Combining wave function and density-functional theories by means of range separation: progress report

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Outline

- Range separation of electron correlation: why and how ?
- long-range WFT / short-range DFT (srDFT)
- Prescriptions for the choice of the range separation
- Performance of srDFT models:

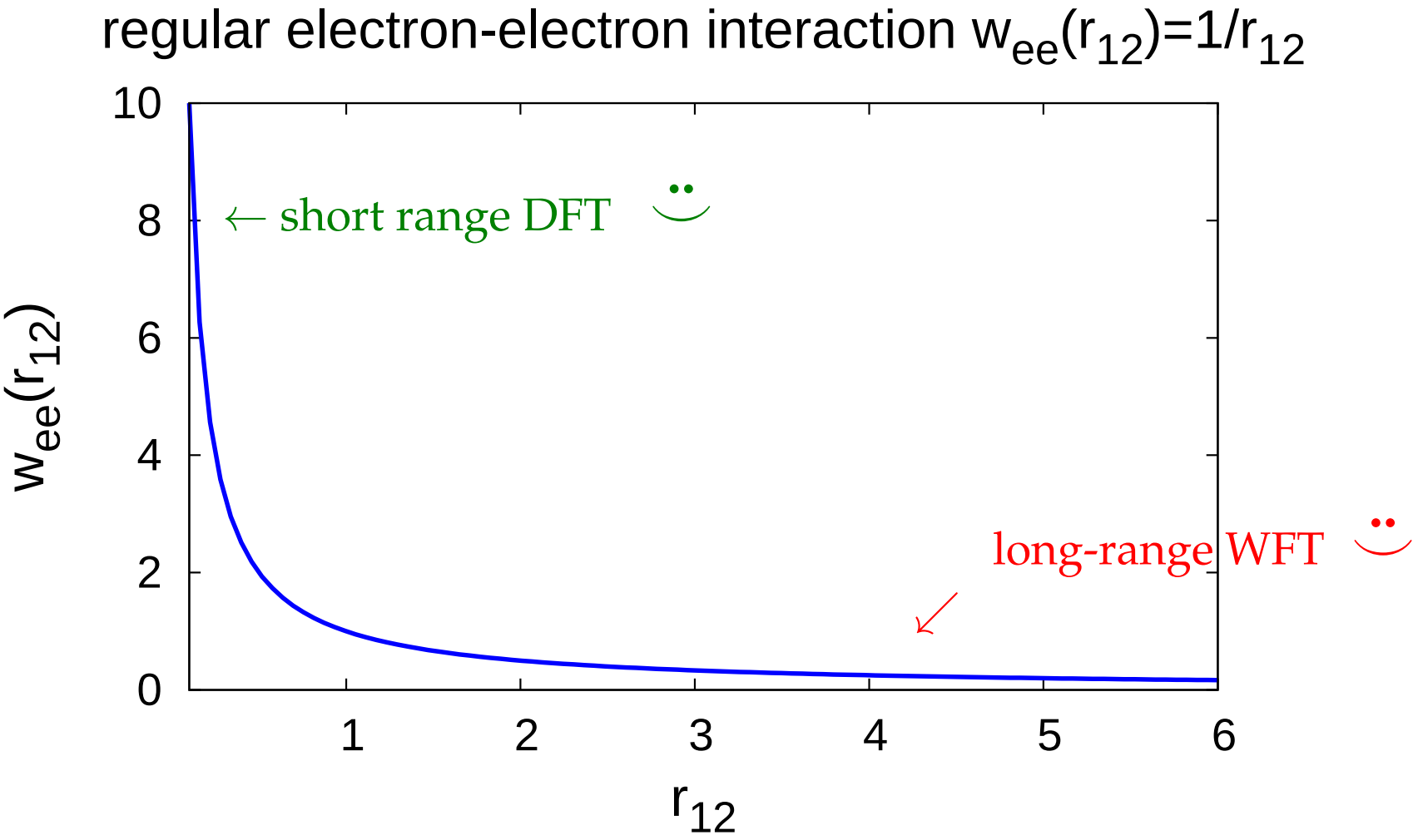
  van der Waals systems

  multireference systems (dissociation)

  multireference van der Waals systems

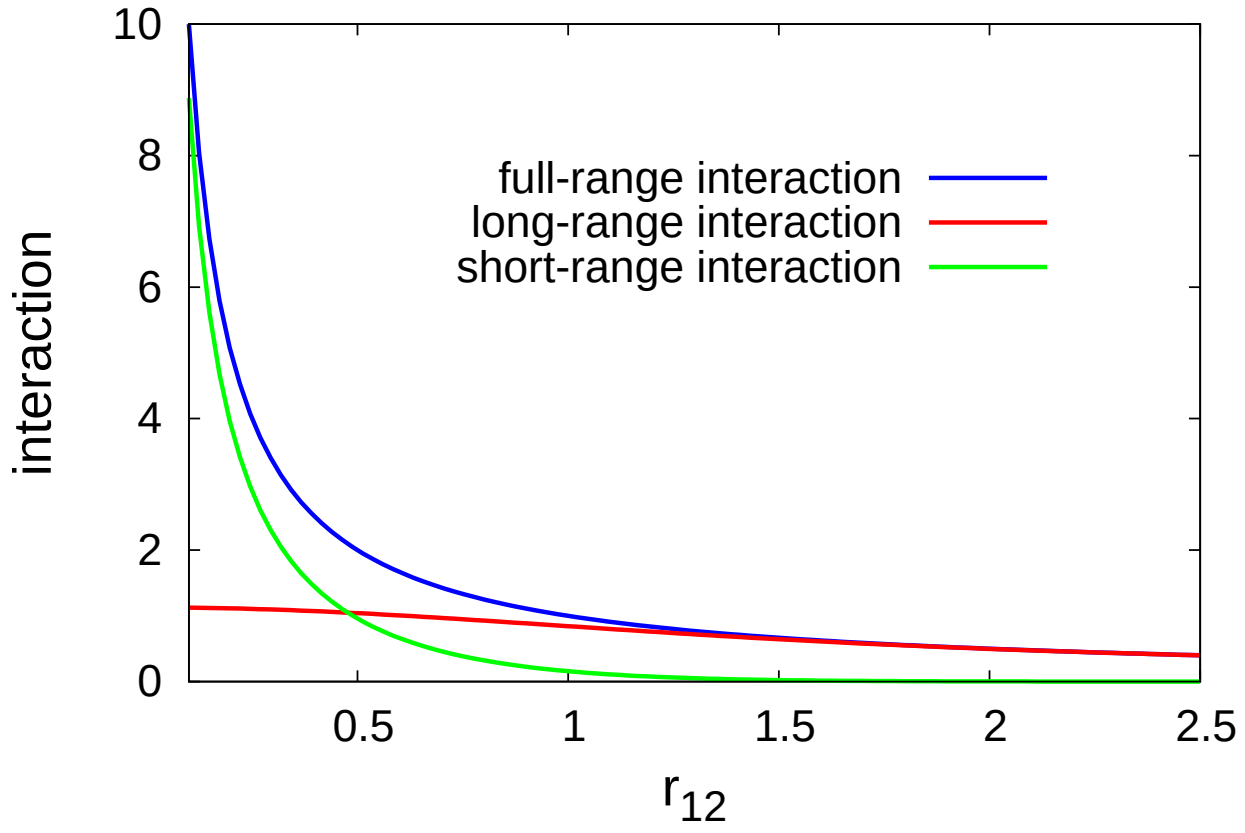
- Conclusion and outlook

Range separation of electron correlation: why and how ?

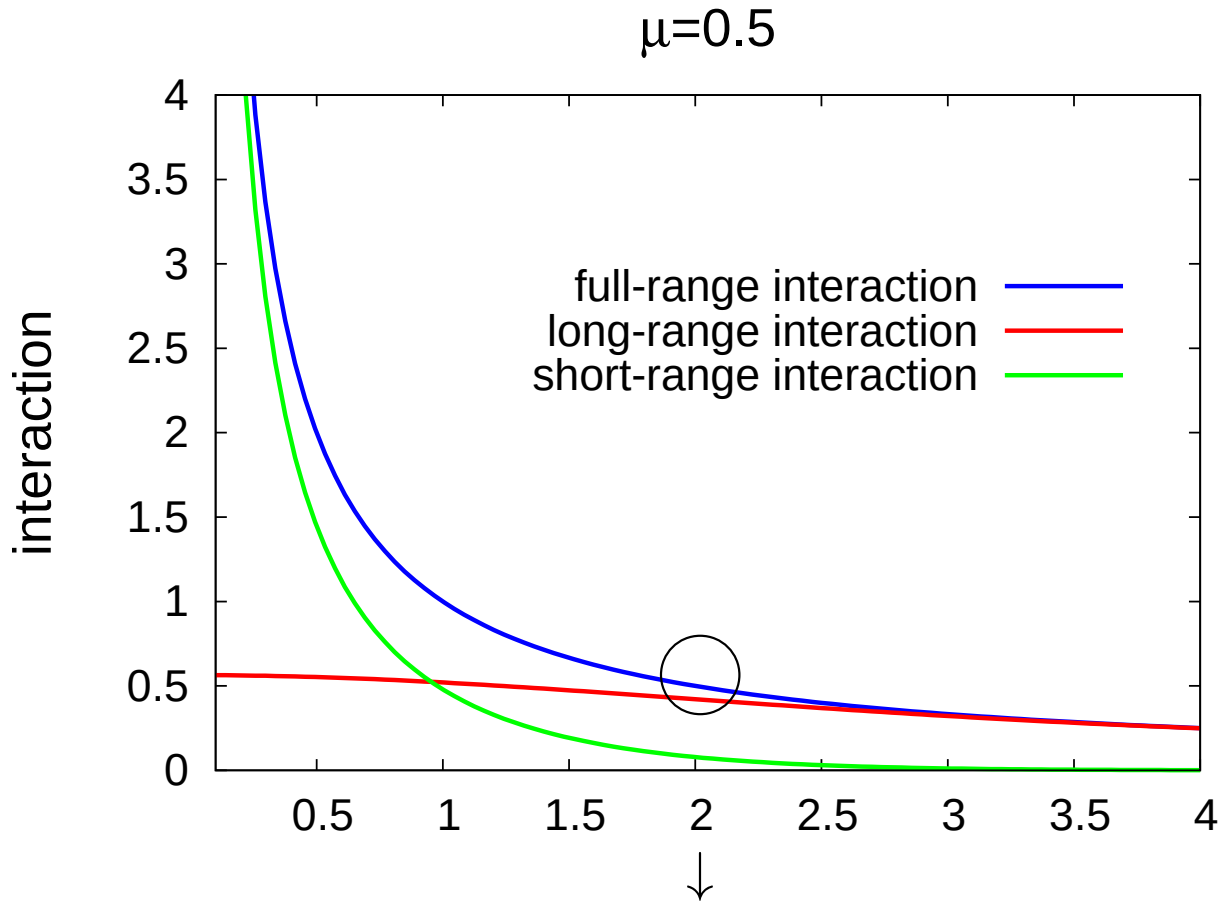


full range interaction $= \frac{1}{r_{12}} = w_{\rm ee}^{\rm lr}(r_{12}) + w_{\rm ee}^{\rm sr}(r_{12})$ as proposed by A. Savin

long-range interaction (WFT) short-range interaction (DFT)



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



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

Long-range WFT / short-range DFT (srDFT)

- We use the general formalism introduced in the first lecture with a modified electron-electron interaction equal to the long-range interaction: $\hat{W}_{\rm ee}^{m} = \hat{W}_{\rm ee}^{{\rm lr},\mu}$

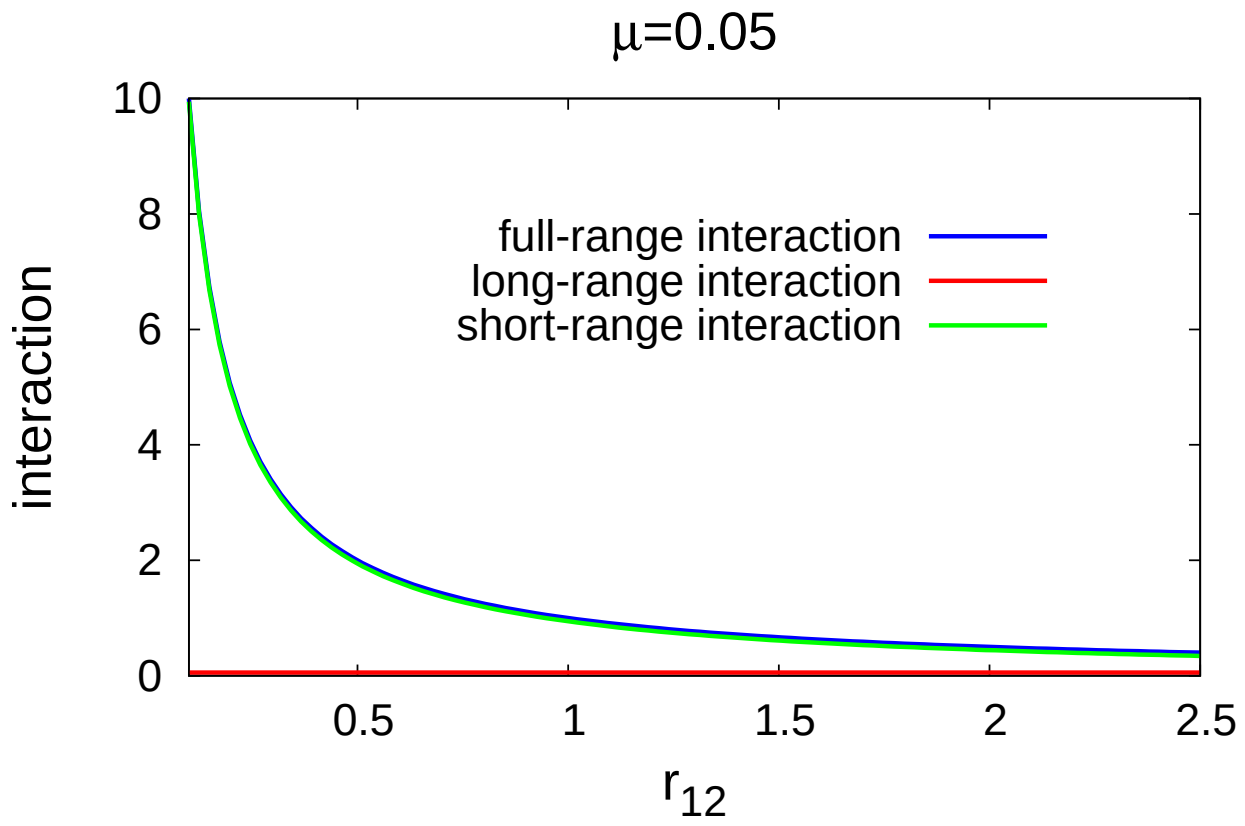
$$\hat{W}_{\rm ee} = \hat{W}_{\rm ee}^{{\rm lr},\mu} + \left(\underbrace{\hat{W}_{\rm ee} - \hat{W}_{\rm ee}^{{\rm lr},\mu}} \right)$$

WFT-based methods $\qquad$ $\hat{W}_{\rm ee}^{{\rm sr},\mu}$ complement of $\hat{W}_{\rm ee}^{{\rm lr},\mu}$ $\rightarrow$ $E_{\rm Hxc}^{{\rm sr},\mu}[n]$

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

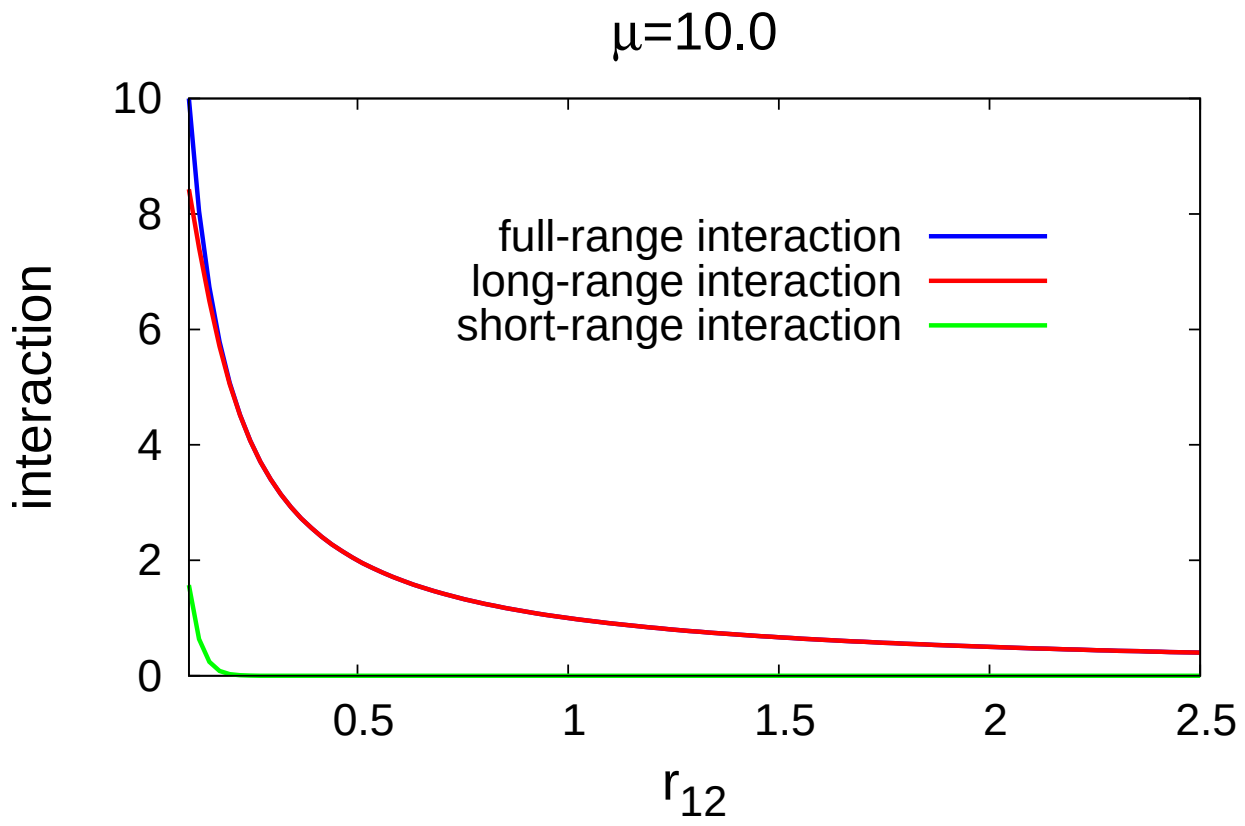
- approximations used in the description of the long-range interaction define the srDFT schemes: HF-srDFT, MP2-srDFT, CC-srDFT, MCSCF-srDFT, ...
- approximations used in the short-range functional: srLDA, srPBE, ...

$\mu = 0$ limit: Kohn-Sham DFT



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

$\mu \to \infty$ limit: WFT



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

- An combined WFT-DFT approach is obtained when $0 < \mu < +\infty$
- Prescription for the choice of μ:

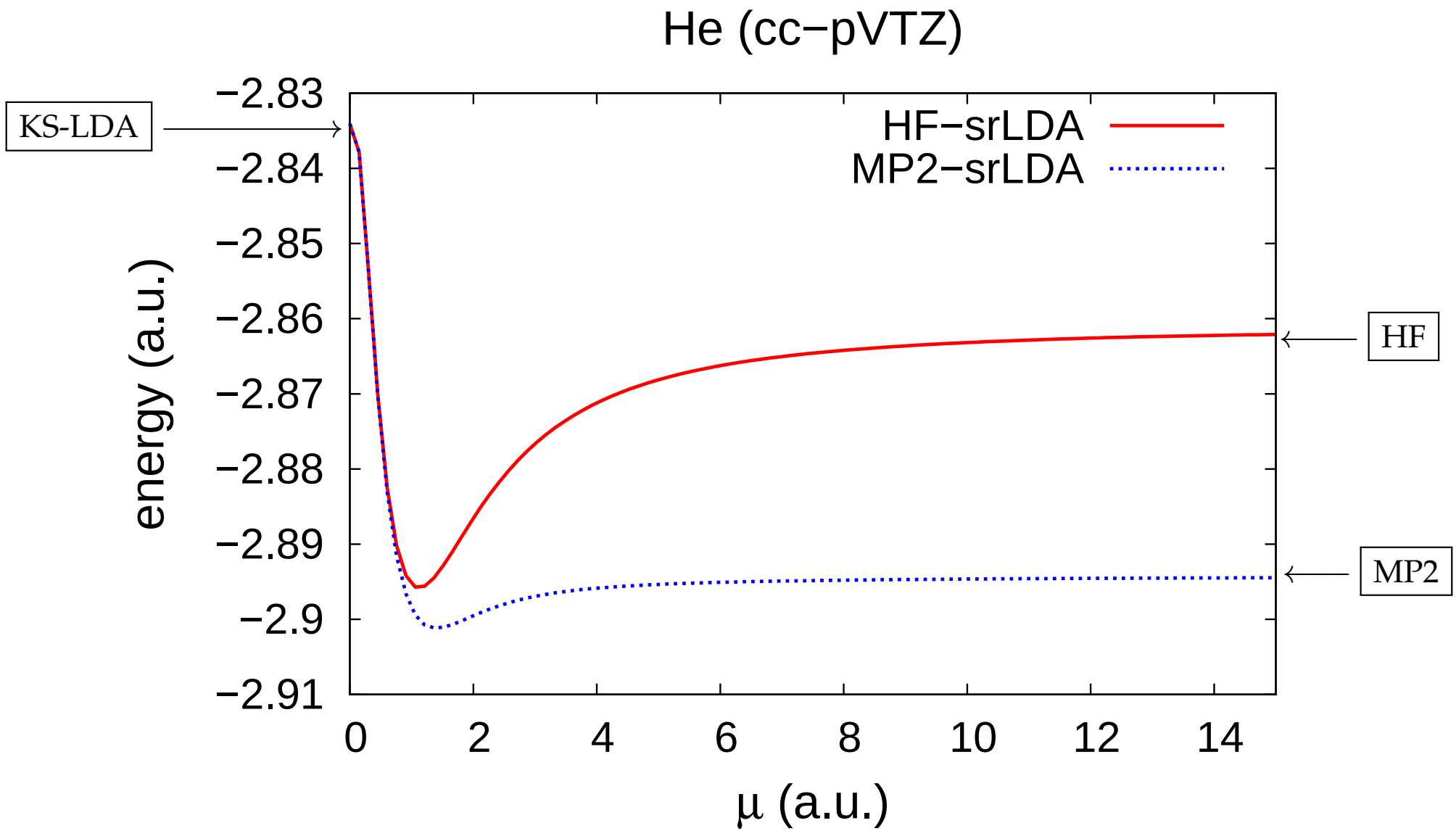
  in order to merge the best of both WFT and DFT worlds, in terms of accuracy and computational cost, μ should be chosen so that

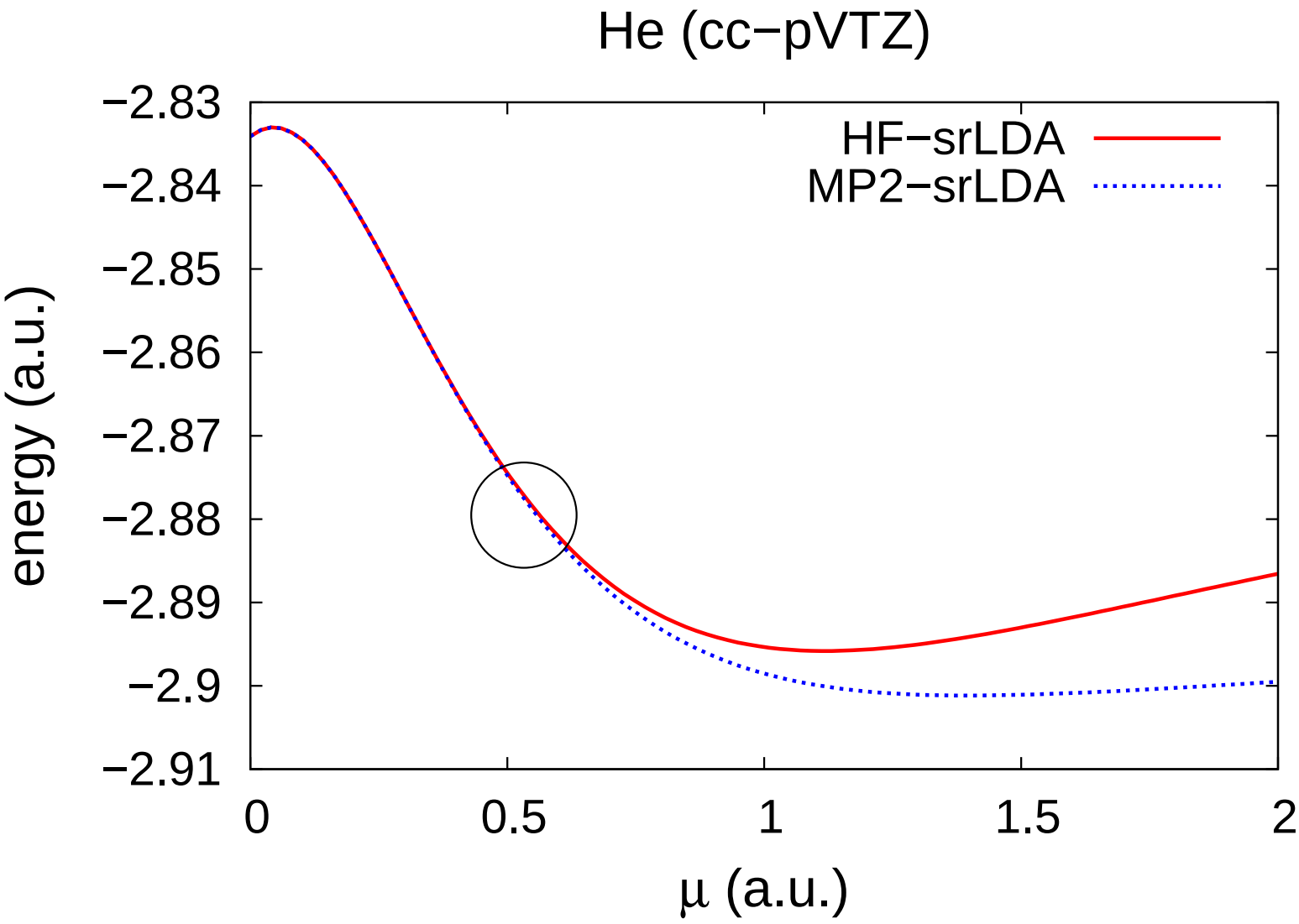
  (i) multireference effects and dispersion interactions are assigned to the long-range interaction, and thus treated within WFT

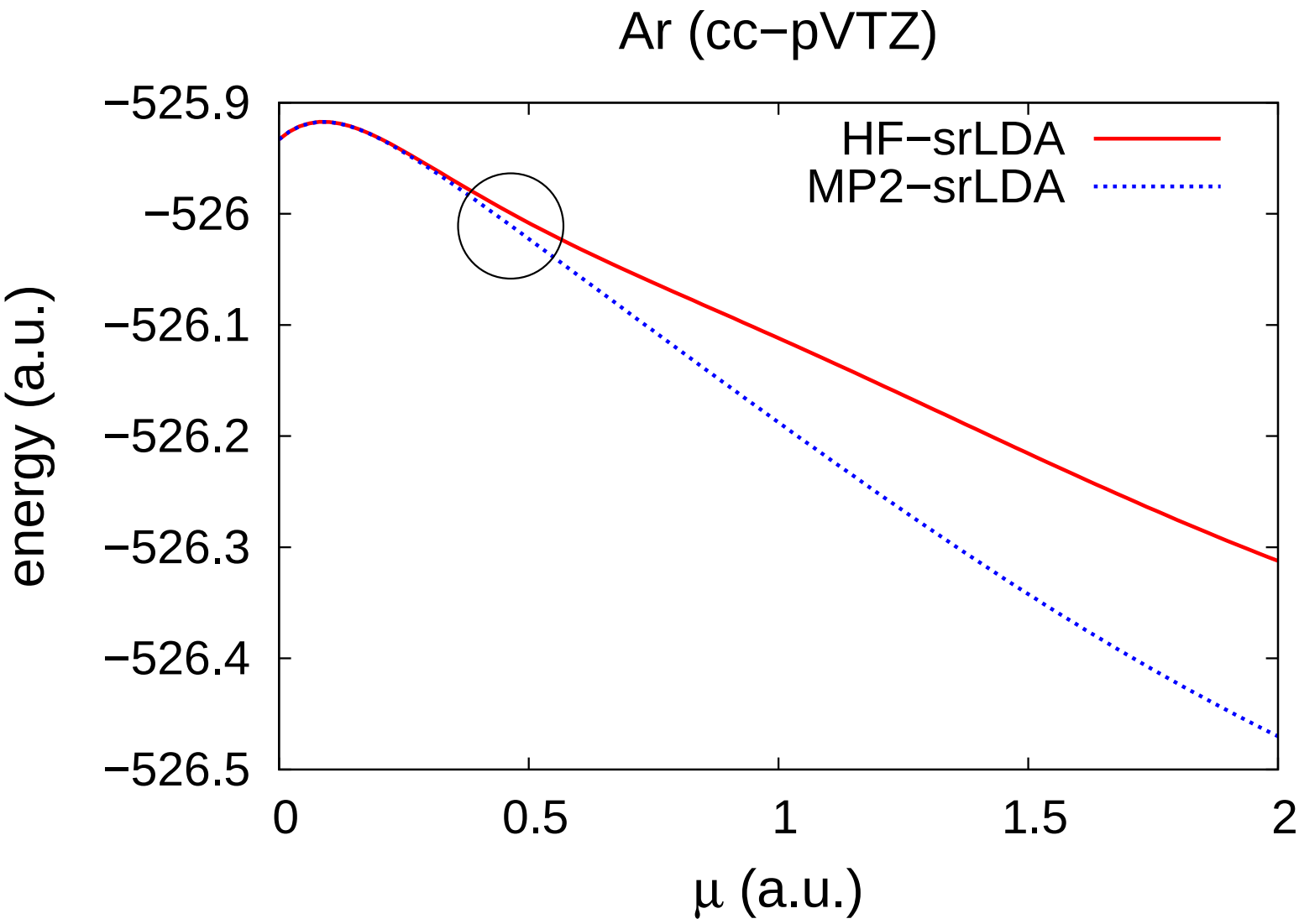
  (ii) short-range electron correlation (related to the singularity of the electron-electron repulsion) is assigned to the short-range interaction, and thus treated within DFT

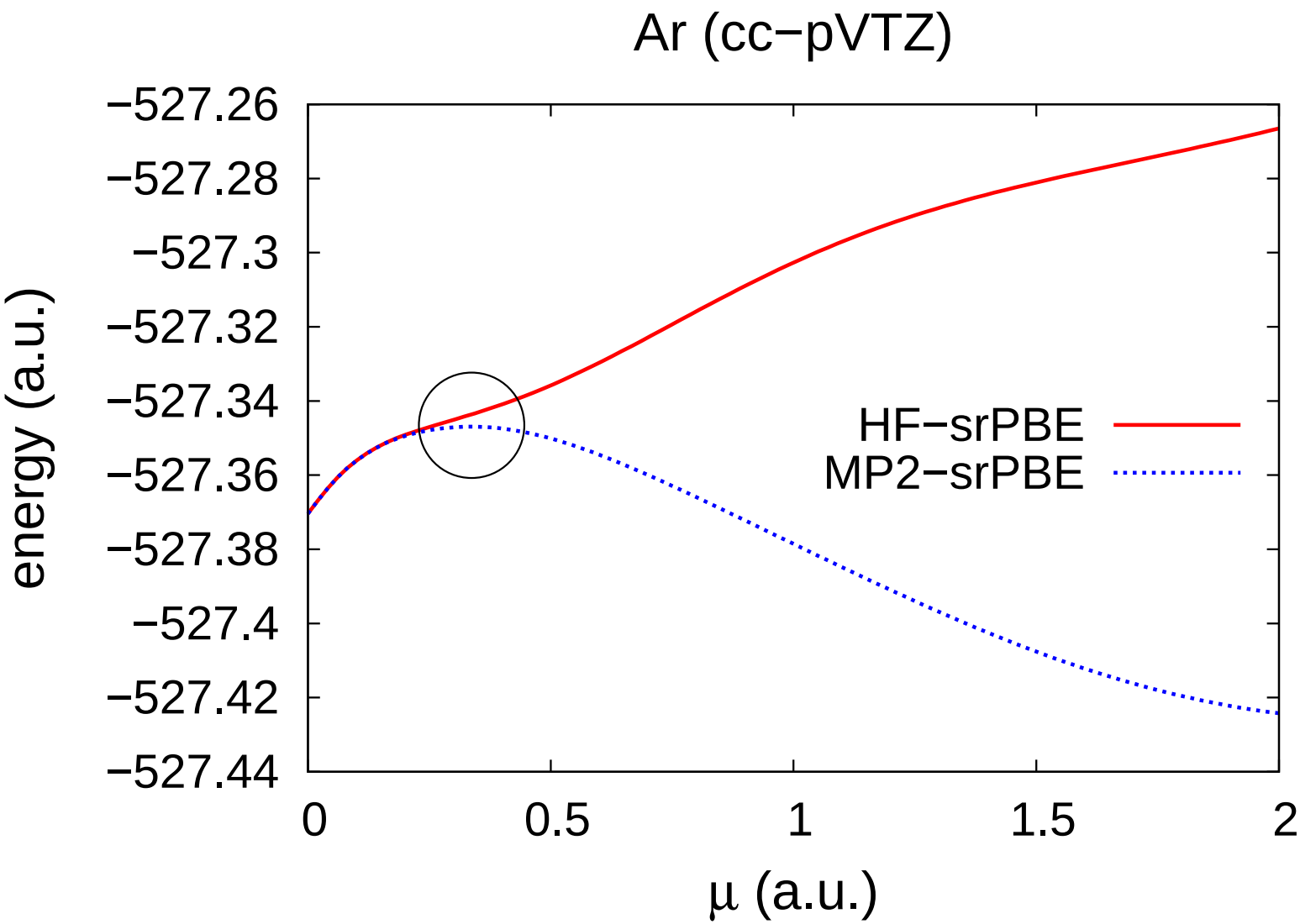
- Following this prescription, we obtain the following necessary condition:

  systems that have no significant long-range correlation effects should be well described within the HF-srDFT scheme (no need for a *post*-HF treatment of the long-range interaction) $\rightarrow$ $\boxed{\mu \leq \mu_{\max}}$


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.)

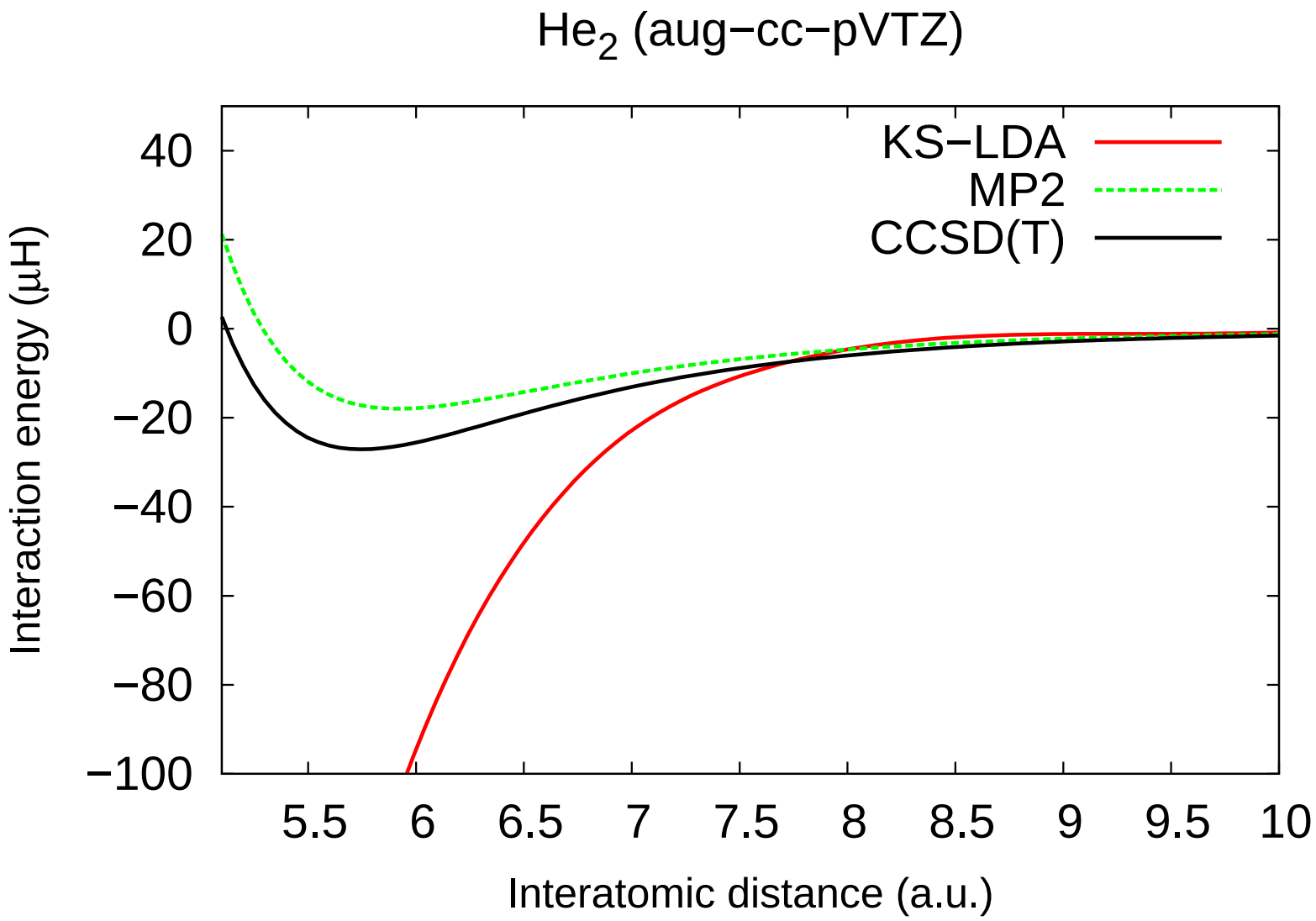

Ar (cc−pVTZ)
HF−srLDA
MP2−srLDA
energy (a.u.)
−525.9
−526
−526.1
−526.2
−526.3
−526.4
−526.5
0
0.5
1
1.5
2
μ (a.u.)

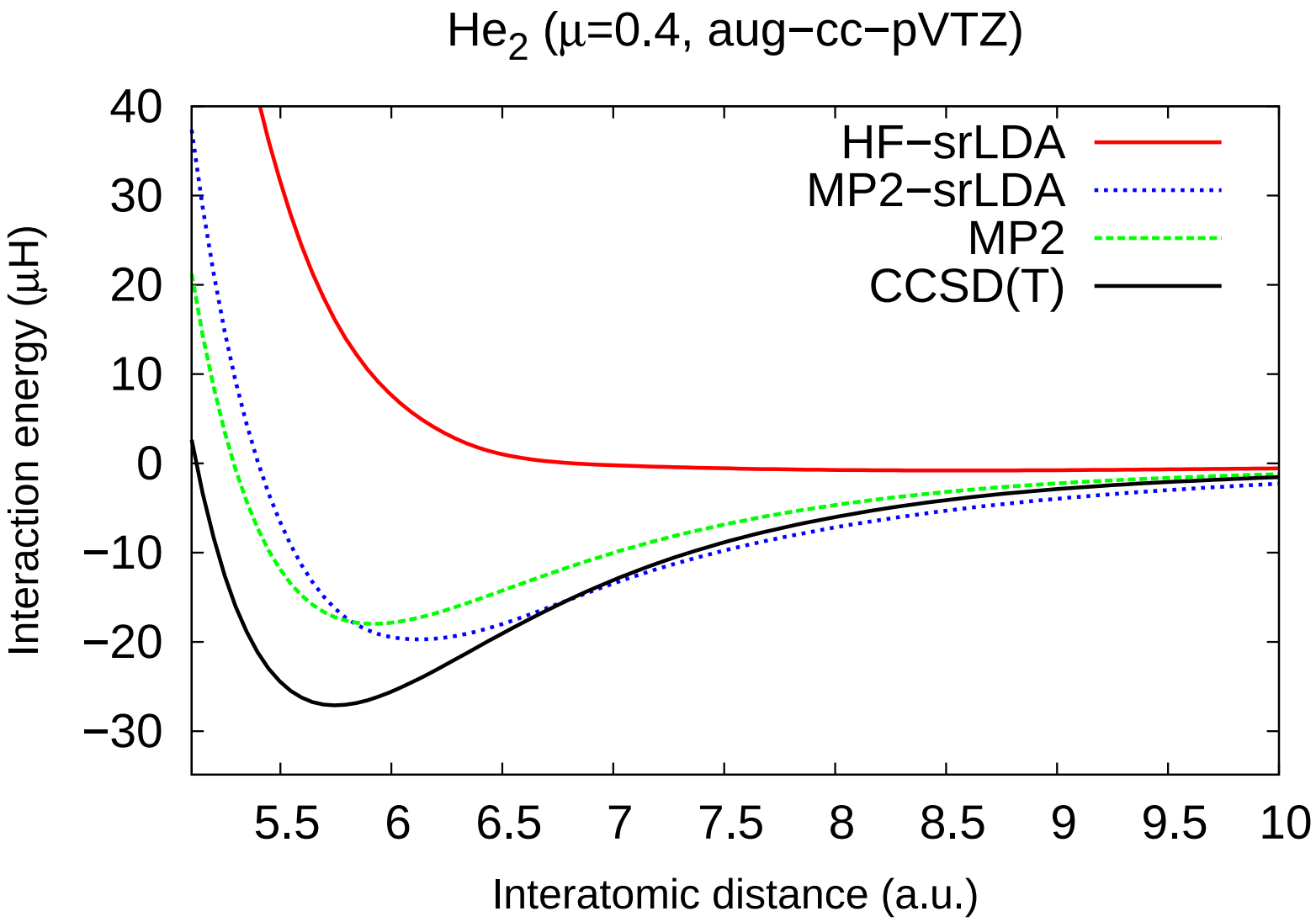

Ar (cc−pVTZ)
energy (a.u.)
−527.26
−527.28
−527.3
−527.32
−527.34
−527.36
−527.38
−527.4
−527.42
−527.44
0
0.5
1
1.5
2
μ (a.u.)
HF−srPBE
MP2−srPBE

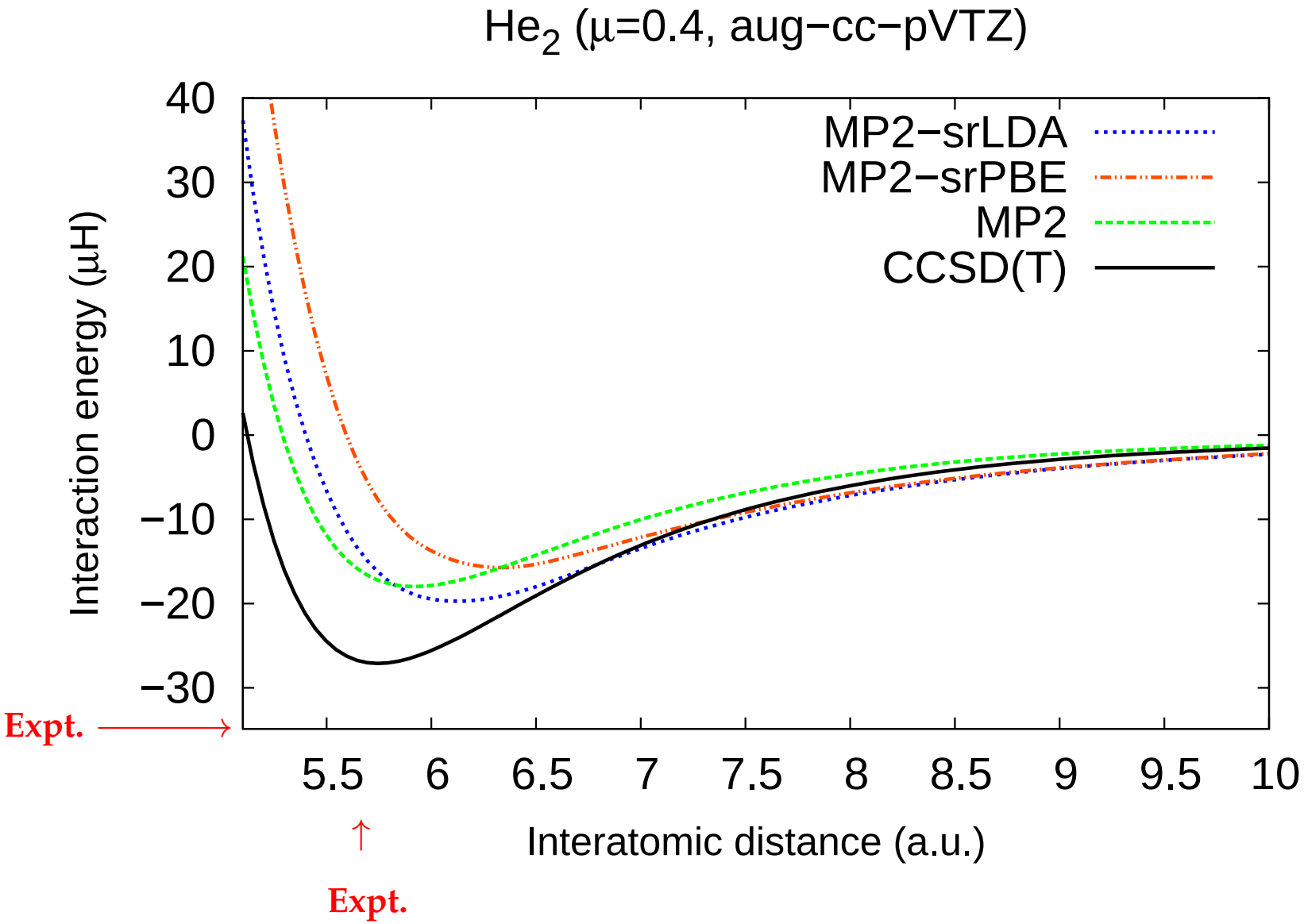
Choice of μ

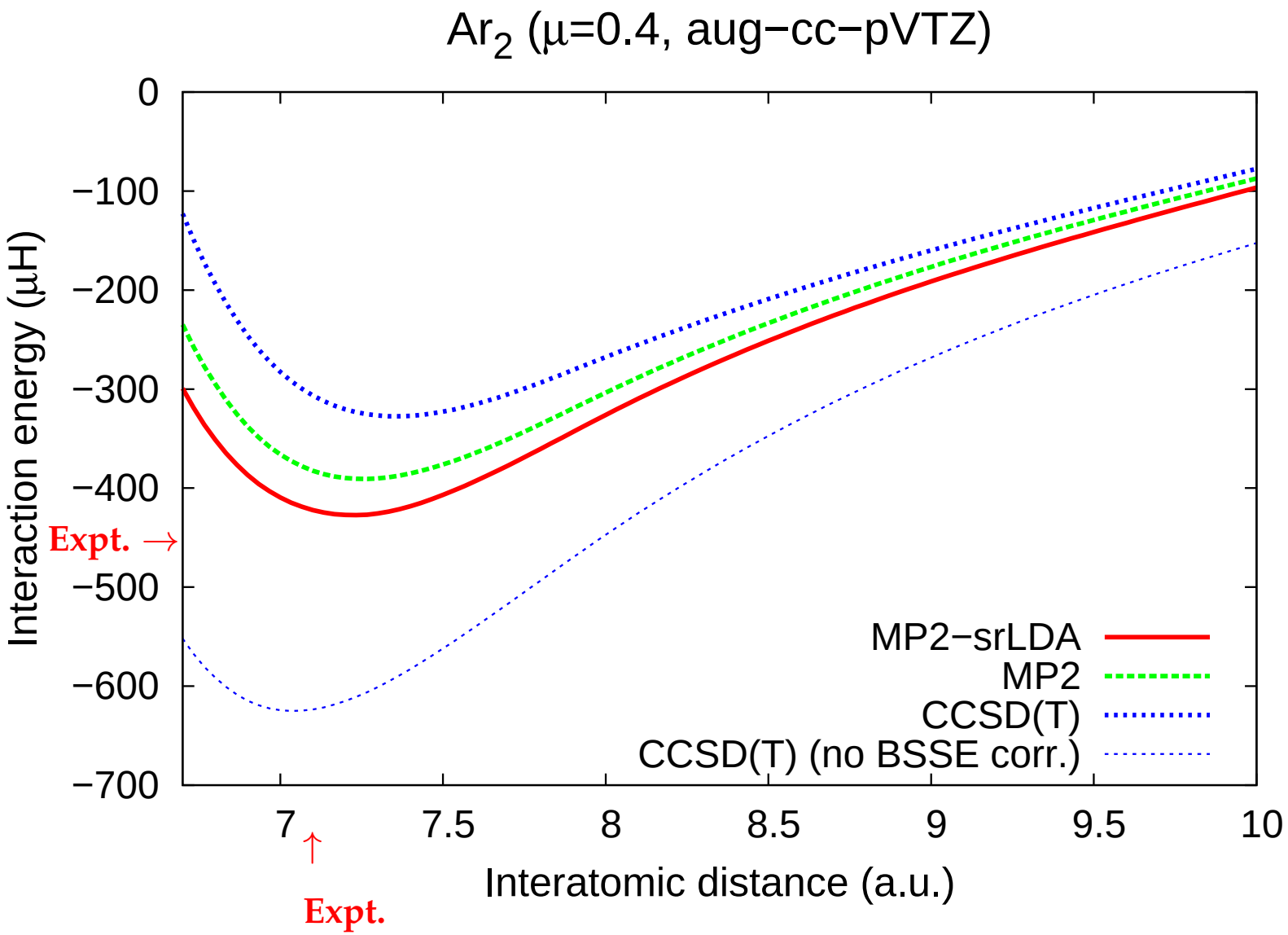
- $\frac{1}{\mu_{\max}} \approx 2.0$ a.u. can be interpreted as an average distance between valence electrons
- For heavier systems, the valence electron density is expected to be more diffuse, leading thus to smaller $\mu_{\max}$ values as we observed (0.2 to 0.3)
- When performing calculations on systems with significant long-range correlation effects, μ should be as large as possible, in order to be sure that the latters are mostly described within WFT (and not DFT)
- For the purpose of defining a general theory, it is highly desirable to define a universal μ value. We currently use $\boxed{\mu = 0.4}$

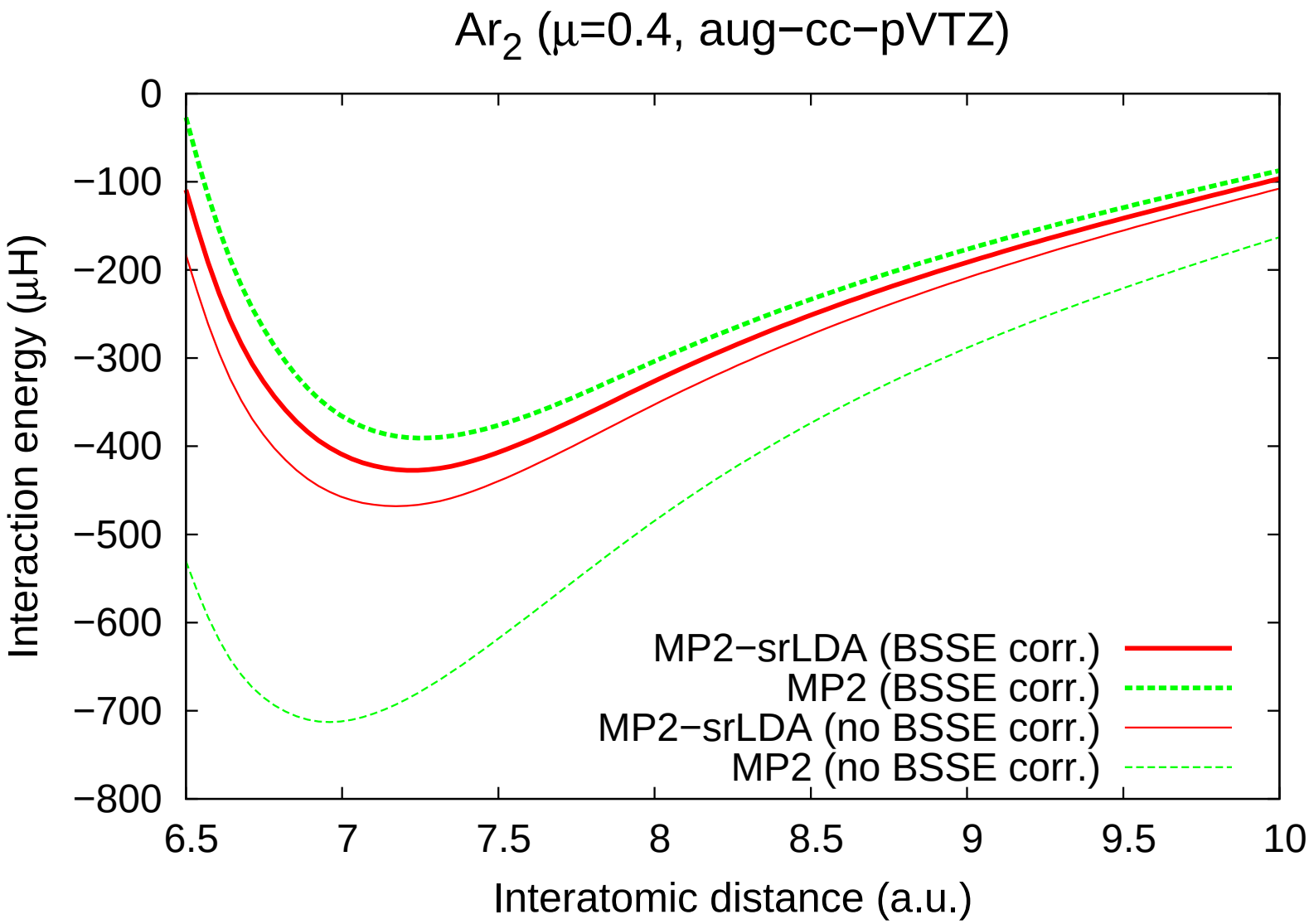
E. Fromager, J. Toulouse, and H. J. Aa. Jensen, *J. Chem. Phys.*, 126 (2007) 074111.

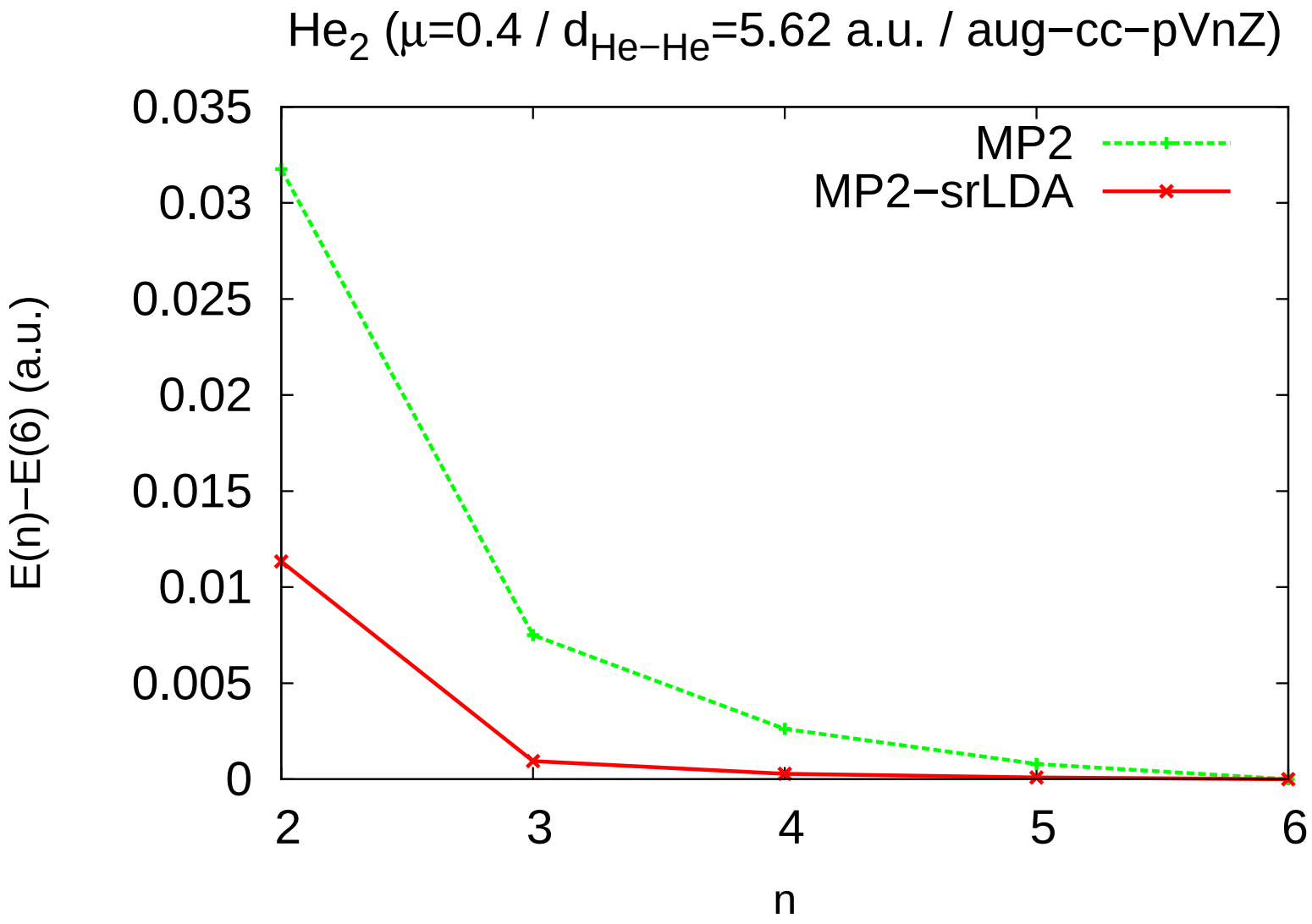

He2 (aug−cc−pVTZ)
KS−LDA
MP2
CCSD(T)
Interaction energy (μH)
40
20
0
−20
−40
−60
−80
−100
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)

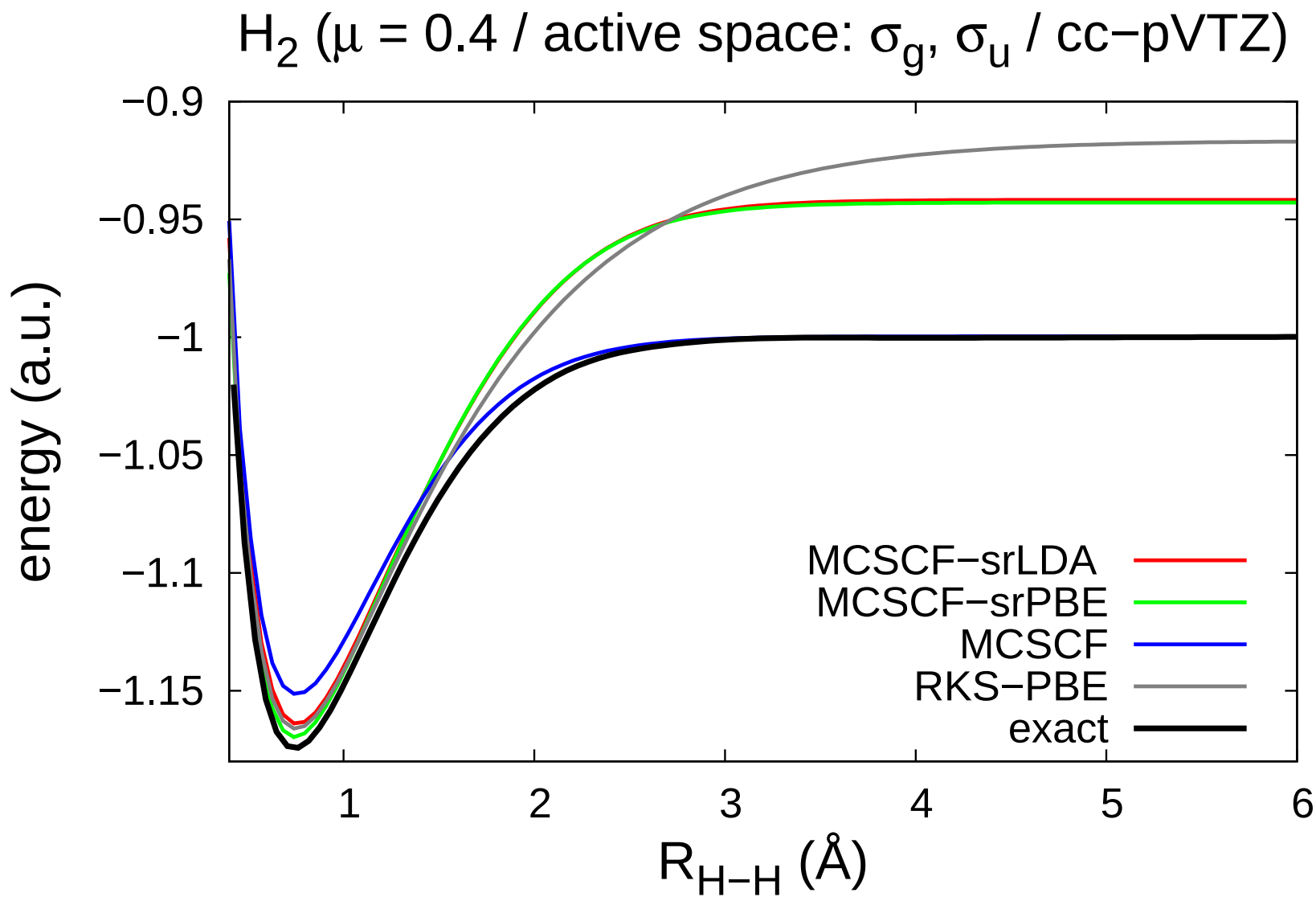

He2 (μ=0.4, aug−cc−pVTZ)
HF−srLDA
MP2−srLDA
MP2
CCSD(T)
Interaction energy (μH)
40
30
20
10
0
−10
−20
−30
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)

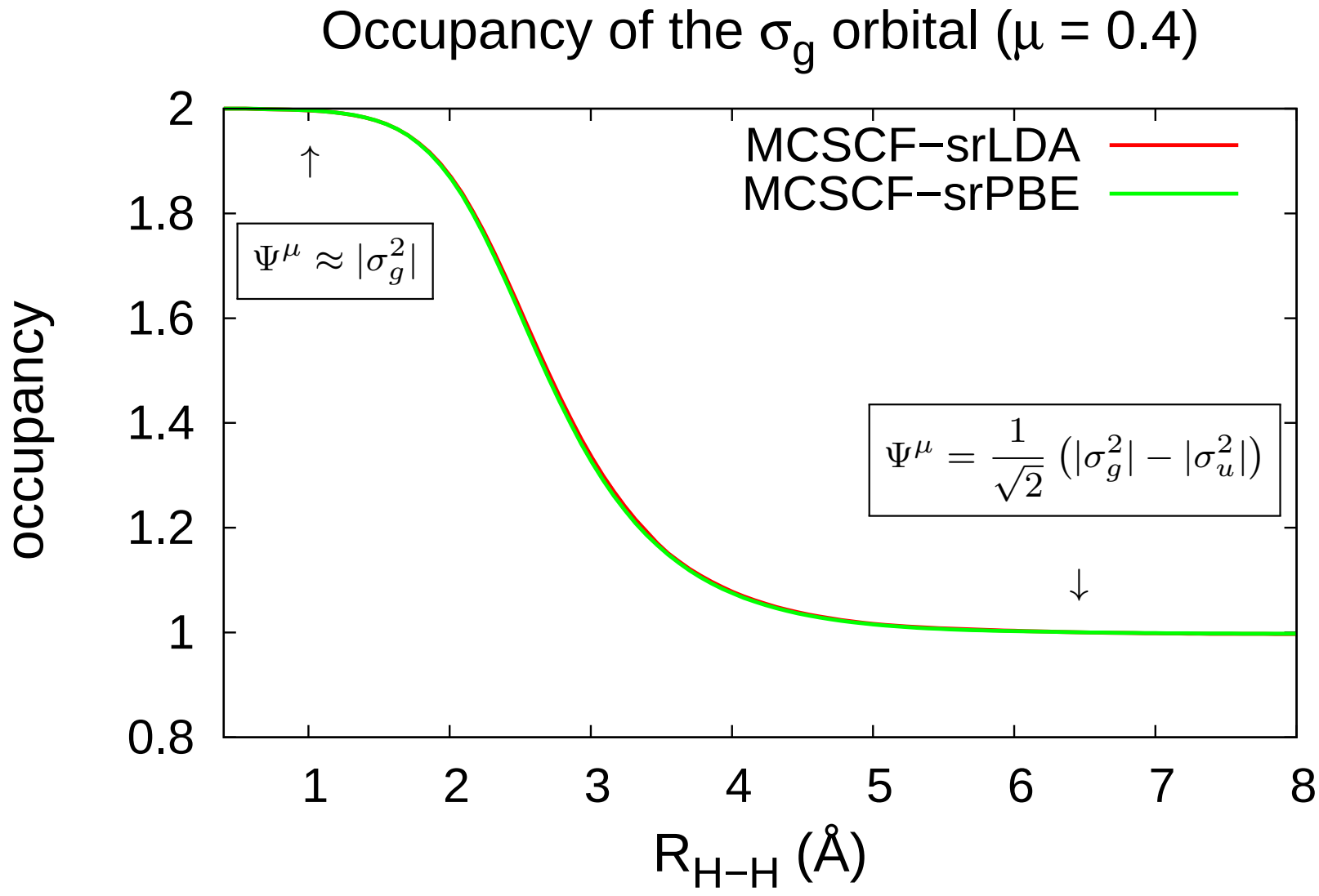

He2 (μ=0.4, aug−cc−pVTZ)
MP2−srLDA
MP2−srPBE
MP2
CCSD(T)
Interaction energy (μH)
40
30
20
10
0
−10
−20
−30
Expt.
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)
Expt.


Ar2 (μ=0.4, aug−cc−pVTZ)
Interaction energy (μH)
0
−100
−200
−300
−400
−500
−600
−700
Expt. →
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)
Expt.
MP2−srLDA
MP2
CCSD(T)
CCSD(T) (no BSSE corr.)


Ar2 (μ=0.4, aug−cc−pVTZ)
Interaction energy (μH)
0
−100
−200
−300
−400
−500
−600
−700
−800
6.5
7
7.5
8
8.5
9
9.5
10
Interatomic distance (a.u.)
MP2−srLDA (BSSE corr.)
MP2 (BSSE corr.)
MP2−srLDA (no BSSE corr.)
MP2 (no BSSE corr.)


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 (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


Occupancy of the σg orbital (μ = 0.4)
occupancy
RH–H (Å)
MCSCF–srLDA
MCSCF–srPBE
Ψμ ≈ |σg2|
Ψμ = 1/√2 (|σg2| − |σu2|)
2
1.8
1.6
1.4
1.2
1
0.8
1
2
3
4
5
6
7
8

$$E_{\rm Hxc}^{{\rm sr},\mu}[n] = \frac{1}{2}\int n(\mathbf{r})n(\mathbf{r}')w_{ee}^{{\rm sr},\mu}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}d\mathbf{r}' \quad + \quad E_{\rm xc}^{{\rm sr},\mu}[n]$$

In the dissociation limit:

$$|\mathbf{r}-\mathbf{r}'| \to +\infty \;\Rightarrow\; w_{ee}^{{\rm sr},\mu}(|\mathbf{r}-\mathbf{r}'|) \to 0$$

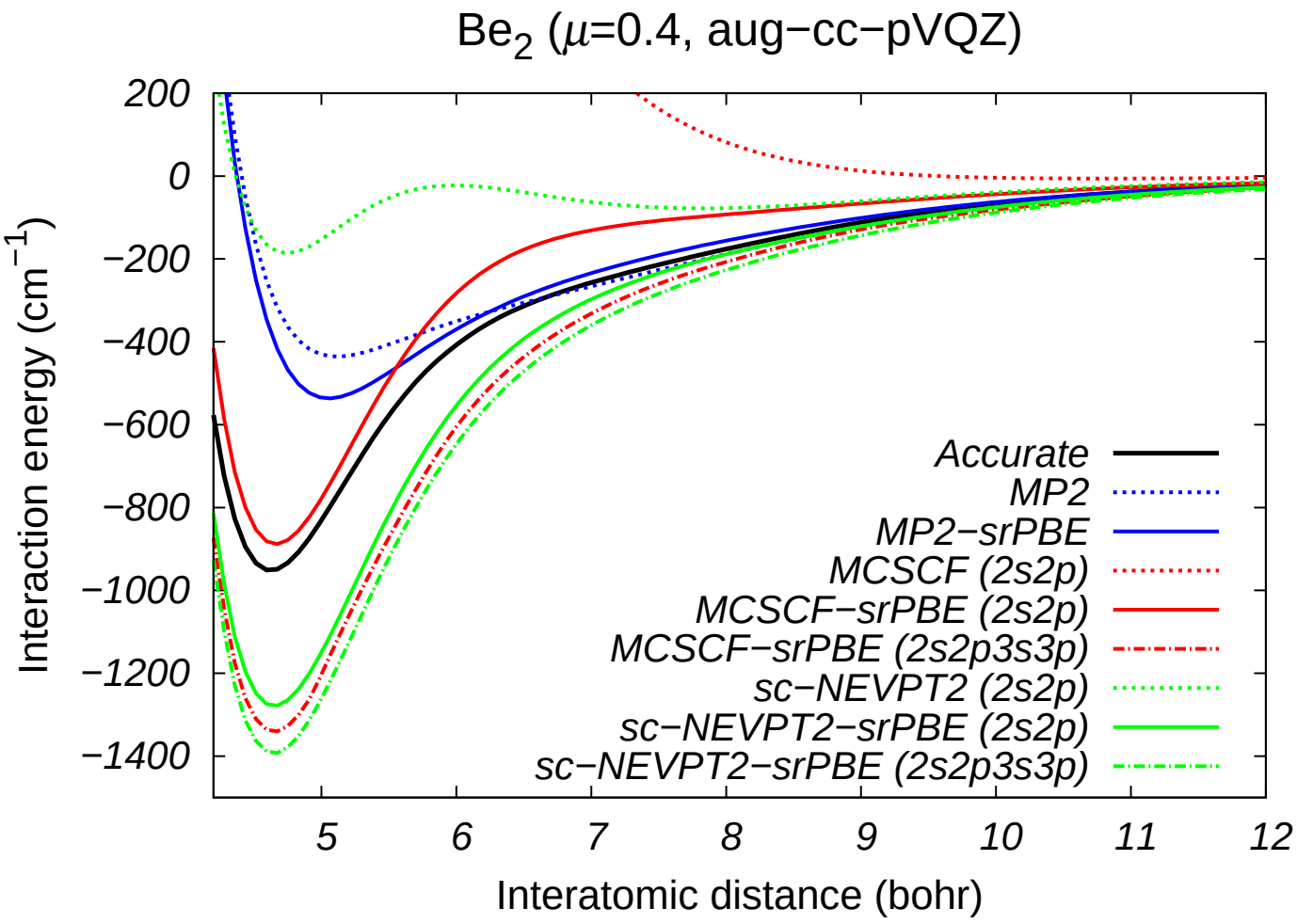
$$|\mathbf{r}-\mathbf{r}'| \to 0 \;\Rightarrow\; w_{ee}^{{\rm sr},\mu}(|\mathbf{r}-\mathbf{r}'|) \sim \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{\rm Hxc}^{{\rm sr},\mu}[n] \approx 2 \times \underbrace{\frac{1}{2}\int \frac{n_{\rm H}(\mathbf{r})n_{\rm H}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}'} \quad + \quad 2 \times \underbrace{E_{\rm xc}^{{\rm sr},\mu}[n_{\rm H}]}$$

self-interaction error

no spin polarization !

sc-NEVPT2 on top of MCSCF-srDFT



E. Fromager, R. Cimiraglia, and H. J. Aa. Jensen, Phys. Rev. A 81, 024502 (2010)

Conclusions and outlook

- Range separation enables a rigorous combination of *post*-HF and DFT methods
- It is possible to choose an optimal range separation in a non-semi-empirical way ($\mu = 0.4$ a.u.)
- MP2-srDFT (and CC-srDFT) promising for describing dispersion interactions (fast basis set convergence, small BSSE)
- MCSCF-srDFT promising too ... but real need for better short-range functionals (exact exchange !?)
- sc-NEVPT2-srDFT: tool for describing multireference weakly bound systems (metal-metal interactions, ...)
- work in progress: TD-MCSCF-srDFT and relativistic MCSCF-srDFT approach