Introduction to multiconfigurational quantum chemistry

Emmanuel Fromager

Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique - Université de Strasbourg / CNRS

M2 lecture, Strasbourg, France.
Variational and non-variational approximations

- The exact electronic ground state $\Psi_0$ and its energy $E_0$ can be obtained two ways:

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \langle \hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$$

- Approximate parametrized ground-state wave function: $\Psi(\lambda_0)$

where $\lambda_0$ denotes the complete set of optimized parameters.

Variational calculation

$$\left. \frac{\partial}{\partial \lambda} \frac{\langle \Psi(\lambda) | \hat{H} | \Psi(\lambda) \rangle}{\langle \Psi(\lambda) | \Psi(\lambda) \rangle} \right|_{\lambda = \lambda_0} = 0$$

↓

Hartree-Fock (HF)
Configuration Interaction (CI)
Multi-Configurational Self-Consistent Field (MCSCF)

Non-variational calculation

$$\hat{H} | \Psi(\lambda) \rangle - E(\lambda) | \Psi(\lambda) \rangle = 0 \quad \text{for} \; \lambda = \lambda_0$$

↓

Many-Body Perturbation Theory (MBPT)
Coupled Cluster (CC)
H$_2$ (1$^1\Sigma_g^+$, aug-cc-pVQZ)

Energy (a.u.) vs. Interatomic distance (a.u.)

- FCI
- HF
- MP2

Institut de Chimie, Strasbourg, France
Short-range dynamical correlation

Ground-state configuration  singly-excited conf.  doubly-excited conf.
Introduction to multiconfigurational quantum chemistry

Static correlation

LUMO
HOMO

LUMO
HOMO

LUMO
HOMO

Institut de Chimie, Strasbourg, France
Static correlation

- $\text{H}_2$ in the equilibrium geometry:

\[
|\Psi_0\rangle = C_0 |1\sigma_g^\alpha 1\sigma_g^\beta \rangle + \ldots \quad \text{where } |C_0|^2 = 98\% \quad \text{no static correlation}
\]

- In the dissociation limit: $\text{H}_A\ldots\text{H}_B$ and \textit{not} $\text{H}_A^-\ldots\text{H}_B^+$ or $\text{H}_A^+\ldots\text{H}_B^-$

\[
\phi_{1\sigma_g}(r) = \frac{1}{\sqrt{2}} \left( \phi_{1s_A}(r) + \phi_{1s_B}(r) \right) \quad \text{and} \quad \phi_{1\sigma_u}(r) = \frac{1}{\sqrt{2}} \left( \phi_{1s_A}(r) - \phi_{1s_B}(r) \right)
\]

\[
|1\sigma_g^\alpha 1\sigma_g^\beta \rangle = \frac{1}{2} \left( |1s_A^\alpha 1s_B^\beta \rangle + |1s_B^\alpha 1s_A^\beta \rangle + |1s_A^\alpha 1s_A^\beta \rangle + |1s_B^\alpha 1s_B^\beta \rangle \right)
\]

\[
- |1\sigma_u^\alpha 1\sigma_u^\beta \rangle = \frac{1}{2} \left( |1s_A^\alpha 1s_B^\beta \rangle + |1s_B^\alpha 1s_A^\beta \rangle - |1s_A^\alpha 1s_A^\beta \rangle - |1s_B^\alpha 1s_B^\beta \rangle \right)
\]

\[
|\Psi_0\rangle = \frac{1}{\sqrt{2}} \left( |1\sigma_g^\alpha 1\sigma_g^\beta \rangle - |1\sigma_u^\alpha 1\sigma_u^\beta \rangle \right) \quad \text{strong static correlation}
\]
**H$_2$ in a minimal basis**

**EXERCISE:**

1. Show that the Hamiltonian matrix for H$_2$ can be written in the basis of the two single-determinant states $|1\sigma_g^\alpha 1\sigma_g^\beta \rangle$ and $|1\sigma_u^\alpha 1\sigma_u^\beta \rangle$ as follows,

$$[\hat{H}] = \begin{pmatrix}
E_g & K \\
K & E_u
\end{pmatrix},$$

where

for $i = g, u$, $E_i = 2h_{ii} + \langle 1\sigma_i 1\sigma_i |1\sigma_i 1\sigma_i \rangle$, $h_{ii} = \langle 1\sigma_i |\hat{h}|1\sigma_i \rangle$, $K = \langle 1\sigma_u 1\sigma_u |1\sigma_g 1\sigma_g \rangle$.

2. In the following, we use the minimal basis consisting of the two 1$s$ atomic orbitals. Explain why, in the dissociation limit, $E_g = E_u$ and $K = \frac{1}{2}\langle 1s 1s |1s 1s \rangle > 0$.

3. Conclude that, in the dissociation limit, the ground state is multiconfigurational and does correspond to two neutral hydrogen atoms with energy $(E_g - K)$. 
Introduction to multiconfigurational quantum chemistry

\[ H_2 (1^1\Sigma^+_g, \text{aug-cc-pVQZ}) \]

\( \text{FCI} \quad \text{HF} \quad \text{CISD 2/2} \)

Energy (a.u.)
Interatomic distance (a.u.)

1  2  3  4  5  6  7  8  9  10
Multi-Configurational Self-Consistent Field model (MCSCF)

- The MCSCF model consists in performing a CI calculation with a reoptimization of the orbitals:

\[
|\Psi(\kappa, C)\rangle = e^{-\hat{\kappa}} \left( \sum_{\xi} C_{\xi} |\text{det}_{\xi}\rangle \right) \quad \text{where} \quad C \equiv \{C_{\xi}\}_{\xi}
\]

- The MCSCF model is a multiconfigurational extension of HF which aims at describing static correlation: a limited number of determinants should be sufficient.

- Short-range dynamical correlation is treated afterwards (post-MCSCF models)

- Choice of the determinants: active space

\[
\begin{align*}
\text{H} & \quad 2 \text{ electrons in 2 orbitals } (1\sigma_g, 1\sigma_u) & \quad \rightarrow & \quad 2/2 \\
\text{Be} & \quad 2 \text{ electrons in 4 orbitals } (2s, 2p_x, 2p_y, 2p_z) & \quad \rightarrow & \quad 2/4
\end{align*}
\]
Multi-Configurational Self-Consistent Field model (MCSCF)

- Complete Active Space (CAS) for Be: $|1s^22s^2\rangle, |1s^22p_x^2\rangle, |1s^22p_y^2\rangle, |1s^22p_z^2\rangle$.
  
  if all the determinants are included in the MCSCF calculation $\rightarrow$ CASSCF
  
  if a Restricted Active Space (RAS) is used $\rightarrow$ RASSCF

- The orbital space is now divided in three:

  **doubly occupied molecular orbitals (inactive)**: $\phi_i, \phi_j, \ldots$  $1s$

  **active molecular orbitals**: $\phi_u, \phi_v, \ldots$  $2s, 2p_x, 2p_y, 2p_z$

  **unoccupied molecular orbitals (virtuals)**: $\phi_a, \phi_b, \ldots$  $3s, 3p, 3d, \ldots$
\[ \Psi_0 \approx |\sigma_g^2| \]
**Multi-Configurational Self-Consistent Field model (MCSCF)**

**EX6:** In order to illustrate with H$_2$ the fact that *active orbitals* can be *partially occupied*, show that the active part of the density matrix $A \mathbf{D}$, defined as

$$
A \mathbf{D}_{vw} = \langle \Psi | \hat{E}_{vw} | \Psi \rangle,
$$

where $|\Psi\rangle = \frac{1}{\sqrt{1+c^2}} \left( |1\sigma_1 \sigma_2 \rangle - c |1\sigma_1 \sigma_2 \rangle \right)$,

equals

$$
A \mathbf{D} = \begin{bmatrix}
\frac{2}{1+c^2} & 0 \\
0 & \frac{2c^2}{1+c^2}
\end{bmatrix}.
$$

**Note:** In the particular case of a single determinantal wave function ($c = 0$) the active density matrix reduces to

$$
\begin{bmatrix}
2 & 0 \\
0 & 0
\end{bmatrix}.
$$
Iterative optimization of the orbital rotation vector $\kappa$ and the CI coefficients $C_i$:

$$|\Psi^{(0)}\rangle = \sum_i C_i^{(0)} |i\rangle \quad \text{← normalized starting wave function}$$

$$|\Psi(\lambda)\rangle = e^{-\hat{\kappa}} \frac{|\Psi^{(0)}\rangle + \hat{Q}|\delta\rangle}{\sqrt{1 + \langle\delta|\hat{Q}|\delta\rangle}} \quad \text{← convenient parametrization} \quad \lambda = \begin{bmatrix} \vdots \\ \kappa_{pq} \\ \vdots \\ \delta_i \\ \vdots \end{bmatrix}_{p > q}$$

$$\hat{Q} = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|, \quad |\delta\rangle = \sum_i \delta_i |i\rangle, \quad \langle\Psi^{(0)}|\hat{Q}|\delta\rangle = 0, \quad \langle\Psi(\lambda)|\Psi(\lambda)\rangle = 1$$

MCSCF energy expression: $E(\lambda) = \langle\Psi(\lambda)|\hat{H}|\Psi(\lambda)\rangle$

Variational optimization:

$$E^{[1]}_{\lambda^+} = \begin{bmatrix} E_{\lambda^+}^{o[1]} \\ E_{\lambda^+}^{c[1]} \end{bmatrix} = 0 \quad \text{where} \quad E_{\lambda^+}^{o[1]} = \frac{\partial E(\lambda)}{\partial \kappa} \bigg|_{\lambda^+}$$

and $E_{\lambda^+}^{c[1]} = \frac{\partial E(\lambda)}{\partial \delta} \bigg|_{\lambda^+}$
Introduction to multiconfigurational quantum chemistry

- Newton method:

\[ E(\lambda) \approx E(0) + \lambda^T E_0^{[1]} + \frac{1}{2} \lambda^T E_0^{[2]} \lambda \quad \rightarrow \quad E_{\lambda+}^{[1]} \approx E_0^{[1]} + E_0^{[2]} \lambda_+ = 0 \quad \rightarrow \quad E_0^{[2]} \lambda_+ = -E_0^{[1]} \]

Newton step

- Convergence reached when \( E_0^{[1]} = 0 \)

**EX7:** Show that \( E_0^{[1]}_{pq} = \langle \Psi^{(0)} | [\hat{E}_{pq} - \hat{E}_{qp}, \hat{H}] | \Psi^{(0)} \rangle \) and \( E_0^{c[1]} = 2 \left( H^{\text{CAS}} - E(0) \right) C^{(0)} \)

where \( H_{ij}^{\text{CAS}} = \langle i|\hat{H}|j \rangle \) and \( C^{(0)} = \begin{bmatrix} \vdots \\ C_i^{(0)} \\ \vdots \end{bmatrix} \)

**Note:** \( E_0^{o[1]} = 0 \) is known as generalized Brillouin theorem.
Introduction to multiconfigurational quantum chemistry

H\textsubscript{2} (1\textsuperscript{1}\Sigma_{g}^{+}, \text{aug-cc-pVQZ})

Institut de Chimie, Strasbourg, France
Multi-Reference Perturbation Theory (MRPT)

- Multiconfigurational extension of MP2:

  unperturbed wave function  \[ |\Phi_0\rangle \rightarrow |\Psi^{(0)}\rangle \]

  unperturbed energy  \[ E^{(0)} = 2 \sum_i \epsilon_i \rightarrow ??? \]

  perturbers  \[ |D\rangle \rightarrow ??? \]

  zeroth-order excited energies  \[ E^{(0)} + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \rightarrow ??? \]

  unperturbed Hamiltonian  \[ \hat{F} \rightarrow E^{(0)}|\Phi_0\rangle\langle\Phi_0| + \sum_D \langle D|\hat{F}|D\rangle|D\rangle\langle D| \rightarrow ??? \]

- Standard approaches are CASPT2\(^a\) and N-electron valence state PT2 (NEVPT2)\(^b\)


$H_2 \left( {1}^1 \Sigma_g^+, \text{aug-cc-pVQZ} \right)$

![Graph showing the energy of $H_2$ as a function of interatomic distance for various methods: FCI, HF, CISD 2/2, MCSCF 2/2, and sc-NEVPT2.](image)

- **Energy (a.u.)**
  - FCI
  - HF
  - CISD 2/2
  - MCSCF 2/2
  - sc-NEVPT2

- **Interatomic distance (a.u.)**
  - Ranges from 1 to 10.
Multi-state MCSCF approach

- **State-averaged** MCSCF model: simultaneous optimization of the ground and the lowest $N-1$ excited states at the MCSCF level.

- Iterative procedure: $N$ initial orthonormal states are built from the same set of orbitals.

\[
|\Psi_I^{(0)}\rangle = \sum_i C_{I,i}^{(0)} |i\rangle, \quad I = 1, \ldots, N
\]

- **Double-exponential** parametrization:

\[
|\Psi_I^{(\kappa, S)}\rangle = e^{-\kappa} e^{-\hat{S}} |\Psi_I^{(0)}\rangle \quad \text{where} \quad \hat{S} = \sum_{J=1}^{N} \sum_{K>J} S_{KJ} \left( |\Psi_K^{(0)}\rangle\langle\Psi_J^{(0)}| - |\Psi_J^{(0)}\rangle\langle\Psi_K^{(0)}| \right)
\]

\[
\sum_i |i\rangle\langle i| = \sum_K |\Psi_K^{(0)}\rangle\langle\Psi_K^{(0)}|
\]
Multi-state MCSCF approach

- Gross–Oliveira–Kohn (GOK) variational principle for an ensemble of ground and excited states:

For any set \( \{ \Psi_I \}_{I=1}^{N} \) of \( N \) orthonormal states, the following inequality holds,

\[
\sum_{I=1}^{N} w_I \langle \Psi_I | \hat{H} | \Psi_I \rangle \geq \sum_{I=1}^{N} w_I E_I
\]

where \( E_1 \leq E_2 \leq \ldots \leq E_N \) are the \( N \) lowest exact eigenvalues of \( \hat{H} \), and the weights are ordered as follows,

\[
w_1 \geq w_2 \geq \ldots \geq w_N > 0.
\]

EXERCISE: Prove the theorem in the particular case of two states by using Theophilou’s variational principle: \( \langle \Psi_1 | \hat{H} | \Psi_1 \rangle + \langle \Psi_2 | \hat{H} | \Psi_2 \rangle \geq E_1 + E_2 \). Hint: Show that

\[
w_1 \langle \Psi_1 | \hat{H} | \Psi_1 \rangle + w_2 \langle \Psi_2 | \hat{H} | \Psi_2 \rangle = w_2 \left[ \langle \Psi_1 | \hat{H} | \Psi_1 \rangle + \langle \Psi_2 | \hat{H} | \Psi_2 \rangle \right] + (w_1 - w_2) \langle \Psi_1 | \hat{H} | \Psi_1 \rangle
\]
**EXERCISE:** Proof of Theophilou’s variational principle for two states

(1) Let \( \Delta = \langle \Psi_1 | \hat{H} | \Psi_1 \rangle + \langle \Psi_2 | \hat{H} | \Psi_2 \rangle - E_1 - E_2 \). We consider the complete basis of the exact eigenvectors \( \{ \tilde{\Psi}_I \}_{I=1,2,...} \) of \( \hat{H} \) with eigenvalues \( \{ E_I \}_{I=1,2,...} \).

Both trial wavefunctions can be expanded in that basis as follows,

\[
| \Psi_K \rangle = \sum_I C_{KI} | \tilde{\Psi}_I \rangle, \quad K = 1, 2.
\]

Show that \( \Delta = \sum_{I=1}^{2} (p_I - 1) E_I + \sum_{I>2} p_I E_I \) where \( p_I = C_{1I}^2 + C_{2I}^2 \).

(2) Show that \( \Delta = \sum_{I=1}^{2} (1 - p_I)(E_2 - E_I) + \sum_{I>2} p_I (E_I - E_2) \). **Hint:** prove first that \( \sum_I p_I = 2 \).

(3) Let us now decompose the two first eigenvectors \( (I = 1, 2) \) in the basis of the trial wavefunctions and the orthogonal complement:

\[
| \tilde{\Psi}_I \rangle = C_{1I} | \Psi_1 \rangle + C_{2I} | \Psi_2 \rangle + \hat{Q}_{12} | \tilde{\Psi}_I \rangle \quad \text{where}
\]

\[
\hat{Q}_{12} = 1 - \sum_{K=1}^{2} | \Psi_K \rangle \langle \Psi_K |.
\]

Explain why \( p_I \leq 1 \) when \( I = 1, 2 \) and conclude.
Multi-state MCSCF approach

- State-averaged energy: 
  \[ E(\kappa, S) = \sum_{I=1}^{N} w_I \langle \Psi_I(\kappa, S) | \hat{H} | \Psi_I(\kappa, S) \rangle \]

  where \( w_I \) are arbitrary weights. In the so-called "equal weight" state-averaged MCSCF calculation \( w_I = \frac{1}{N} \).

- Variational optimization: 
  \[ \frac{\partial E(\kappa, S)}{\partial \kappa} = \frac{\partial E(\kappa, S)}{\partial S} = 0 \]

- Note that, in contrast to the exact theory, converged individual energies (and therefore excitation energies) may vary with the weights. This is due to the orbital optimization.

- Short-range dynamical correlation is usually recovered within multi-reference perturbation theory (multi-state CASPT2 or NEVPT2 for example)