

# Introduction to multiconfigurational quantum chemistry

*Emmanuel Fromager*



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

M2 lecture, Strasbourg, France.

YouTube video: <https://www.youtube.com/watch?v=c-48MoitBBU>

Slides used in the video (part 2): [https://quantique.u-strasbg.fr/ISTPC/lib/exe/fetch.php?media=istpc2021:istpc2021\\_mc\\_quantum\\_chem.pdf](https://quantique.u-strasbg.fr/ISTPC/lib/exe/fetch.php?media=istpc2021:istpc2021_mc_quantum_chem.pdf)

## Variational and non-variational approximations

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

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

- Approximate parametrized** ground-state wave function:  $\Psi(\boldsymbol{\lambda}_0)$

where  $\boldsymbol{\lambda}_0$  denotes the complete set of **optimized** parameters.

### Variational calculation

$$\left. \frac{\partial}{\partial \boldsymbol{\lambda}} \frac{\langle \Psi(\boldsymbol{\lambda}) | \hat{H} | \Psi(\boldsymbol{\lambda}) \rangle}{\langle \Psi(\boldsymbol{\lambda}) | \Psi(\boldsymbol{\lambda}) \rangle} \right|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}_0} = 0$$

↓

Hartree-Fock (HF)

Configuration Interaction (CI)

Multi-Configurational Self-Consistent Field (MCSCF)

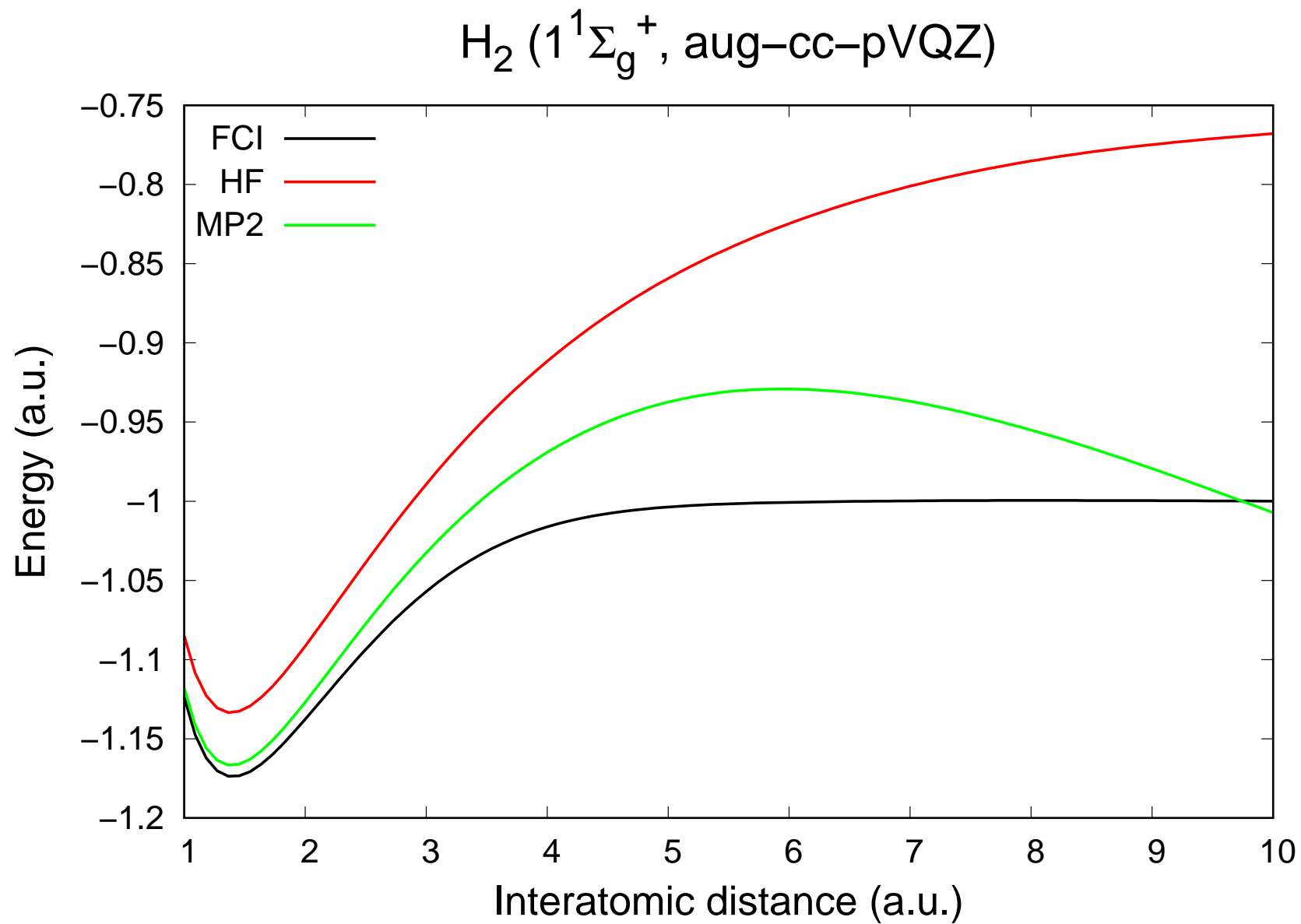
### Non-variational calculation

$$\hat{H} | \Psi(\boldsymbol{\lambda}) \rangle - E(\boldsymbol{\lambda}) | \Psi(\boldsymbol{\lambda}) \rangle = 0 \quad \text{for } \boldsymbol{\lambda} = \boldsymbol{\lambda}_0$$

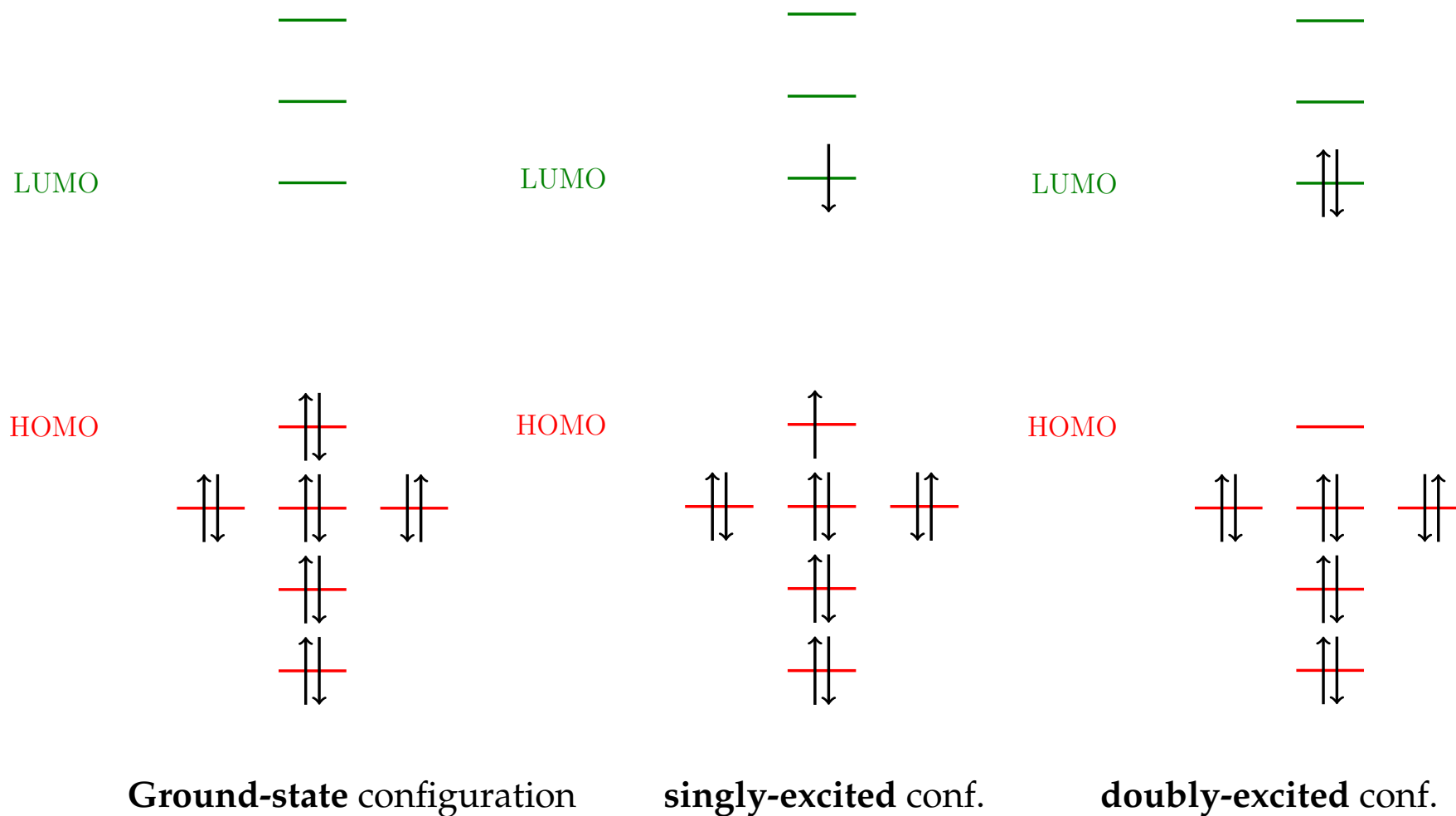
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Many-Body Perturbation Theory (MBPT)

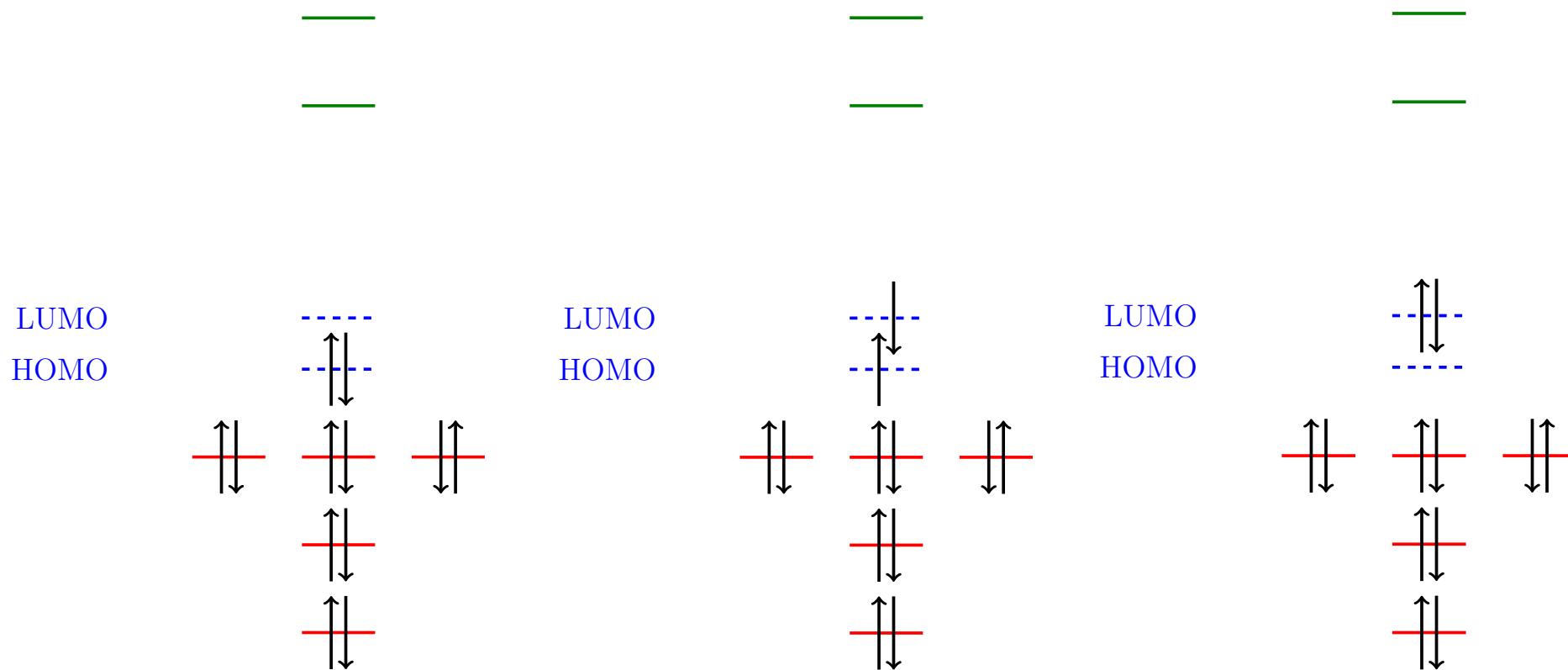
Coupled Cluster (CC)



## Short-range dynamical correlation



## Static correlation



## Static correlation

- H<sub>2</sub> in the equilibrium geometry:

$$\boxed{|\Psi_0\rangle = C_0|1\sigma_g^\alpha 1\sigma_g^\beta\rangle + \dots} \quad \text{where } |C_0|^2 = 98\% \quad \text{no static correlation}$$

- In the dissociation limit: H<sub>A</sub>...H<sub>B</sub> and *not* H<sub>A</sub><sup>-</sup>...H<sub>B</sub><sup>+</sup> or H<sub>A</sub><sup>+</sup>...H<sub>B</sub><sup>-</sup>

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

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

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

$$\boxed{|\Psi_0\rangle = \frac{1}{\sqrt{2}} \left( |1\sigma_g^\alpha 1\sigma_g^\beta\rangle - |1\sigma_u^\alpha 1\sigma_u^\beta\rangle \right)} \quad \text{strong static correlation}$$

H<sub>2</sub> in a minimal basis**EXERCISE:**

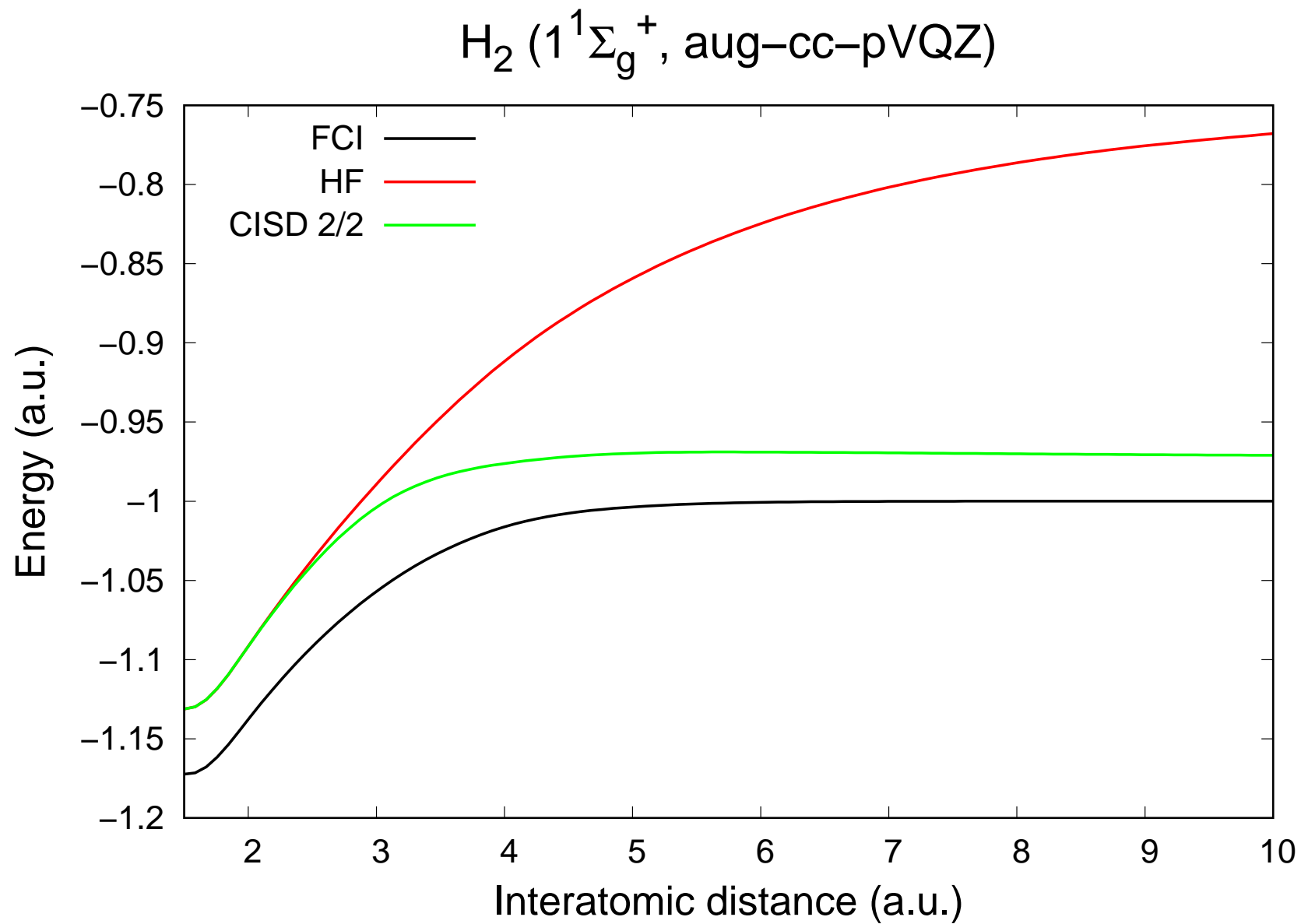
(1) Show that the Hamiltonian matrix for H<sub>2</sub> can be written in the basis of the two single-determinant states  $|1\sigma_g^\alpha 1\sigma_g^\beta\rangle$  and  $|1\sigma_u^\alpha 1\sigma_u^\beta\rangle$  as follows,

$$[\hat{H}] = \begin{bmatrix} E_g & K \\ K & E_u \end{bmatrix}, \quad \text{where}$$

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 1s 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  $(E_g - K)$ .





## Multi-Configurational Self-Consistent Field model (MCSCF)

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

$$|\Psi(\boldsymbol{\kappa}, \mathbf{C})\rangle = e^{-\hat{\kappa}} \left( \sum_{\xi} C_{\xi} |\text{det}_{\xi}\rangle \right) \quad \text{where} \quad \mathbf{C} \equiv \{C_{\xi}\} \quad \text{and} \quad \boldsymbol{\kappa} \equiv \{\kappa_{pq}\}.$$

- The parameters  $\mathbf{C}$  and  $\boldsymbol{\kappa}$  are optimized *variationally* i.e. by minimizing  $\frac{\langle \Psi(\boldsymbol{\kappa}, \mathbf{C}) | \hat{H} | \Psi(\boldsymbol{\kappa}, \mathbf{C}) \rangle}{\langle \Psi(\boldsymbol{\kappa}, \mathbf{C}) | \Psi(\boldsymbol{\kappa}, \mathbf{C}) \rangle}$ .
- 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*

H...H                      2 electrons in 2 orbitals ( $1\sigma_g, 1\sigma_u$ )                       $\longrightarrow$  2/2

Be                              2 electrons in 4 orbitals ( $2s, 2p_x, 2p_y, 2p_z$ )                       $\longrightarrow$  2/4

## Multi-Configurational Self-Consistent Field model (MCSCF)

- Complete Active Space (**CAS**) for Be:  $|1s^2 2s^2\rangle, |1s^2 2p_x^2\rangle, |1s^2 2p_y^2\rangle, |1s^2 2p_z^2\rangle,$

if all the determinants are included in the MCSCF calculation  $\longrightarrow$  CASSCF

if a Restricted Active Space (**RAS**) is used  $\longrightarrow$  RASSCF

- The orbital space is now divided in three:

doubly occupied molecular orbitals ( <b>inactive</b> )	$\phi_i, \phi_j, \dots$	$1s$
<b>active</b> molecular orbitals	$\phi_u, \phi_v, \dots$	$2s, 2p_x, 2p_y, 2p_z$
unoccupied molecular orbitals ( <b>virtu</b> als)	$\phi_a, \phi_b, \dots$	$3s, 3p, 3d, \dots$

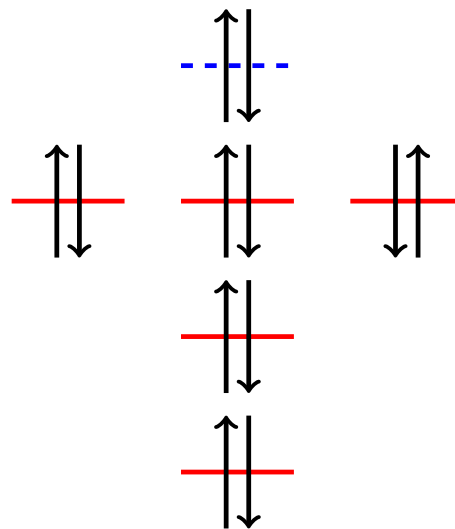
$a, b, \dots$

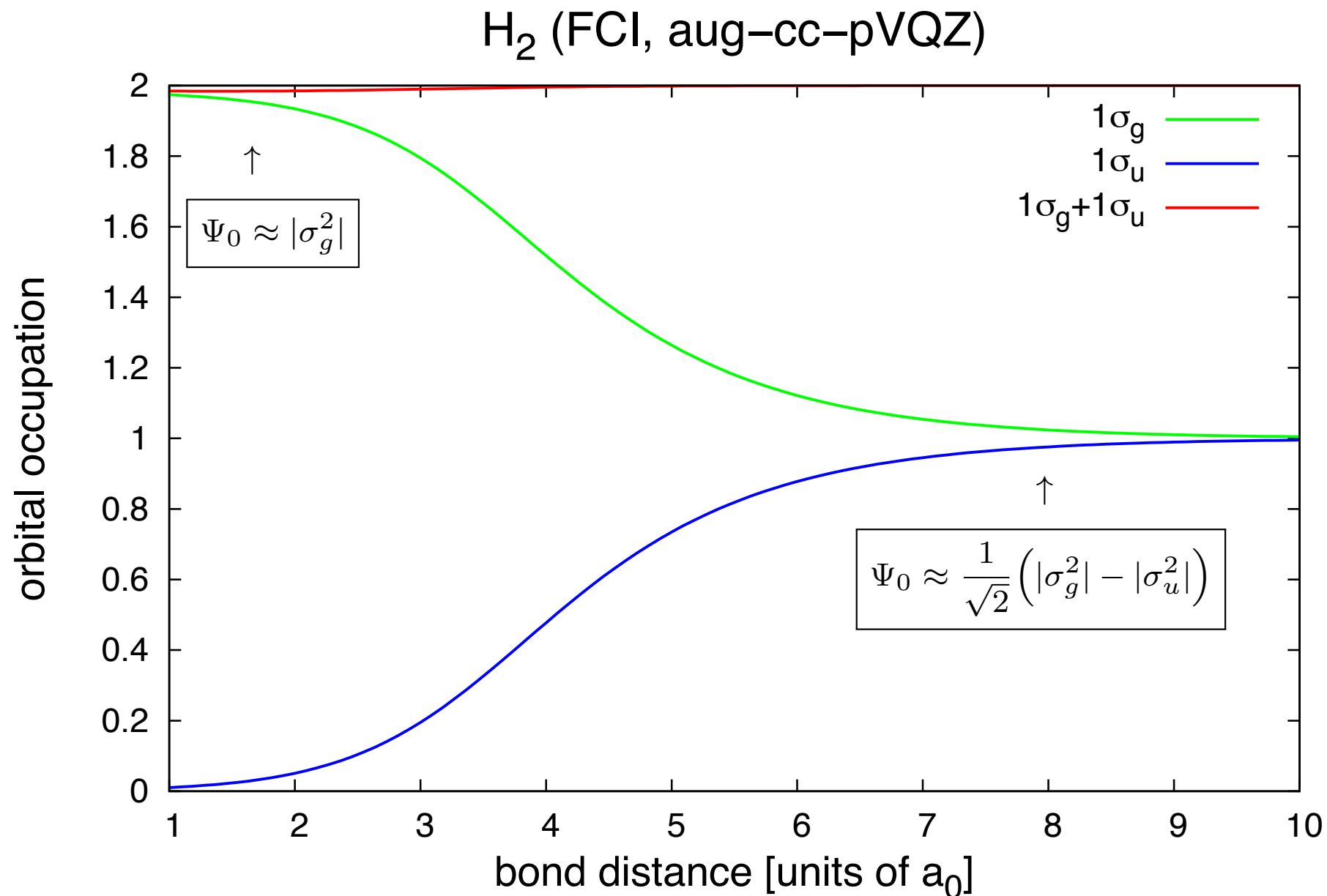


$u, v, \dots$



$i, j, \dots$





## Multi-Configurational Self-Consistent Field model (MCSCF)

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

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

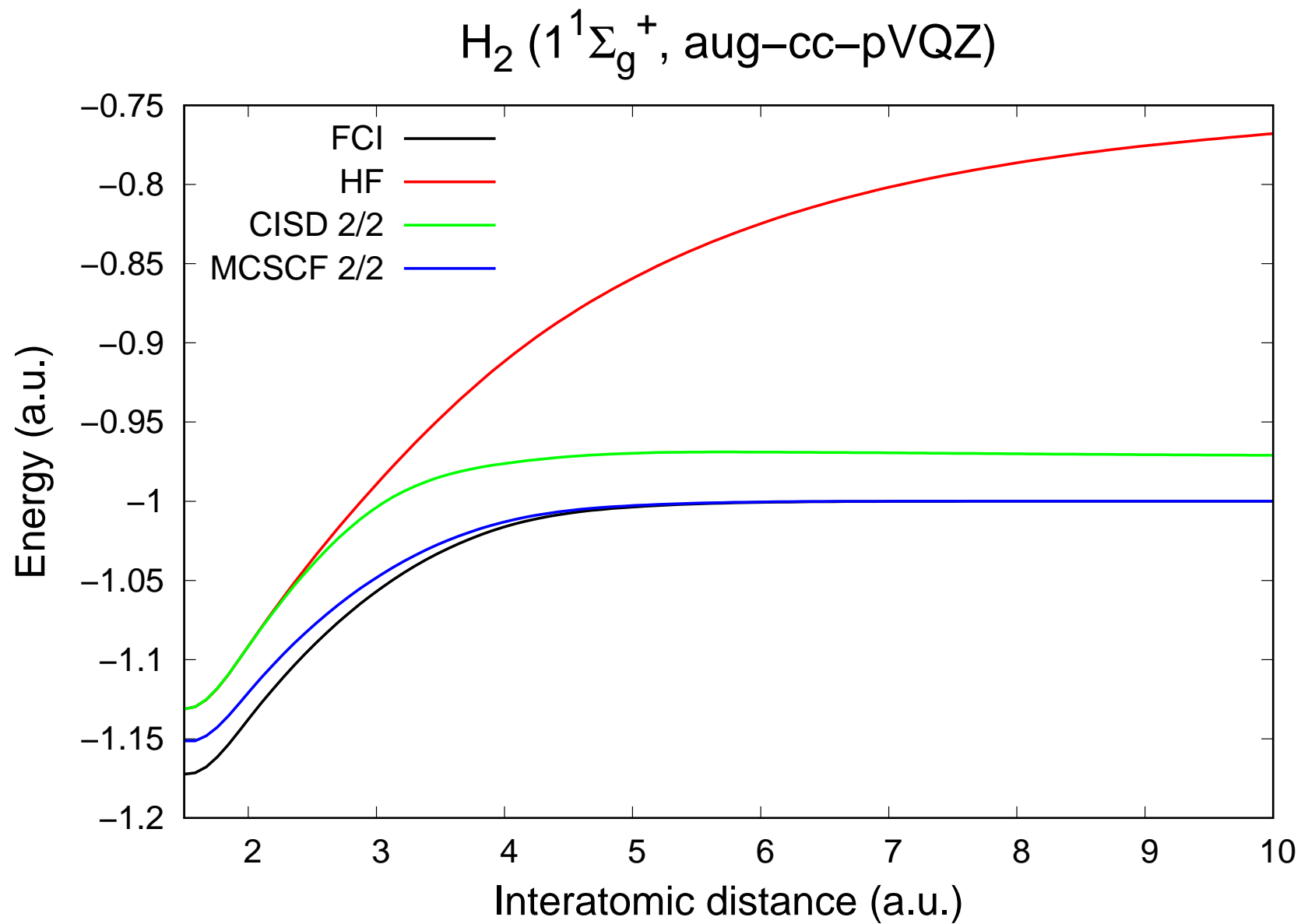
where  $|\Psi\rangle = \frac{1}{\sqrt{1+c^2}} \left( |1\sigma_g^\alpha 1\sigma_g^\beta\rangle - c |1\sigma_u^\alpha 1\sigma_u^\beta\rangle \right)$ ,

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  $\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}$ .



## Multi-Reference Perturbation Theory (MRPT)

- General *perturbative energy expression through second order*:

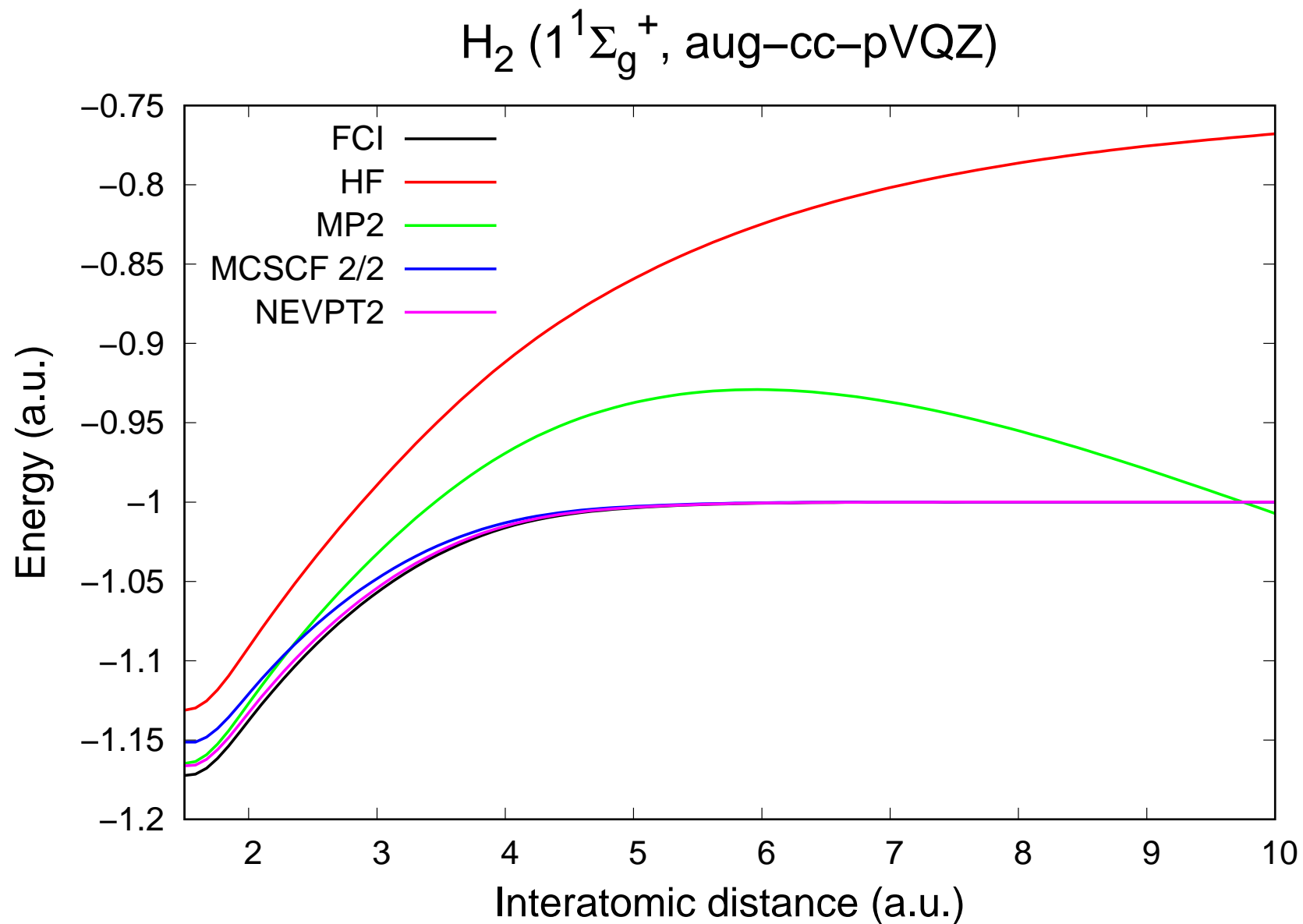
$$E_0 \approx \langle \Psi_{\text{MC}} | \hat{H} | \Psi_{\text{MC}} \rangle + \sum_{\mathcal{P}}^{\text{perturbers}} \frac{\langle \Psi_{\mathcal{P}} | \hat{H} | \Psi_{\text{MC}} \rangle^2}{\mathcal{E}_{\text{MC}} - \mathcal{E}_{\mathcal{P}}}$$

- **Multi-reference** extension of MP2:

unperturbed wave function	$ \Phi_{\text{HF}}\rangle$	$\longrightarrow$	$ \Psi_{\text{MC}}\rangle$
unperturbed energy	$E^{(0)} = 2 \sum_i \varepsilon_i$	$\longrightarrow$	$\mathcal{E}_{\text{MC}} = ???$
perturbers	$ D\rangle$	$\longrightarrow$	$ \Psi_{\mathcal{P}}\rangle = ??? \xleftarrow{\text{NEVPT2}^b} \hat{H}  \Psi_{\text{MC}}\rangle$
zeroth-order excited energies	$E^{(0)} + \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$	$\longrightarrow$	$\mathcal{E}_{\mathcal{P}} = ???$
unperturbed Hamiltonian	$\hat{H}_0 = \hat{F}$	$\longrightarrow$	$\mathcal{E}_{\text{MC}}  \Psi_{\text{MC}}\rangle \langle \Psi_{\text{MC}}  + \sum_{\mathcal{P}}^{\text{perturbers}} \mathcal{E}_{\mathcal{P}}  \Psi_{\mathcal{P}}\rangle \langle \Psi_{\mathcal{P}}  = ???$

- Standard approaches are **CASPT2**<sup>a</sup> and *N-electron valence state* PT2 (**NEVPT2**)<sup>b</sup>.

<sup>a</sup> K. Andersson, P. Å. Malmqvist, and B. O. Roos, J.Chem. Phys. 96, 1218 (1992). <sup>b</sup> C. Angeli, R. Cimiraglia, and J.P. Malrieu, J. Chem. Phys. 117, 9138 (2002).





## State-averaged MCSCF approach

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

For any set  $\{\Psi_I\}_{I=1,\mathcal{N}}$  of  $\mathcal{N}$  orthonormal states, the following inequality holds [Phys. Rev. A 37, 2805 (1988)],

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

where  $E_1 \leq E_2 \leq \dots \leq E_{\mathcal{N}}$  are the  $\mathcal{N}$  lowest **exact** eigenvalues of  $\hat{H}$ , and the weights are ordered as follows,

$$w_1 \geq w_2 \geq \dots \geq w_{\mathcal{N}} > 0.$$

- The state-averaged MCSCF model consists in using a **MCSCF parameterization** for each  $\Psi_I$ .
- All the states are usually described with the **same** set of (so-called **state-averaged**) molecular orbitals.
- **Short-range dynamical correlation** is usually recovered within multi-reference perturbation theory (**multi-state** CASPT2 or NEVPT2, for example).

*Complements*

- Iterative optimization of the orbital rotation vector  $\kappa$  and the CI coefficients  $C_i$ :

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

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

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

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

- Variational optimization:  $E_{\lambda_+}^{[1]} = \begin{bmatrix} E_{\lambda_+}^{o[1]} \\ E_{\lambda_+}^{c[1]} \end{bmatrix} = 0$  where  $E_{\lambda_+}^{o[1]} = \left. \frac{\partial E(\lambda)}{\partial \kappa} \right|_{\lambda_+}$

and  $E_{\lambda_+}^{c[1]} = \left. \frac{\partial E(\lambda)}{\partial \delta} \right|_{\lambda_+}$

- Newton method:

$$E(\boldsymbol{\lambda}) \approx E(0) + \boldsymbol{\lambda}^T E_0^{[1]} + \frac{1}{2} \boldsymbol{\lambda}^T E_0^{[2]} \boldsymbol{\lambda} \quad \rightarrow \quad E_{\boldsymbol{\lambda}_+}^{[1]} \approx E_0^{[1]} + E_0^{[2]} \boldsymbol{\lambda}_+ = 0 \quad \rightarrow \quad E_0^{[2]} \underbrace{\boldsymbol{\lambda}_+}_{\text{Newton step}} = -E_0^{[1]}$$

**Newton step**

- Convergence reached when  $E_0^{[1]} = 0$

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

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

Note:  $E_0^{o[1]} = 0$  is known as **generalized Brillouin theorem**.

**EXERCISE:** Prove GOK's 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  $\{ \tilde{\Psi}_I \}_{I=1,2,\dots}$  of  $\hat{H}$  with eigenvalues  $\{ E_I \}_{I=1,2,\dots}$

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:  $|\tilde{\Psi}_I\rangle = C_{1I}|\Psi_1\rangle + C_{2I}|\Psi_2\rangle + \hat{Q}_{12}|\tilde{\Psi}_I\rangle$  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.

## State-averaged MCSCF approach

- **State-averaged** MCSCF model: **simultaneous optimization** of the ground and the lowest  $\mathcal{N} - 1$  excited states at the MCSCF level.
- Iterative procedure:  $\mathcal{N}$  initial orthonormal states are built from the same set of orbitals.

$$|\Psi_I^{(0)}\rangle = \sum_i C_{I,i}^{(0)} |i\rangle, \quad I = 1, \dots, \mathcal{N}$$

- **Double-exponential** parametrization:

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

$$\text{and} \quad \sum_i |i\rangle \langle i| = \sum_K |\Psi_K^{(0)}\rangle \langle \Psi_K^{(0)}|$$

## State-averaged MCSCF approach

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

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

- Variational optimization: 
$$\frac{\partial E(\boldsymbol{\kappa}, \mathbf{S})}{\partial \boldsymbol{\kappa}} = \frac{\partial E(\boldsymbol{\kappa}, \mathbf{S})}{\partial \mathbf{S}} = 0$$
- 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**.