g$  and  $N_u$  are normalization constants.
- Closed-shell RHF configuration  $1\sigma_g^2$ ,
  - $\Phi_{\text{RHF}} = |1\sigma_g\alpha 1\sigma_g\beta| (a_{1\sigma_g\alpha}^+ a_{1\sigma_g\beta}^+ |vac\rangle)$ .
  - “restricted HF” (RHF) wave function (proper eigenfunctions of spin and spatial operator).

# Molecular Orbitals for H<sub>2</sub>

$$\text{RHF, } \Psi = \Phi_{\text{RHF}} = |1\sigma_g\alpha 1\sigma_g\beta| \quad (a_{1\sigma_g\alpha}^+ a_{1\sigma_g\beta}^+ |vac\rangle)$$

At equilibrium

$\Phi_{\text{RHF}}$  is a good approximation to the exact wave function.

$R \rightarrow \infty$

- Correct/exact wave function:

$$\Phi_{\text{cov}} = \frac{1}{\sqrt{2}} (|1s_A\alpha 1s_B\beta| + |1s_B\alpha 1s_A\beta|)$$

- $1\sigma_g \rightarrow \frac{1}{\sqrt{2}}(1s_A + 1s_B)$

- $\Phi_{\text{RHF}} \rightarrow$

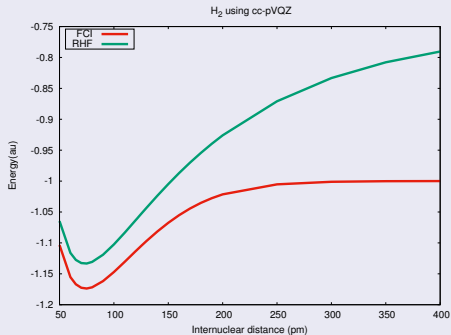
$$\frac{1}{2} (|1s_A\alpha 1s_B\beta| + |1s_B\alpha 1s_A\beta| + |1s_A\alpha 1s_A\beta| + |1s_B\alpha 1s_B\beta|),$$

- Unphysical 50:50 mixture of “covalent” and “ionic” terms.
- Consequence of the electrons in HF do not correlate the motion

# Molecular Orbitals for H<sub>2</sub>

RHF

Potential curves using RHF and FCI for H<sub>2</sub>, cc-pVQZ basis



# Molecular Orbitals for H<sub>2</sub>

## UHF

### Orbitals and wave function(Coulson and Fischer-Hjalmar)

- MOs are not symmetry adapted.
- $\psi_1 = N(1s_A + \lambda 1s_B)$ ,  $\psi_2 = N(\lambda 1s_A + 1s_B)$ .
- $\Phi_{\text{UHF}} = |\psi_1 \bar{\psi}_2|$ .
- Not an eigenfunction of  $\hat{S}^2$ .

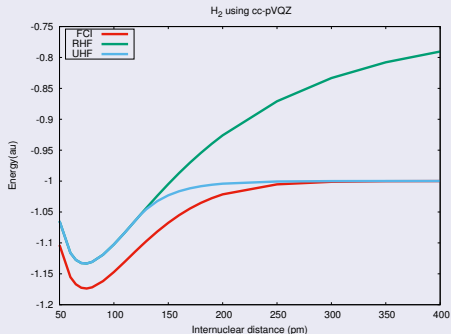
### $\lambda = ?$

- Optimize energy with respect to  $\lambda$  at each value of  $R$ .
- Near  $R_e$   $\lambda = 1$ , whereas as  $R \rightarrow \infty$ ,  $\lambda \rightarrow 0$ .
- $\Phi_\lambda$  for optimum  $\lambda$  is an example of an **unrestricted Hartree-Fock** (UHF) wave function.

# Molecular Orbitals for H<sub>2</sub>

UHF

Potential curves using UHF, RHF and FCI for H<sub>2</sub>, cc-pVQZ basis





# Molecular Orbitals for H<sub>2</sub>

## UHF

### Advantages

- Wave function and energy at dissociation: dissociates to two H atoms.
- Wave function becomes RHF wave function around equilibrium → good approximation here.

### Disadvantages

- Does not display inversion symmetry → symmetry-broken approximation.
- $\Phi_{\text{UHF}}$  is an eigenfunction of  $\hat{S}_z$  but not of  $\hat{S}^2$  → spin-broken approximation.
- Large errors in region where bonds are broken.

# The symmetry problem: to break or not to break

## Symmetry and HF

### Do worry-restrict

- Argument: symmetry-properties are important, so keep them.
- Once a symmetry property is lost, it may be hard to regain it.

### Do not worry- unrestricted

- We are making so many approximations, so why worry?
- (Life is too short for symmetry adaptation.)
- As correlation is added, symmetry will be recovered.
- Gives a very simple wave function - a single determinant.

### Projected and extended Hartree-Fock

- Project on correct symmetry (Projected HF) and perhaps reoptimize (Extended HF). Recent work by G. Scuseria.

# The symmetry problem: to break or not to break

## UHF in practice

- UHF is cheap and straightforward. Deficiencies are easy to monitor (look at  $\langle S^2 \rangle$ ).
- Doubles the number of parameters compared to RHF. Not a big problem in UHF, but increases the work in correlated calculations built on UHF.
- Loss of spin and spatial symmetries (corrected as correlation is introduced).
- Cannot do low-spin biradicals, etc.
- Cannot do general excited states.
- Possible bifurcations and non-analytic behaviour of potential curves and surfaces.

# Contents

Wednesday, Sept. 11

- Molecular orbitals for H<sub>2</sub> using RHF and UHF
- **Introduction to the MCSCF method**
- The CASSCF method
- Examples of some simple CASSCF calculations

# MCSCF

## Introduction

### The Multi configurational Self Consistent Field Method

- Introduce a small number of orbitals (active orbitals), say 10 -20, 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 two.
- Select the configurations that will be included.
- Form of wave function:  $|\tilde{0}\rangle = \sum_I C_I |\tilde{I}\rangle$  where  $|I\rangle$  are Slater determinants (ONV's) or configuration state functions.
- Optimize the orbitals and the CI coefficients  $C_I$ .

# MCSCF

## Introduction

### A choice of the configuration spaces: CASSCF

- First simplifying assumption: we will choose a subspace of the MOs, the *active space*, from which all configurations will be built.
- Then include *all* configurations generated by allocating electrons to these orbitals: a *full CI* in the active space.
- We still have to choose the active orbitals, but then configuration generation is automatic.
- A nice naive approach would be the valence AOs for all atoms, but this quickly gets very large. . .
- MCSCF optimization using this sort of *complete active space* (CAS) — a CASSCF calculation — is 'easy'

# MCSCF

## Introduction

### What can be expected from MCSCF? (correlation)

- MCSCF does not describe the short-range terms that arise as  $r_{12} \rightarrow 0$ : *dynamical correlation*.
- (Convergence of dynamical correlation in an orbital-based expansion requires huge orbital-expansions.)
- MCSCF includes the *nondynamical* (or “static”) correlation that comes from configurational near-degeneracies or from gross deficiencies in the RHF wave function.
- (Static correlation is converged if the near-degenerate orbitals are included)
- **Aims at describing part of correlation energy that changes, not the complete correlation energy**

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# The CASSCF method

## Simple to define

- Number of orbitals (per symmetry) and number of electrons in the active space.
- There is usually also a number of double occupied orbitals: inactive orbitals.

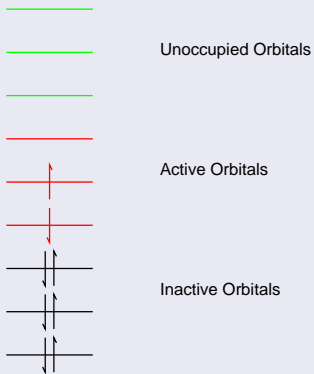
## The active orbital space

- 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.

# The CASSCF method

## The Orbital Spaces for CAS Wave Functions

### Inactive, active, and secondary orbitals



# The CASSCF method

Our H<sub>2</sub> cas

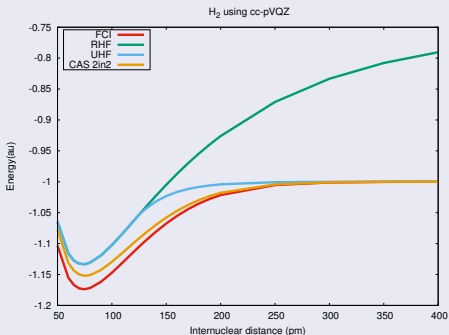
## 2 electrons in 2 active orbitals

- $\Phi_0 = c_g |1\sigma_g \overline{1\sigma_g}| + c_u |1\sigma_u \overline{1\sigma_u}|$
- Both CI coefficients and orbitals are optimized.
- 2 in 2 CAS.
- Describes wave function well both at equilibrium and at dissociation.
- Well defined spatial and spin symmetry.
- More complicated to optimize than UHF.

# The CASSCF method

Our H<sub>2</sub> cas

Potential curves using UHF, RHF, CAS 2in2 and FCI for H<sub>2</sub>,  
cc-pVQZ basis



# The CASSCF method

The size of the configuration expansion

Number of Slater determinants (aka ONV's) for 2k electrons in 2k orbitals

2	4
4	36
6	400
8	4.900
10	63.504
12	853.776
14	11.778.896
16	165.636.896
18	2.363.904.260
20	34.134.777.856
24	7.312.459.672.336

- # SD's =  $\binom{2k}{k}^2$
- For large  $k$ : # SD's =  $\frac{16^k}{k\pi}$
- Adding one Cr atom ( $2k=6$ )  $\sim$  18 years of computer development
- Standard CI: largest calc: 24 in 24, practical: 20 in 20
- DMRG and Monte Carlo CI allow larger spaces.

# The CASSCF method

## Choosing active spaces

### Simple diatomics

- Sometimes the problem seems and is simple: H<sub>2</sub> ground-state potential curve will need  $(\sigma_g, \sigma_u)^2$ , or the two 1s orbitals, as the active space.
- Bigger diatomics seem similarly easy: N<sub>2</sub> ground state will need  $(\sigma_g, \pi_u, \pi_g, \sigma_u)^6$  or the 2p orbitals.
- C<sub>2</sub> will need the 2s orbitals as well, because of the 2s/2p near-degeneracy in C atom.
- F<sub>2</sub>:  $(\sigma_g, \sigma_u)^2$  (the bonding/antibonding pair) and  $(\sigma_g, \pi_u, \pi_g, \sigma_u)^{10}$  gives only a qualitative result (bonding. . .). The 3p orbitals are needed!
- Even diatomics are not straightforward.

# The CASSCF method

## Choosing active spaces

### A bit on polyatomic molecules

- In most polyatomics, the full valence space is too large.
- Identify the orbitals involved in the process.
- Spectroscopy of C<sub>6</sub>H<sub>6</sub>: use the six  $\pi$  MOs.
- Breaking a CH or CC bond in a hydrocarbon: use  $\sigma, \sigma^*$
- May have to refine this choice (we will see how). Clearly very far from a black-box approach!

### Even larger active spaces

- More than about 20 in 20 is very demanding.
- Consider alternative expansions, RAS, GAS.
- Or alternative ways for FCI: DMRG, Monte Carlo CI.

# Contents

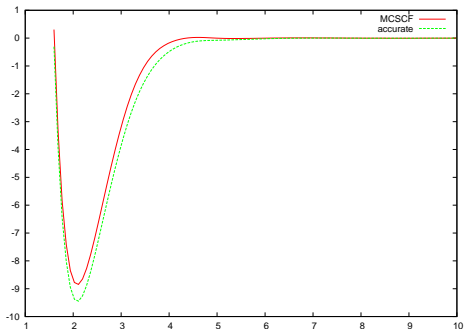
## Wednesday, Sept. 11

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# Examples of CASSCF calculations

## The N<sub>2</sub> ground state

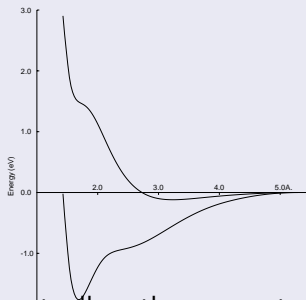


- Curves have been shifted to be identical at infinite separation.
- Qualitative, but not quantitative correct.

# Examples of CASSCF calculations

## The Cr<sub>2</sub> ground state

### MCSCF vs accurate potential curve



- Wave function is actually rather accurate..

# Examples of CASSCF calculations

N<sub>2</sub> excitation energies (eV)

	MCSCF	MCSCF(av)	accurate
${}^3\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$	7.91	7.76	7.57
${}^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$	11.36	11.15	10.32

- ${}^3\Sigma_u^+$  and  ${}^1\Sigma_g^+$  dissociate to  ${}^4S + {}^4S$ ;  ${}^1\Sigma_u^+$  dissociates to  ${}^2D + {}^2D$ .
- Differential dynamical correlation error.

# Examples of CASSCF calculations

## M(CO)<sub>n</sub> binding energies

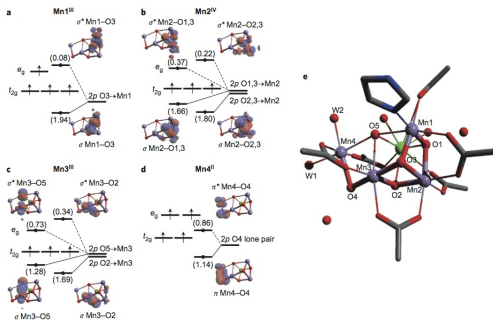
- Dissociation



- For Ni(CO)<sub>4</sub>, Fe(CO)<sub>5</sub> and Cr(CO)<sub>6</sub> CASSCF predicts very little binding (about 100 kJ/mol) compared to accurate results of 550–650.
- Bond lengths too long.
- In fact, much of the CASSCF binding comes from basis set superposition error even in very large basis sets!

# Examples of CASSCF calculations

## The Mn<sub>4</sub>O<sub>5</sub>Ca complex using DMRG



- CAS with 44 electrons in 35 orbitals
- The first detailed investigation into the bonding and oxidation states
- Yanai *et al*, Nature Chem. p 660, 5 (2013)

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# MCSCF Calculations on Excited States

Separate calculations on the individual states

## Problems

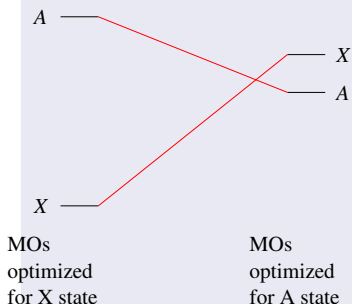
- Calculations on states that are not the lowest of their spin and spatial symmetry are more difficult. . .
  - 1 Convergence to a saddle point (normally the Hessian has  $n - 1$  negative eigenvalues in state  $n$ ).
  - 2 *Root flipping* may occur- the excited state become the lowest root in the CI
  - 3 Converged MCSCF wave functions for two roots of the same symmetry are in general not orthogonal.

# MCSCF Calculations on Excited States

Separate calculations on the individual states

## Root flipping, example: LiH

- Ground state:  $c_1 1\sigma^2 2\sigma^2 + c_2 1\sigma^2 3\sigma^2$  ( $X^1\Sigma^+$ ),  
excited state:  $1\sigma^2 2\sigma^1 3\sigma^1$  ( $A^1\Sigma^+$ ).



- Orbitals for the excited state differs very much from the ground state orbitals  $\rightarrow$  excited state becomes lowest state
- Can be handled by methods using the complete Hessian
- However, the upper energy property is lost for the excited state



# MCSCF Calculations on Excited States

## State-averaged MCSCF

### Purpose

Obtain orbitals that describe several states

### Procedure

- Introduce a (weighted) average of the energies of  $M$  states:

$$E_{aver} = \sum_{I=1}^M \omega_I E_I$$

- States will have identical orbitals- but different CI coefs.
- A standard single state program is easily modified to perform state-averaged MCSCF calculations

### Problem

- 1 MOs in different states may be *very* different!
- 2 May therefore require large active spaces

# MCSCF Calculations on Excited States

## State-averaged MCSCF

### An Example: N,V, states of C<sub>2</sub>H<sub>4</sub>

- Simplest choice  $\pi_u, \pi_g$  with two active electrons.
- N state:  $C_1(\pi_u)^2 + C_2(\pi_g)^2$
- V state:  $(\pi_u\pi_g)_{(S=0)}$
- For the ground (N) state:  $\langle \pi_g | z^2 | \pi_g \rangle = 1.69$
- For the excited (V) state:  $\langle \pi_g | z^2 | \pi_g \rangle = 9.13$
- A single  $\pi_g$  MO cannot do both jobs! At least two  $\pi_g$ -orbitals are needed (and the V state is actually more difficult than this).

# Contents

Thursday, Sept. 12

- Extensions of the CASSCF method
- Optimization of CASSCF wave functions
- The CASSI/RASSI method

# Extensions of the CASSCF method

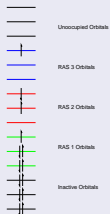
The RAS construction: Three active orbital spaces

RAS1 orbitals: Max number of holes

RAS2 orbitals:  $n_{occ}$  varies

RAS3 orbitals: Max number of electrons

Many type of CI expansions within a common framework.



# The GASSCF method

Some further developments of active spaces

## The Generalized Active Space

- Allows an arbitrary number of active orbital spaces
- Allows arbitrary types of occupation restrictions
- An American cousin is ORMAS( occupation restricted multiple active spaces)

It is all right now, in fact it is a GAS  
Jagger/Richards

# Common aspects of the RASSCF and GASSCF methods

## Advantages

- Much larger number of active orbitals may now be employed
- Expansions that are tailored a given problem may be devised
- Part of the dynamic correlation may be calculated

## Disadvantages

- Dynamic correlation is not obtained with high accuracy - an active space of valence orbitals + 1s1p1d per (light) atom recovers about 70 % of correlation energy
- Convergence of the optimization procedure is typically much slower due to strong coupling between CI and orbital changes

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# Optimization of MCSCF Wave Functions

The wave function to be optimized

- $|\tilde{0}\rangle = \sum_m |\tilde{m}\rangle c_m$

The optimization problem

- Determine the MOs and the MC coefficients using the variational principle
- $\delta E = \delta \left( \frac{\langle \tilde{0} | \hat{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle} \right) = 0$



# Optimization of MCSCF Wave Functions

The energy

## Non-Relativistic Hamiltonian (Second Quantization)

- $\hat{H} = \hat{h} + \hat{g} + h_{nuc} =$   
 $\sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} (E_{pq} E_{rs} - \delta_{qr} E_{ps}) + h_{nuc}$

## Contribution from one-electron operator

- $\langle 0 | \hat{h} | 0 \rangle = \sum_{pq} h_{pq} D_{pq}$
- $D_{pq} = \langle 0 | E_{pq} | 0 \rangle$ : The *first order reduced density matrix*.

## Contribution from the two-electron operator

- $\langle 0 | \hat{g} | 0 \rangle = \sum_{pqrs} g_{pqrs} P_{pqrs}$
- $P_{pqrs} = \frac{1}{2} \langle 0 | E_{pq} E_{rs} - \delta_{qr} E_{ps} | 0 \rangle$ : *second order density matrix*

# Optimization of MCSCF Wave Functions

## The energy

### Summary

- Total MCSCF energy from sum over occupied orbitals

$$E = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle = \sum_{pq} h_{pq} D_{pq} + \sum_{pqrs} g_{pqrs} P_{pqrs} + h_{nuc}.$$

- Can be written as summations over active orbitals

$$E = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle = \sum_{vw} F_{vw}^I D_{vw} + \sum_{vwxy} g_{vwxy} P_{vwxy} + E_{core}.$$

- The molecular orbital coefficients appear in the  $h_{pq}$  and  $g_{pqrs}$ .
- The CI coefficients appear in  $\mathbf{D}$  and  $\mathbf{P}$ .
- Energy depends on MOs  $\tilde{\varphi}$  and CI coefficients  $c$

# Optimization of MCSCF Wave Functions

## Unitary Transformation of MOs

### Exponential parameterization

- MOs are orthonormal and we wish to preserve this.
- A unitary transformation of the orbitals  $\tilde{\varphi} = \varphi \mathbf{U}$ ,  $\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$ , ensures orthonormality.
- Any unitary matrix can be written in the form.  $\mathbf{U} = \exp \mathbf{T}$  with  $\mathbf{T}^\dagger = -\mathbf{T}$ , ( $\mathbf{T}$  is anti-hermitian).
- Real MOs: *orthogonal* transformation and *antisymmetric* matrix  $\mathbf{T}^T = -\mathbf{T}$ .
- Creation operators are transformed as  $\hat{a}_p^\dagger = \exp(\hat{T}) a_p^\dagger \exp(-\hat{T})$ ,  
 $\hat{T} = \sum_{pq} T_{pq} E_{pq} = \sum_{p>q} T_{pq} (E_{pq} - E_{qp})$ .
- For CAS: only inactive  $\rightarrow$  active and secondary, active  $\rightarrow$  secondary excitations are included (nonredundant excitations).

# Optimization of MCSCF Wave Functions

## Unitary Transformation of CI vector

### An exponential ansatz for normalized expansions

- The wave function is  $|0\rangle = \sum_m |m\rangle C_m$  with  $\sum_m |C_m|^2 = 1$ .
- The *complementary space*  $|K\rangle$  is orthogonal to  $|0\rangle$ :  $\langle 0|K\rangle = 0$ .
- Define  $\hat{S} = \sum_{K \neq 0} S_{K0} (|K\rangle \langle 0| - |0\rangle \langle K|)$ .
- $S_{K0}$  are variational parameters and  $\hat{S}^\dagger = -\hat{S}$ .
- unitary transformation of  $|0\rangle$ :  $|\tilde{0}\rangle = e^{\hat{S}} |0\rangle$ .
- $|\tilde{0}\rangle$  remains normalized.

# Optimization of MCSCF Wave Functions

The wave function ansatz and energy function

$$|\tilde{0}\rangle = e^{\hat{T}} e^{\hat{S}} |0\rangle$$

## Comments

- Transformation of both orbital and configuration space.
- The operators  $\hat{T}, \hat{S}$  are antihermitian.
- Wave function is normalized.
- The parameters  $T_{pq}, p > q$  and  $S_{K0}$  can vary independently.
- Other forms are normally used..

## The energy function

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

# Optimization of MCSCF Wave Functions

The wave function ansatz and energy function

The energy function (from last slide)

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

The optimal energy

- Vary  $\mathbf{T}$  and  $\mathbf{S}$  such that the energy becomes stationary.

$$\frac{\partial E}{\partial T_{pq}} = 0 \quad \frac{\partial E}{\partial S_{K0}} = 0$$

Nonlinear set of equations

- Must be solved iteratively.
- Large arsenal of methods from numerical analysis, including
  - 1 The Newton-Raphson method.
  - 2 Approximate /Quasi Newton methods.

# Optimization of MCSCF Wave Functions

## The Newton-Raphson Optimization Method

### The Newton-Raphson method in general

- We wish to find a stationary point of a function  $E(\mathbf{p})$ , where  $\mathbf{p}$  is a set of parameters that can be freely varied.
- Start with a guess, which for simplicity here we set to zero  $\mathbf{p}_0 = \mathbf{0}$ .
- Expand  $E$  through second order around this point

$$\begin{aligned} E(\mathbf{p}) &\approx E^{(2)} = E(0) + \sum_i \left( \frac{\partial E}{\partial p_i} \right)_0 p_i + \frac{1}{2} \sum_{ij} p_i \left( \frac{\partial^2 E}{\partial p_i \partial p_j} \right)_0 p_j \\ &= E(0) + \mathbf{g}^\dagger \mathbf{p} + \frac{1}{2} \mathbf{p}^\dagger \mathbf{H} \mathbf{p} \end{aligned}$$

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

# Optimization of MCSCF Wave Functions

## The Newton-Raphson Optimization Method

### The Newton-Raphson method in general

- An approximation to the stationary point is found by finding the stationary point of  $E^{(2)}$ .
- $\frac{\partial E^{(2)}}{\partial p_i} = 0 \rightarrow \mathbf{g} + \mathbf{H}\mathbf{p} = \mathbf{0}$  ( $\mathbf{p} = -\mathbf{H}^{-1}\mathbf{g}$ )
- For this  $\mathbf{p}$ , the new  $\mathbf{g}$  and  $\mathbf{H}$  are constructed,...
- Continue until convergence:  $|\mathbf{g}| \approx 0$ .

### Comments

- Approximating  $E$  with  $E^{(2)} \rightarrow$  only valid for small  $\mathbf{p} \rightarrow$  problems far from convergence.
- Converges quadratically when  $\mathbf{p}$  is small.
- The linear equations must often be solved using iterative methods.



# Optimization of MCSCF Wave Functions

## Taylor Expansion of the MCSCF Energy

### The wave function and energy

- $|\tilde{0}\rangle = e^{\hat{T}} e^{\hat{S}} |0\rangle$
- $E = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle = \langle 0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | 0 \rangle$

### The BCH expansion for operators

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

### Expand $E$ through second order in $\hat{T}, \hat{S}$ using the BCH expansion

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

# Optimization of MCSCF Wave Functions

## Taylor Expansion of the MCSCF Energy

From last slide

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

The orbital gradient

- $\hat{T} = \sum_{p>q} T_{pq} (E_{pq} - E_{qp}) = \sum_{p>q} T_{pq} \cdot E_{pq}^-$
- $\frac{\partial E}{\partial T_{pq}} = g_{pq}^o = \langle 0 | [\hat{H}, E_{pq}^-] | 0 \rangle$
- $g_{pq}^o$  vanishes trivially for e.g. inactive-inactive excitations.

The Extended Brillouin Theorem for CASSCF wave functions

- For the adjoint of a non-redundant rotations  $E_{qp} | 0 \rangle = 0$ , so  $g_{pq}^o = \langle 0 | [\hat{H}, (E_{pq} - E_{qp})] | 0 \rangle = 2 \langle 0 | \hat{H} E_{pq} | 0 \rangle$ .
- At convergence the matrix elements between the wave-function and single excited states vanish.

# Optimization of MCSCF Wave Functions

## The orbital gradient

### Calculated using (yet) a Fock-matrix

- $g_{pq}^o = 2(F_{pq} - F_{qp})$ .
- Most demanding part: active(v)  $\rightarrow$  secondary(a).
- $F_{va} = \sum_w F_{wa}^I D_{vw} + \sum_{wxy} d_{vwxy} g_{awxy}$ .
- Sum is over active orbitals.
- Requires integrals with 3 active indices.
- If integrals and density-matrices are known: scales as  $N_{act}^4 N_{sec}$ .
- No problem in constructing and storing.

# Optimization of MCSCF Wave Functions

## Taylor Expansion of the MCSCF Energy

From last slide

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

The CI gradient

- $\hat{S} = \sum_{K \neq 0} S_{K0} (|K\rangle \langle 0| - |0\rangle \langle K|)$ ,  $\langle K | 0 \rangle = 0$ .
- $\frac{\partial E}{\partial S_{K0}} = g_K^c = \langle 0 | ([\hat{H}, |K\rangle \langle 0| - |0\rangle \langle K|]) | 0 \rangle = 2 \langle K | \hat{H} | 0 \rangle$
- $|K\rangle$  is orthogonal complement to  $|0\rangle$  so:  
 $\mathbf{g}^c = \mathbf{0} \rightarrow (1 - |0\rangle \langle 0|) \hat{H} | 0 \rangle = 0$ .
- $\mathbf{HC} = E\mathbf{C}$ .
- The optimal CI-coefficients constitute a solution to the standard CI eigenvalue problem.

# Optimization of MCSCF Wave Functions

## Taylor Expansion of the MCSCF Energy

From last slide

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

The Hessian: Partition into orbital (o) and CI (c) parts

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

# Optimization of MCSCF Wave Functions

## The Newton-Raphson Equations for MCSCF

### Form

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

### Number of elements in $\mathbf{H}$ for medium scale calculation

- Assume: 200 orbitals, 20 occupied orbitals,  $10^6$  SD's.
- Number of orbital rotations:  $20 \times 200 = 4000$ .

$\mathbf{H}^{oo}$ :  $4000 \times 4000 = 16 \times 10^6$  - not problematic.

$\mathbf{H}^{oc}$ :  $4000 \times 10^6 = 4 \times 10^9$  - may be stored.

$\mathbf{H}^{cc}$ :  $10^6 \times 10^6 = \times 10^{12}$  - difficult to store, (but is sparse).

Cannot be solved using standard methods like LU decomposition.

# Optimization of MCSCF Wave Functions

## Solving the Newton-Raphson Equations for MCSCF

### Form

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

- Too large to solve using standard decomposition methods.

### Make approximations and/or use iterative methods

**Iterative full second-order** Set up a scheme to calculate Hessian times vector directly.

**Decouple CI and Orbital part** Neglect orbital-configuration coupling. Construct  $\mathbf{H}^{oo}$  and solve configuration part by standard CI.

**Further approximations** Approximate  $\mathbf{H}^{oo}$ ; done in the super-CI approach.

# Optimization of MCSCF Wave Functions

## Solving the Newton-Raphson Equations for MCSCF

### Various codes

- Virtually no package offers *only* a naive NR: can switch off CI/orbital coupling, use damping techniques, etc. Diagonalization of augmented Hessian (norm-extended optimization).
- *Trust-region* approaches that offer guaranteed convergence:
  - DALTON CASSCF/RASSCF (second-order) NEO/NR, coupling.
  - MOLPRO general MCSCF (second-order+ in MOs), coupling.
- *Quasi-Newton* approaches:
  - MOLCAS CASSCF/RASSCF (No coupling, first-order+ in MOs).
- Note: Number of iterations does not indicate complexity.



# Optimization of MCSCF Wave Functions

## Excited states

- DALTON: only separate calculation on each state. Second-order procedure allows convergence to excited states.
- MOLCAS: separate calculations, or averaging over states of same spin and spatial symmetry.
- MOLPRO: separate calculations, or averaging over any mixture of states (spin, symmetry and charge can all be different).
- Averaging is often used to ensure nonabelian symmetry- (can be done in a much simpler and more efficient manner).

# Contents

Thursday, Sept. 12

- MCSCF calculations on excited states
- Extensions of the CASSCF method
- Optimization of CASSCF wave functions
- **The CASSI/RASSI method**

# RASSI/CASSI: The RASSCF (CASSCF) State Interaction Method

## Matrix elements between different XASSCF(X=C,R) states

- Assume we have obtained XASSCF wave function,  $|X\rangle$  and  $|Y\rangle$ , for two electronic states.
- To determine transitions between the states, we must calculate the the *transition moment*:  $\langle X | \hat{\mu} | Y \rangle$
- $\hat{\mu}$  is for example the dipole operator:  $\hat{\mu} = \sum_{pq} \vec{\mu}_{pq} E_{pq}$ .
- Transition matrix element is  $\langle X | \hat{\mu} | Y \rangle = \sum_{pq}^{XY} D_{pq}^{XY} \vec{\mu}_{pq}$ .
- $D_{pq}^{XY} = \langle X | E_{pq} | Y \rangle$  is a transition density matrix.

# RASSI/CASSI: The RASSCF (CASSCF) State Interaction Method

## The Nonorthogonality Problem

- The calculation of the transition density matrix is easy when the two states are described in the same MO basis.
- The same holds when the MOs are not the same but they are *biorthonormal*:  $\langle p^X | q^Y \rangle = \delta_{pq}$
- For CASSCF or RASSCF wave functions, the CI-coefficients may be counter-rotated, so a wave functions may be re-expressed in the biorthonormal basis.

# RASSI/CASSI: The RASSCF (CASSCF) State Interaction Method

The CI-transformation technique of Prof. Malmqvist

## The idea

- A CI-vector is given for a given set of orbitals
- The orbitals are now changed to a new basis
- Change the CI-coefficients so the state with transformed orbitals is identical to the original state

## Complexity of the problem

- For a pair of states, the operation count for the transformation corresponds to CI with a one-electron operator
- That is: Peanuts..

# RASSI/CASSI: The RASSCF (CASSCF) State Interaction Method

## The algorithm allows

- The computation of transition densities  $\mathbf{D}^{XY}$  and  $\mathbf{P}^{XY}$ .
- Also: overlap integrals:  $\langle A|B\rangle$  and Hamiltonian matrix elements  $\langle X|\hat{H}|Y\rangle$ .
- Allows the solution of the XAS *state interaction* secular problem 
$$\begin{pmatrix} \mathbf{H}_{XX} - E\mathbf{1} & \mathbf{H}_{XY} - E\mathbf{S}_{XY} \\ \mathbf{H}_{YX} - E\mathbf{S}_{YX} & \mathbf{H}_{YY} - E\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{c}_X \\ \mathbf{c}_Y \end{pmatrix} = 0$$
- The resulting states are orthogonal, and non-interacting through the Hamiltonian.
- Hundreds of XASSCF states can be handled.

# Contents

## Friday, Sept. 13

- Introduction to dynamic correlation
- The multi-reference CI method
- Nearly size-extensive multi-reference methods
- Perturbation theory, general and multireference methods
- CASPT2
- NEVPT2

# Introduction to Dynamical correlation

## And it is

The short-range correlation that arise as  $r_{12} \rightarrow 0$  - the Coulomb cusp.

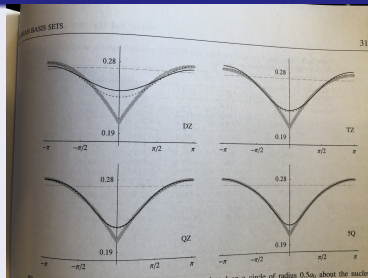
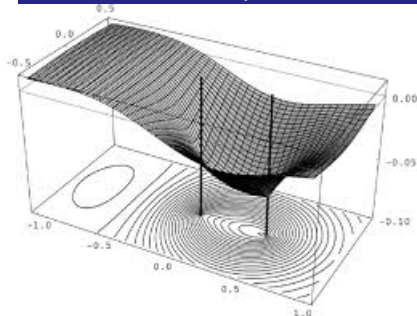
## Characteristica

- Wave function is non-differentiable when the coordinates of two electrons are identical
- At these points, the convergence of the wave function in an orbital-based expansion is very slow.
- Using optimized orbitals does not help for the last %



# Introduction to Dynamical correlation

## The Coulomb cusp for He



- Left: One electron is fixed. The other electron moves in two-dim-plane.
- Right: One electron is fixed. The other electron moves in circle with the same radius as fixed electron.

# Introduction to Dynamical correlation

## Methods to determine dynamic correlation

**Single-reference(SR)** Based on excitations out from a reference state containing a single determinant/CSF

**Multi-reference (MR)** Based on excitations out from a reference state containing a several determinant/CSF

**Variational** SRCI and MRCI

**Perturbation** Møller-Plesset and various Multireference schemes

**Projection** SR or MR Coupled cluster

Methods containing two-electron functions (F12, geminals, ..) may be combined with the above

The challenge have been to develop methods that accurate include both static and dynamic correlation

# Introduction to Dynamical correlation

## Wishing list for correlation methods

### Size extensivity, definition

- Consider two molecules A, B, infinite apart
- Perform calculation with method X on the two molecules separately  $\rightarrow E_A, E_B$
- Perform also calculation with method X on supermolecule containing both A,B  $\rightarrow E_{AB}$
- If  $E_A + E_B = E_{AB}$  then method X is *size-extensive*

### Size-extensive methods

- RHF, UHF, FCI, CC, Perturbation theory (not CASPT2..)
- Active spaces may be chosen, so CAS is size-extensive
- CI, Including MRCI, is not size-extensive

# Introduction to Dynamical correlation

Combined with static correlation

- We want a method to treat dynamical correlation built on top of MCSCF methods.
- (Or use UHF-based methods and hope. . .)
- Need “multireference” methods for CC, CI, PT.
- Should preferable be both size-extensive and size-consistent
- Or perhaps some sort of DFT on top of MCSCF (not discussed here).

# Contents

## Friday, Sept. 13

- Introduction to dynamic correlation
- **The multi-reference CI method**
- Nearly size-extensive multi-reference methods
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- CASPT2
- NEVPT2

# The Multireference CI Method

## Introduction

### The wave function space

- Select a number of reference configurations  $\Phi(I)$  based on an MCSCF calculation.
- Generate all singly,  $\Phi(I)_i^x$  and doubly,  $\Phi(I)_{ij}^{xy}$  excited configuration state functions (CSFs).  $i, j$  are occupied orbitals and  $x, y$  occupied or external orbitals.
- Obtained from operators  $\hat{E}_{xi}$ ,  $\hat{E}_{xi}\hat{E}_{yj}$  operating on each  $\Phi(I)$ .
- The above set of CSFs is redundant - same CSFs obtained several times.
- E.g., H<sub>2</sub> two-reference,  $\hat{E}_{x\sigma_g}\hat{E}_{y\sigma_g}$  and  $\hat{E}_{x\sigma_u}\hat{E}_{y\sigma_u}$  give the same doubly-excited configuration.

# The Multireference CI Method

## Introduction

### The wave function

- A linear combination of the configurations

$$\Psi_{MRCI} = \sum_I \left[ C(I)\Phi(I) + \sum_{ix} C_i^x(I)\Phi(I)_i^x + \sum_{ijxy} C_{ij}^{xy}(I)\Phi(I)_{ij}^{xy} \right]$$

- Includes both dynamic and static correlation energy
- Linear expansion  $\rightarrow$  problems with size-extensivity

### The parameters $C$

- Are determined using the variational principle
- Leads to the eigenvalue problem  $(\mathbf{H} - E\mathbf{1})\mathbf{C} = \mathbf{0}$

# The Multireference CI Method

## The Direct CI Method

### Idea

- It is not possible to store the Hamiltonian matrix **H**
- Obtain instead selected roots using iterative methods

### Efficient direct CI methods require

- Efficient numerical algorithms to obtain the lowest eigenvalues
- Efficient routines for the calculation of **HC** from integrals

### $\sigma = \mathbf{HC}$

- $\hat{H} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} (pq|rs) (\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps})$
- $\sigma_{\mu} = \sum_{\nu} \left[ \sum_{pq} h_{pq} A_{pq}^{\mu\nu} + \frac{1}{2} \sum_{pqrs} (pq|rs) A_{pqrs}^{\mu\nu} \right] C_{\nu}$
- $A_{pq}^{\mu\nu}$  and  $A_{pqrs}^{\mu\nu}$  are the *direct CI coupling coefficients*.



# The Multireference CI Method

## Internal contraction

### Problem with MRCI

Number of configurations runs easily into millions and billions

### Internal contraction

- Apply excitation operators to the MCSCF wave function  $\Psi_0$ , instead of to the configurations in the reference space
- The 'configurations' obtained in this way are much more complicated objects.
- There are much fewer coefficients to optimize:  $C_{ij}^{xy}(I) \rightarrow C_{ij}^{xy}$ , more-or-less independent of the number of CSFs in  $\Psi_0$ .
- This approach is termed *internally contracted* MRCI.

# The Multireference CI Method

## Internal contraction

### The pro and cons

- Internal contraction reduces variational freedom and will raise the energy.
- This is rarely an issue, especially in implementations that “relax” the coefficients in  $\Psi_0$  during the iterations.
- Occasional problems, particularly with singles coefficients and these are sometimes then uncontracted.
- MOLPRO: internally contracted MRCI  
MOLCAS: no contraction in MRCI  
A number of new programs coming (BAGEL)

# The Multireference CI method

## Advantages

- Probably the most accurate method available for small molecules.
- Balanced calculations for several electronic states.

## Disadvantages

- MRCI is not size-extensive.
- The size of the uncontracted CI expansion grows quickly with the number of reference configurations.
- Even with internal contraction large multiconfiguration reference functions become intractable.
- Becomes less and less practical for large molecules.

# Contents

## Friday, Sept. 15

- Introduction to dynamic correlation
- The multi-reference CI method
- **Nearly size-extensive multi-reference methods**
- Perturbation theory, general, MP2 and multireference methods
- CASPT2
- NEVPT2

# Nearly size-extensivene multireference methods

## Multireference ACPF and relatives

### Idea

- Use MRCI form of wave function:  $\Psi = \Psi_0 + \Psi_a + \Psi_e$
- $\Psi_a$  is in reference space,  $\Psi_e$  contain the external excitations
- Modify energy-expression

### The energy expression

- $E = \frac{\langle \Psi_0 + \Psi_a + \Psi_e | H - E_0 | \Psi_0 + \Psi_a + \Psi_e \rangle}{1 + g_a \langle \Psi_a | \Psi_a \rangle + g_e \langle \Psi_e | \Psi_e \rangle}$  (Numerator is size-extensive)

### $g \rightarrow$ methods (N is number of electrons)

MRCI:  $g_a = 1, g_e = 1.$

MRLCCM: no  $\Psi_a, g_e = 0.$

MRACPF:  $g_a = 1, g_e = 2/N.$

QDVPT:  $g_a = 1, g_e = 0.$

MRCEPA(0):  $g_a = 0, g_e = 0.$

# Other (nearly) size-extensive multireference methods

## Multireference Davidson corrections

### Idea

- Perform a MRCI calculation as usual
- Add a correction to the obtained correlation energy to obtain a better (lower) energy

### Two forms

- Two forms of corrections:

$$\Delta E_{\text{corr}} = (E_{\text{MRCI}} - E_{\text{REF}}) \{1 - \sum_R (c_R^{\text{MRCI}})^2\}$$

$$\Delta E_{\text{corr}} = (E_{\text{MRCI}} - E_{\text{REF}}) \{1 - \sum_R (c_R^{\text{MRCI}} c_R^{\text{REF}})\}$$

- Both trivial to compute.

### Problems

- Weak theoretical foundation- but works often anyhow!!

# Contents

## Friday, Sept. 13

- Introduction to dynamic correlation
- The mult- reference CI method
- Nearly size-extensive multi-reference methods
- Perturbation theory, general and multireference methods
- CASPT2
- NEVPT2

# Multi-reference perturbation theory

## Rayleigh-Schrödinger Perturbation Theory

### Split Hamiltonian

- $\hat{H} = \hat{H}_0 + \lambda \hat{V}$ .
- $\hat{H}_0 |0_0\rangle = E_0 |0_0\rangle$

### First-order correction to wave function and second-order correction to energy

- $|0_1\rangle = \sum_{\mu} C_{\mu}^1 |\mu\rangle, \langle \mu | 0_0\rangle = 0$
- $C_{\mu}^1 = -\sum_{\nu} (\mathbf{H}_0 - E_0 \mathbf{S})_{\mu\nu}^{-1} \langle \nu | \hat{V} | 0_0\rangle$
- $(\mathbf{H}_0)_{\mu\nu} = \langle \mu | \hat{H}_0 | \nu\rangle, S_{\mu\nu} = \langle \mu | \nu\rangle$
- $E_2 = \langle 0_1 | \hat{V} | 0_0\rangle$



# Multi-reference perturbation theory

## Various forms

Many forms, differs by choices of

- 1 Reference state
- 2 Form of  $\hat{H}_0$
- 3 Form of wave function corrections
- 4 (Use of intermediate Hamiltonian, buffer states ...)

Reference state

- CASSCF/RASSCF/GASSCF...
- Incomplete spaces

Is usually not convergent, but low-order corrections (2+3) are useful

# Multi-reference perturbation theory

## Various forms

### Form of $\hat{H}_0$

- Fock-type one-electron operator in all orbital spaces(CASPT)
- Fock-type one-electron operator in inactive and secondary spaces, full two-electron Hamilton operator in active space (NEVPT)

### Form of wave function corrections

- Complete internal contraction - MOLCAS-CASPT, NEVPT
- Complete internal contraction - MOLPRO-CASPT, NEVPT
- No internal contraction: many approaches

# Contents

## Friday, Sept. 13

- Introduction to dynamic correlation
- The multi-reference CI method
- Nearly size-extensive multi-reference methods
- Perturbation theory, general and multireference methods
- CASPT2
- NEVPT2

# CASPT2

Form of reference state, correction, and  $\hat{H}_0$

## Reference state, $|0_0\rangle$

- CAS state - with or without optimized orbitals

## Form of first-order correction

- $|0_1\rangle = \sum_{\mu} C_{\mu}^1 \mathcal{O}_{\mu} |0_0\rangle$
- $\mathcal{O}_{\mu}$  contains the single and double excitations from  $|0_0\rangle$
- Only SD space in first-order correction: interacts with  $|0_0\rangle$

## The zero-order Hamiltonian

- $\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_K \hat{F} \hat{P}_K + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_X \hat{F} \hat{P}_X$ 
  - $\hat{F}$  is a Fock-type one-electron operator, several choices
  - Projections are needed for a zero-order eigenvalue equation
  - $\hat{P}_0$  projects on  $|0_0\rangle$ ,  $\hat{P}_K$  projects on other states in the CASpace,  $\hat{P}_{SD}$  projects on single and doubles,  $\hat{P}_X$  on the rest.

# CASPT2

The Fock Operator, simplest choice

Defined as

- $\hat{f} = \sum_{pq} f_{pq} E_{pq}$
- $f_{pq} = \sum_{\sigma} \langle 0_0 | [a_{p\sigma}, [H, a_{q\sigma}^{\dagger}]_+] | 0_0 \rangle = h_{pq} + \sum_{rs} D_{rs} [(pq|rs) - \frac{1}{2}(pr|qs)]$ .
- Becomes standard MP  $\hat{H}_0$  if  $|0_0\rangle$  is HF wave function

Properties of  $\mathbf{f}$

Inactive orbitals	$f_{pp} = -IP_p$
External orbitals	$f_{pp} = EA_p$
$n_p^{occ} = 1$ :	$f_{pp} = \frac{1}{2}(-IP_p + EA_p)$

- Unpaired electrons are favoured, so binding energies are too low.

# CASPT2

## Fock matrix Elements and the First-Order Equation

### The first-order equation

- $(\mathbf{H}_0 - E_0 \mathbf{S})\mathbf{C}^1 = -\mathbf{V}$
- Eight types of double excitations
- Equations may be split into 8 blocks, one for each of 8 excitation types
- The coupling of the blocks is introduced in a second iterative step.

### Fock matrix Elements, $\mathbf{H}_0$

- Contain up to fourth-order density matrices:  

$$\langle pqrs | \hat{F} | p'q'r's' \rangle = \sum_{mn} f_{mn} \langle 0_0 | \hat{E}_{sr} \hat{E}_{qp} \hat{E}_{mn} \hat{E}_{p'q'} \hat{E}_{r's'} | 0_0 \rangle$$
- May be rearranged to require three-body density

# CASPT2

## Computational steps in a CASPT2 calculation

- 1 Perform a CASSCF calculation, single-state or state-average.
- 2 Determine orbitals that block-diagonalizes the Fock matrix.
- 3 Transform integrals to obtain two-electron integrals with at least two indices corresponding to occupied orbitals (second order transformation).
- 4 Compute  $\mathbf{S}$  and some additional matrices and diagonalize them.
- 5 Compute the second-order energy in the "diagonal" approximation.
- 6 Solve the large system of linear equations introducing the coupling arising from the non-diagonal blocks of  $\mathbf{H}_0$ .

# CASPT2

## Intruder states in CASPT2

- CASPT2 will only be an adequate method when the perturbation is small.
- All large CI coefficients should thus be included in the CAS space.
- When large coefficients appear in the first-order wave function (weight of the reference function is small), the active space should in general be increased.
- A large coefficient may arise from artifacts of  $\hat{H}_0$
- This is the *intruder state* problem in CASPT2.
- May be removed using level-shifting and/or other choices of  $\hat{F}$



# CASPT2

## Multi-State (MS) CASPT2

### Idea

- Diagonalize approx. Hamiltonian in space of CASPT2 states
- First perturb, then diagonalize scheme
- Natural extension of XASSI (X=C,R)

### The method

- Assume a number of CASSCF states,  $E_i, \Psi_i, i = 1, N$ ,
- The CASPT first-order wave functions are denoted  $\chi_i, i = 1, N$ .
- Use  $\Psi_i + \chi_i$  as basis functions in a approx. var. calc.
- Effective Hamiltonians:  $(H_{eff})_{ij} = \delta_{ij}E_i + \langle \Psi_i | \hat{H} | \chi_j \rangle$
- Recommended for treating several states of one symmetry.

# CASPT2

## Advantages of CASPT2

- A CAS wave function is the reference so static correlation may be included.
- The size of the contracted SD space is never large and is independent of the CAS CI space.
- The formalism is nearly size-extensive. Therefore a large number of electrons may be correlated (more than 100 in practical applications).
- The method has the same orbital invariance as the CASSCF method.
- May be extended to RAS and GAS wave functions.
- Requires often tuning of the level-shift parameter.

# CASPT2

## Applications of CASPT2

- Energy surfaces for ground and excited states.
- Electronic spectroscopy, including all types of excited states (singly, doubly, etc. excited, valence and Rydberg states, charge transfer, etc.).
- The whole periodic system from H to Pu (scalar relativity in CASSCF, spin-orbit with RASSI).
- Radicals and biradicals, positive and negative ions.
- Large molecules where MRCI is not applicable (calculations on systems with up to 50 atoms have been performed).

# CASPT2

## Problems with CASPT2

- The active space may become prohibitively large (today's limit 14-16 active orbitals).
- The intruder state problem.
- The zeroth-order Hamiltonian has a (small) systematic error (has recently been fixed with a shifted Hamiltonian, the IPEA shift).
- Transition properties are obtained at the CASSCF level, not CASPT2.
- It is not a “black box” method. (But is this really a problem/disadvantage...?)

# CASPT2

## Applications

### N<sub>2</sub> ground-state spectroscopic constants

	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
CASSCF	1.102	2329	8.91
CASPT2	1.100	2312	9.43
ACPF	1.099	2330	9.79
CCSD(T)	1.099	2332	9.82
Expt	1.098	2359	9.90

# Contents

## Friday, Sept. 13

- Introduction to dynamic correlation
- The multi-reference CI method
- Nearly size-extensive multi-reference methods
- Perturbation theory, general and multireference methods
- CASPT2
- **NEVPT2**

# NEVPT2

## Use Dyall's zero-order operator

- $\hat{H}_0 = \sum_{ij} f_{ij} E_{ij} + \sum_{ab} f_{ab} E_{ab} + \sum_{vw} h_{vw} E_{vw} + \frac{1}{2} \sum_{vwxy} g_{vwxy} (E_{vw} E_{xy} - \delta_{wx} E_{vy})$
- Fock-operator in inactive (indices ij) and secondary orbitals (indices ab)
- Full Hamiltonian in active orbitals (indices vwxy)
- Requires five-body terms over active orbitals.

## Expansion of first-order wave-function

- Advantageous to use internal contraction
- Due to the accurate treatment of interactions between active orbitals, the CAS CI coefficients may be re-optimized
- Overall formalism very similar to the CASPT formalism.

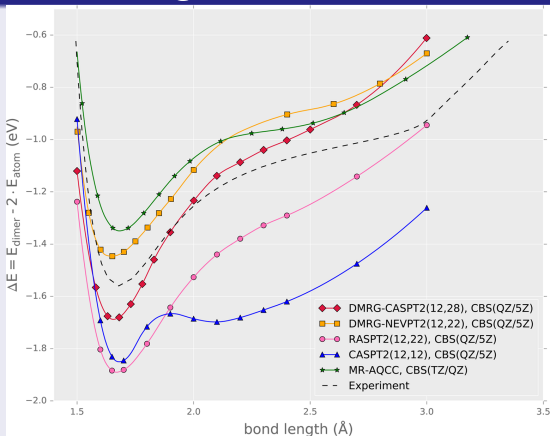
# NEVPT2

## Pro and cons compared to CASPT2-theoretical aspects

- More complicated and involved computations due to the 2-electron term over active orbitals - Not decisive these days.
- Treats the orbitals given rise to static correlation accurately.
- But treats the different types of orbitals differently.
- Allows relaxation of the CAS-coefficients
- Less developed codes (no multistate version?, No RAS/GAS extensions).
- zero-order eigenvalue equation automatically fulfilled.
- Rigourously size-extensive.
- No (very few) intruder states.



## NEVPT2

Cr<sub>2</sub> potential curve using CASPT2 and NEVPT2

# NEVPT2

## Pro and cons compared to CASPT-accuracy

- The theoretical advances of the NEVPT formalism does not in general lead to improved accuracy.
- CASPT has a tendency to overshoot correlation effects, which often leads to very good results in smaller basis sets.
- For complicated transition metal systems, the current advice is to stick to the CASPT method.
- I am not sure that the final verdict on the relative merits has been made.