

Multi-configurational calculations

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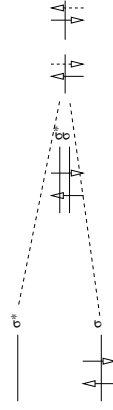
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General considerations

Again H_2 in a minimal basis:

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



- 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 $|s_A s_B\rangle + |s_B s_A\rangle$ without the ionic configurations $|s_A s_A\rangle$
and $|s_B s_B\rangle$

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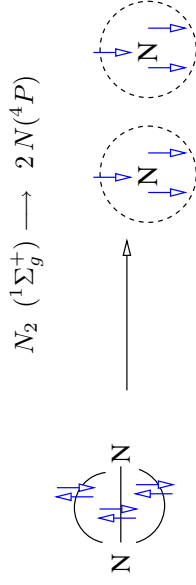
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General considerations

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

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



Need for multiconfigurational wavefunctions

Non-dynamical correlation

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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)

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Super-CI method

Alternative to the diagonalization of the Fock matrix

1. Starting orbitals
2. Orthogonalize 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

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

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

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Super-CI method

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

- Orbitals change through mono-excitations
- Excitation operator

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

- 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

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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} :

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

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Generalization

- First-order density matrix

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

- Second-order density matrix

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

- 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

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

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Density matrices

Hartree-Fock:

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

fits in the same expression as above with the 1-particle density matrix

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

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

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

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

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

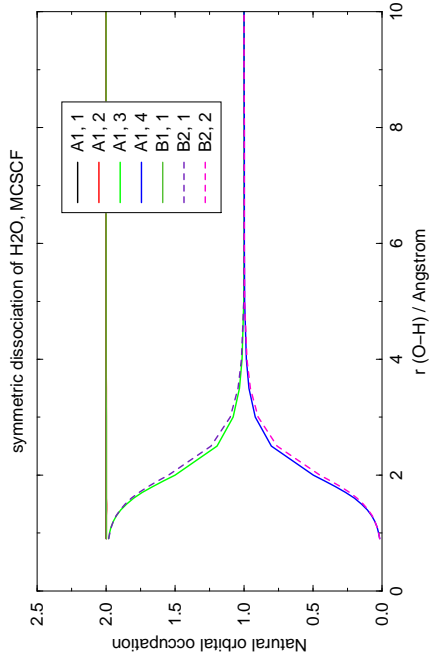
- Dipole moment

$$\mu = \sum_{\alpha\beta} D_{\alpha\beta} \langle \chi_\alpha | \hat{r} | \chi_\beta \rangle = \sum_{i \in \text{occ}} D_{ii} \langle \phi_i | \hat{r} | \phi_i \rangle$$

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



Ψ

Orbitals



Remains to work

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

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

$$T^\dagger = -T \quad ; \quad U = e^{\hat{T}}$$

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

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

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

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

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

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Finally the optimization

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

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

- Expansion of the exponentials to 2nd order:

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

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

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Finally the optimization

- Newton-Raphson procedure:

$$E(\mathbf{x}) = E(0) + \mathbf{a}^T \cdot \mathbf{x} + \frac{1}{2} \mathbf{x}^T \mathbf{B} \mathbf{x}$$

$$\mathbf{a} + \mathbf{B} \cdot \mathbf{x} = 0$$

$$\mathbf{x} = -\mathbf{B}^{-1} \cdot \mathbf{a}$$

- Identify:

$$\mathbf{a}_{T_{ij}} = \left(\frac{\partial E}{\partial T_{ij}} \right) = \langle \Psi_0 | [\hat{H}, \hat{E}_{ij} - \hat{E}_{ji}] | \Psi_0 \rangle$$

$$\mathbf{a}_{S_{K0}} = \left(\frac{\partial E}{\partial S_{K0}} \right) = 2 \langle \Psi_0 | \hat{H} | \Psi_K \rangle$$

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

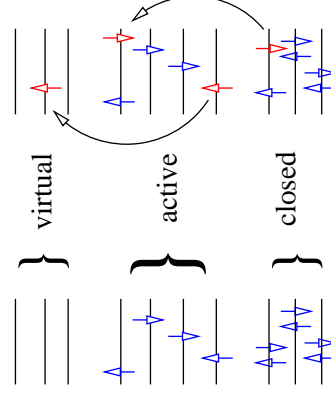
Has to be implemented

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Adding dynamical correlation

- Add excitations



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

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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