Multi-configurational self-consistent field

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Notations

- Molecular orbitals: $\phi_p(\mathbf{r}) = \sum_\mu C_{\mu p}\, \chi_\mu(\mathbf{r})$ $\langle \phi_p | \phi_q \rangle = \delta_{pq}$
- Non-orthogonal set of atomic orbitals (Gaussian functions): $\langle \chi_\mu | \chi_\nu \rangle = S_{\mu\nu}$
- Hamiltonian in second quantization:

$$\hat{H} = \sum_{p,q} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle pr|qs \rangle \Big(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \Big)$$

where $$h_{pq} = \int \mathrm{d}\mathbf{r}\ \phi_p(\mathbf{r}) \Big[-\frac{1}{2}\nabla^2_{\mathbf{r}}\ +\ v_{\mathrm{ne}}(\mathbf{r}) \Big] \phi_q(\mathbf{r})$$

and $$\langle pr|qs \rangle = \int\!\!\int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\ \phi_p(\mathbf{r_1})\phi_r(\mathbf{r_2})\ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\ \phi_q(\mathbf{r_1})\phi_s(\mathbf{r_2}) = (pq|rs)$$

Variational and non-variational approximations

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

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

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

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

Variational calculation

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

↓

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

Non-variational calculation

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

↓

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

Spin-orbital rotation

- Let $\{|P\rangle\}$ denote an orthonormal basis of spin-orbitals and $\{|\tilde{P}\rangle\}$ another orthonormal basis obtained by unitary transformation:

$$|\tilde{P}\rangle = \sum_{Q} U_{QP} |Q\rangle$$

- **U** can be written as $\boxed{\mathbf{U} = e^{-\boldsymbol{\kappa}} \quad \text{with} \quad \boldsymbol{\kappa}^{\dagger} = -\boldsymbol{\kappa}}$ $\leftarrow$ $\boldsymbol{U}^{\dagger} = \left(e^{-\boldsymbol{\kappa}}\right)^{\dagger} = e^{-\boldsymbol{\kappa}^{\dagger}} = e^{\boldsymbol{\kappa}} = \boldsymbol{U}^{-1}$

- κ_{PQ} can be used rather than U_{PQ} for parametrizing the spin-orbital rotation

EX1: Using **EX2**, show that in second quantization the unitary transformation can be simply written as

$$\hat{a}^{\dagger}_{\tilde{P}} = \sum_{Q} \left(e^{-\boldsymbol{\kappa}}\right)_{QP} \hat{a}^{\dagger}_{Q} = \boxed{e^{-\hat{\kappa}}\ \hat{a}^{\dagger}_{P}\ e^{\hat{\kappa}} = \hat{a}^{\dagger}_{\tilde{P}}} \qquad \text{where} \qquad \hat{\kappa} = \sum_{PQ} \kappa_{PQ}\ \hat{a}^{\dagger}_{P} \hat{a}_{Q}$$

Spin-orbital rotation

- Note that the rotation operator $\hat{\kappa}$ is anti-Hermitian:

$$\hat{\kappa}^{\dagger} = \sum_{PQ} \kappa^{*}_{PQ}\, \hat{a}^{\dagger}_{Q}\hat{a}_{P} = \sum_{PQ} \kappa^{\dagger}_{QP}\, \hat{a}^{\dagger}_{Q}\hat{a}_{P} = -\sum_{PQ} \kappa_{QP}\, \hat{a}^{\dagger}_{Q}\hat{a}_{P} = -\hat{\kappa}$$

- Unitary transformation for a N-electron Slater determinant:

$$|\tilde{P}_1\tilde{P}_2\ldots\tilde{P}_N\rangle = \hat{a}^{\dagger}_{\tilde{P}_1}\hat{a}^{\dagger}_{\tilde{P}_2}\ldots\hat{a}^{\dagger}_{\tilde{P}_N}|\mathrm{vac}\rangle = e^{-\hat{\kappa}}\hat{a}^{\dagger}_{P_1}\, e^{\hat{\kappa}}e^{-\hat{\kappa}}\hat{a}^{\dagger}_{P_2}\, e^{\hat{\kappa}}\ldots e^{-\hat{\kappa}}\hat{a}^{\dagger}_{P_N}\, e^{\hat{\kappa}}|\mathrm{vac}\rangle$$

$$= e^{-\hat{\kappa}}\hat{a}^{\dagger}_{P_1}\hat{a}^{\dagger}_{P_2}\ldots\hat{a}^{\dagger}_{P_N}\, \underbrace{e^{\hat{\kappa}}|\mathrm{vac}\rangle}_{|\mathrm{vac}\rangle}$$

$$\boxed{|\tilde{P}_1\tilde{P}_2\ldots\tilde{P}_N\rangle = e^{-\hat{\kappa}}\, |P_1P_2\ldots P_N\rangle}$$

Spin-restricted orbital rotation

- In a restricted formalism the same set of orbitals is used for α and β spins:

$$\hat{\kappa} = \sum_{PQ} \kappa_{PQ}\ \hat{a}^{\dagger}_{P}\hat{a}_{Q} = \sum_{pq}\sum_{\sigma\sigma'} \underbrace{\kappa_{p,\sigma q,\sigma'}}_{\kappa_{pq}\delta_{\sigma\sigma'}}\ \hat{a}^{\dagger}_{p,\sigma}\hat{a}_{q,\sigma'} = \sum_{pq}\kappa_{pq}\hat{E}_{pq}$$

- Since $\kappa_{pq} = -\kappa_{qp}$ (real algebra)

$$\hat{\kappa} = \sum_{p>q}\kappa_{pq}\hat{E}_{pq} - \sum_{p<q}\kappa_{qp}\hat{E}_{pq}$$

$$\boxed{\hat{\kappa} = \sum_{p>q}\kappa_{pq}\left(\hat{E}_{pq} - \hat{E}_{qp}\right)}$$

Hartree-Fock approximation

- For simplicity we consider here the particular case of a non-degenerate singlet closed-shell ground state
- The HF method consists then in approximating the exact wave function Ψ_0 by a single Slater determinant Φ_0. The orbital space is thus divided in two:

doubly occupied molecular orbitals $\phi_i, \phi_j, \ldots$ **unoccupied molecular orbitals** $\phi_a, \phi_b, \ldots$

$$|\Phi_0\rangle = \prod_i^{\text{occ.}} \prod_{\sigma=\alpha,\beta} \hat{a}^\dagger_{i,\sigma} |\text{vac}\rangle$$

- The initial set of molecular orbitals is usually not optimized → the optimized HF molecular orbitals will be obtained by means of unitary transformations (orbital rotation)

Hartree-Fock approximation

- Exponential parametrization: $|\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}}\,|\Phi_0\rangle$ with $\hat{\kappa} = \sum_{p>q} \kappa_{pq}\left(\hat{E}_{pq} - \hat{E}_{qp}\right)$

$\boldsymbol{\kappa} = \begin{bmatrix} \vdots \\ \kappa_{pq} \\ \vdots \end{bmatrix}_{p>q}$ denotes the column vector containing all the parameters to be optimized

- occupied-occupied and unoccupied-unoccupied rotations:

$$\hat{\kappa} = \underbrace{\sum_{i>j} \kappa_{ij}\left(\hat{E}_{ij} - \hat{E}_{ji}\right)}_{\hat{\kappa}^{\text{occ.}}} + \sum_{i,a} \kappa_{ai}\left(\hat{E}_{ai} - \hat{E}_{ia}\right) + \underbrace{\sum_{a>b} \kappa_{ab}\left(\hat{E}_{ab} - \hat{E}_{ba}\right)}_{\hat{\kappa}^{\text{unocc.}}}$$

$\hat{\kappa}^{\text{occ.}}|\Phi_0\rangle = \hat{\kappa}^{\text{unocc.}}|\Phi_0\rangle = 0 \rightarrow$ only occupied-unoccupied rotations will be optimized $\rightarrow \boldsymbol{\kappa} = \begin{bmatrix} \vdots \\ \kappa_{ai} \\ \vdots \end{bmatrix}$

Hartree-Fock approximation

- Hartree-Fock energy expression:

$$E(\boldsymbol{\kappa}) = \frac{\langle\Phi(\boldsymbol{\kappa})|\hat{H}|\Phi(\boldsymbol{\kappa})\rangle}{\langle\Phi(\boldsymbol{\kappa})|\Phi(\boldsymbol{\kappa})\rangle} = \frac{\langle\Phi_0|e^{-\hat{\kappa}^\dagger}\ \hat{H}\ e^{-\hat{\kappa}}|\Phi_0\rangle}{\langle\Phi_0|e^{-\hat{\kappa}^\dagger}\ e^{-\hat{\kappa}}|\Phi_0\rangle} = \boxed{\langle\Phi_0|e^{\hat{\kappa}}\hat{H}e^{-\hat{\kappa}}|\Phi_0\rangle = E(\boldsymbol{\kappa})}$$

- Variational optimization of $\boldsymbol{\kappa}$: $E^{[1]}_{\boldsymbol{\kappa}_+} = \left.\dfrac{\partial E(\boldsymbol{\kappa})}{\partial\boldsymbol{\kappa}}\right|_{\boldsymbol{\kappa}_+} = 0$

- Iterative procedure (Newton method):

$$E(\boldsymbol{\kappa}) \approx E(0) + \boldsymbol{\kappa}^T E^{[1]}_0 + \frac{1}{2}\boldsymbol{\kappa}^T E^{[2]}_0 \boldsymbol{\kappa} \quad \rightarrow \quad E^{[1]}_{\boldsymbol{\kappa}_+} \approx E^{[1]}_0 + E^{[2]}_0 \boldsymbol{\kappa}_+ = 0 \quad \rightarrow \quad E^{[2]}_0 \underbrace{\boldsymbol{\kappa}_+}_{\textbf{Newton step}} = -E^{[1]}_0$$

- Update the HF determinant: $\Phi_0 \leftarrow \Phi(\boldsymbol{\kappa}_+)$

- HF calculation converged when $\boxed{E^{[1]}_0 = 0}$

Hartree-Fock approximation

Note: The exponential parametrization can also be used in Kohn-Sham DFT

$$\langle\Phi(\boldsymbol{\kappa})|\hat{H}|\Phi(\boldsymbol{\kappa})\rangle \quad \longrightarrow \quad \langle\Phi(\boldsymbol{\kappa})|\hat{T}+\hat{V}_{\rm ne}|\Phi(\boldsymbol{\kappa})\rangle + E_{\rm Hxc}[n(\boldsymbol{\kappa})]$$

where $|\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}}|\Phi^{\rm KS}\rangle,\qquad n(\boldsymbol{\kappa},\mathbf{r}) = \langle\Phi(\boldsymbol{\kappa})|\hat{n}(\mathbf{r})|\Phi(\boldsymbol{\kappa})\rangle,$

$$\hat{n}(\mathbf{r}) = \hat{E}_{\mathbf{rr}} = \sum_{\sigma}\hat{\Psi}^{\dagger}(\mathbf{r},\sigma)\hat{\Psi}(\mathbf{r},\sigma) = \sum_{p,q}\phi_p(\mathbf{r})\phi_q(\mathbf{r})\hat{E}_{pq} \qquad \longleftarrow \text{density operator}$$

Hartree-Fock approximation

EX2: Using the Taylor expansion of $\hat{f}(x) = e^{-x\hat{A}}\,\hat{B}\,e^{x\hat{A}}$ about $x = 0$, prove the *Baker-Campbell-Hausdorff* (BCH) expansion:

$$e^{-\hat{A}}\,\hat{B}\,e^{\hat{A}} = \hat{B} + \sum_{n=1}^{+\infty} \frac{1}{n!} [\![\hat{B},\hat{A}]\!]_n \qquad [\![\hat{B},\hat{A}]\!]_{n+1} = [[\![\hat{B},\hat{A}]\!]_n,\hat{A}], \quad [\![\hat{B},\hat{A}]\!]_1 = [\hat{B},\hat{A}]$$

$$= \hat{B} + [\hat{B},\hat{A}] + \frac{1}{2}[[\hat{B},\hat{A}],\hat{A}] + \dots$$

- Analytical formulas for the gradient and the hessian:

$$E(\boldsymbol{\kappa}) = E(0) + \underbrace{\langle\Phi_0|[\hat{\kappa},\hat{H}]|\Phi_0\rangle} + \frac{1}{2}\langle\Phi_0|[\hat{\kappa},[\hat{\kappa},\hat{H}]]|\Phi_0\rangle + \dots$$

$$\sum_{ai} \kappa_{ai}\langle\Phi_0|[\hat{E}_{ai} - \hat{E}_{ia},\hat{H}]|\Phi_0\rangle \quad \rightarrow \quad E^{[1]}_{0,ai} = \langle\Phi_0|[\hat{E}_{ai} - \hat{E}_{ia},\hat{H}]|\Phi_0\rangle$$

$$= -2\langle\Phi_0|\hat{H}\hat{E}_{ai}|\Phi_0\rangle = 0 \ \textbf{(Brillouin theorem)}$$

Fock matrix and canonical orbitals

EX3: Using the simplified commutator expression $[\hat{E}_{pq}, \hat{E}_{rs}] = \delta_{qr}\hat{E}_{ps} - \delta_{ps}\hat{E}_{rq}$, show that

$$E^{[1]}_{0,ai} = 2\langle\Phi_0|[\hat{E}_{ai}, \hat{H}]|\Phi_0\rangle = \boxed{-4f_{ia} = E^{[1]}_{0,ai}}$$

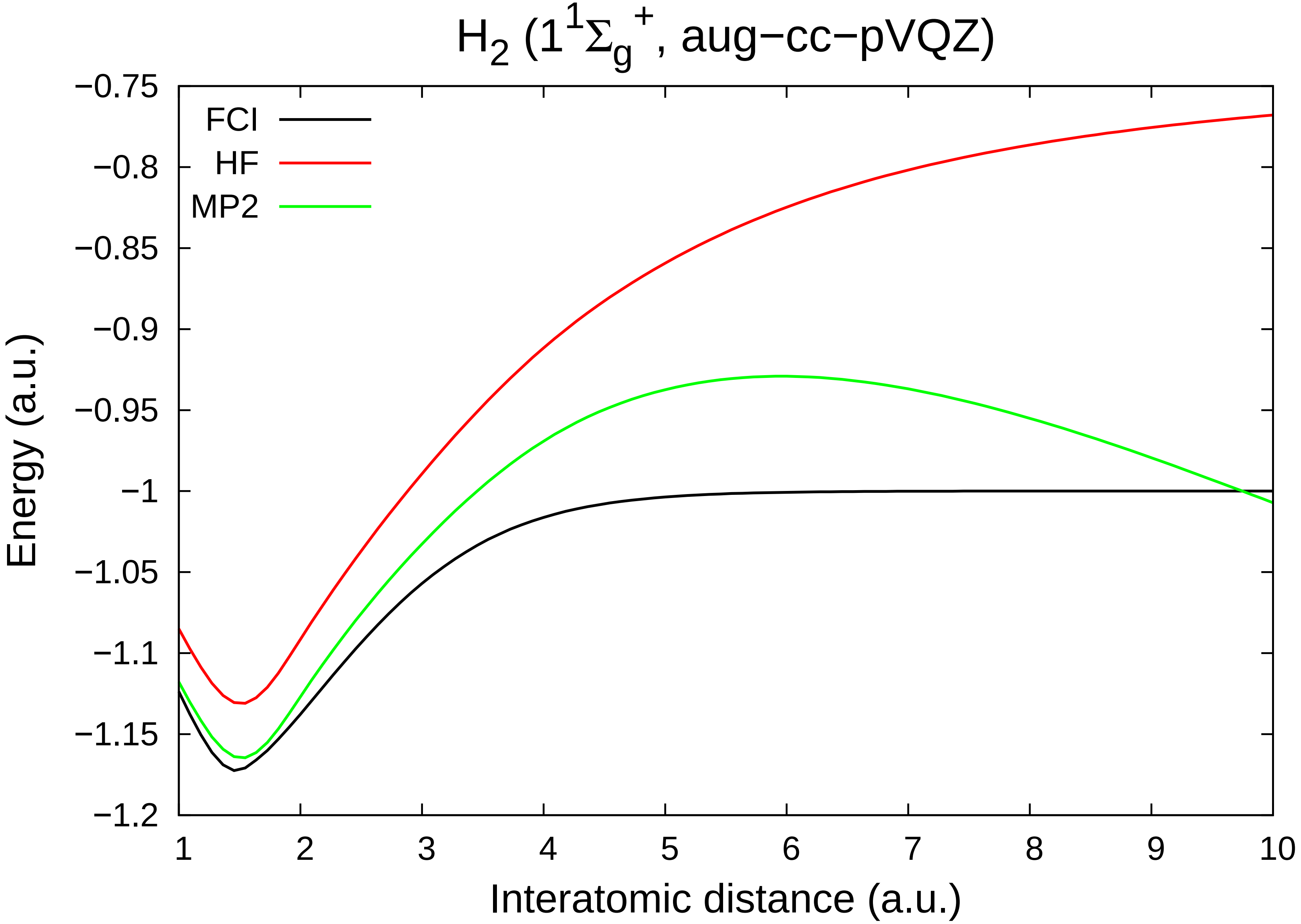
where the Fock matrix elements are defined as $f_{pq} = h_{pq} + \sum_{rs}\Big(\langle pr|qs\rangle - \frac{1}{2}\langle pr|sq\rangle\Big)D_{rs}$,

$D_{rs} = \langle\Phi_0|\hat{E}_{rs}|\Phi_0\rangle$ ← one-electron density matrix

- Canonical HF orbitals:

$$\mathbf{D} = \begin{bmatrix} \mathbf{D}^{\text{occ.}} & 0 \\ 0 & 0 \end{bmatrix} \quad \mathbf{f} = \begin{bmatrix} \mathbf{f}^{\text{occ.}} & 0 \\ 0 & \mathbf{f}^{\text{unocc.}} \end{bmatrix} \quad \longrightarrow \quad \mathbf{D}' = \mathbf{D}, \quad \mathbf{f}' = \begin{bmatrix} \mathbf{f}'^{\text{occ.}} & 0 \\ 0 & \mathbf{f}'^{\text{unocc.}} \end{bmatrix}$$

$$\mathbf{D}^{\text{occ.}}_{ij} = 2\delta_{ij} \qquad \mathbf{f}^{\text{occ.}}_{ij} = f_{ij}, \quad \mathbf{f}^{\text{unocc.}}_{ab} = f_{ab} \qquad \mathbf{f}'^{\text{occ.}}_{ij} = \delta_{ij}\varepsilon_i, \quad \mathbf{f}'^{\text{unocc.}}_{ab} = \delta_{ab}\varepsilon_a$$


H2 (1¹Σg+, aug−cc−pVQZ)
Energy (a.u.)
Interatomic distance (a.u.)
−0.75
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
3
4
5
6
7
8
9
10
FCI
HF
MP2

Static correlation

- H_2 in the equilibrium geometry:

$\boxed{|\Psi_0\rangle = C_0|1\sigma_g^\alpha 1\sigma_g^\beta\rangle + \ldots}$ 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:

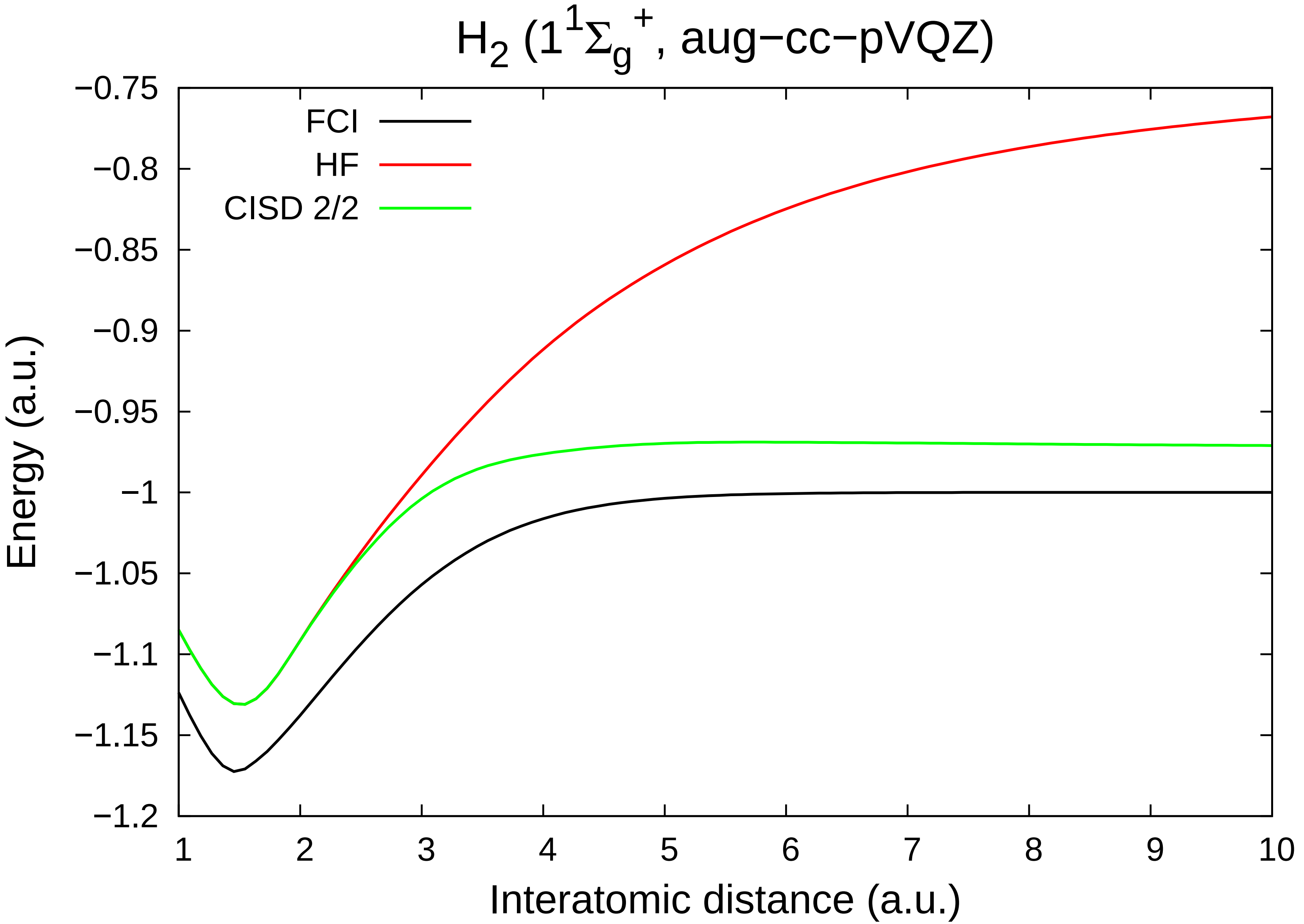
(1) Show that the Hamiltonian matrix for H_2 can be written in the basis of the two single-determinant states $|1\sigma_g^\alpha 1\sigma_g^\beta\rangle$ and $|1\sigma_u^\alpha 1\sigma_u^\beta\rangle$ as follows,

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

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 $E_g - K$.


H_2 ($1^1\Sigma_g^+$, aug−cc−pVQZ)
Energy (a.u.)
Interatomic distance (a.u.)
FCI
HF
CISD 2/2
−0.75
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
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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

$$|\Psi(\boldsymbol{\kappa}, \mathbf{C})\rangle = e^{-\hat{\kappa}} \left(\sum_i C_i |i\rangle \right)$$

- 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)

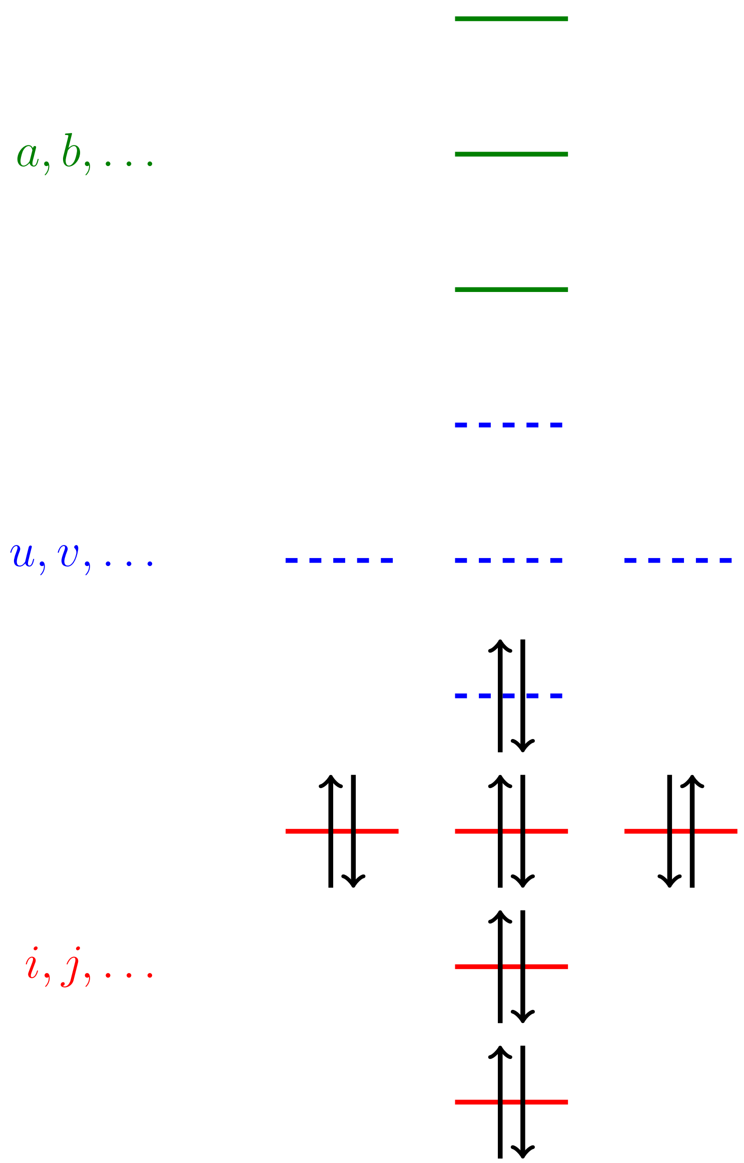
- Complete Active Space (CAS) for Be: $|1s^2 2s^2\rangle, |1s^2 2p_x^2\rangle, |1s^2 2p_y^2\rangle, |1s^2 2p_z^2\rangle,$

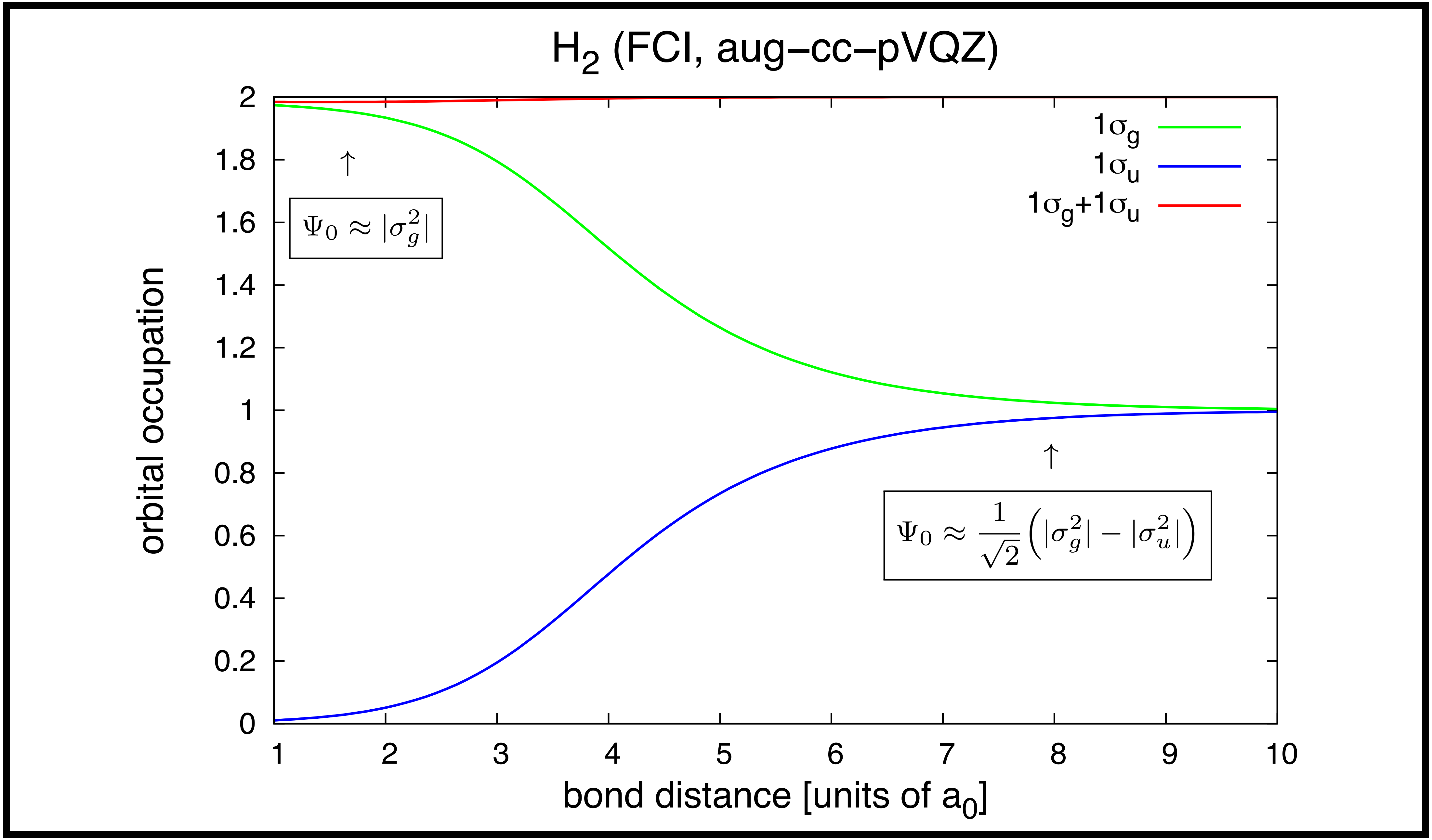
  if all the determinants are included in the MCSCF calculation $\longrightarrow$ CASSCF

  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	$\phi_a, \phi_b, \ldots$	$3s, 3p, 3d, \ldots$


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


H_2 (FCI, aug–cc–pVQZ)
orbital occupation
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
bond distance [units of a_0]
$1\sigma_g$
$1\sigma_u$
$1\sigma_g$+$1\sigma_u$
↑
$\Psi_0 \approx |\sigma_g^2|$
↑
$\Psi_0 \approx \frac{1}{\sqrt{2}}\left(|\sigma_g^2| - |\sigma_u^2|\right)$

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

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

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

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

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

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

- 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 $E_0^{[1]} = 0$

$\boxed{\textbf{EX7:}}$ 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.

Multi-Configurational Self-Consistent Field model (MCSCF)

EX8: We consider in this exercise a different parametrization of the MCSCF wave function:

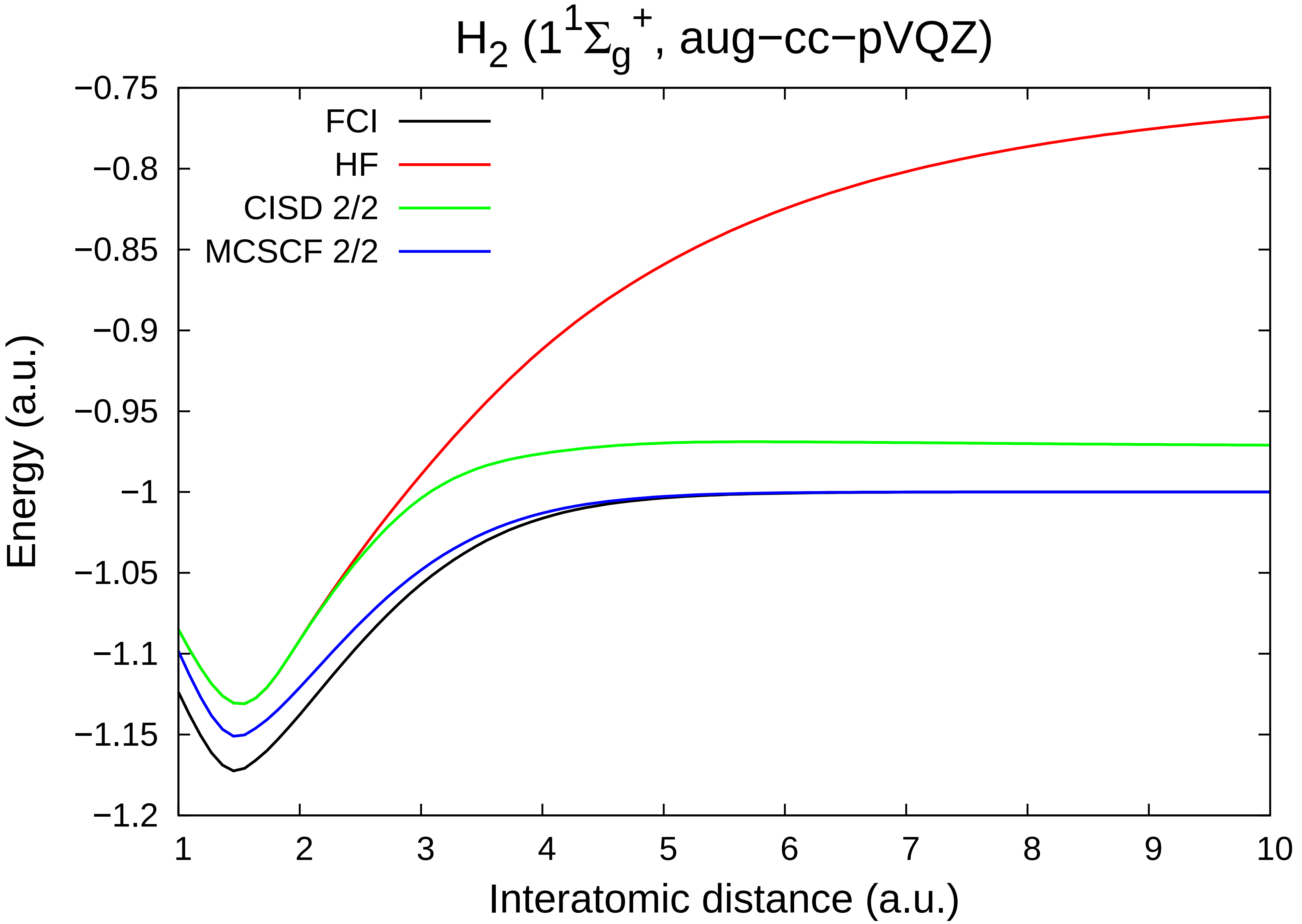
$$|\Psi(\boldsymbol{\kappa},\mathbf{S})\rangle = e^{-\hat{\kappa}}\, e^{-\hat{S}}|\Psi^{(0)}\rangle$$

where $\hat{S} = \sum_K S_K \Big(|K\rangle\langle\Psi^{(0)}| - |\Psi^{(0)}\rangle\langle K|\Big)$, $\quad\langle\Psi^{(0)}|K\rangle = 0,\quad \langle K|K'\rangle = \delta_{KK'}$ and

$$\sum_i |i\rangle\langle i| = |\Psi^{(0)}\rangle\langle\Psi^{(0)}| + \sum_K |K\rangle\langle K|$$

Derive the corresponding MCSCF gradient and show that the optimized MCSCF wave functions obtained with this parametrization and the previous one are the same.

Note: This double exponential form is convenient for computing response properties at the MCSCF level and performing state-averaged MCSCF calculations.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10
Interatomic distance (a.u.)

Recovering dynamical correlation effects

- Standard approach: post-MCSCF treatment based either on perturbation theory (MRPT) or Coupled Cluster theory (MRCC).
- Combining MCSCF with DFT is not easy ...

$$E_0 = \min_{\boldsymbol{\lambda}} \left\{ \langle \Psi(\boldsymbol{\lambda}) | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi(\boldsymbol{\lambda}) \rangle + \underbrace{E_c^{\text{CAS}}[n_{\Psi(\boldsymbol{\lambda})}]}_{\text{not universal !}} \right\}$$

thus leading to the so-called "double counting problem"

- Range-separated MCSCF-DFT[1]: two-electron repulsion at long range assigned to MCSCF and, at short range, assigned to DFT ⟶ correlations are separated in real space !
- CASDFT method based on orbitals occupation[2] rather than the electron density ⟶ correlations are separated in the orbital space !

[1] E. Fromager, J. Toulouse, and H. J. Aa. Jensen, J. Chem. Phys. **126**, 074111 (2007).

[2] E. Fromager, Mol. Phys. **113**, 419 (2015).

Multi-state 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.

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

- Double-exponential parametrization:

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

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

Multi-state MCSCF approach

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

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

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

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,

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

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

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

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
$\hat{Q}_{12} = 1 - \sum_{K=1}^{2} |\Psi_K\rangle\langle\Psi_K|$. $\quad$ Explain why $\quad p_I \leq 1 \quad$ when $\quad I = 1, 2 \quad$ and conclude.

Multi-state 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.

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