

Multi-reference Methods

Peter Reinhardt

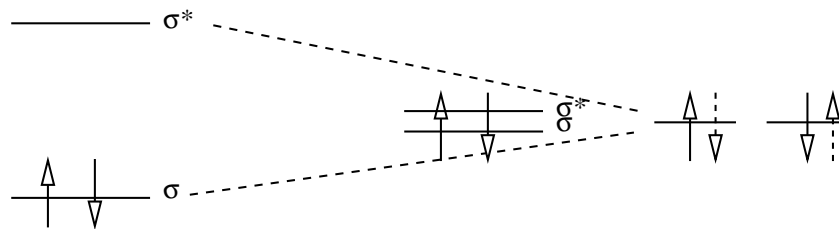
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MCSCF : general considerations

Again H₂ in a minimal basis:

$$\sigma = s_A + s_B$$

$$\sigma^* = s_A - s_B$$



- Equilibrium distance:

- Hartree-Fock $|\Phi_0\rangle = |\sigma\bar{\sigma}\rangle$

- CISD (=Full CI): $|\Psi\rangle = \sqrt{1 - \epsilon^2}|\sigma\bar{\sigma}\rangle + \epsilon|\sigma^*\bar{\sigma}^*\rangle$

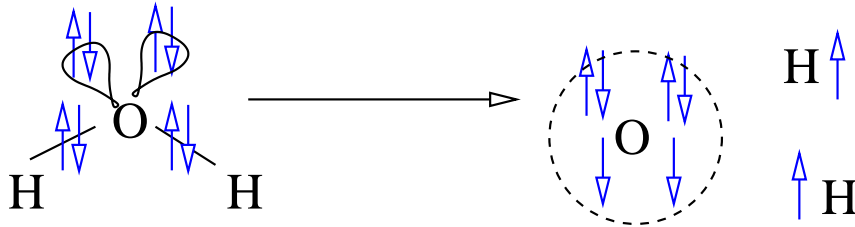
Long distance:

$$|\Psi\rangle = a|\sigma\bar{\sigma}\rangle + b|\sigma^*\bar{\sigma}^*\rangle \quad \text{with } |a| \approx |b| \approx 1/\sqrt{2}$$

in order to have $|s_A\bar{s}_B\rangle + |s_B\bar{s}_A\rangle$ without the ionic configurations $|s_A\bar{s}_A\rangle$ and $|s_B\bar{s}_B\rangle$

General considerations

More general: few electrons in a few orbitals to consider
 H_2O : 4 electrons in 4 orbitals to start with



- Better: 8 electrons in 6 orbitals (s on H, $2sp$ on O)
- Full CI in this subspace

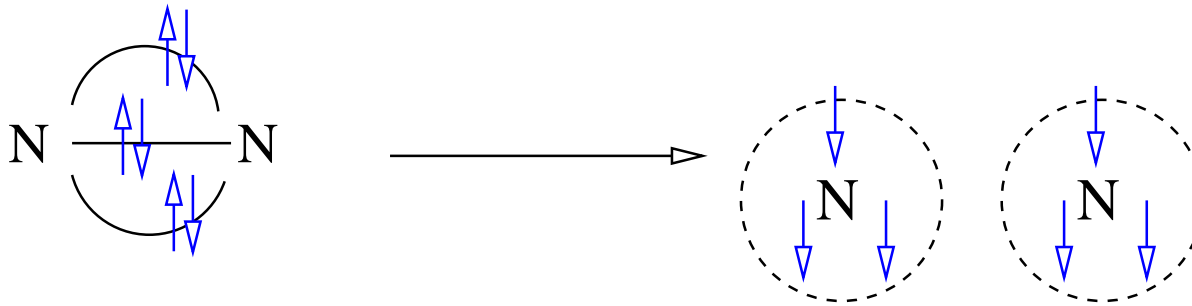
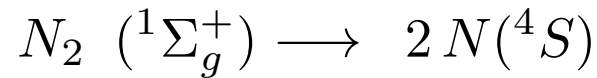
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Triple bond in N₂: 6 electrons of the 14 possible in 6 atomic *2p* orbitals



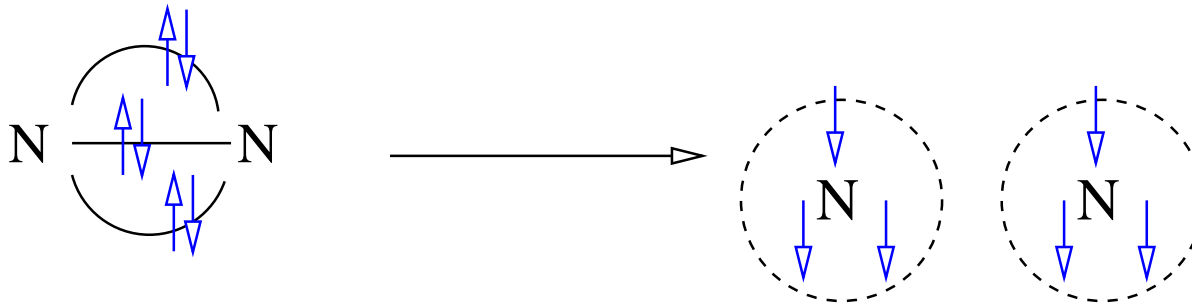
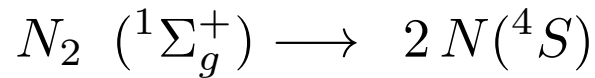
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Need for multiconfigurational wavefunctions

Non-dynamical correlation

General considerations

2 ingredients needed:

- Where to look for orbitals?
- Which determinants to take?

Hartree-Fock orbitals optimized for one single determinant.

- Average over different occupations?
- But how to treat open-shell determinants? No spin eigenfunctions!

Simultaneous optimization of orbitals and wavefunctions:

Multiconfigurational Self-Consistent Field (M C S C F)

Super-CI method

Alternative to the diagonalization of the Fock matrix

1. Starting orbitals
2. Orthonormalize the orbitals
3. Construct Fock matrix, calculate total energy
4. Construct CI matrix of single excitations

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle \approx F_{ab} \delta_{ij} - F_{ij} \delta_{ab}$$

5. Use the CI coefficients of

$$|\Psi\rangle = |\Phi_0\rangle + \frac{1}{\sqrt{2}} \sum_{ia} c_i^a (|\Phi_i^a\rangle + |\Phi_i^{\bar{a}}\rangle)$$

to correct the orbitals (occupied and virtual ones) through

$$\phi'_i = \phi_i + \sum_a c_i^a \phi_a ; \quad \phi'_a = \phi_a - \sum_i c_i^a \phi_i$$

6. Go to step 2

Super-CI method

If canonical orbitals are required, then diagonalize **once** the converged Fock matrix

- Orbitals change through mono-excitations
- Excitation operator

$$\begin{aligned}\hat{E}_{ia} &= \frac{1}{\sqrt{2}} \left(\hat{a}_{a,\alpha}^\dagger \hat{a}_{i,\alpha} + \hat{a}_{a,\beta}^\dagger \hat{a}_{i,\beta} \right) \\ \hat{E}_{ia} |\Phi_0\rangle &= \frac{1}{\sqrt{2}} \left(|\Phi_i^a\rangle + |\Phi_i^{\bar{a}}\rangle \right) \\ |\Psi\rangle &= \left(1 + \sum_{ia} c_i^a \hat{E}_{ia} \right) |\Phi_0\rangle\end{aligned}$$

- Convergence achieved if Brillouin's theorem is satisfied

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = F_{ia} \longrightarrow 0$$

or total energy changes smaller than a given threshold

Generalization

Matrix elements between determinants $|\Phi_m\rangle$ and $|\Phi_n\rangle$

- Monoelectronic operator \hat{h} :

$$\begin{aligned}\langle \Phi_m | \hat{h} | \Phi_n \rangle &= \sum_{ij} h_{ij} \langle \Phi_m | \hat{E}_{ij} | \Phi_n \rangle \\ &= \sum_{ij} h_{ij} D_{ij}^{mn}\end{aligned}$$

- Bi-electronic operator \hat{G} :

$$\begin{aligned}\langle \Phi_m | \hat{G} | \Phi_n \rangle &= \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle \Phi_m | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Phi_n \rangle \\ &= \sum_{ijkl} g_{ijkl} P_{ijkl}^{mn}\end{aligned}$$

Generalization

- First-order density matrix (or 1-particle density matrix)

$$D_{ij} = \langle \Psi | \hat{E}_{ij} | \Psi \rangle = \sum_{mn} c_m^* c_n D_{ij}^{mn}$$

- Second-order density matrix (or 2-particle density matrix)

$$P_{ijkl} = \frac{1}{2} \langle \Psi | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Psi \rangle = \sum_{mn} c_m^* c_n P_{ijkl}^{mn}$$

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- Total energy

$$E_{\text{tot}} = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{ij} h_{ij} D_{ij} + \sum_{ijkl} g_{ijkl} P_{ijkl}$$

- h_{ij} and g_{ijkl} depend only on the molecular orbitals
- D_{ij} and P_{ijkl} depend only on the wavefunction expansion coefficients in

$$|\Psi\rangle = |\Phi_0\rangle + \sum_n c_n |\Phi_n\rangle$$

Density matrices

Hartree-Fock:

$$E_{HF} = 2 \sum_{i \in occ} h_{ii} + \sum_{ij \in occ} 2(ii|jj) - (ij|ji)$$

fits in the same expression as above with the density matrices

$$D_{ij} = \begin{cases} 2 & i = j; i \in occ. \\ 0 & \text{otherwise} \end{cases}$$

$$P_{ijkl} = \begin{cases} 2 & i = j, k = l, i \neq k; all \in occ. \\ 1 & i = j = k = l; i \in occ. \\ -1 & i = l, j = k, i \neq j; i, j \in occ. \\ 0 & \text{otherwise} \end{cases}$$

Only entries 0, 1, 2 or -1 in these matrices in the 1-determinant case.

$$E_{HF} = \sum_{ij \in all} D_{ij} h_{ij} + \sum_{ijkl \in all} P_{ijkl} (ij|kl)$$

Density matrices

- One-electron properties:

Multipolar moments, electrostatic potentials as $\sum_{ij} D_{ij} \langle \phi_i | \hat{O} | \phi_j \rangle$

- Integrals of the operator in molecular orbitals
- Alternative: integrals and density matrix in atomic orbitals

$$F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\delta} D_{\gamma\delta} [2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta)]$$

- Mulliken population analysis

$$N_A = \sum_{\alpha\beta \in A} D_{\alpha\beta} S_{\alpha\beta}$$

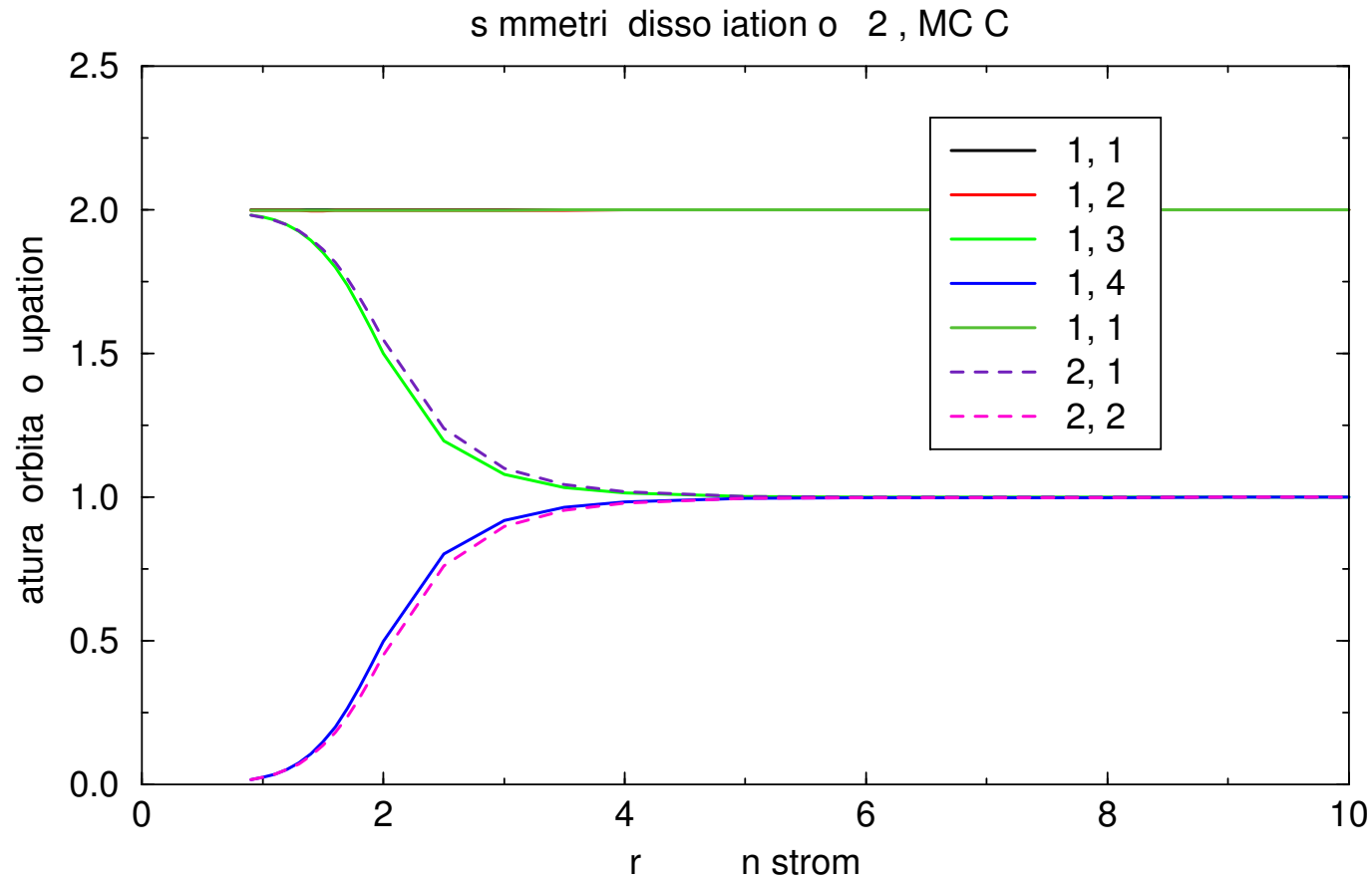
- Dipole moment

$$\vec{\mu} = \sum_{\alpha\beta} D_{\alpha\beta} \langle \chi_\alpha | \hat{r} | \chi_\beta \rangle = \sum_{i,j \in all} D_{ij} \langle \phi_i | \hat{r} | \phi_j \rangle$$

Natural orbitals

We may diagonalize the multi-determinantal 1-particle matrix D_{ij} : orbitals with fractional occupation numbers.

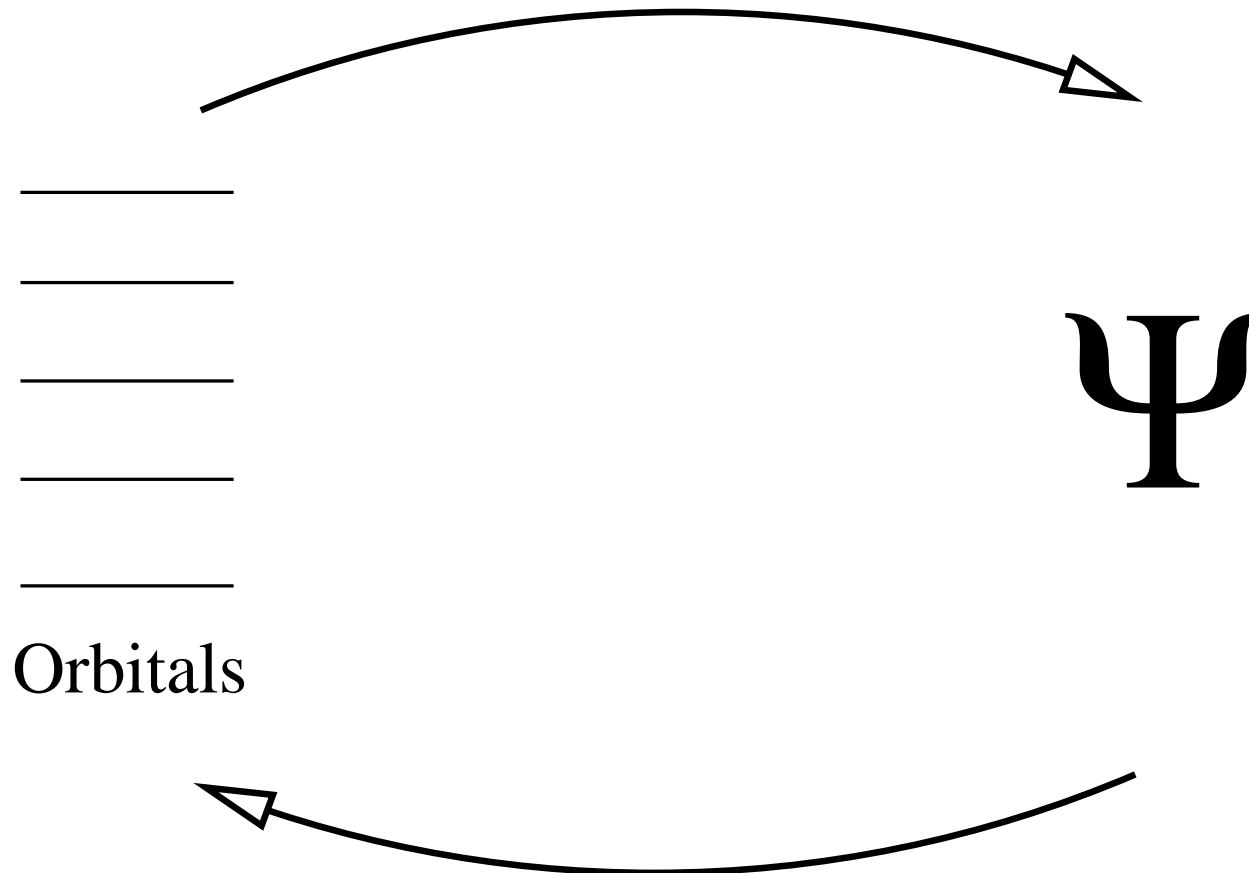
- ≈ 2 electrons: closed shell
- ≈ 1 electron : singly occupied orbital
- ≈ 0 electrons: virtual orbitals



Remains to work

Derivatives of the total energy with respect to orbitals and CI coefficients:

- Derivatives of h_{ij} and g_{ijkl} wrt orbital expansion coefficients
- Derivatives of the density matrices wrt to WF expansion coefficients
- Alternate between orbital and WF optimization steps



Remains to work

Rotations in the parameter space via unitary matrices U with $U^\dagger U = U U^\dagger = 1$.

- Conserves orthonormality
- Can be expressed as exponential of an anti-hermitian matrix T ,

$$T^\dagger = -T \quad : \quad U = e^T$$

- Orbital rotations (parameters are the matrix elements T_{ij}):

$$\hat{T} = \sum_{i>j} T_{ij} \left(\hat{E}_{ij} - \hat{E}_{ji} \right)$$

- Wavefunction rotations: $\hat{S} = \sum_{K \neq 0} S_{K0} \left(|\Psi_K\rangle\langle\Psi_0| - |\Psi_0\rangle\langle\Psi_K| \right)$

- Transformation of a general multireference state $|\Psi_0\rangle$ into another

$$|\Psi\rangle = e^{\hat{T}} e^{\hat{S}} |\Psi_0\rangle$$

Finally the optimization

- Total energy after application of the rotations on an initial multi-configurational state $|\Psi_0\rangle$:

$$E_{\text{tot}} = \langle \Psi_0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | \Psi_0 \rangle$$

- Expansion of the exponentials to 2nd order:

$$\begin{aligned} E_{\text{tot}} = & \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | [\hat{H}, \hat{T}] | \Psi_0 \rangle + \langle \Psi_0 | [\hat{H}, \hat{S}] | \Psi_0 \rangle + \\ & + \frac{1}{2} \langle \Psi_0 | [[\hat{H}, \hat{T}], \hat{T}] | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | [[\hat{H}, \hat{S}], \hat{S}] | \Psi_0 \rangle \\ & + \langle \Psi_0 | [[[\hat{H}, \hat{T}], \hat{S}]] | \Psi_0 \rangle + \dots \end{aligned}$$

- Taylor expansion in the rotational parameters T_{ij} and S_{K0}

Finally the optimization

- Newton-Raphson procedure:

$$\begin{aligned} E(\mathbf{x}) &= E(0) + \mathbf{a}^\dagger \cdot \mathbf{x} + \frac{1}{2} \mathbf{x}^\dagger \mathbf{B} \mathbf{x} \\ \mathbf{a} + \mathbf{B} \cdot \mathbf{x} &= 0 \\ \mathbf{x} &= -\mathbf{B}^{-1} \cdot \mathbf{a} \end{aligned}$$

- Identify:

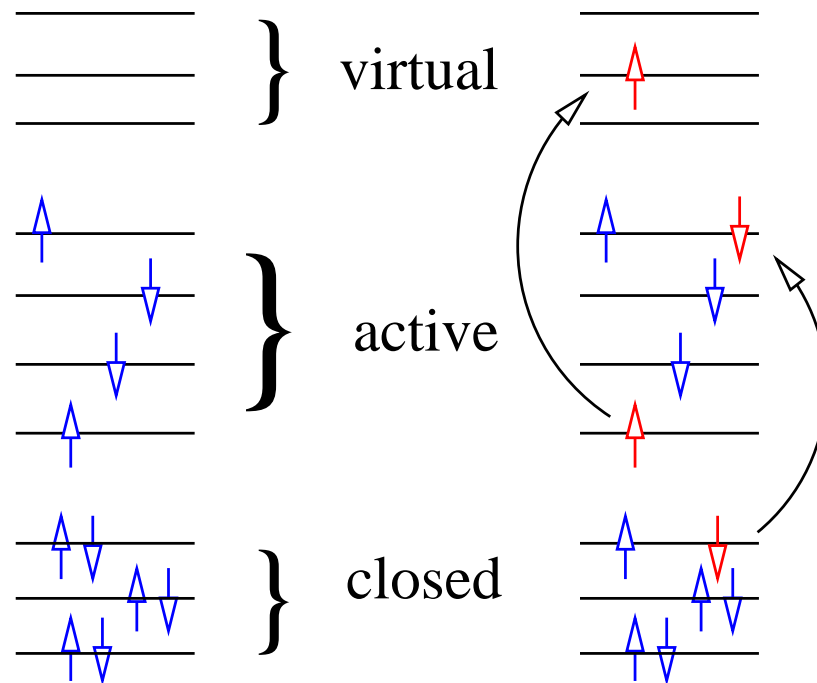
$$\begin{aligned} \mathbf{a}_{T_{ij}} &= \left(\frac{\partial E}{\partial T_{ij}} \right) = \langle \Psi_0 | [\hat{H}, \hat{E}_{ij} - \hat{E}_{ji}] | \Psi_0 \rangle \\ \mathbf{a}_{S_{K0}} &= \left(\frac{\partial E}{\partial S_{K0}} \right) = 2 \langle \Psi_0 | \hat{H} | \Psi_K \rangle \end{aligned}$$

Three types of 2nd derivatives: orbital–orbital, WF–orbital, WF–WF

Has to be implemented

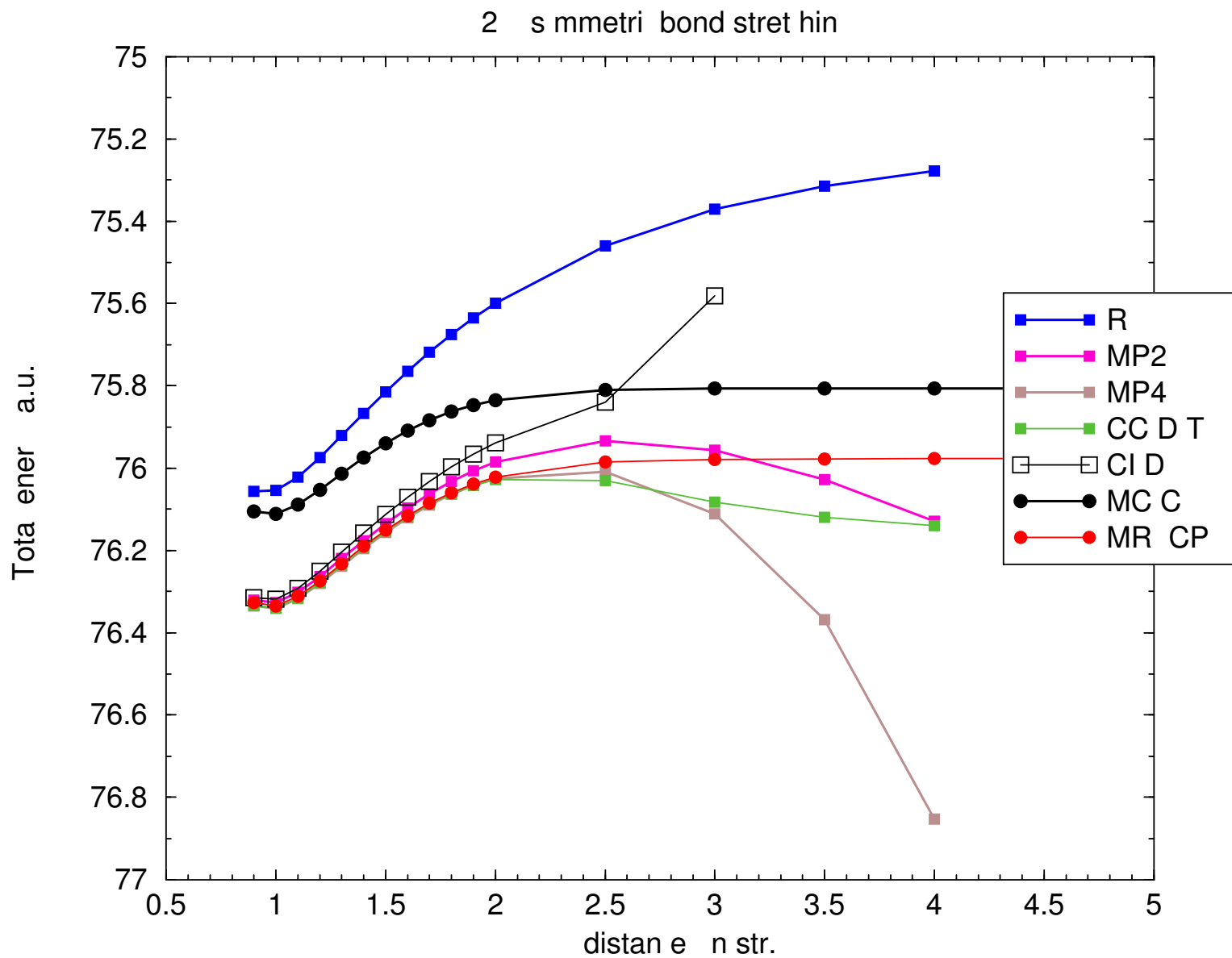
Adding dynamical correlation

- Add excitations



- CISD like in the mono-reference case
- Dressing techniques available: MR-CEPA, MR-ACPF, MR-AQCC
- Same size-consistence problems as for mono-reference case

Adding dynamical correlation



Selecting excitations

- Weight of excitations closed \longrightarrow virtual small:

$$\Delta E \sim \frac{1}{\epsilon_j + \epsilon_i - \epsilon_a - \epsilon_b}$$

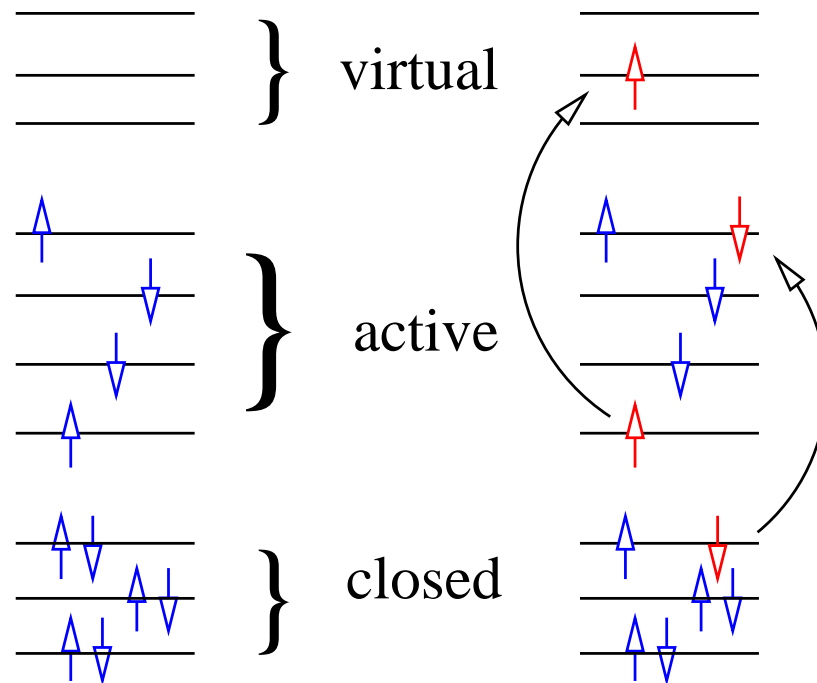
- Selection of important excitations via perturbation theory
- Determinant by determinant
- CIPSI (Malrieu, Toulouse), MRDCI (Peyerimhoff, Bonn)

Practical aspects

- Much more expensive than RHF
- Grows exponentially with number of active orbitals
- Definition of active space not straightforward: all valence electrons in all valence atomic orbitals may be too large
- Convergence not assured
- Active space may change for different points on a potential surface
- Starting point for calculations on
 - Open-shell systems
 - Electronically excited states
 - Resonant singlet systems

Adding dynamical correlation

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Adding dynamical correlation

- MR perturbation theory ?
 - How to define \hat{H}_0 ?
 - What is the $E_0^{(0)}$ of an MCSCF state: barycentric?

$$\frac{1}{N_{det}} \sum_{I=1}^{N_{det}} \langle \Phi_I | \hat{H} | \Phi_I \rangle$$

- CASPT2
 - NEVPT2
- Still not uniquely defined: MR-CC methods

Electronic spectroscopy

Several states to consider, all composed of

$$\Psi = \Psi_{\text{vib}} \Psi_{\text{elec}} \Psi_{\text{spin}}$$

Transition probability is

$$\begin{aligned} M_{12} &= \langle \Psi_1 | \hat{\mu} | \Psi_2 \rangle \\ &= \langle \Psi_{\text{vib},1} | \Psi_{\text{vib},2} \rangle \langle \Psi_{\text{elec},1} | \hat{\mu} | \Psi_{\text{elec},2} \rangle \langle \Psi_{\text{spin},1} | \Psi_{\text{spin},2} \rangle \end{aligned}$$

- $|\langle \Psi_{\text{vib},1} | \Psi_{\text{vib},2} \rangle|^2$ Franck-Condon factor (0.1 ... 1)
- $\langle \Psi_{\text{spin},1} | \Psi_{\text{spin},2} \rangle$ spin selection rules $\Delta S = 0$
- $\langle \Psi_{\text{elec},1} | \hat{\mu} | \Psi_{\text{elec},2} \rangle$ dipole transition moment, orbital selection
- Molecular extinction coefficient ϵ (in cm^2/mol)

10^{-5} to 1 spin forbidden

1 to 10^3 spin allowed, but orbital forbidden

10^3 to 10^5 totally allowed

General considerations

State specific versus state-averaged

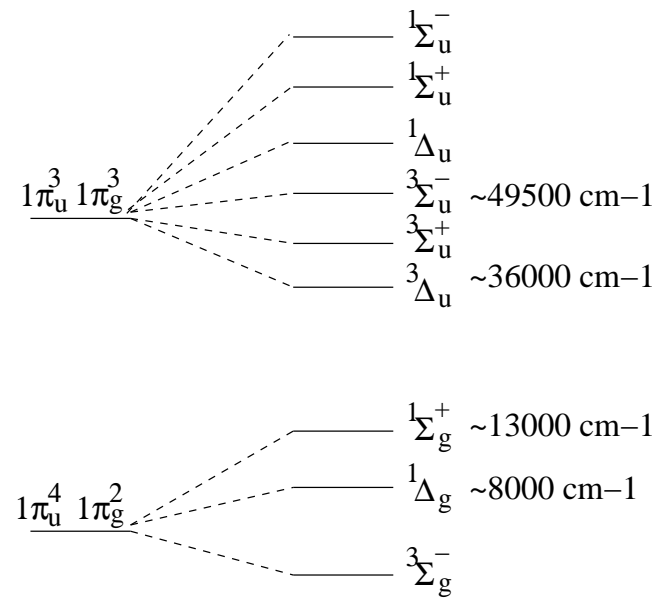
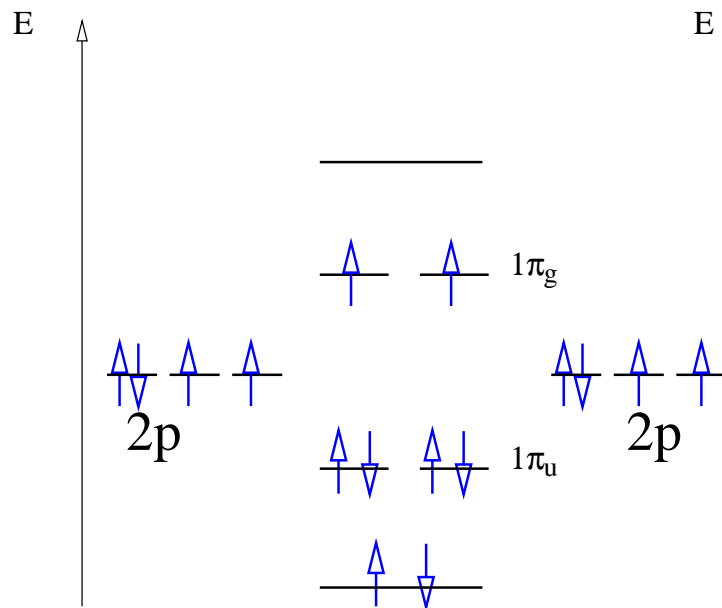
- State-averaged calculation: same orbitals for different spectroscopic states.
 - Systematic errors common to all states
 - Differences between states coherently calculated
 - Wavefunction can not relax during a transition (10^{-15} s)
- State specific: each state (symmetry) treated via a separate calculation
 - Ground state of each symmetry
 - Perturbation theory, Coupled-Cluster
 - Dressing of CI matrices
- Units: $1 \text{ eV} = 8065.5447 \text{ cm}^{-1} = 96.485 \text{ kJ/mol}$; $1 \text{ u.a.} = 27.21 \text{ eV} = 627.51 \text{ kcal/mol}$

Example O₂

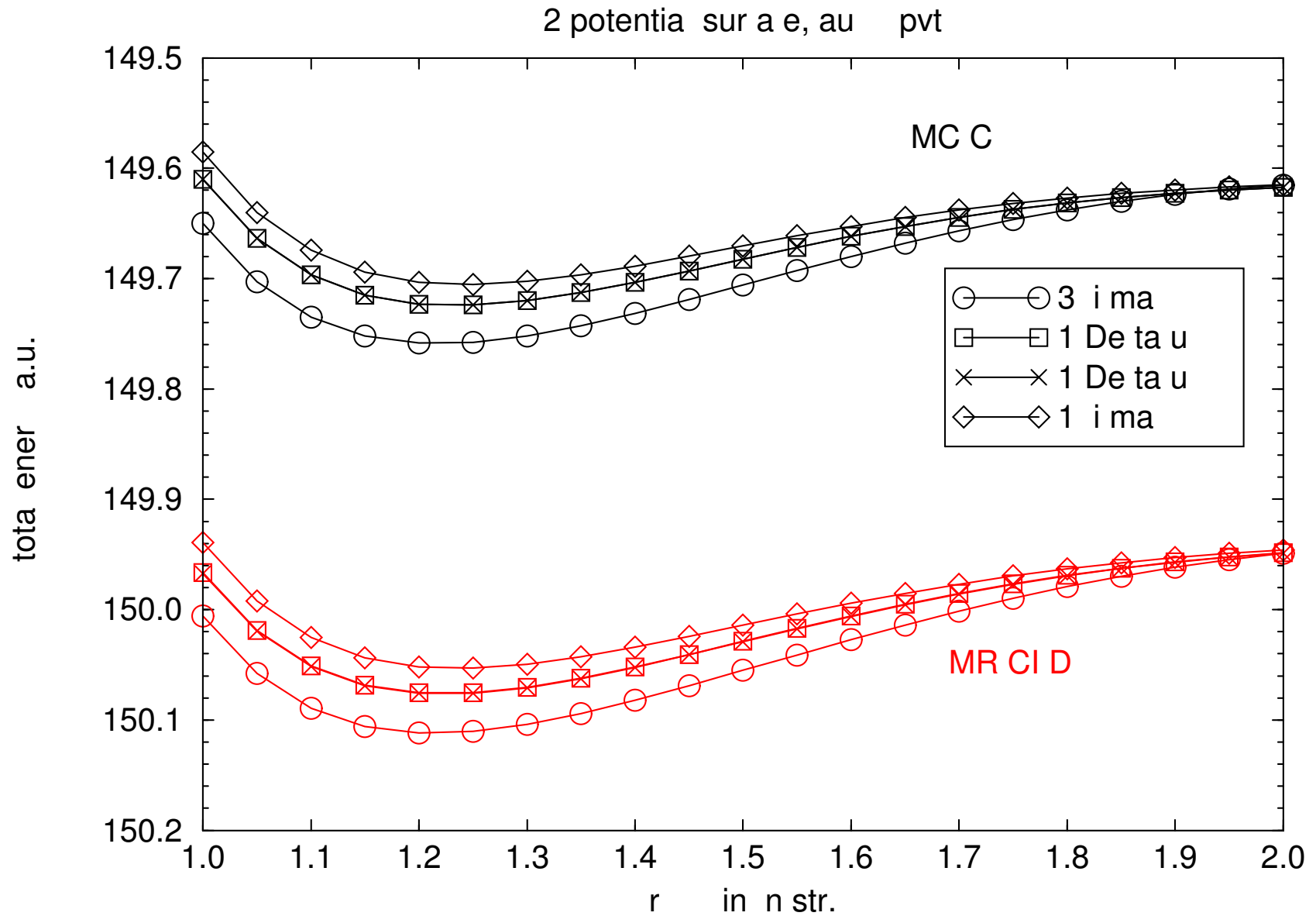
Linear diatomic molecule, point group D_{∞h}. Calculation in D_{2h}.

Correspondance:

D _{∞h}	Σ _g ⁺	Σ _g ⁻	Σ _u ⁺	Σ _u ⁻	Π _g	Π _u	Δ _g	Δ _u
D _{2h}	A _g	B _{1g}	B _{1u}	A _u	$\begin{cases} B_{2g} \\ B_{3g} \end{cases}$	$\begin{cases} B_{2u} \\ B_{3u} \end{cases}$	$\begin{cases} A_g \\ B_{1g} \end{cases}$	$\begin{cases} A_u \\ B_{1u} \end{cases}$



Example O₂



Example O₂

method	symm.	state to $^3\Sigma_g^-$	state ave.	state sp.
MCSCF	B _{1g}	$^1\Delta_g$	-7778.29	-7840.77
MCSCF	A _g	$^1\Delta_g$	-7778.29	-7840.77
MCSCF	A _g	$^1\Sigma_g^+$	-12129.20	-12154.80
MRCI	B _{1g}	$^1\Delta_g$	-7983.99	-8053.04
MRCI	A _g	$^1\Delta_g$	-7873.34	-7942.93
MRCI	A _g	$^1\Sigma_g^+$	-13138.70	-13036.70

Reproduction of the two observed weak bands of O₂: 7918.1 cm⁻¹,
13195.1 cm⁻¹

- Spin changes from triplet to singlet (spin forbidden)
- Direct product of electronic function and dipole moment does not contain a totally symmetric component: orbital forbidden as well
- Observation with $\epsilon \approx 10^{-4}$: violation of the selection rules

Current developments

- Local orbitals: reducing the cost to linear scaling
- Breaking down the correlation energy to increments
- Development of MR-Coupled-Cluster methods
- Coupling of wavefunction-based correlation methods with DFT
- Coupling Full CI with Monte-Carlo methods
- Perturbation theory for open-shell cases
- Calculation of general properties