Introduction to multiconfigurational quantum chemistry

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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

Variational and non-variational approximations

- The exact electronic ground state Ψ_0 and its energy E_0 can be obtained two ways:

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

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

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

Variational calculation

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

$\downarrow$

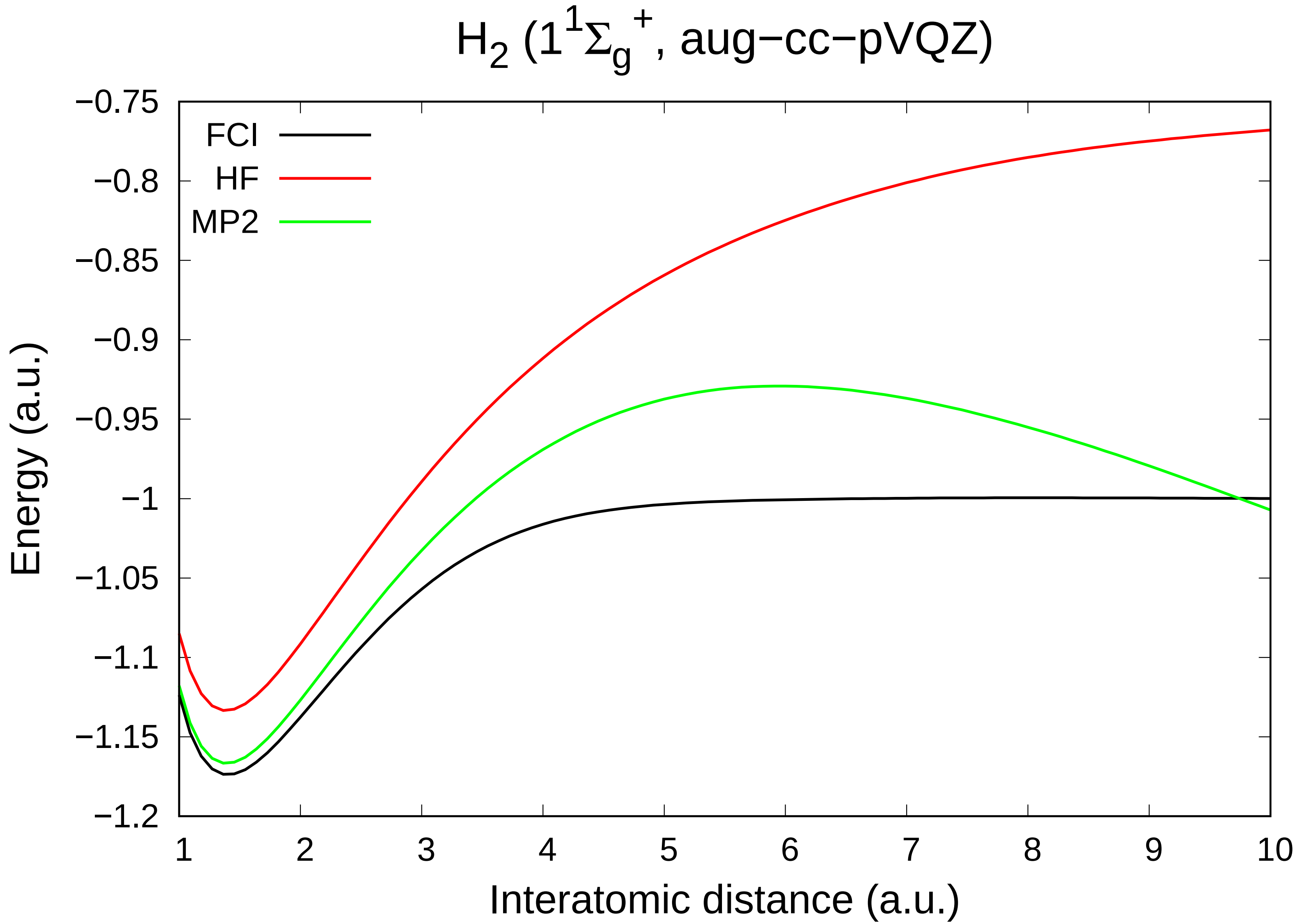
Hartree-Fock (HF)
Configuration Interaction (CI)
Multi-Configurational Self-Consistent Field (MCSCF)

Non-variational calculation

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

$\downarrow$

Many-Body Perturbation Theory (MBPT)
Coupled Cluster (CC)


H2 (1 1Σg+, aug−cc−pVQZ)
FCI
HF
MP2
Energy (a.u.)
−0.75
−0.8
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−0.95
−1
−1.05
−1.1
−1.15
−1.2
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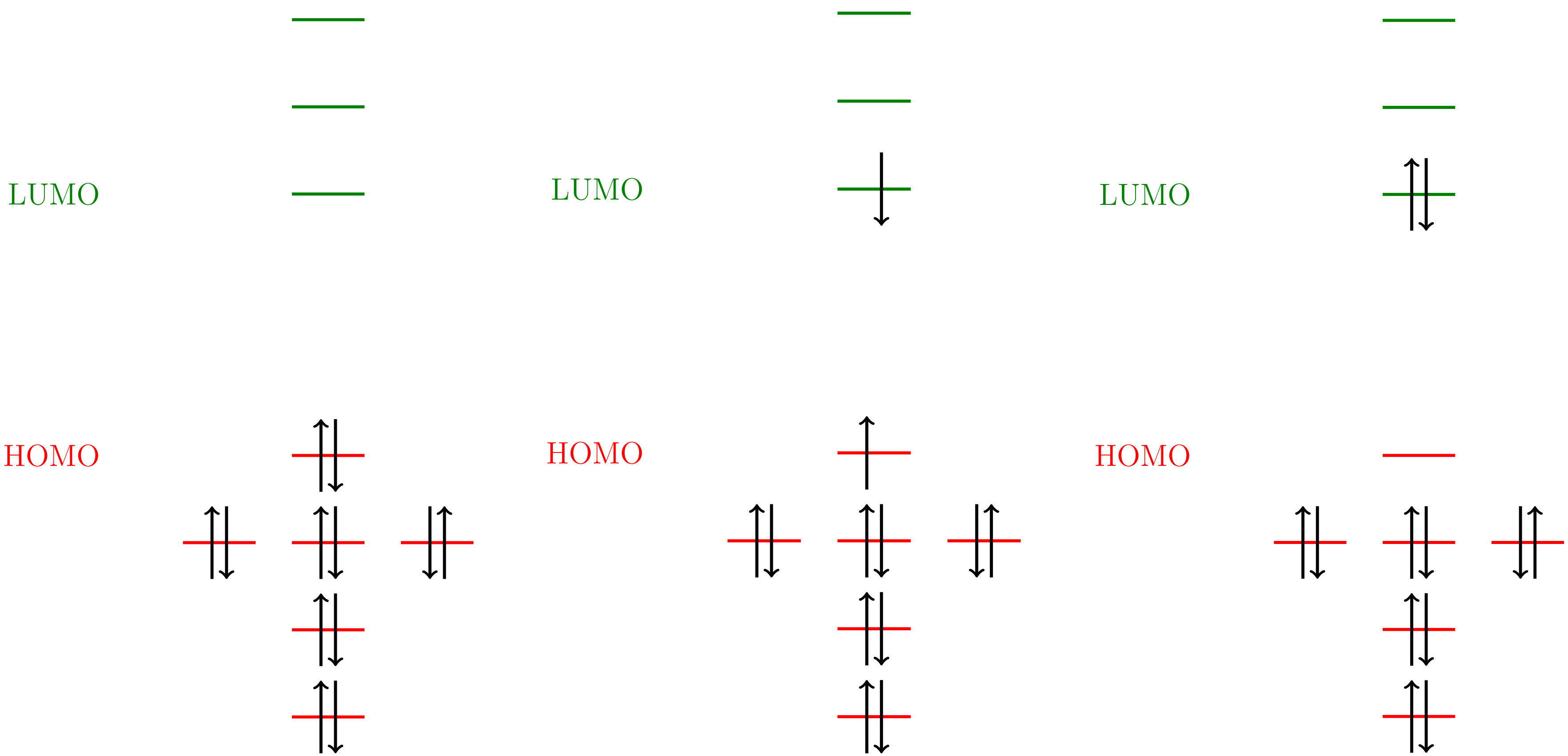
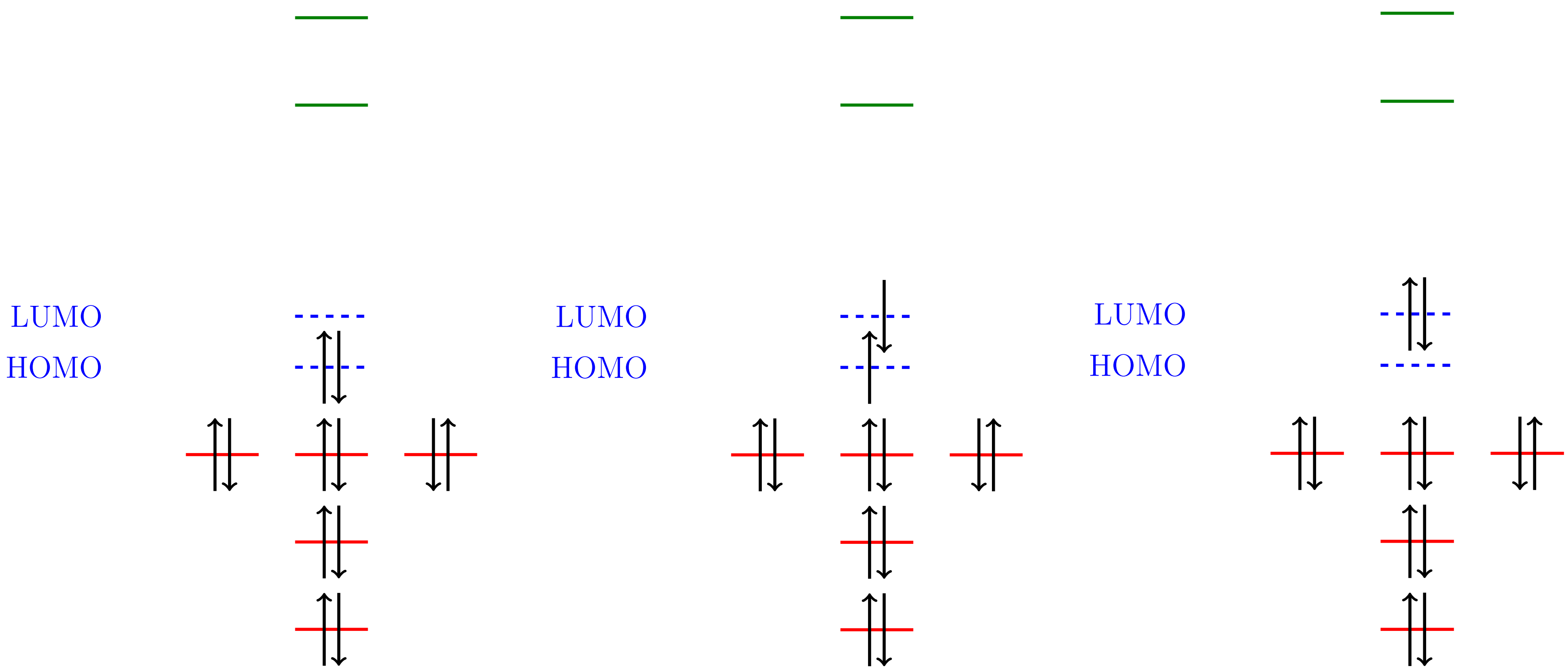
10
Interatomic distance (a.u.)

Short-range dynamical correlation



Ground-state configuration **singly-excited** conf. **doubly-excited** conf.

Static correlation



Static correlation

- H_2 in the equilibrium geometry:

$$\boxed{|\Psi_0\rangle = C_0|1\sigma_g^\alpha 1\sigma_g^\beta\rangle + \ldots} \quad \text{where } |C_0|^2 = 98\%$$

no static correlation

- In the dissociation limit: $H_A \ldots H_B$ and *not* $H_A^- \ldots H_B^+$ or $H_A^+ \ldots H_B^-$

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

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

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

$$\boxed{|\Psi_0\rangle = \frac{1}{\sqrt{2}}\Big(|1\sigma_g^\alpha 1\sigma_g^\beta\rangle - |1\sigma_u^\alpha 1\sigma_u^\beta\rangle\Big)}$$

strong static correlation

H_2 in a minimal basis

EXERCISE:

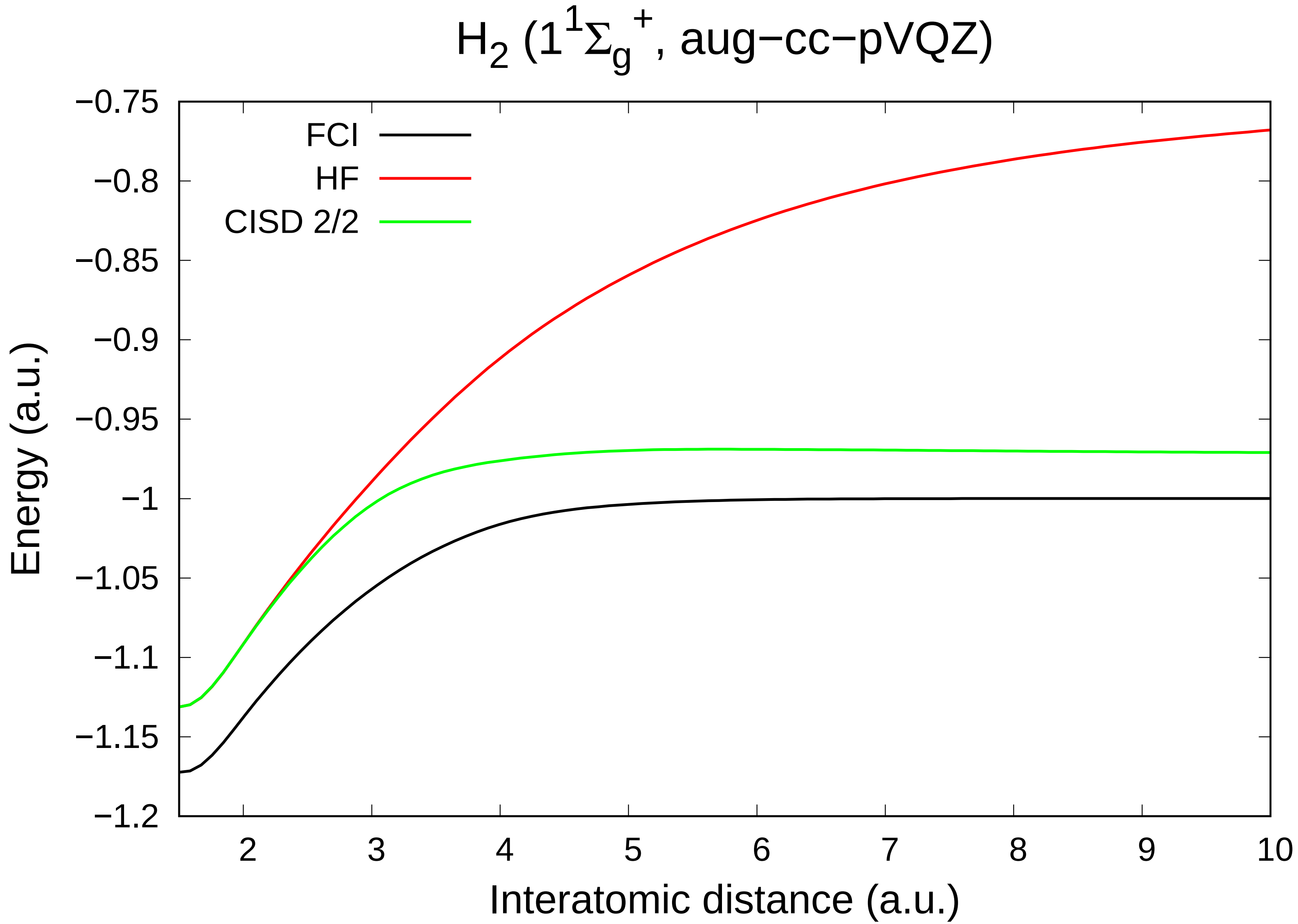
(1) Show that the Hamiltonian matrix for H_2 can be written in the basis of the two single-determinant states $|1\sigma_g^\alpha 1\sigma_g^\beta\rangle$ and $|1\sigma_u^\alpha 1\sigma_u^\beta\rangle$ as follows,

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

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 $K = \frac{1}{2}\langle 1s1s|1s1s\rangle > 0$.

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


H2 (1 1Σg +, aug−cc−pVQZ)
FCI
HF
CISD 2/2
Energy (a.u.)
Interatomic distance (a.u.)
−0.75
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−0.95
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Multi-Configurational Self-Consistent Field model (MCSCF)

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

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

- 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)

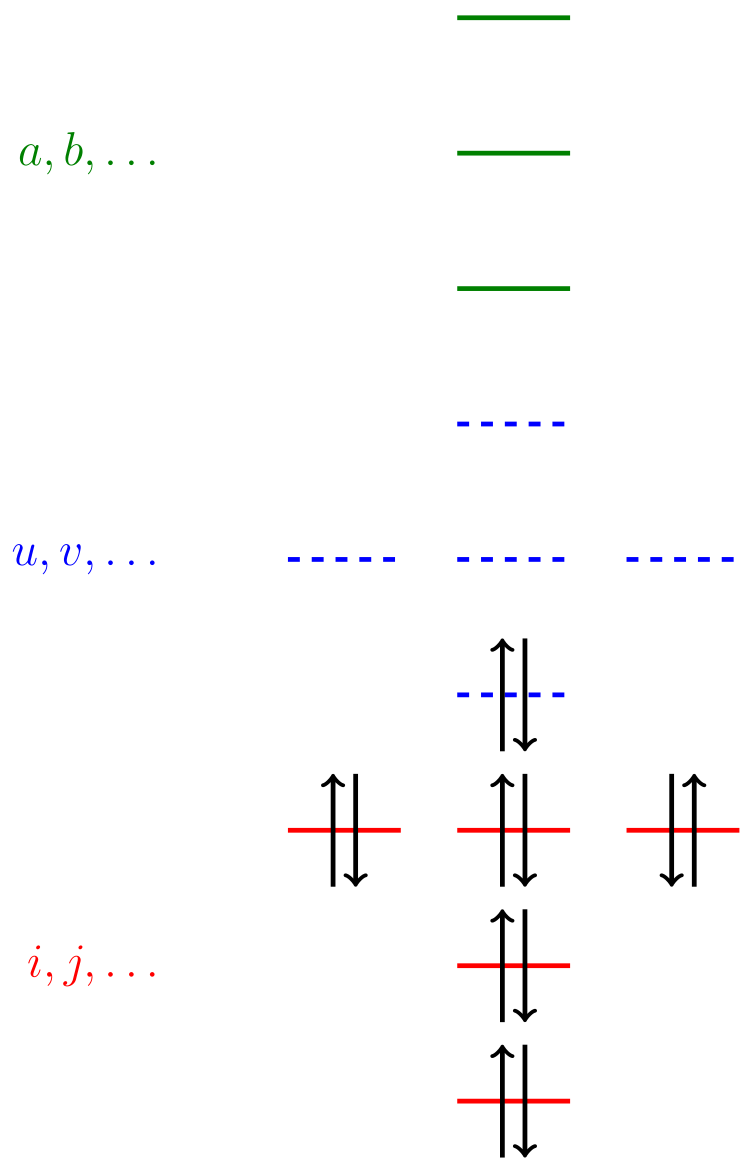
- Complete Active Space (CAS) for Be: $|1s^2 2s^2\rangle, |1s^2 2p_x^2\rangle, |1s^2 2p_y^2\rangle, |1s^2 2p_z^2\rangle$,

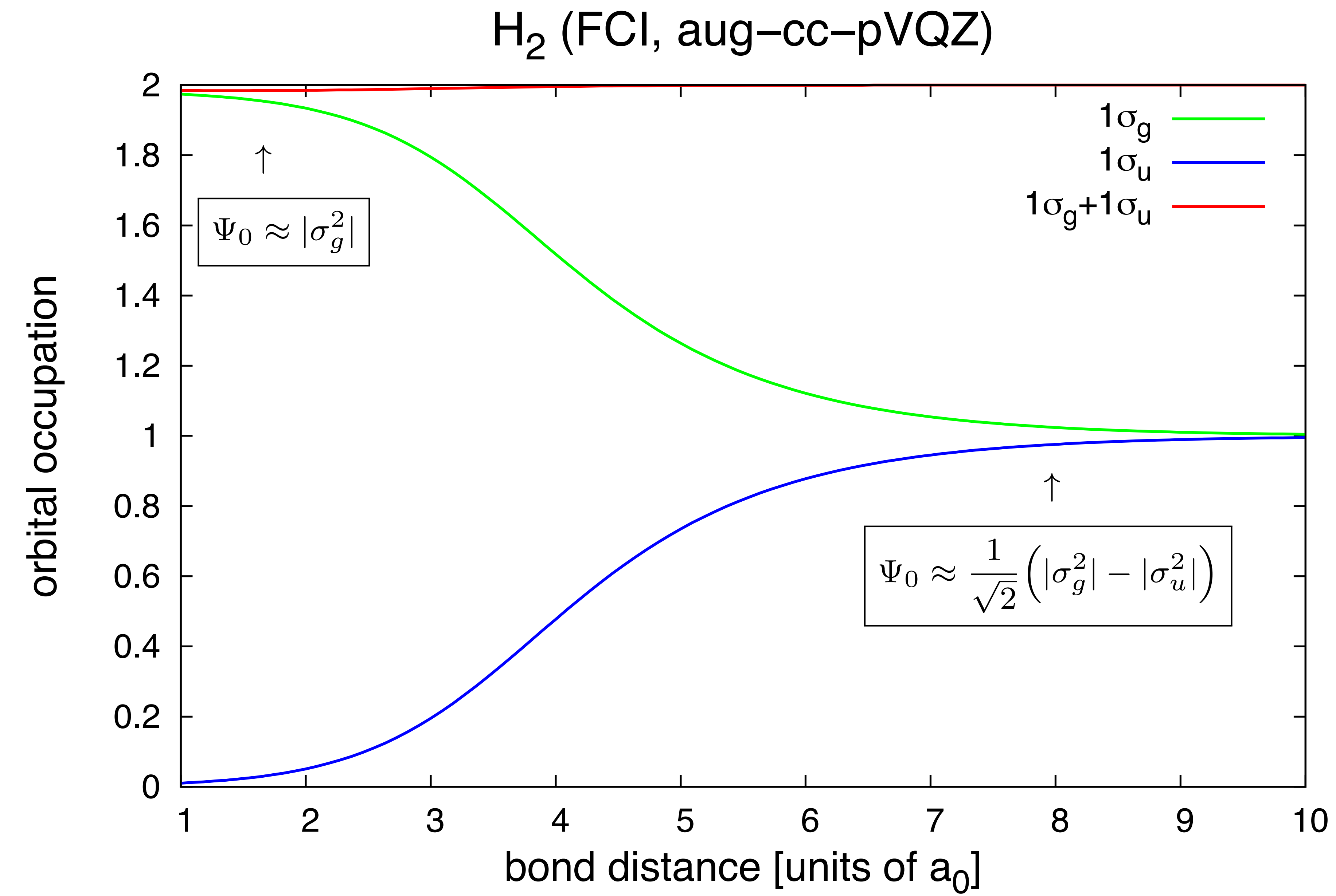
  if all the determinants are included in the MCSCF calculation $\longrightarrow$ CASSCF

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

- The orbital space is now divided in three:

doubly occupied molecular orbitals (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)	$\phi_a, \phi_b, \ldots$	$3s, 3p, 3d, \ldots$


$a, b, \ldots$
$u, v, \ldots$
$i, j, \ldots$


H2 (FCI, aug–cc–pVQZ)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
orbital occupation
1σg
1σu
1σg+1σu
$\Psi_0 \approx |\sigma_g^2|$
$\Psi_0 \approx \frac{1}{\sqrt{2}}\left(|\sigma_g^2| - |\sigma_u^2|\right)$
1
2
3
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5
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9
10
bond distance [units of a0]

Multi-Configurational Self-Consistent Field model (MCSCF)

EXERCISE: 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

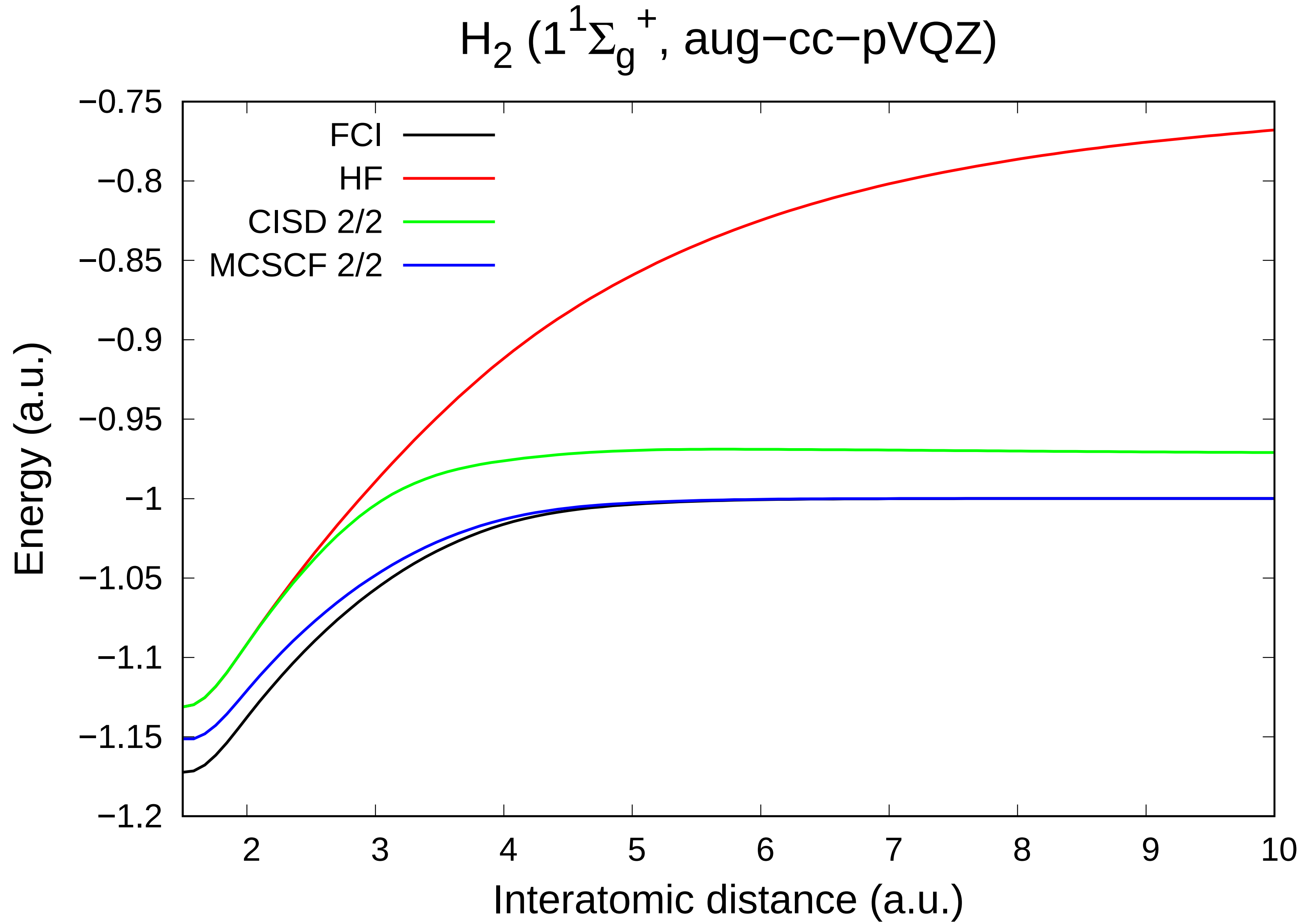
$$ {}^A\mathbf{D}_{vw} = \langle \Psi | \hat{E}_{vw} | \Psi \rangle, $$

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

equals

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

Note: In the particular case of a single determinantal wave function ($c = 0$) the active density matrix reduces to $\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}$.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CISD 2/2
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Interatomic distance (a.u.)

Multi-Reference Perturbation Theory (MRPT)

- *General perturbative energy expression through second order:*

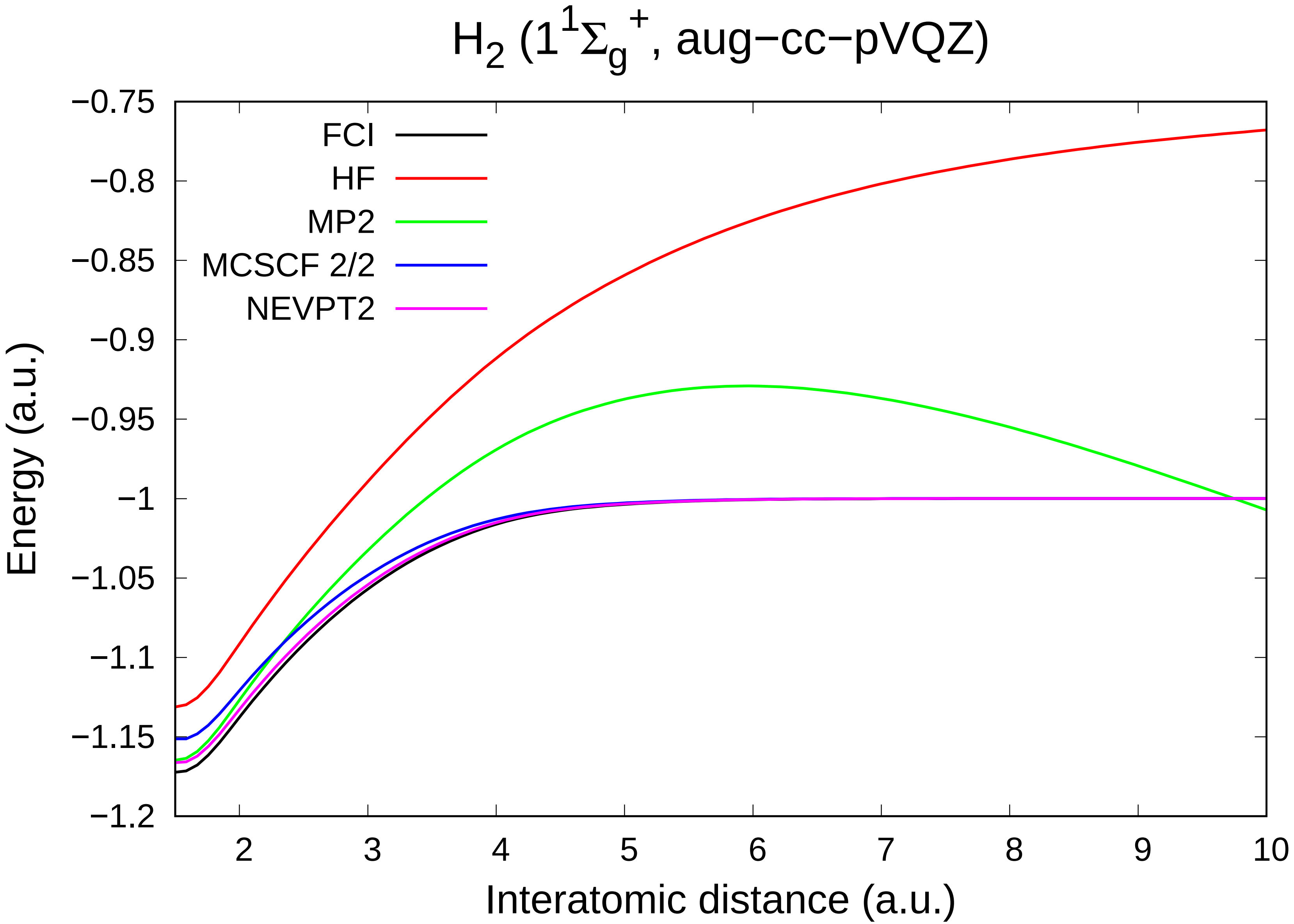
$$E_0 \approx \langle \Psi_{\rm MC}|\hat{H}|\Psi_{\rm MC}\rangle + \sum_{\mathcal{P}}^{\text{perturbers}} \frac{\langle \Psi_{\mathcal{P}}|\hat{H}|\Psi_{\rm MC}\rangle^2}{\mathcal{E}_{\rm MC} - \mathcal{E}_{\mathcal{P}}}$$

- Multi-reference extension of MP2:

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

- Standard approaches are CASPT2[a] and *N-electron valence state* PT2 (NEVPT2)[b].

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



H2 (1 1Σg +, aug−cc−pVQZ)
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−0.8
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−1.05
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Energy (a.u.)
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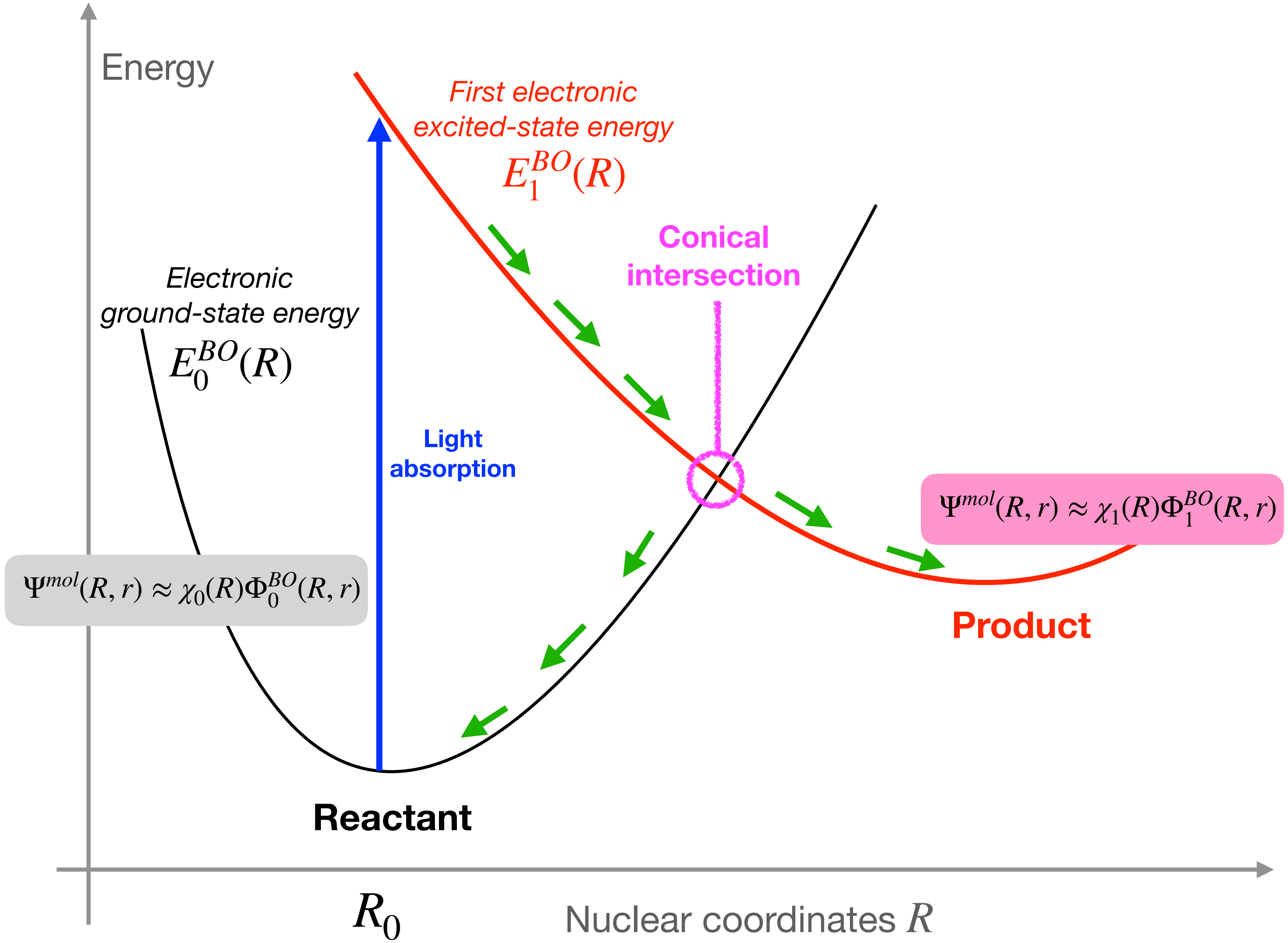
Interatomic distance (a.u.)
FCI
HF
MP2
MCSCF 2/2
NEVPT2

Schematics of a photochemical process



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)],

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

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

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

- The state-averaged MCSCF model consists in using a *MCSCF parameterization* for each Ψ_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 $\boldsymbol{\kappa}$ and the CI coefficients C_i:

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

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

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

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

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

and $E^{\mathrm{c}[1]}_{\boldsymbol{\lambda}_+} = \left.\dfrac{\partial E(\boldsymbol{\lambda})}{\partial \boldsymbol{\delta}}\right|_{\boldsymbol{\lambda}_+}$

- Newton method:

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

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

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

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

Note: $E_0^{\mathrm{o}[1]} = 0$ 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

$$w_1\langle\Psi_1|\hat{H}|\Psi_1\rangle + w_2\langle\Psi_2|\hat{H}|\Psi_2\rangle = w_2\Big[\langle\Psi_1|\hat{H}|\Psi_1\rangle + \langle\Psi_2|\hat{H}|\Psi_2\rangle\Big] + (w_1 - w_2)\langle\Psi_1|\hat{H}|\Psi_1\rangle$$

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 $\left\{ \tilde{\Psi}_I \right\}_{I=1,2,\ldots}$ of $\hat{H}$ with eigenvalues $\{E_I\}_{I=1,2,\ldots}$
Both trial wavefunctions can be expanded in that basis as follows,

$$|\Psi_K\rangle = \sum_I C_{KI} |\tilde{\Psi}_I\rangle, \qquad K = 1, 2.$$

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

(**2**) Show that $\quad \Delta = \sum_{I=1}^{2} (1 - p_I)(E_2 - E_I) + \sum_{I>2} p_I (E_I - E_2). \quad$ **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: $\quad |\tilde{\Psi}_I\rangle = C_{1I} |\Psi_1\rangle + C_{2I} |\Psi_2\rangle + \hat{Q}_{12} |\tilde{\Psi}_I\rangle \quad$ where $\hat{Q}_{12} = 1 - \sum_{K=1}^{2} |\Psi_K\rangle\langle\Psi_K|.$ Explain why $\quad p_I \leq 1 \quad$ when $\quad I = 1, 2 \quad$ 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.

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

- Double-exponential parametrization:

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

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

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 $w_I = \dfrac{1}{\mathcal{N}}$.

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

- 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.