Multideterminant range-separated density-functional theory and beyond

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cnrs advancing the frontiers

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- ^1S ground state of the helium atom:

$$\Psi_0(\mathbf{r_1}, \sigma_1, \mathbf{r_2}, \sigma_2) = \Psi_0(r_1, r_2, r_{12}) \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1 \alpha} \delta_{\sigma_2 \beta} - \delta_{\sigma_2 \alpha} \delta_{\sigma_1 \beta} \right)$$

- Hamiltonian expressed in terms of r_1, r_2 and $r_{12} = |\mathbf{r_1} - \mathbf{r_2}|$:

$$\hat{H} \equiv -\frac{1}{2} \sum_{i=1}^{2} \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + \frac{2Z}{r_i} \right) - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{1}{r_{12}} \right)$$

$$- \left(\frac{\mathbf{r_1}}{r_1} \cdot \frac{\mathbf{r_{12}}}{r_{12}} \frac{\partial}{\partial r_1} + \frac{\mathbf{r_2}}{r_2} \cdot \frac{\mathbf{r_{21}}}{r_{21}} \frac{\partial}{\partial r_2} \right) \frac{\partial}{r_{12}}$$

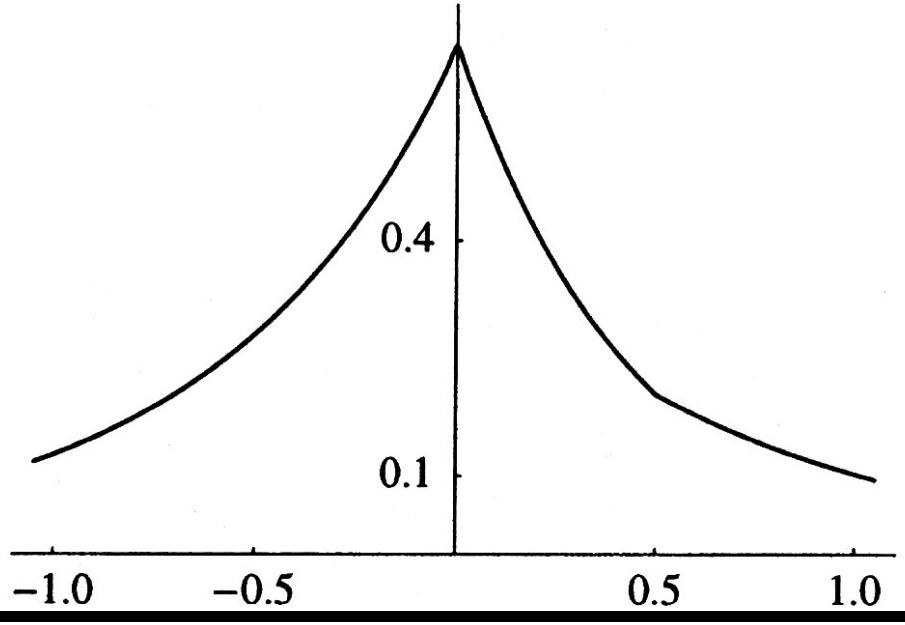
- $E_0 = \dfrac{\hat{H}\Psi_0(r_1, r_2, r_{12})}{\Psi_0(r_1, r_2, r_{12})} =$ constant, especially when $r_i = 0$ or $r_{12} = 0$

- Nuclear cusp conditions: $\left. \dfrac{\partial \Psi_0}{\partial r_1} \right|_{r_1=0} = -Z\Psi_0(0, r_2, r_2)$, $\left. \dfrac{\partial \Psi_0}{\partial r_2} \right|_{r_2=0} = -Z\Psi_0(r_1, 0, r_1)$

- Coulomb cusp condition: $\boxed{\left. \dfrac{\partial \Psi_0(r_1, r_1, r_{12})}{\partial r_{12}} \right|_{r_{12}=0} = \frac{1}{2}\Psi_0(r_1, r_1, 0)}$

- Expansion of the wave function around $r_2 = r_1 = 0.5$ a.u. and $r_{12} = 0$ for a collinear arrangement of the nucleus and the two electrons :

$$
\begin{aligned}
\Psi_0(r_1, r_2, r_{12}) &= \Psi_0(r_1, r_2, |r_1 - r_2|) \\
&\approx \Psi_0(r_1, r_1, 0) + (r_2 - r_1) \left.\frac{\partial \Psi_0(r_1, r_2, 0)}{\partial r_2}\right|_{r_2=r_1} + |r_1 - r_2| \left.\frac{\partial \Psi_0(r_1, r_1, r_{12})}{\partial r_{12}}\right|_{r_{12}=0} \\
&\approx \Psi_0(r_1, r_1, 0) + (r_2 - r_1) \left.\frac{\partial \Psi_0(r_1, r_2, 0)}{\partial r_2}\right|_{r_2=r_1} + \frac{1}{2}|r_1 - r_2| \Psi_0(r_1, r_1, 0) + \ldots
\end{aligned}
$$



Short-range dynamical correlation

- The HF determinant does not fulfill the Coulomb cusp condition:

$$\Phi_0(r_1, r_2, r_{12}) = \phi_{1s}(r_1)\phi_{1s}(r_2) = e^{-\zeta(r_1+r_2)} = \Phi_0(r_1, r_2) \quad \longrightarrow \quad \frac{\partial \Phi_0}{\partial r_{12}} = 0 \quad \longrightarrow \quad \text{no cusp !}$$

- Describing short-range dynamical correlation is about recovering the Coulomb cusp

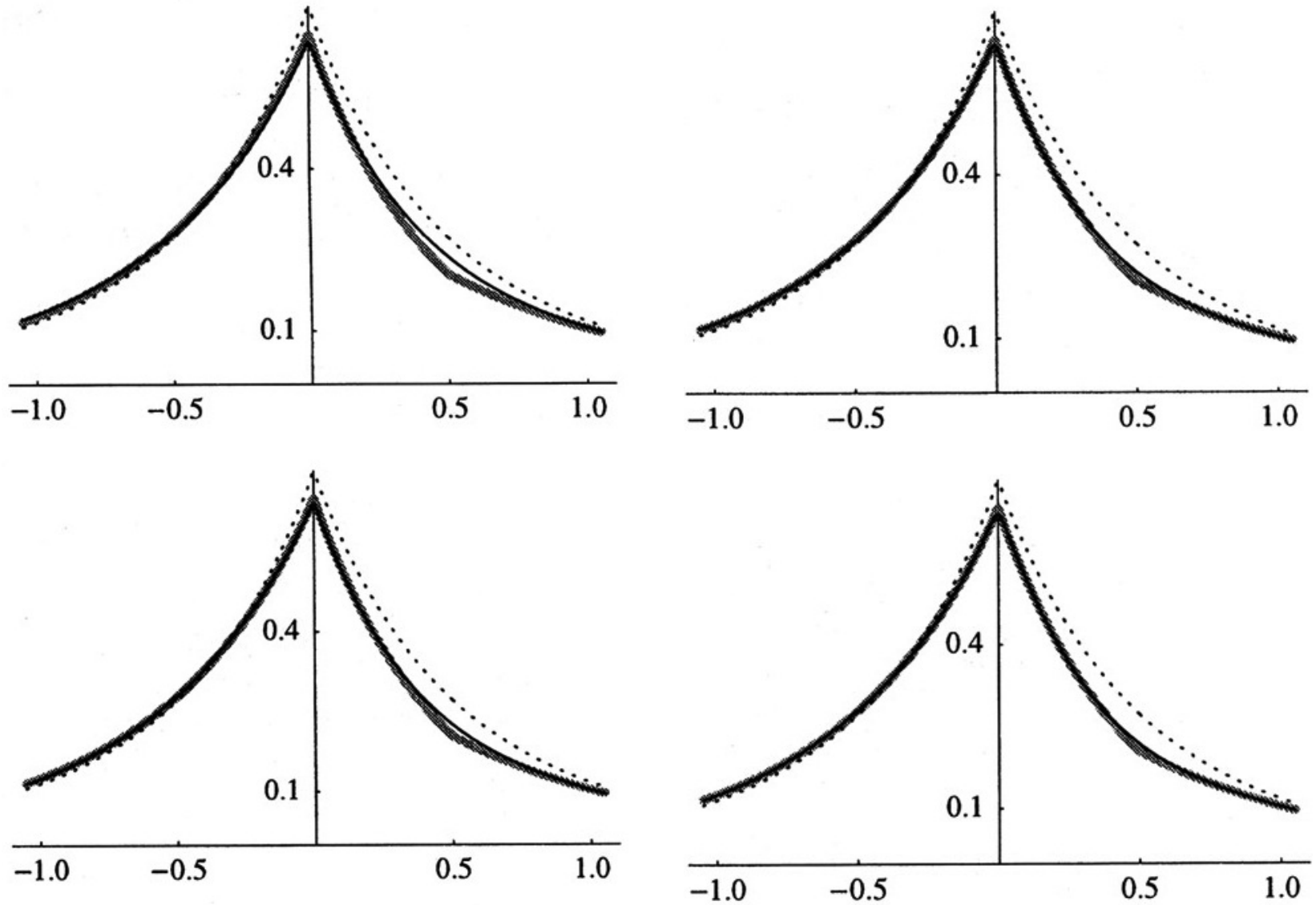
- **First approach:** expand the wave function in the basis of Slater determinants built from atomic orbitals $\phi_p(\mathbf{r})$ expressed as $r^{n-1}e^{-\zeta r}Y_l^m(\theta, \varphi)$. This is known as Configuration Interaction (CI)

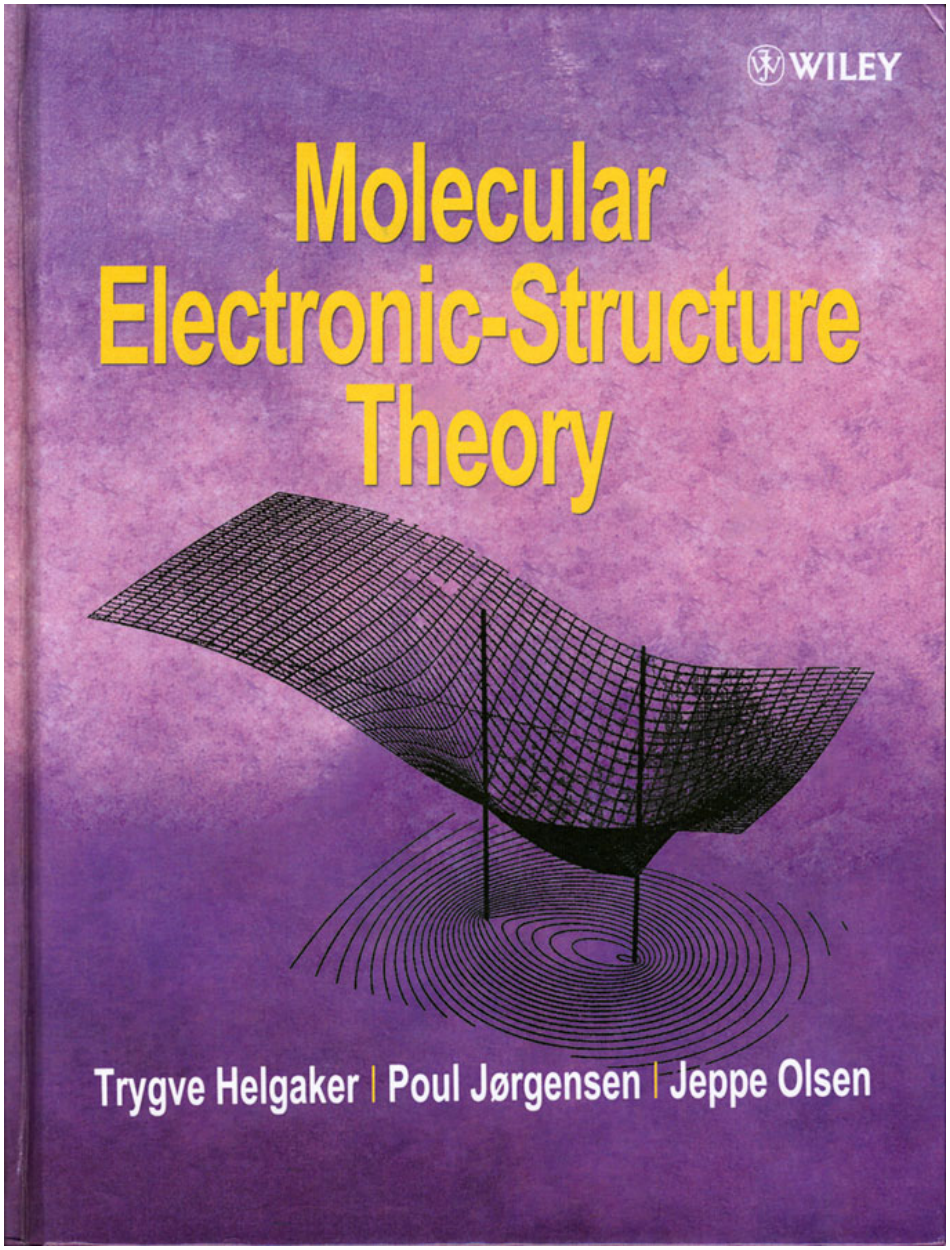
$$\Psi_0^{\text{CI}}(r_1, r_2, r_{12}) = C_0\Phi_0(r_1, r_2)$$

$$+ \sum_a C_a \Big(\phi_a(\mathbf{r_1})\phi_{1s}(\mathbf{r_2}) + \phi_a(\mathbf{r_2})\phi_{1s}(\mathbf{r_1})\Big) \qquad \longleftarrow \text{ single excitations}$$

$$+ \sum_{a \leq b} C_{ab} \Big(\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_a(\mathbf{r_2})\phi_b(\mathbf{r_1})\Big) \qquad \longleftarrow \text{ double excitations}$$

Short-range dynamical correlation




WILEY
Molecular Electronic-Structure Theory
Trygve Helgaker | Poul Jørgensen | Jeppe Olsen

Short-range dynamical correlation

Slow convergence with respect to the number of Slater determinants ...

$$\frac{4\pi}{2l+1}\left(\sum_{m=-l}^{l}(-1)^m Y_l^m(\theta_1,\varphi_1)Y_l^{-m}(\theta_2,\varphi_2)\right) = P_l(\cos\theta_{12}) = a_l\,(\cos\theta_{12})^l + a_{l-1}\,(\cos\theta_{12})^{l-1} + \ldots$$

where $r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}$

$$\left.\frac{\partial \Psi_0^{\rm CI}(r_1, r_1, r_{12})}{\partial r_{12}}\right|_{r_{12}=0} \sim \left.\frac{\partial r_{12}^2}{\partial r_{12}}\right|_{r_{12}=0} = 0 \quad \longrightarrow \quad \text{no cusp strictly speaking !}$$

Short-range dynamical correlation

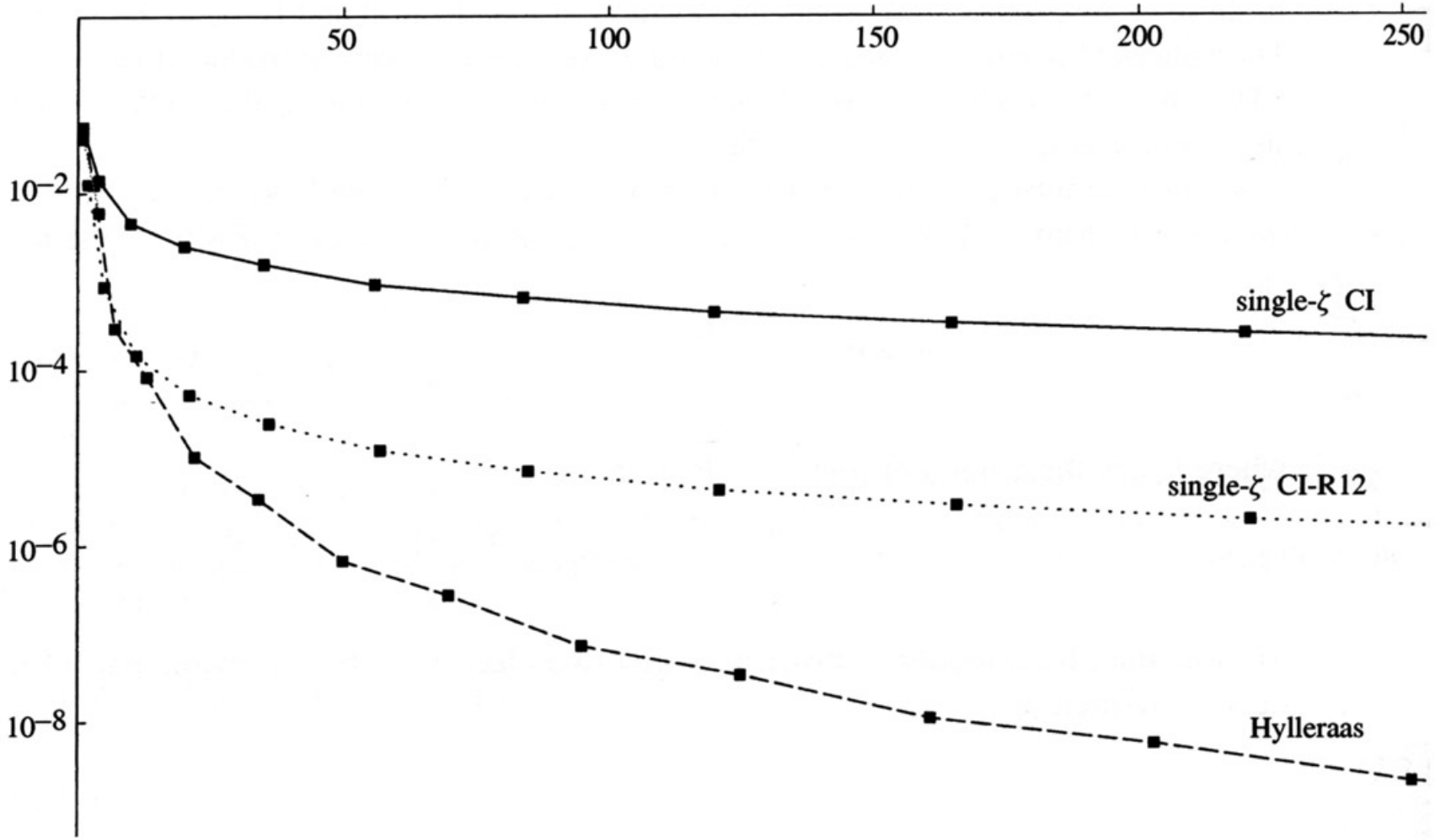
- **Second approach:** introduce r_{12} explicitly in the wave function.
  This is known as explicitly correlated method. For example:

$$\tilde{\Phi}_0(r_1, r_2, r_{12}) = \left(1 + \frac{1}{2} r_{12}\right) \Phi_0(r_1, r_2) \quad \text{or} \quad \tilde{\Phi}_0(r_1, r_2, r_{12}) = e^{\frac{1}{2} r_{12}} \Phi_0(r_1, r_2)$$

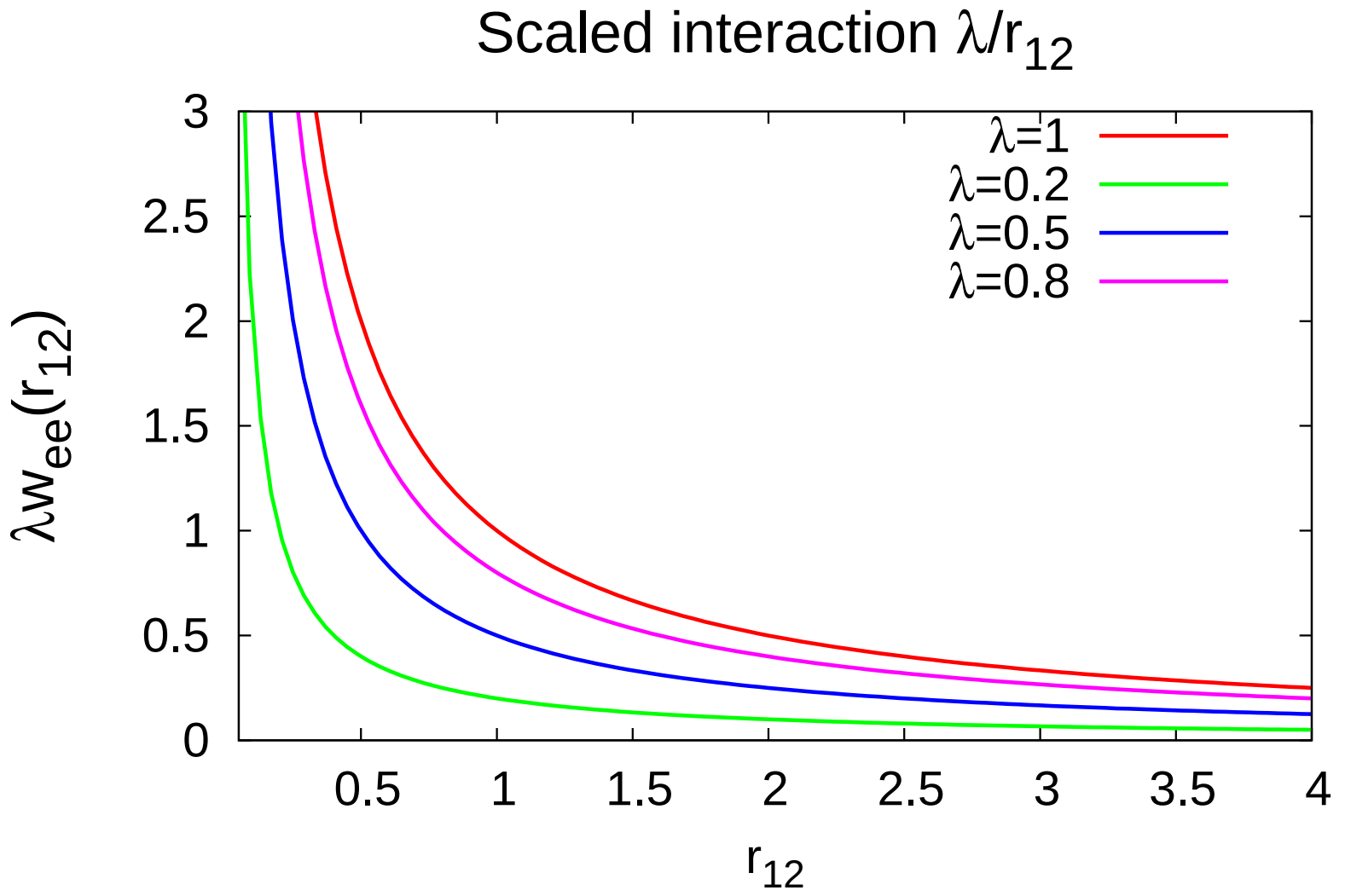
$$\left. \frac{\partial \tilde{\Phi}_0(r_1, r_1, r_{12})}{\partial r_{12}} \right|_{r_{12}=0} = \frac{1}{2} \Phi_0(r_1, r_1) = \frac{1}{2} \tilde{\Phi}_0(r_1, r_1, 0) \quad \longrightarrow \quad \text{cusp !}$$

- **Third approach:** combine the two first approaches

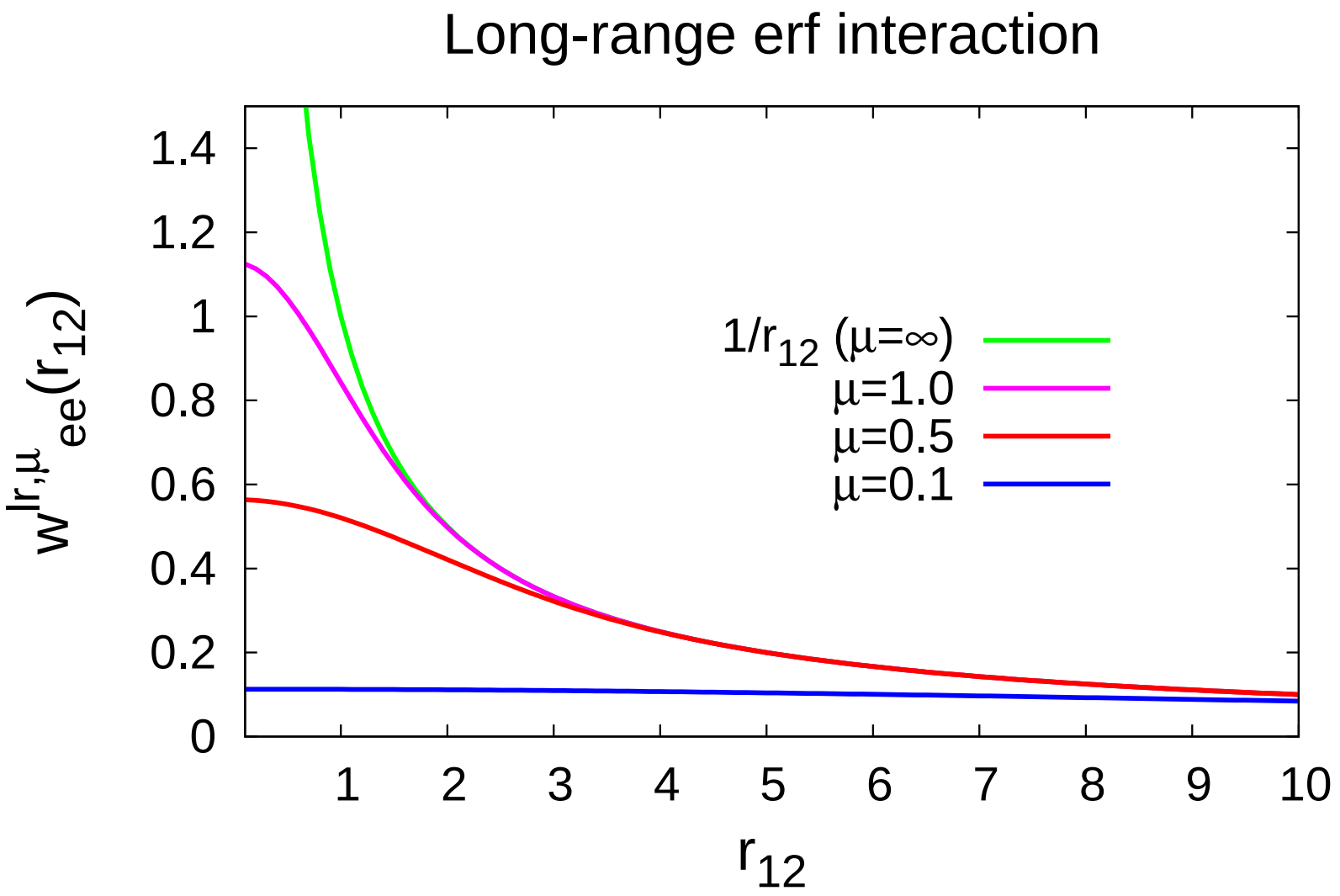
$$\tilde{\Psi}_0^{\mathrm{CI}}(r_1, r_2, r_{12}) = \Psi_0^{\mathrm{CI}}(r_1, r_2, r_{12}) + c_{12}\, r_{12}\, \Phi_0(r_1, r_2)$$



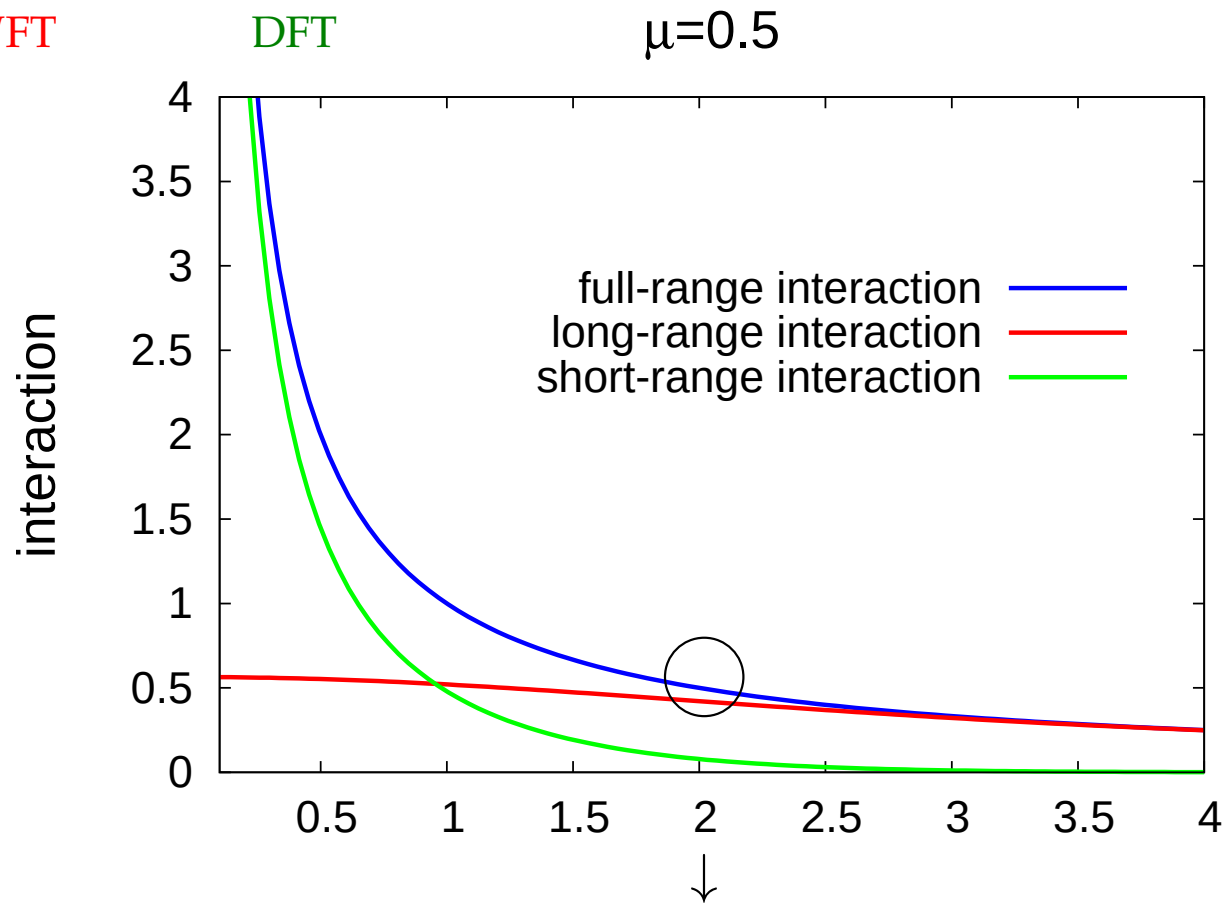
The error in the electronic energy of the ground-state helium atom (E_h). The error is plotted on a logarithmic scale as a function of the number of terms in the expansions.


Scaled interaction λ/r12
λw_ee(r_12)
r12
λ=1
λ=0.2
λ=0.5
λ=0.8
0
0.5
1
1.5
2
2.5
3
0.5
1
1.5
2
2.5
3
3.5
4

$$\lambda/r_{12} \rightarrow \mathrm{erf}(\mu r_{12})/r_{12}$$



$$\frac{1}{r_{12}} = \underbrace{\frac{\mathrm{erf}(\mu r_{12})}{r_{12}}}_{\text{WFT}} + \underbrace{\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}}_{\text{DFT}} \qquad \text{where} \qquad \mathrm{erf}(\mu r_{12}) = \frac{2}{\sqrt{\pi}} \int_0^{\mu r_{12}} e^{-t^2}\, dt$$



$\frac{1}{\mu}$: reference distance in a.u.

Generalized adiabatic connection (*A. Savin*)

$$\left(\hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right) \Psi = E \Psi \qquad \boxed{\mu \to +\infty}$$

$$\nwarrow$$

$$\left(\hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \sum_{i=1}^{N} v^{\mu}(\mathbf{r}_i) \times \right) \Psi^{\mu} = \mathcal{E}^{\mu} \Psi^{\mu} \qquad \boxed{0 < \mu < +\infty}$$

$$\nwarrow$$

$$\left(\hat{T} + \sum_{i=1}^{N} v^{0}(\mathbf{r}_i) \times \right) \Phi^{\rm KS} = \mathcal{E}^{0} \Phi^{\rm KS} \qquad \boxed{\mu = 0}$$

Density constraint: $\boxed{\forall \mu \in [0, +\infty[\qquad n_{\Psi} = n_{\Psi^{\mu}} = n_{\Phi^{\rm KS}} = n}$

- μ-dependent decomposition of the universal Hohenberg-Kohn functional:

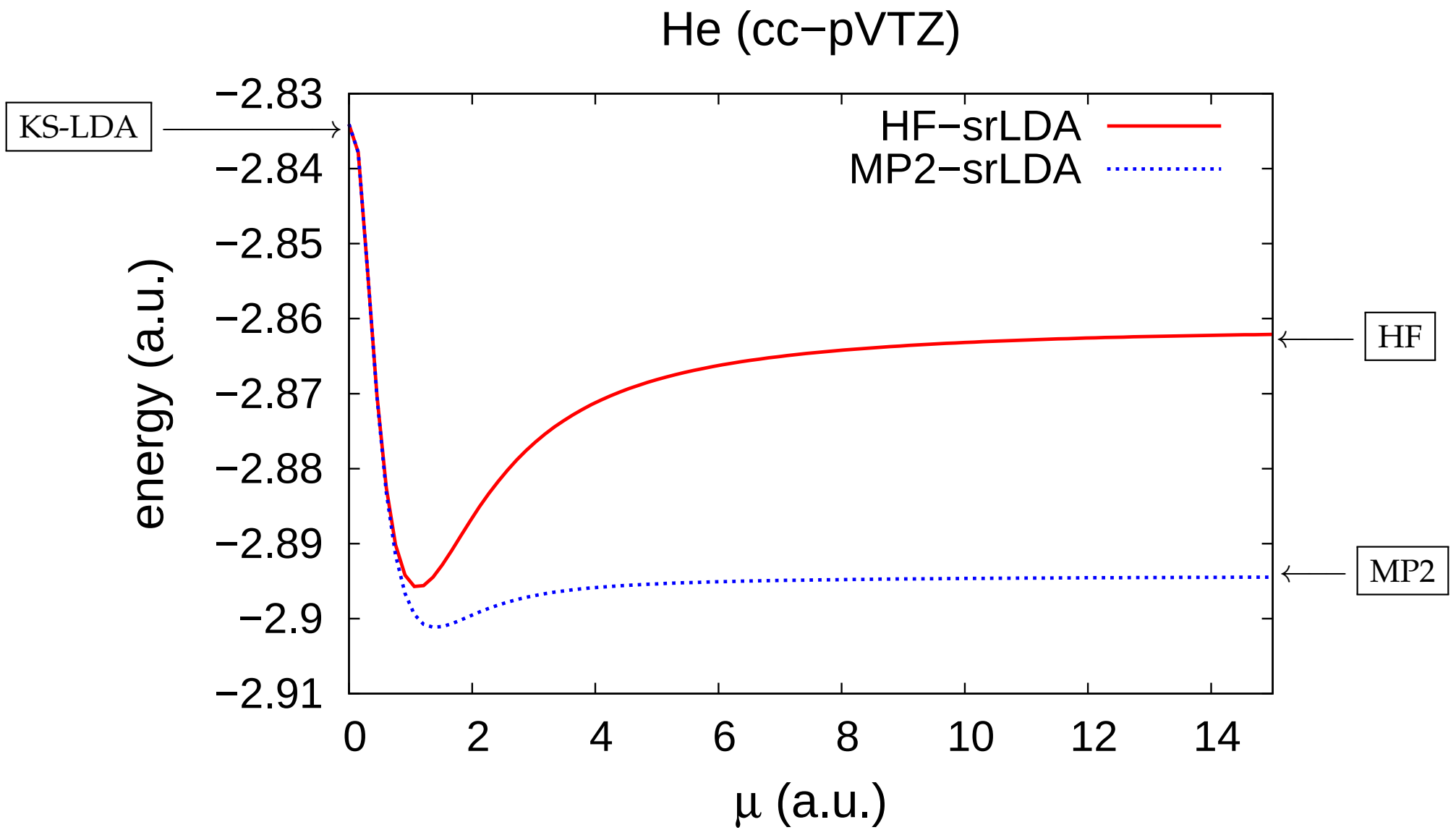
$$F[n] = \langle \Psi^{\mu}[n] | \hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} | \Psi^{\mu}[n] \rangle + \underbrace{E_{\rm Hxc}[n] - E_{\rm Hxc}^{\rm lr,\mu}[n]}_{E_{\rm Hxc}^{\rm sr,\mu}[n]} \xrightarrow{\mu=0} \underbrace{F[n] = \langle \Phi^{\rm KS}[n] | \hat{T} | \Phi^{\rm KS}[n] \rangle + E_{\rm Hxc}[n]}_{\text{Kohn-Sham DFT !}}$$

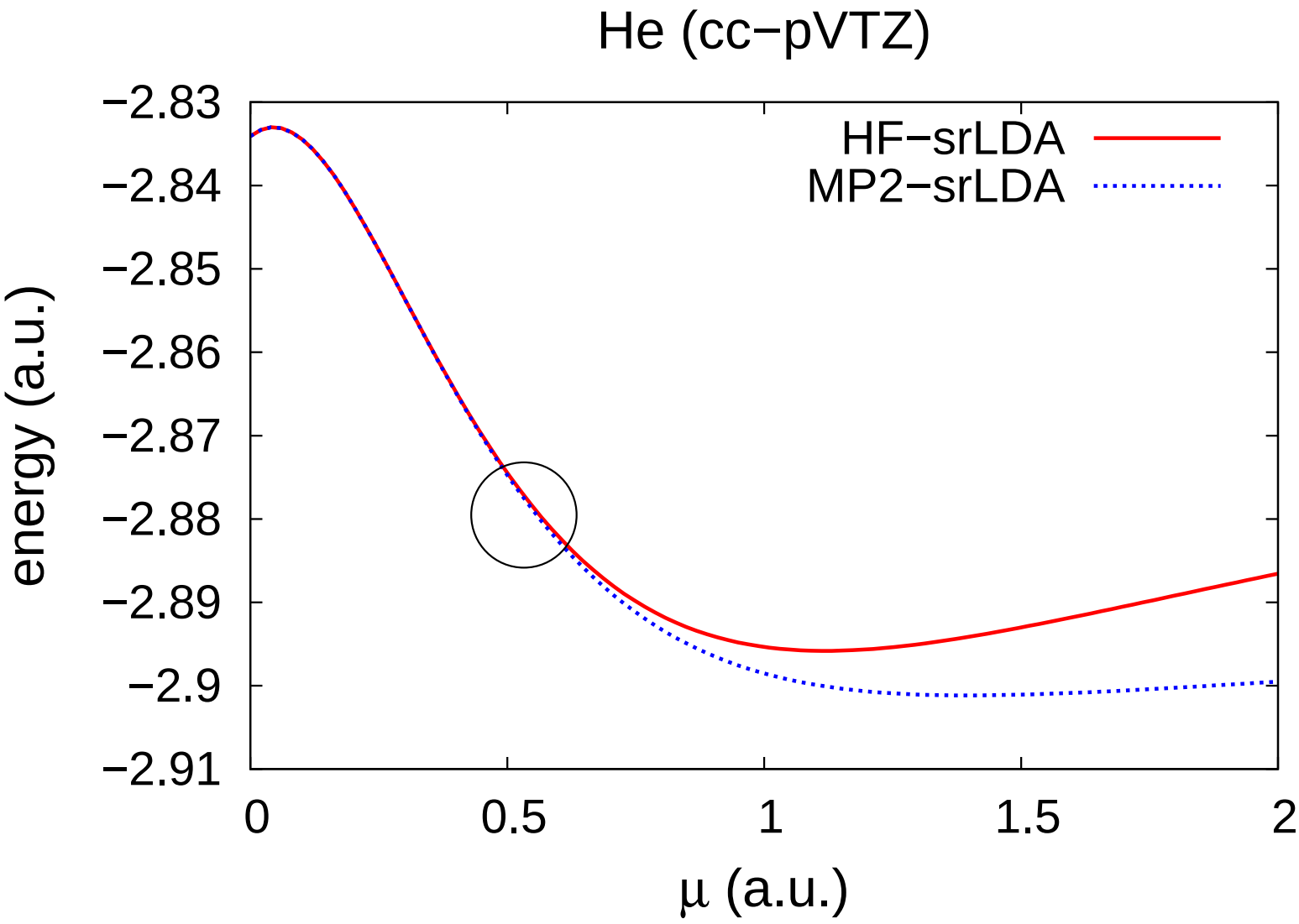
short-range Hxc

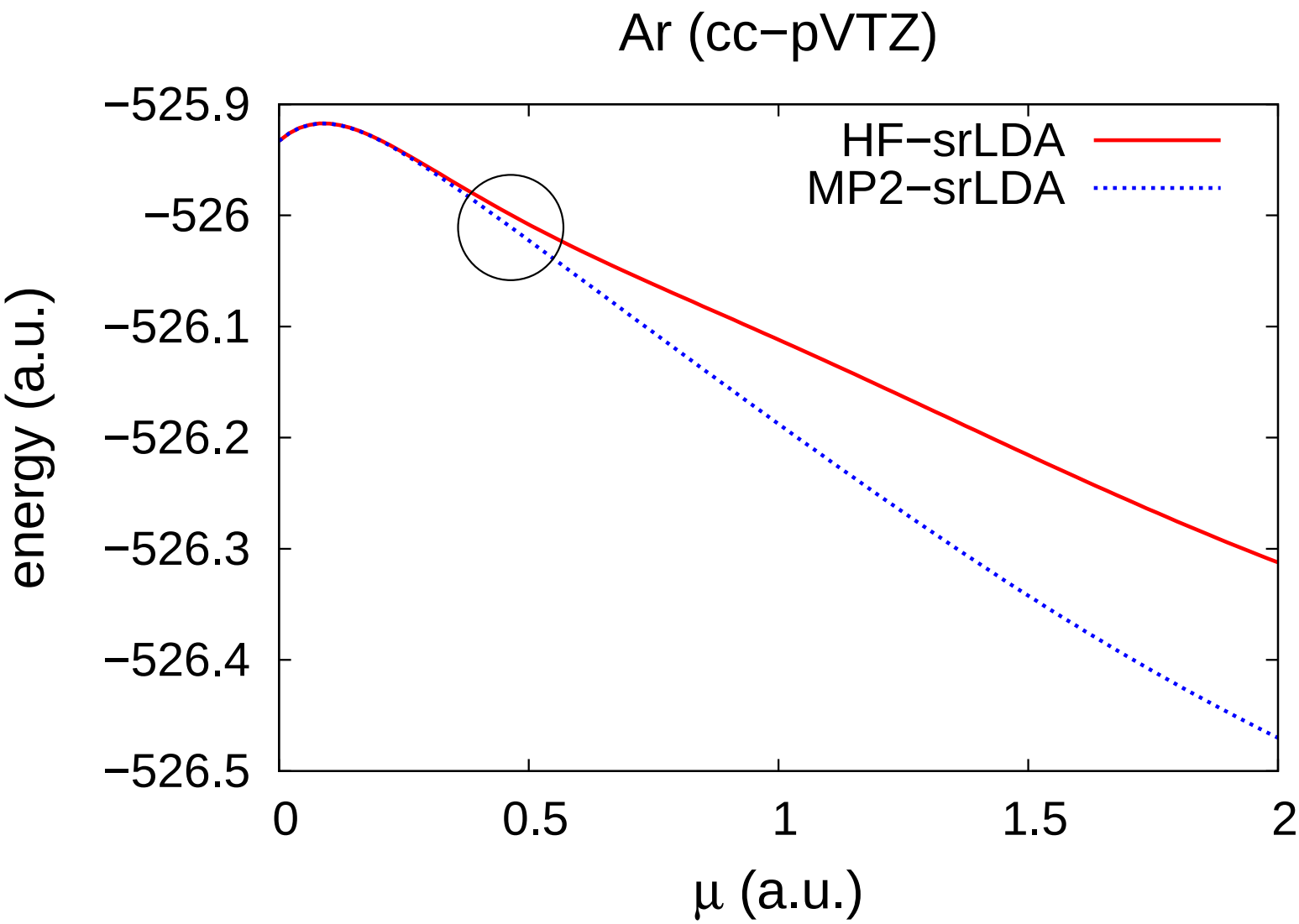
- Variational principle: $E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} | \Psi \rangle + E_{\rm Hxc}^{\rm sr,\mu}[n_{\Psi}] \right\}$

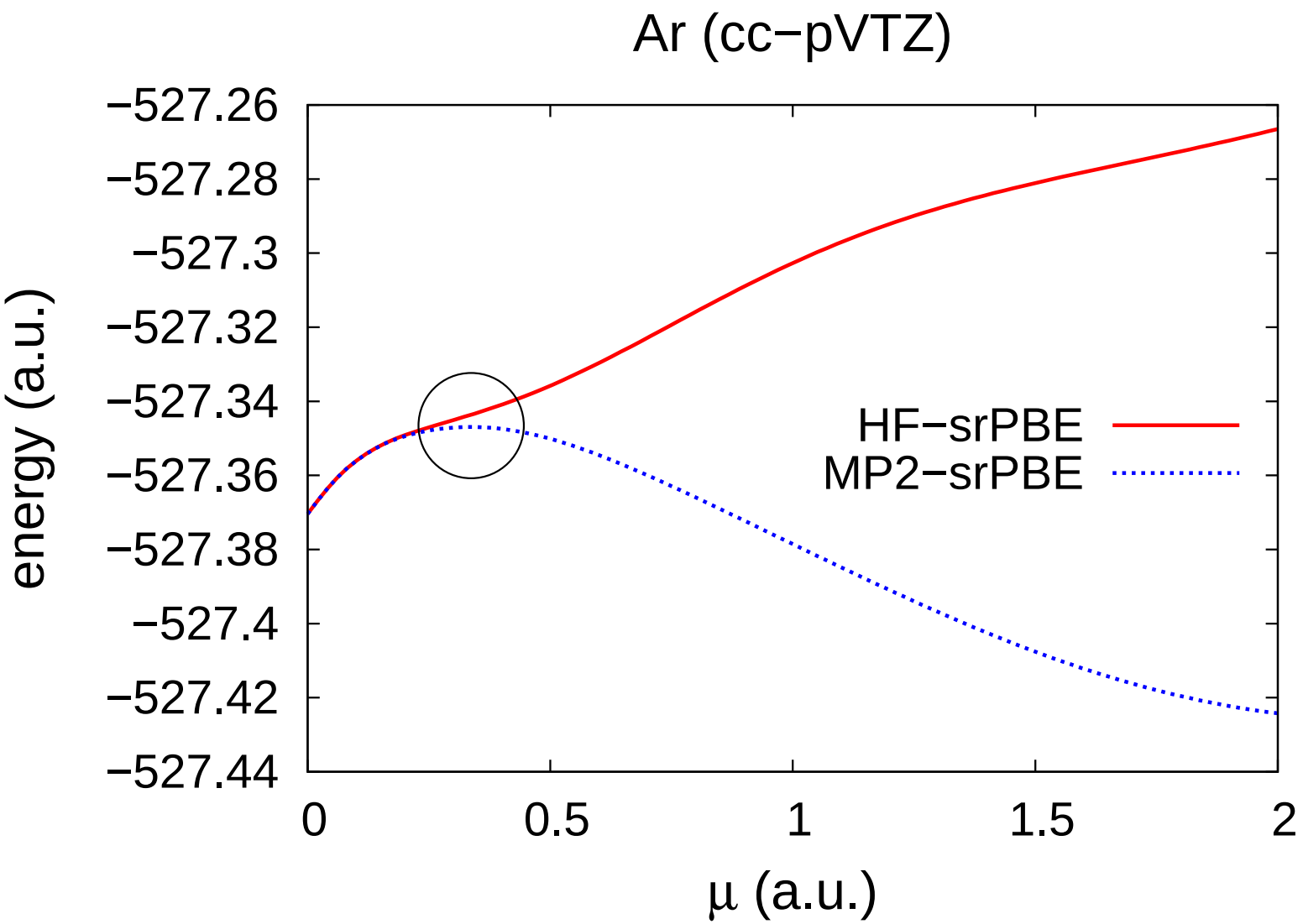
  The exact minimizing wave function is multideterminantal !
  It can be approximated by HF/MP2/CI/CC/MCSCF-type wavefunctions

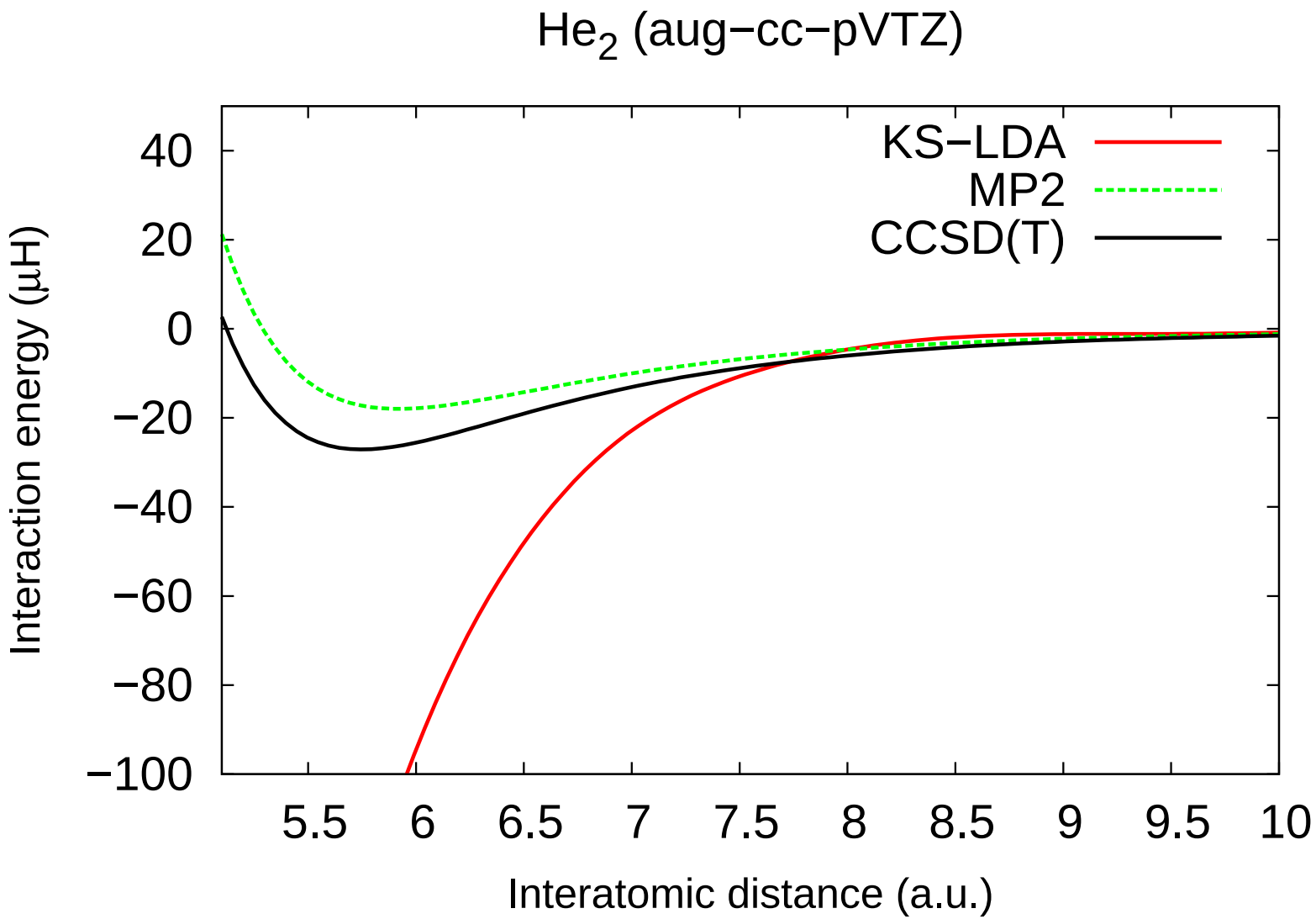
- Models discussed in the following: HF-srDFT, MP2-srDFT (*Ángyán*) and MCSCF-srDFT (*Jensen and Fromager*)
- Short-range functionals: srLDA, srGGA, sr-meta-GGA (*Savin, Toulouse, Gori-Giorgi, Stoll, Goll, Scuseria, ...*)

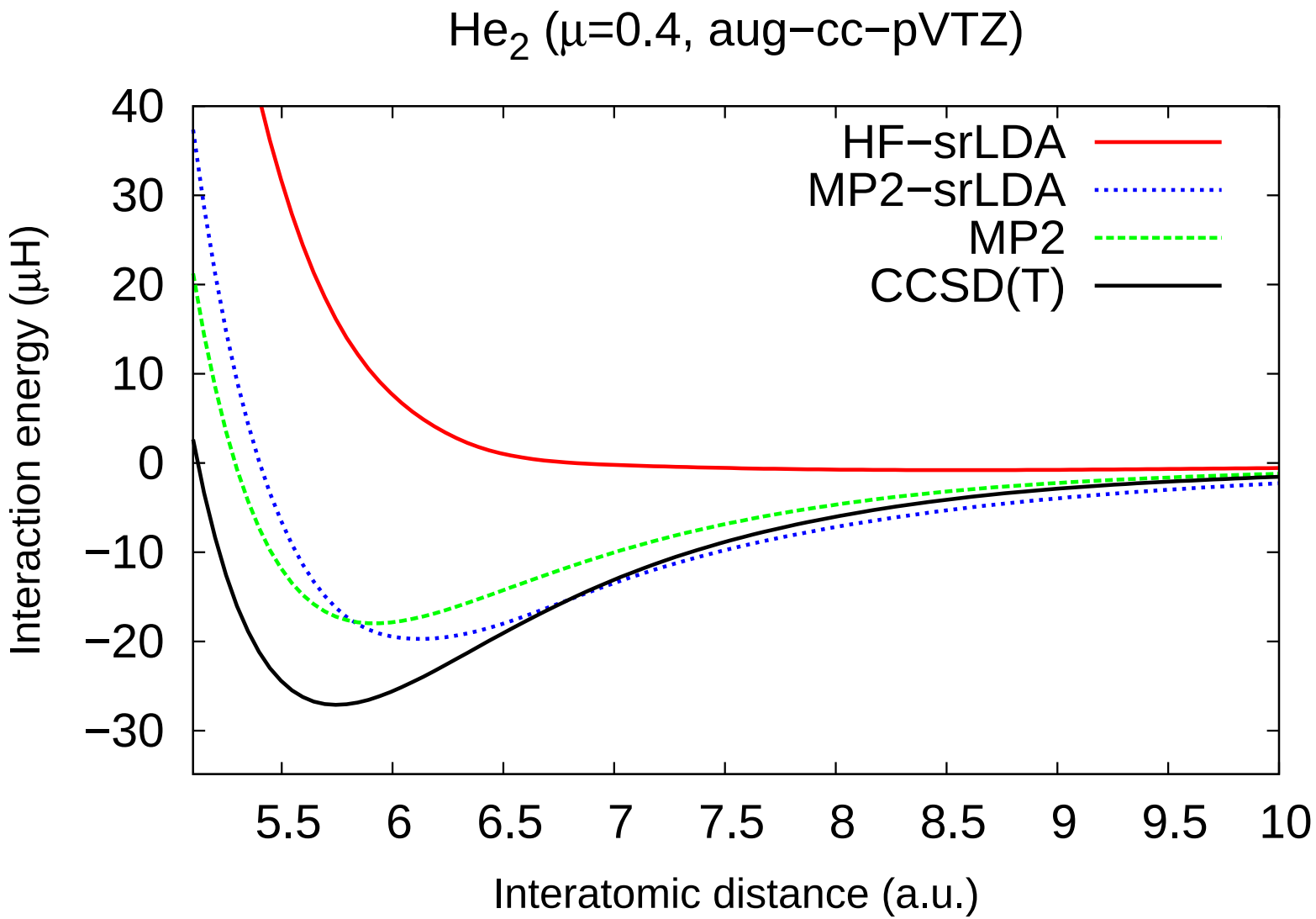

He (cc−pVTZ)
KS-LDA
HF−srLDA
MP2−srLDA
HF
MP2
energy (a.u.)
−2.83
−2.84
−2.85
−2.86
−2.87
−2.88
−2.89
−2.9
−2.91
0
2
4
6
8
10
12
14
μ (a.u.)

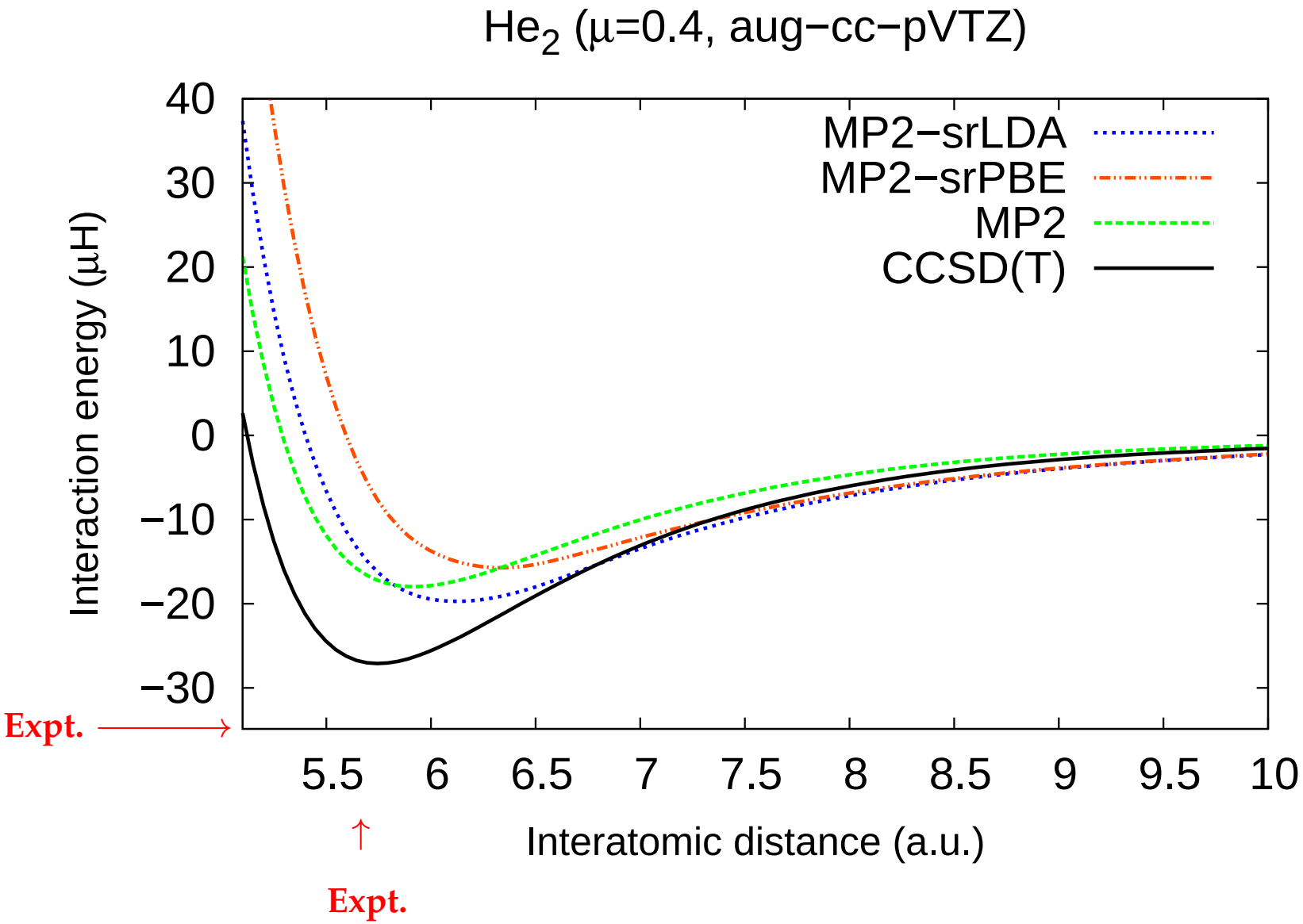

He (cc−pVTZ)
HF−srLDA
MP2−srLDA
energy (a.u.)
−2.83
−2.84
−2.85
−2.86
−2.87
−2.88
−2.89
−2.9
−2.91
0
0.5
1
1.5
2
μ (a.u.)

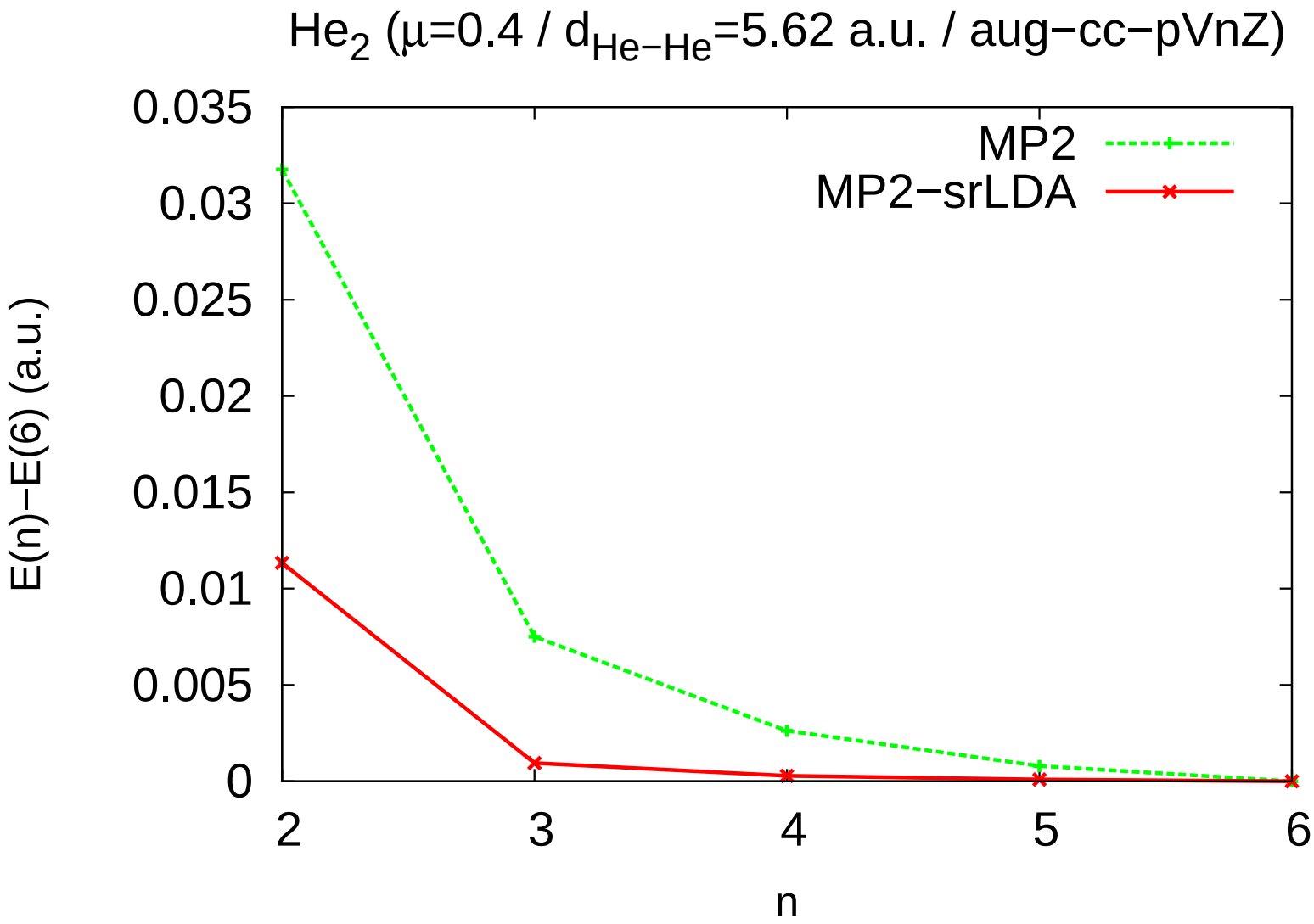

Ar (cc−pVTZ)
HF−srLDA
MP2−srLDA
energy (a.u.)
−525.9
−526
−526.1
−526.2
−526.3
−526.4
−526.5
0
0.5
1
1.5
2
μ (a.u.)

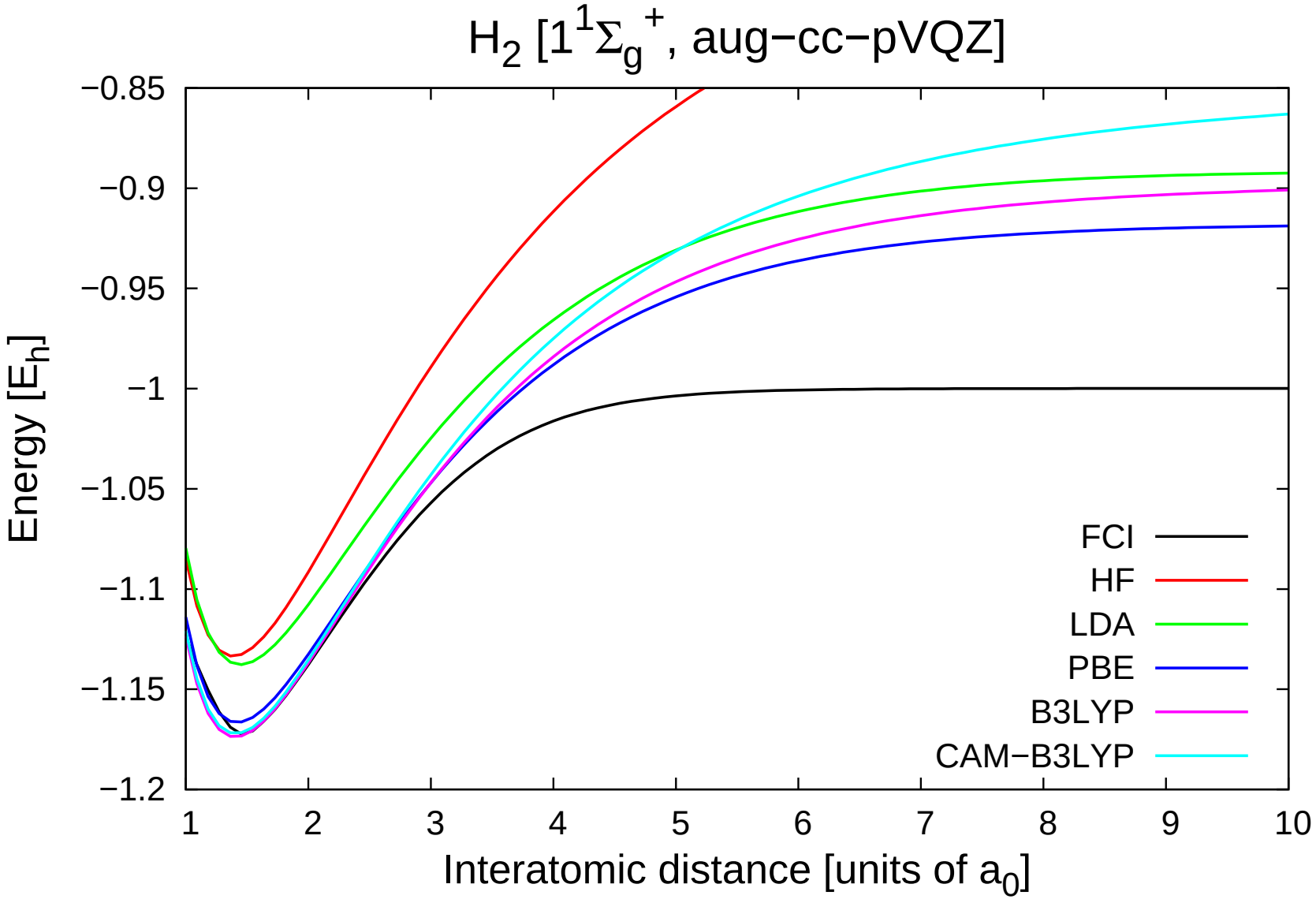

Ar (cc−pVTZ)
energy (a.u.)
−527.26
−527.28
−527.3
−527.32
−527.34
−527.36
−527.38
−527.4
−527.42
−527.44
0
0.5
1
1.5
2
μ (a.u.)
HF−srPBE
MP2−srPBE

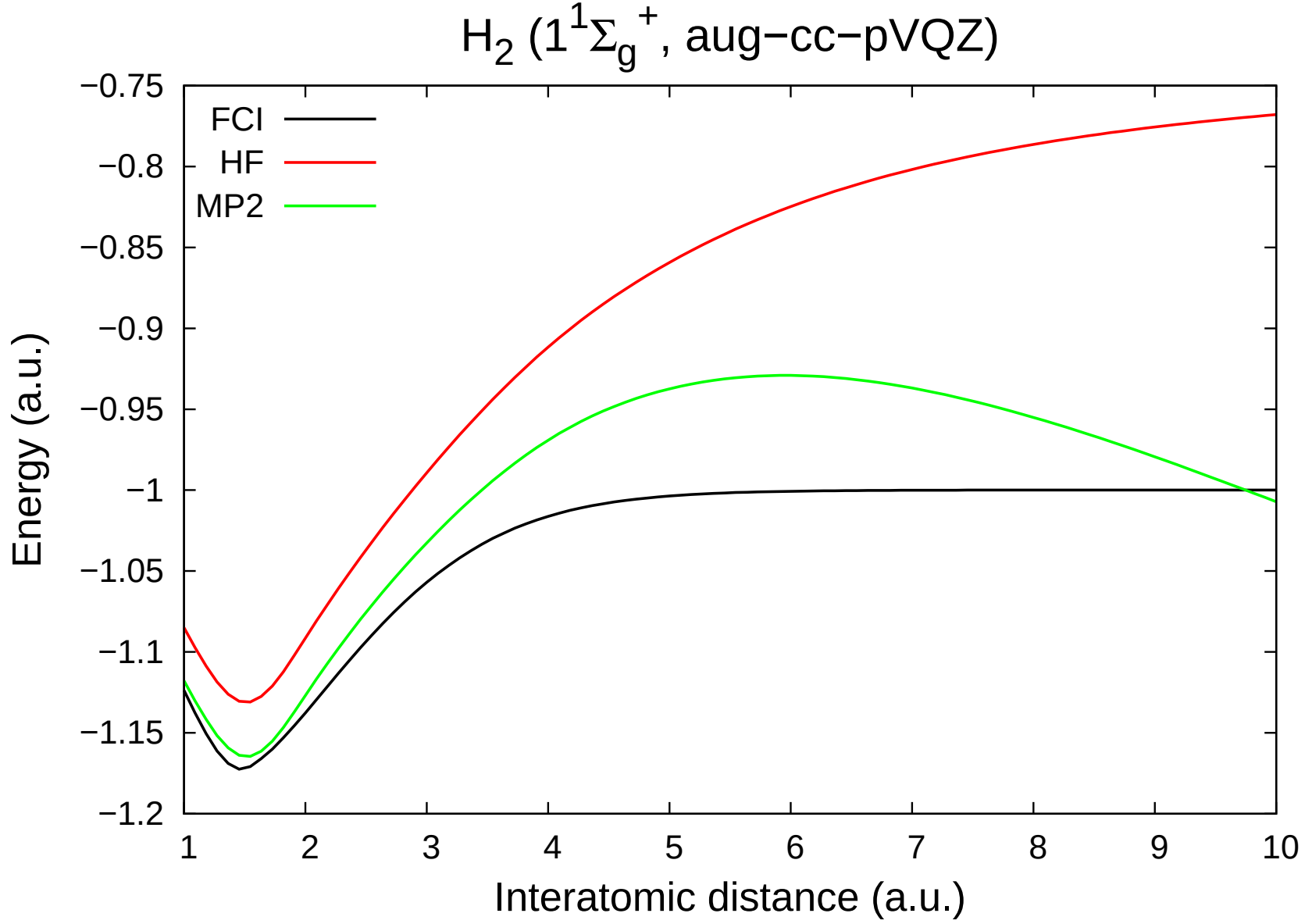

He2 (aug−cc−pVTZ)
KS−LDA
MP2
CCSD(T)
Interaction energy (μH)
40
20
0
−20
−40
−60
−80
−100
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)


He2 (μ=0.4, aug−cc−pVTZ)
HF−srLDA
MP2−srLDA
MP2
CCSD(T)
Interaction energy (μH)
40
30
20
10
0
−10
−20
−30
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)


He2 (μ=0.4, aug−cc−pVTZ)
MP2−srLDA
MP2−srPBE
MP2
CCSD(T)
Interaction energy (μH)
40
30
20
10
0
−10
−20
−30
Expt.
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)
Expt.


He2 (μ=0.4 / dHe−He=5.62 a.u. / aug−cc−pVnZ)
MP2
MP2−srLDA
E(n)−E(6) (a.u.)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
2
3
4
5
6
n


H2 [1 1Σg +, aug−cc−pVQZ]
Energy [Eh]
−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
Interatomic distance [units of a0]
FCI
HF
LDA
PBE
B3LYP
CAM−B3LYP


H_2 ($1^1\Sigma_g^+$, aug−cc−pVQZ)
FCI
HF
MP2
Energy (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
Interatomic distance (a.u.)

Strong electron correlation in molecules

- Example: H_2 molecule

at equilibrium geometry: $\boxed{\Psi_0 = C_0|1\sigma_g^\alpha 1\sigma_g^\beta| + \ldots}$ 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 $H_A^+ \ldots H_B^-$

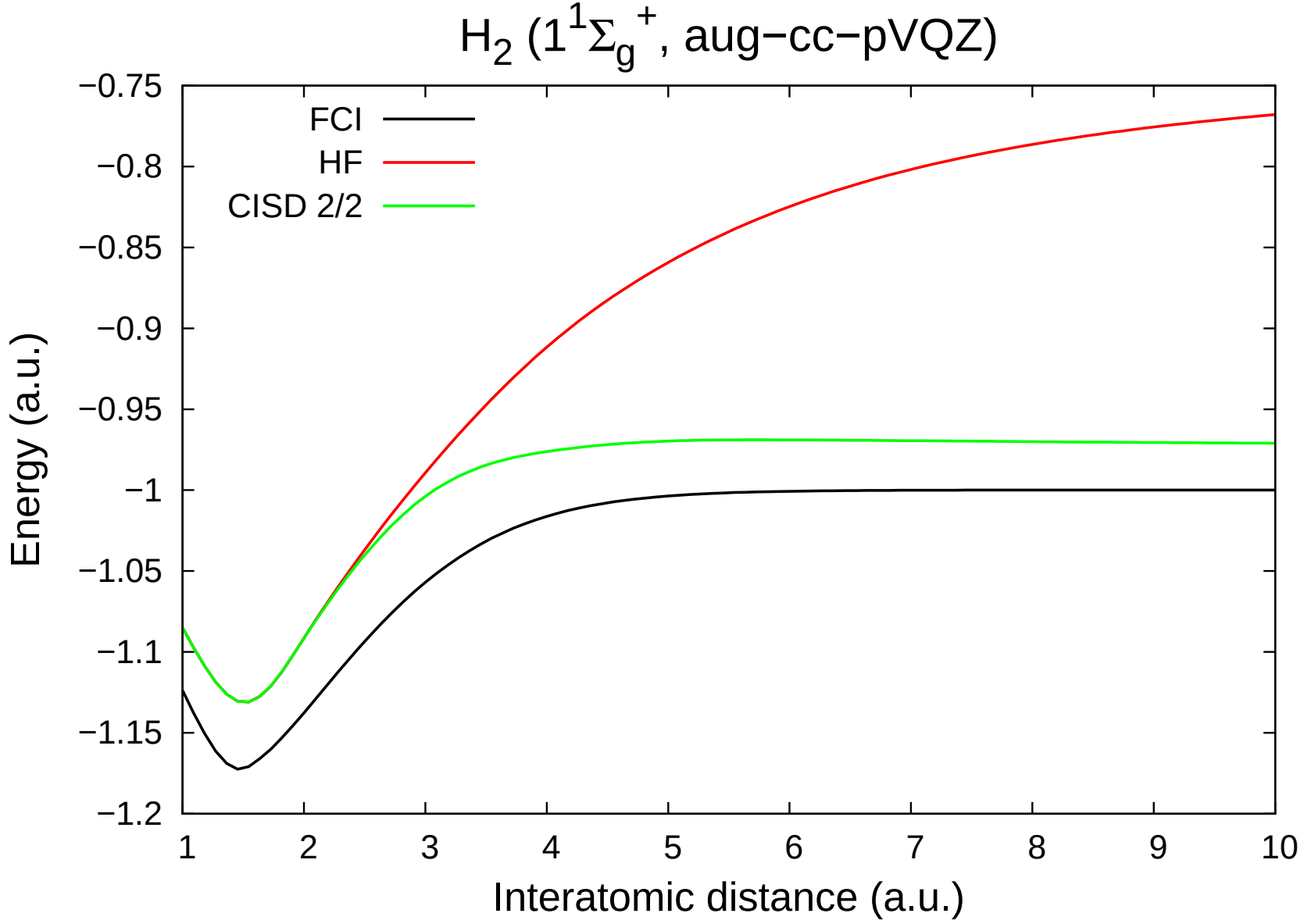
$1\sigma_g = \frac{1}{\sqrt{2}}(1s_A + 1s_B)$ and $1\sigma_u = \frac{1}{\sqrt{2}}(1s_A - 1s_B)$

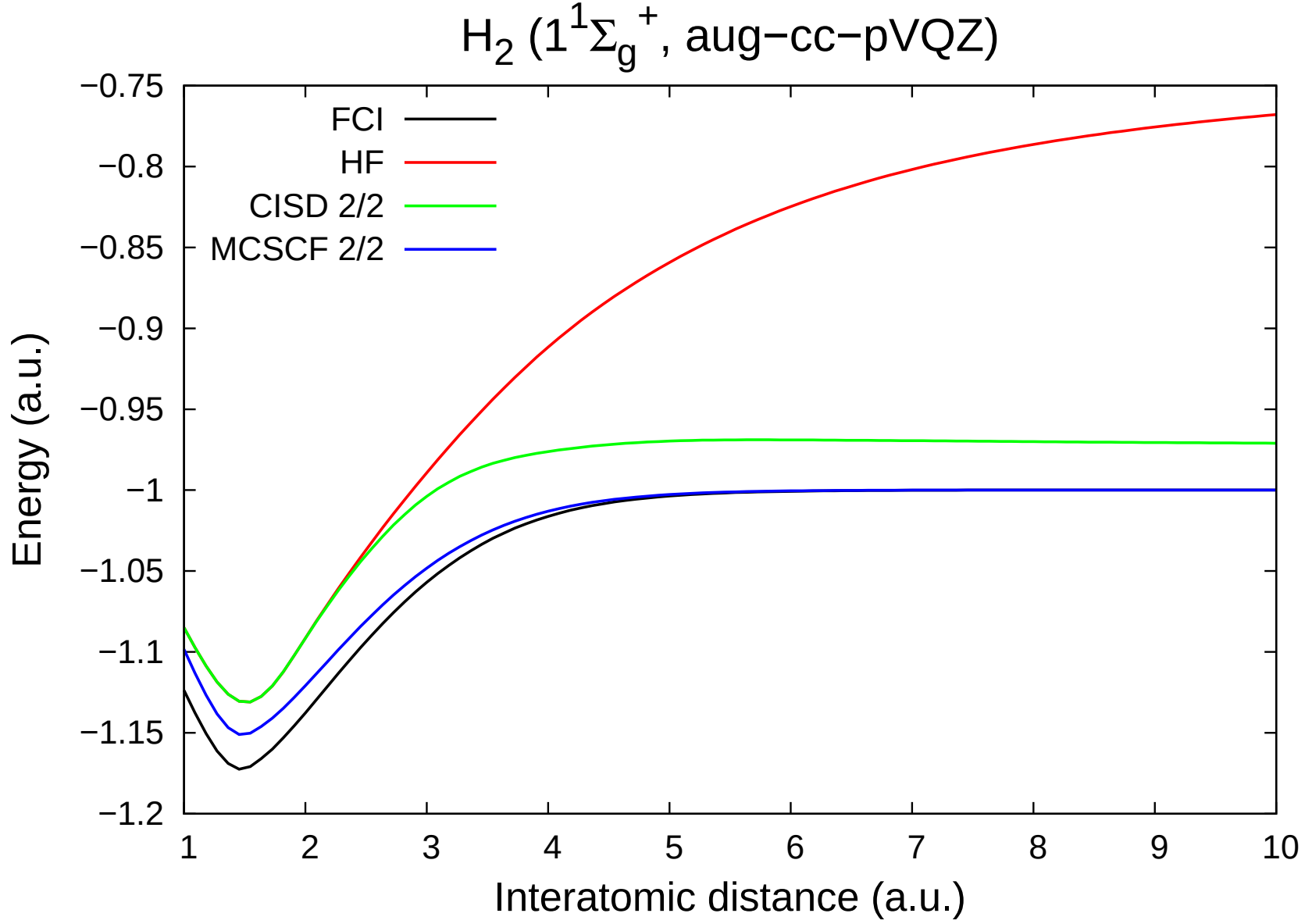
$$|1\sigma_g^\alpha 1\sigma_g^\beta| = \tfrac{1}{2}\left(|1s_A^\alpha 1s_B^\beta| + |1s_B^\alpha 1s_A^\beta| + |1s_A^\alpha 1s_A^\beta| + |1s_B^\alpha 1s_B^\beta|\right)$$

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

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

strong static correlation


H2 (1 1Σg +, aug−cc−pVQZ)
FCI
HF
CISD 2/2
Energy (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
Interatomic distance (a.u.)


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

Merging MCSCF with DFT

- A proper description of multiconfigurational systems requires more than a single determinant
  $\rightarrow$ a complete active space (CAS) must be defined

  H. . .H CAS = $|\sigma_g^2|, |\sigma_u^2|$

  Be CAS = $|1s^2 2s^2|, |1s^2 2p_x^2|, |1s^2 2p_y^2|, |1s^2 2p_z^2|$

- Multiconfigurational extension of KS-DFT: the MCSCF point of view ...

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

leads to a "double counting problem"

Combining long-range WFT with short-range DFT (srDFT)

- As proposed by *Savin*[a], rather than obtaining the density from a non-interacting KS system, one may use a **fictitious long-range interacting system** with ground-state wavefunction Ψ^μ whose density n_{Ψ^μ} equals the exact physical one n_0. Consequently, the exact ground-state energy can be expressed as

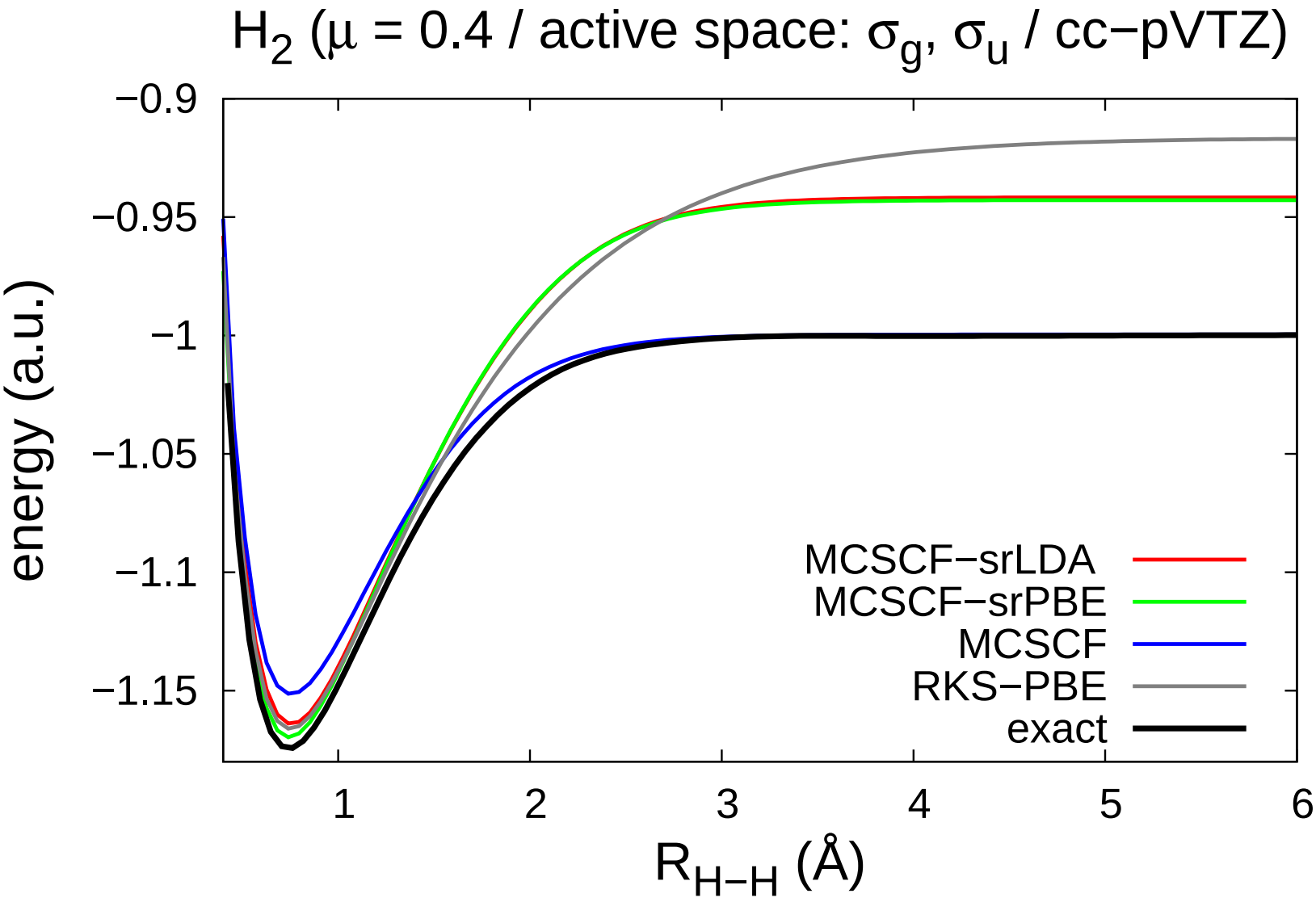
$$\begin{aligned} E_0 &= \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} | \Psi \rangle + E_{\rm Hxc}^{\rm sr,\mu}[n_\Psi] \right\} \\ &= \langle \Psi^\mu | \hat{T} + \hat{W}_{\rm ee}^{\rm lr,\mu} + \hat{V}_{\rm ne} | \Psi^\mu \rangle + E_{\rm Hxc}^{\rm sr,\mu}[n_{\Psi^\mu}] \end{aligned}$$

- In this context, it became possible to **merge rigorously** MCSCF with LDA and PBE approximations[b,c].

[a] A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996), p. 327

[b] J. K. Pedersen, Ph.D. thesis, University of Southern Denmark, 2004.

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


H2 (μ = 0.4 / active space: σg, σu / cc−pVTZ)
energy (a.u.)
−0.9
−0.95
−1
−1.05
−1.1
−1.15
1
2
3
4
5
6
RH−H (Å)
MCSCF−srLDA
MCSCF−srPBE
MCSCF
RKS−PBE
exact

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,

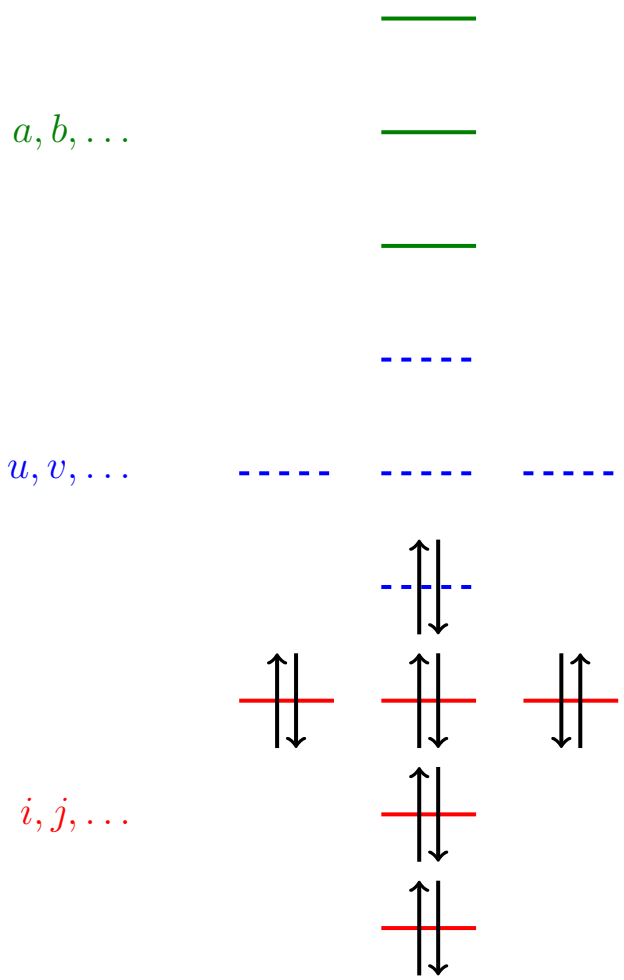
$$[\hat{H}] = \begin{bmatrix} E_g & K \\ K & E_u \end{bmatrix}, \quad \text{where}$$

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 $E_g - K$.

Multiconfigurational DFT in the orbital space



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

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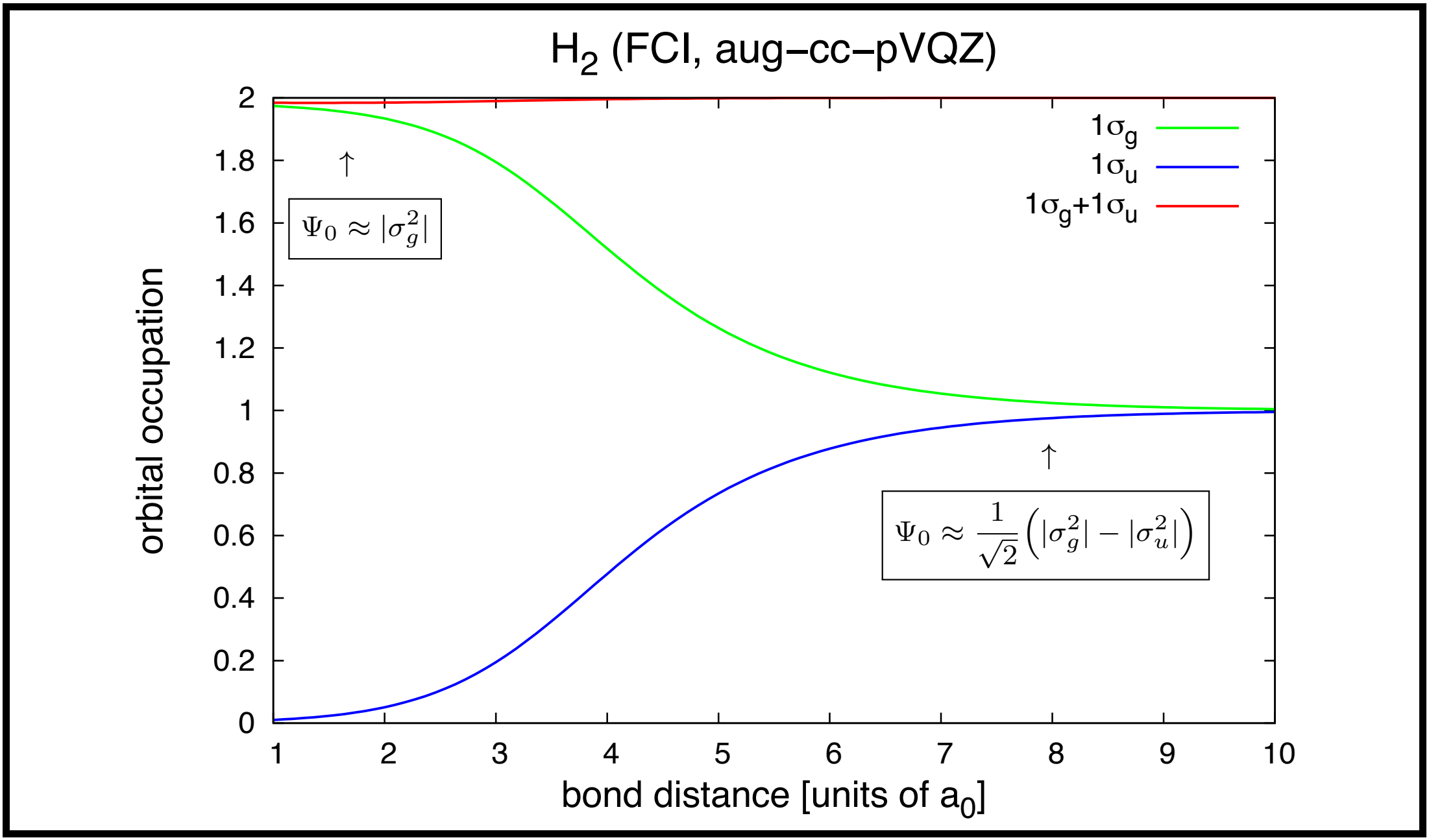
H2 (FCI, aug–cc–pVQZ)
orbital occupation
bond distance [units of a0]
1σg
1σu
1σg+1σu
Ψ0 ≈ |σg2|
Ψ0 ≈ 1/√2 (|σg2| − |σu2|)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
1
2
3
4
5
6
7
8
9
10