Multi-reference Methods

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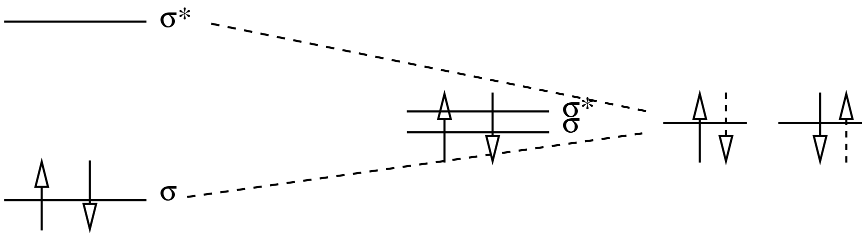
MCSCF : general considerations

Again H_2 in a minimal basis:

$$\sigma \;=\; s_A + s_B \qquad\qquad \sigma^* \;=\; s_A - s_B$$



- 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:

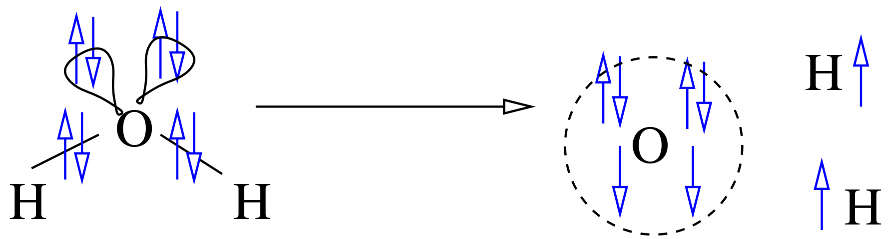
$$|\Psi\rangle \;=\; a|\sigma\bar{\sigma}\rangle + b|\sigma^*\bar{\sigma}^*\rangle \;\text{ with }\; |a| \approx |b| \approx 1/\sqrt{2}$$

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



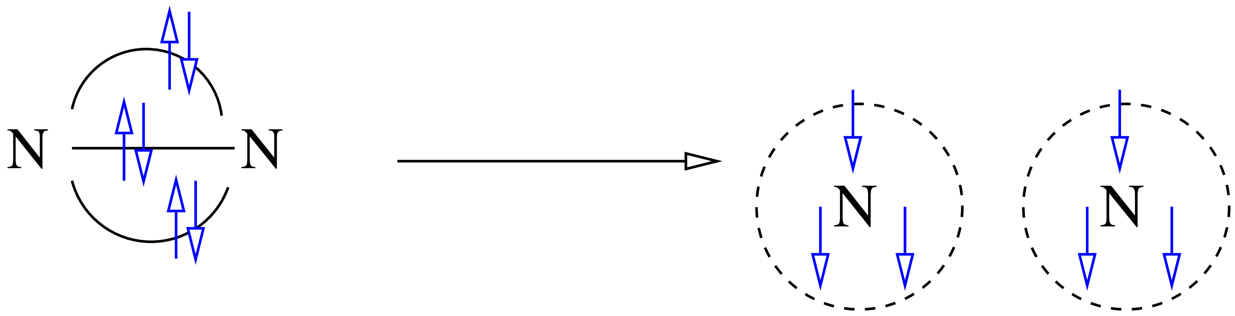
- Better: 8 electrons in 6 orbitals (s on H, $2sp$ on O)
- Full CI in this subspace

General considerations

More general: few electrons in a few orbitals to consider

Triple bond in N_2: 6 electrons of the 14 possible in 6 atomic $2p$ orbitals

$$N_2 \ \left({}^1\Sigma_g^+\right) \longrightarrow \ 2\,N({}^4S)$$



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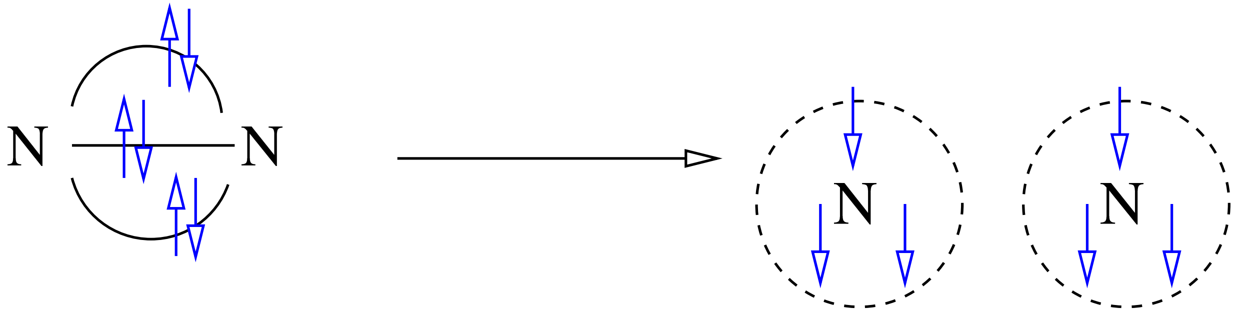

Need for multiconfigurational wavefunctions

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

$$|\Psi\rangle \;=\; |\Phi_0\rangle + \frac{1}{\sqrt{2}} \sum_{ia} c_i^a \,\left(|\Phi_i^a\rangle + |\Phi_{\bar{i}}^{\bar{a}}\rangle \right)$$

to correct the orbitals (occupied and virtual ones) through

$$\phi_i' \;=\; \phi_i + \sum_a c_i^a \,\phi_a \;\; ; \qquad \phi_a' \;=\; \phi_a - \sum_i c_i^a \,\phi_i$$

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

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

- 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

Second quantization

- $$\hat{E}_{ji} = \left(\hat{a}^{\dagger}_{j,\alpha}\hat{a}_{i,\alpha} + \hat{a}^{\dagger}_{j,\beta}\hat{a}_{i,\beta}\right) \qquad \text{(spin-free generators)}$$

  destroying and orbital i and creating an orbital j
- Second quantization starts with the vacuum $|\,\rangle$
- One creates electrons with the creation operator
- $|\phi_1\phi_2\rangle = \hat{a}^{\dagger}_1\hat{a}^{\dagger}_2|\,\rangle$
- $|\phi_2\phi_1\rangle = \hat{a}^{\dagger}_2\hat{a}^{\dagger}_1|\,\rangle = -|\phi_1\phi_2\rangle$ (Pauli's principle)
- Therefore $\hat{a}^{\dagger}_j\hat{a}^{\dagger}_i = -\hat{a}^{\dagger}_i\hat{a}^{\dagger}_j$
- Electron count operator $\hat{n} = \sum_i \hat{a}^{\dagger}_i\hat{a}_i$

Second quantization

-

$$\begin{aligned}\hat{a}_i|n_1\ldots n_i\ldots\rangle &= (-1)^{\sum_{k<i} n_k} n_i|n_1\ldots 0_i\ldots\rangle = \theta_i\, n_i\,|n_1\ldots 0_i\ldots\rangle \\ \hat{a}_i^\dagger|n_1\ldots n_i\ldots\rangle &= \theta_i\,(1-n_i)\,|n_1\ldots 1_i\ldots\rangle\end{aligned}$$

- phase factor θ_i; $n_1,\ldots,=0$ or 1
- anti-commutation relation (recall $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$)

$$\begin{aligned}\hat{a}_j\hat{a}_i + \hat{a}_i\hat{a}_j &= 0 \\ \hat{a}_j^\dagger\hat{a}_i^\dagger + \hat{a}_i^\dagger\hat{a}_j^\dagger &= 0 \\ \hat{a}_j^\dagger\hat{a}_i + \hat{a}_i\hat{a}_j^\dagger &= \delta_{ij} \qquad .\end{aligned}$$

- and thus $\hat{E}_{pq}^\dagger = \hat{E}_{qp}$

Generalization

$$\Psi = \sum_n c_n \Phi_n \qquad \longrightarrow E_\Psi = \langle \Psi \,|\, \hat{H} \,|\, \Psi \rangle$$

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

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

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

$$|\Psi\rangle \;=\; \sum_n c_n \, |\Phi_n\rangle$$

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

Mulliken population analysis:

- Total number of electrons $N = 2\sum_{i\in occ.}\langle\phi_i|\phi_i\rangle$
- $|\phi_i\rangle = \sum_\alpha c_{\alpha i}|\chi_\alpha\rangle$ expansion over basis functions, located on atoms
-

$$\begin{aligned} N &= 2\sum_{i\in occ.}\sum_{\alpha\beta} c_{\alpha i}c_{\beta i}\langle\chi_\alpha|\chi_\beta\rangle \\ &= \sum_{\alpha\beta}\underbrace{2\sum_{i\in occ.} c_{\alpha i}c_{\beta i}}_{=D_{\alpha\beta}}\underbrace{\langle\chi_\alpha|\chi_\beta\rangle}_{=S_{\alpha\beta}} \\ &= \sum_A \underbrace{\sum_{\alpha\in A}\sum_\beta D_{\alpha\beta}S_{\alpha\beta}}_{\text{Population of atom } A} \end{aligned}$$

- One possible decomposition scheme

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

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

- Mulliken population analysis

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

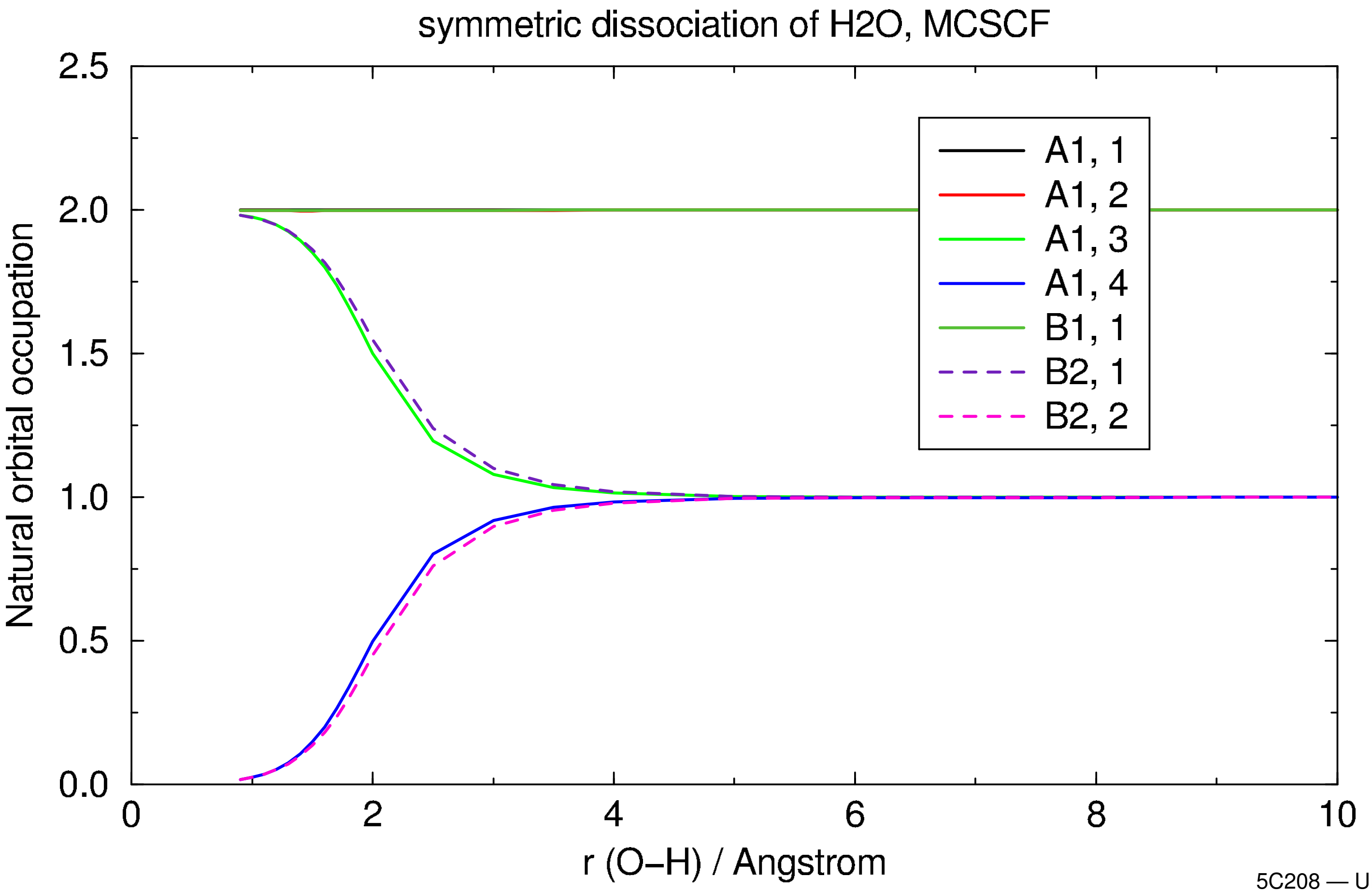
- Dipole moment

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

Natural orbitals

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

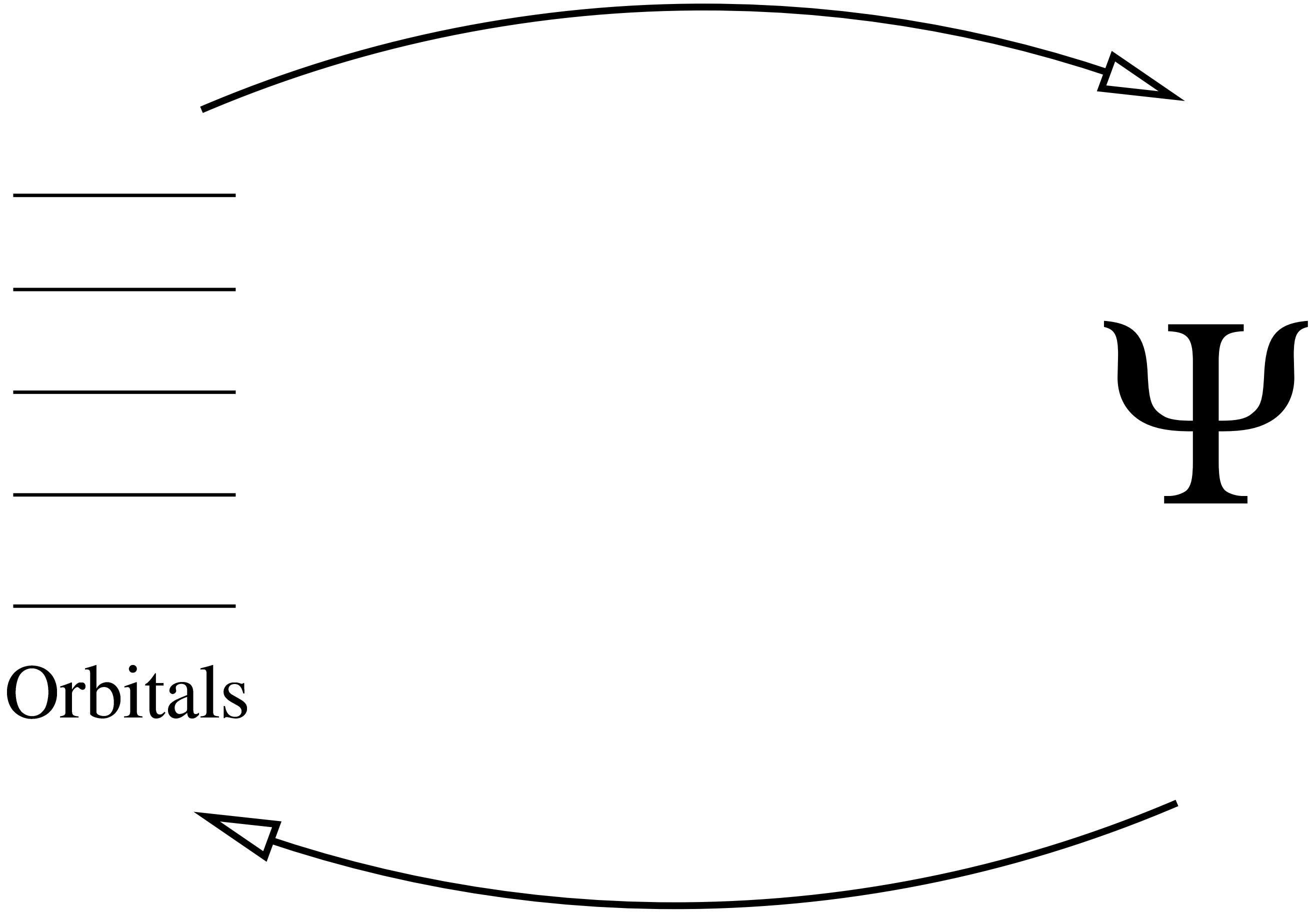
- $\approx$2 electrons: closed shell
- $\approx$1 electron : singly occupied orbital
- $\approx$0 electrons: virtual orbitals



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 $U^\dagger U = UU^\dagger = 1$.

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

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

- 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: $\hat{S} = \sum_{K\neq 0} S_{K0} \; (\,|\Psi_K\rangle\langle\Psi_0| - |\Psi_0\rangle\langle\Psi_K|\,)$
- 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 $|\Psi_0\rangle$:

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

- Expansion of the exponentials to 2nd order:

$$\begin{aligned} E_{\rm tot} \quad &= \quad \langle\,\Psi_0\,|\,\hat{H}\,|\,\Psi_0\,\rangle + \langle\,\Psi_0\,|\,\left[\hat{H},\hat{T}\right]\,|\,\Psi_0\,\rangle + \langle\,\Psi_0\,|\,\left[\hat{H},\hat{S}\right]\,|\,\Psi_0\,\rangle + \\ & \quad + \frac{1}{2}\langle\,\Psi_0\,|\,\left[\left[\hat{H},\hat{T}\right],\hat{T}\right]\,|\,\Psi_0\,\rangle + \frac{1}{2}\langle\,\Psi_0\,|\,\left[\left[\hat{H},\hat{S}\right],\hat{S}\right]\,|\,\Psi_0\,\rangle \\ & \quad + \langle\,\Psi_0\,|\,\left[\left[\hat{H},\hat{T}\right],\hat{S}\right]\,|\,\Psi_0\,\rangle + \;\ldots \end{aligned}$$

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

Finally the optimization

- Newton-Raphson procedure:

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

- Identify:

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

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

Has to be implemented ....

$$\left(\frac{\partial E}{\partial T_{pq}}\right) + \sum_{r>s}\left(\frac{\partial^2 E}{\partial T_{pq}\partial T_{rs}}\right) T_{rs} = 0 \tag{18}$$

The rotation between two orbitals is described via a rotation matrix

$$\begin{pmatrix} \tilde{p} \\ \tilde{q} \end{pmatrix} = \begin{pmatrix} \cos T_{pq} & \sin T_{pq} \\ -\sin T_{pq} & \cos T_{pq} \end{pmatrix} \begin{pmatrix} p \\ q \end{pmatrix}$$

The rotation matrix itself may be written as matrix exponential $e^{T_{pq}\left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)}$ as

$$\begin{aligned} \begin{pmatrix} \cos T_{pq} & \sin T_{pq} \\ -\sin T_{pq} & \cos T_{pq} \end{pmatrix} &= e^{T_{pq}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}} \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + T_{pq}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \frac{1}{2}T_{pq}^2\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}^2 + \ldots \end{aligned} \tag{19}$$

$$\hat{T} = \sum_{p>q} T_{pq}\left(\hat{E}_{pq} - \hat{E}_{qp}\right)$$

$$E = \left\langle \Psi_0 \middle| e^{-\hat{T}}\hat{H}e^{\hat{T}} \middle| \Psi_0 \right\rangle$$

$$
\begin{aligned}
E(T) &= \left\langle \Psi_0 \,\middle|\, \hat{H} \,\middle|\, \Psi_0 \right\rangle + \left\langle \Psi_0 \,\middle|\, \left[\hat{H},\hat{T}\right] \,\middle|\, \Psi_0 \right\rangle + \frac{1}{2}\left\langle \Psi_0 \,\middle|\, \left[\left[\hat{H},\hat{T}\right],\hat{T}\right] \,\middle|\, \Psi_0 \right\rangle + \quad .. \qquad (21)\\
&= E(0) + \sum_{p<q} T_{pq} \left\langle \Psi_0 \,\middle|\, \left[\hat{H},(\hat{E}_{pq}-\hat{E}_{qp})\right] \,\middle|\, \Psi_0 \right\rangle \qquad (22)\\
&\quad + \frac{1}{2}\sum_{p<q}\sum_{r<s} T_{pq}T_{rs} \left\langle \Psi_0 \,\middle|\, \left[\left[\hat{H},(\hat{E}_{pq}-\hat{E}_{qp})\right],(\hat{E}_{rs}-\hat{E}_{sr})\right] \,\middle|\, \Psi_0 \right\rangle + \quad \ldots \qquad (23)\\
&= E(0) + \sum_{p>q} \left(\frac{\partial E}{\partial T_{pq}}\right)_0 T_{pq} + \frac{1}{2}\sum_{p<q}\sum_{r<s} \left(\frac{\partial^2 E}{\partial T_{pq}\partial T_{rs}}\right)_0 T_{pq}T_{rs} + \quad \ldots \qquad (24)
\end{aligned}
$$

$$\begin{aligned}\left(\frac{\partial E}{\partial T_{pq}}\right)_0 &= \left\langle \Psi_0 \left| \hat{H}(\hat{E}_{pq}-\hat{E}_{qp}) \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| (\hat{E}_{pq}-\hat{E}_{qp})\hat{H} \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \hat{H}(\hat{E}_{pq}-\hat{E}_{qp}) \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| (\hat{E}^\dagger_{qp}-\hat{E}^\dagger_{pq})\hat{H} \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \hat{H}(\hat{E}_{pq}-\hat{E}_{qp}) \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{H}(\hat{E}_{qp}-\hat{E}_{pq}) \right| \Psi_0 \right\rangle \\ &= 2\left\langle \Psi_0 \left| \hat{H}(\hat{E}_{pq}-\hat{E}_{qp}) \right| \Psi_0 \right\rangle \qquad (25)\end{aligned}$$

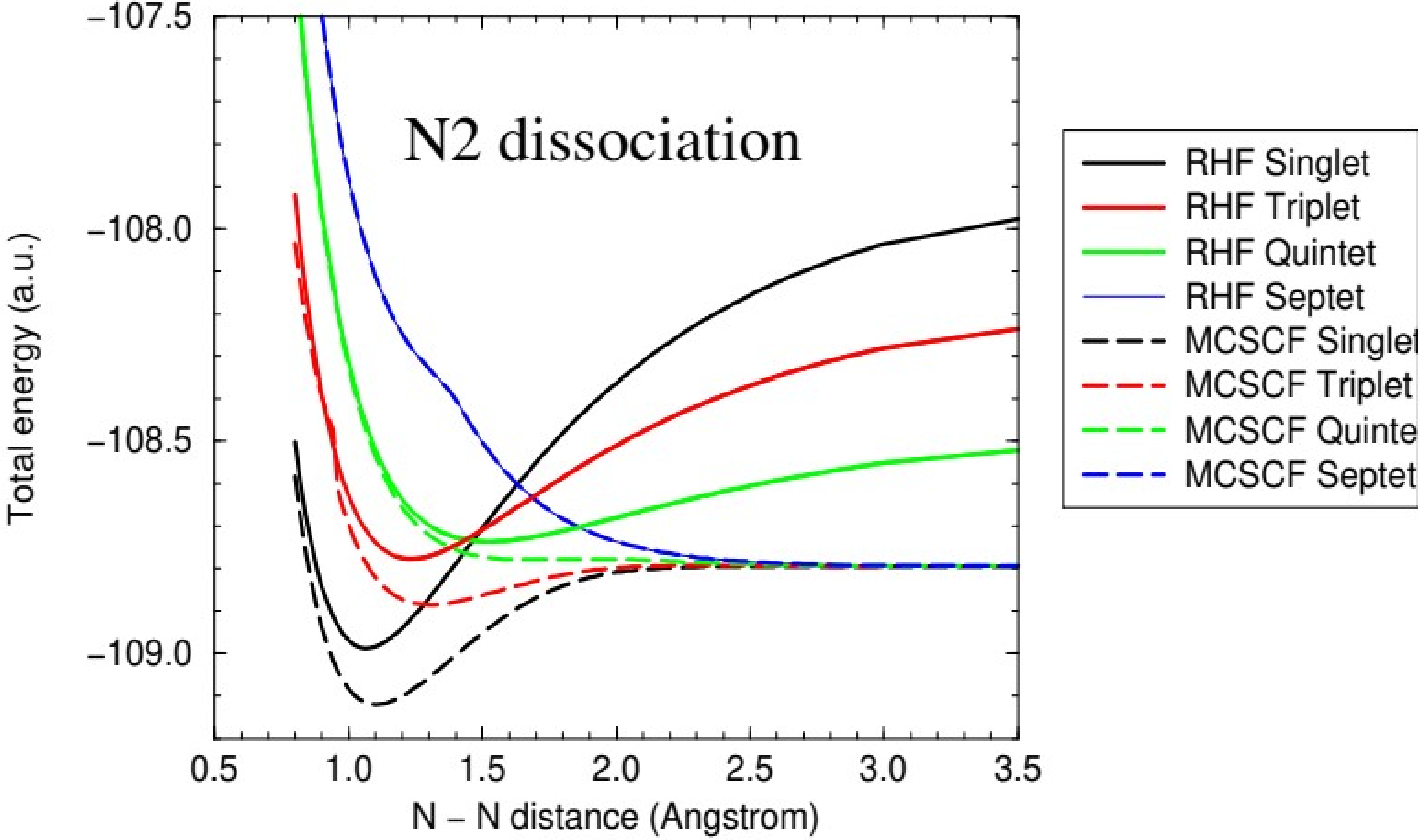
$$\begin{aligned}\left(\frac{\partial^2 E}{\partial T_{pq}\partial T_{rs}}\right)_0 &= 2\left\langle \Psi_0 \left| (\hat{E}_{qp}-\hat{E}_{pq})\hat{H}(\hat{E}_{rs}-\hat{E}_{sr}) \right| \Psi_0 \right\rangle \\ &\quad + \left\langle \Psi_0 \left| (\hat{E}_{qp}-\hat{E}_{pq})(\hat{E}_{sr}-\hat{E}_{rs})\hat{H} \right| \Psi_0 \right\rangle \\ &\quad + \left\langle \Psi_0 \left| (\hat{E}_{sr}-\hat{E}_{rs})(\hat{E}_{qp}-\hat{E}_{pq})\hat{H} \right| \Psi_0 \right\rangle \qquad (26)\end{aligned}$$

$$\hat{H} = \sum_{pq} h_{pq}\hat{E}_{pq} + \frac{1}{2}\sum_{pqrs}(pq|rs)\left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\right)$$

$$
\begin{aligned}
\hat{E}_{pp}|\mu\rangle &= (n_{p,\alpha} + n_{p,\beta})|\mu\rangle = n_p|\mu\rangle \\
\hat{E}_{pa} &= 0 \\
\hat{E}_{ip} &= 2\delta_{ip} \\
\hat{E}_{pq}^{\dagger} &= \hat{E}_{qp} \\
\left[\hat{E}_{pq}, \hat{E}_{rs}\right] &= \delta_{qr}\hat{E}_{ps} - \delta_{ps}\hat{E}_{rq} \\
\hat{E}_{pa}\hat{E}_{bq} &= \delta_{ab}\hat{E}_{pq} \\
\hat{E}_{ip}\hat{E}_{qj} &= \delta_{ij}\left(2\delta_{pq} - \hat{E}_{qp}\right) + 2\delta_{ip}\hat{E}_{qj}
\end{aligned}
$$

That’s all ….

6 electrons / 6 orbitals



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