Density-functional approximations

Emmanuel Fromager

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

EUR: Theory of extended systems

Local density-functional approximations

- Any density-functional energy contribution $S[n]$ can be written as

$$S[n] = \int \mathrm{d}\mathbf{r}\ s[n](\mathbf{r})n(\mathbf{r}),$$

where $s[n](\mathbf{r})$ is an energy contribution *per particle*.

Proof: take $\quad s[n](\mathbf{r}) = \dfrac{\delta S[n]}{\delta n(\mathbf{r})} + \dfrac{S[n] - \displaystyle\int \mathrm{d}\mathbf{r}\ \dfrac{\delta S[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\displaystyle\int \mathrm{d}\mathbf{r}\ n(\mathbf{r})} := \dfrac{\delta S[n]}{\delta n(\mathbf{r})} + C_{\mathrm{LZ}}[n] \qquad \leftarrow$ Levy–Zahariev shift*

- Note that $s[n](\mathbf{r})$ is in principle a *functional* of the density, *not just a function* of $n(\mathbf{r})$.

* M. Levy and F. Zahariev, Phys. Rev. Lett. 113, 113002 (2014).

Local density-functional approximations

- The *local density approximation* (LDA) consists in approaching $s[n](\mathbf{r})$ with a function $s\big(n(\mathbf{r})\big)$ of $n(\mathbf{r})$:

$$S[n] \approx \int \mathrm{d}\mathbf{r}\ s\big(n(\mathbf{r})\big)n(\mathbf{r})$$

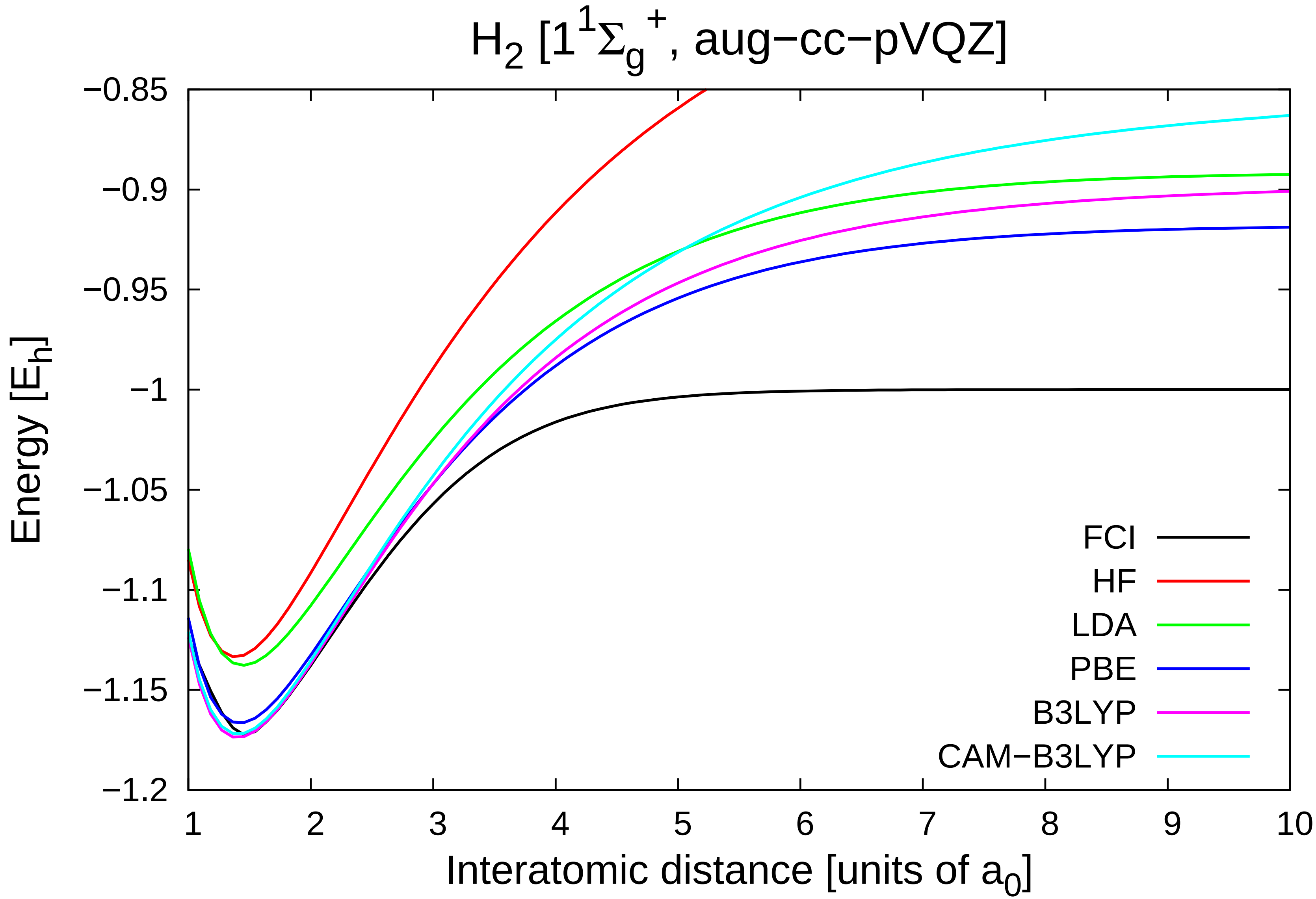
- Simple LDAs to the non-interacting kinetic and exchange energies:

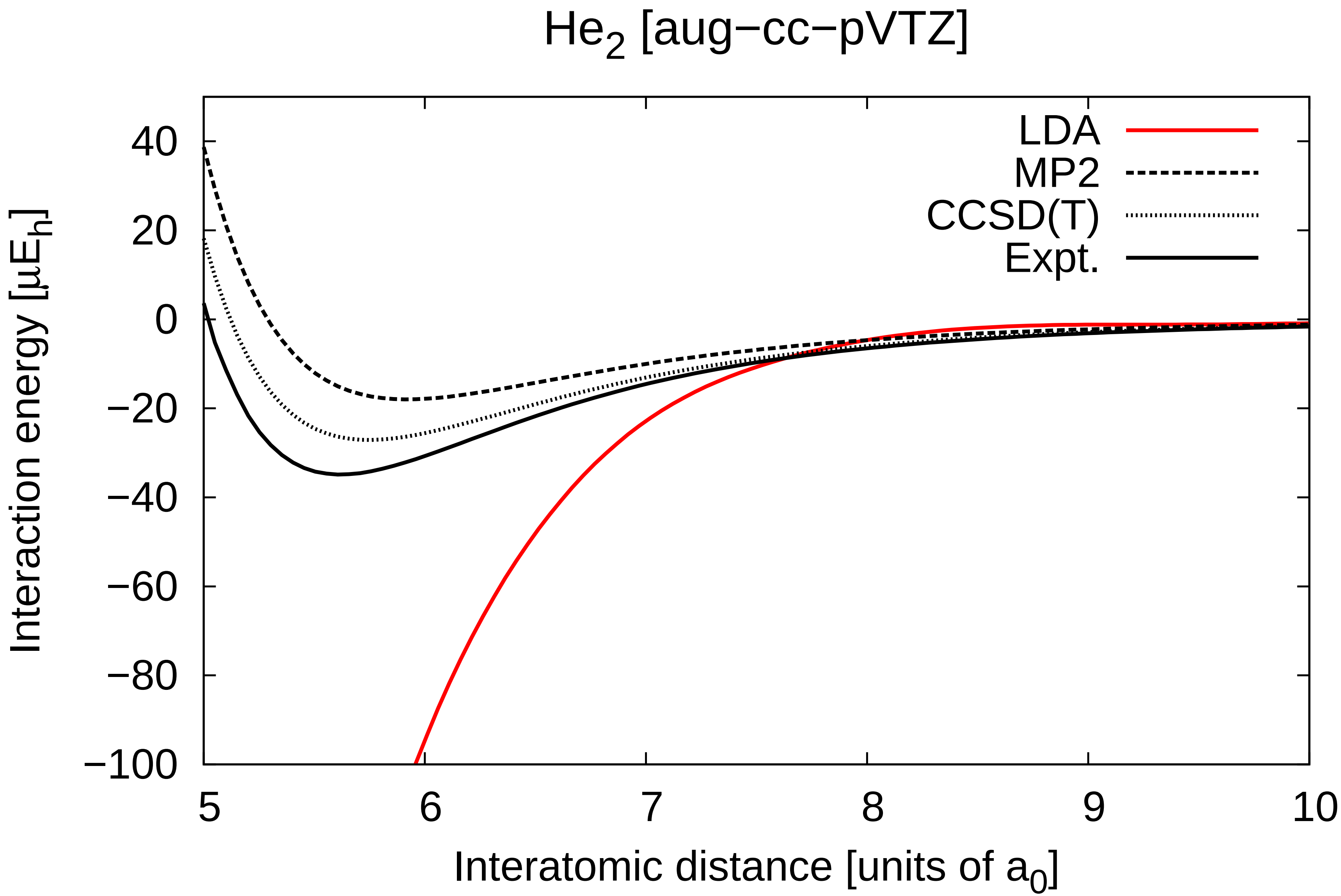
$$T_{\mathrm{s}}[n] \approx T_{\mathrm{s}}^{\mathrm{LDA}}[n] = A\int \mathrm{d}\mathbf{r}\ n^{\alpha}(\mathbf{r}), \qquad E_{\mathrm{x}}[n] \approx E_{\mathrm{x}}^{\mathrm{LDA}}[n] = B\int \mathrm{d}\mathbf{r}\ n^{\beta}(\mathbf{r})$$

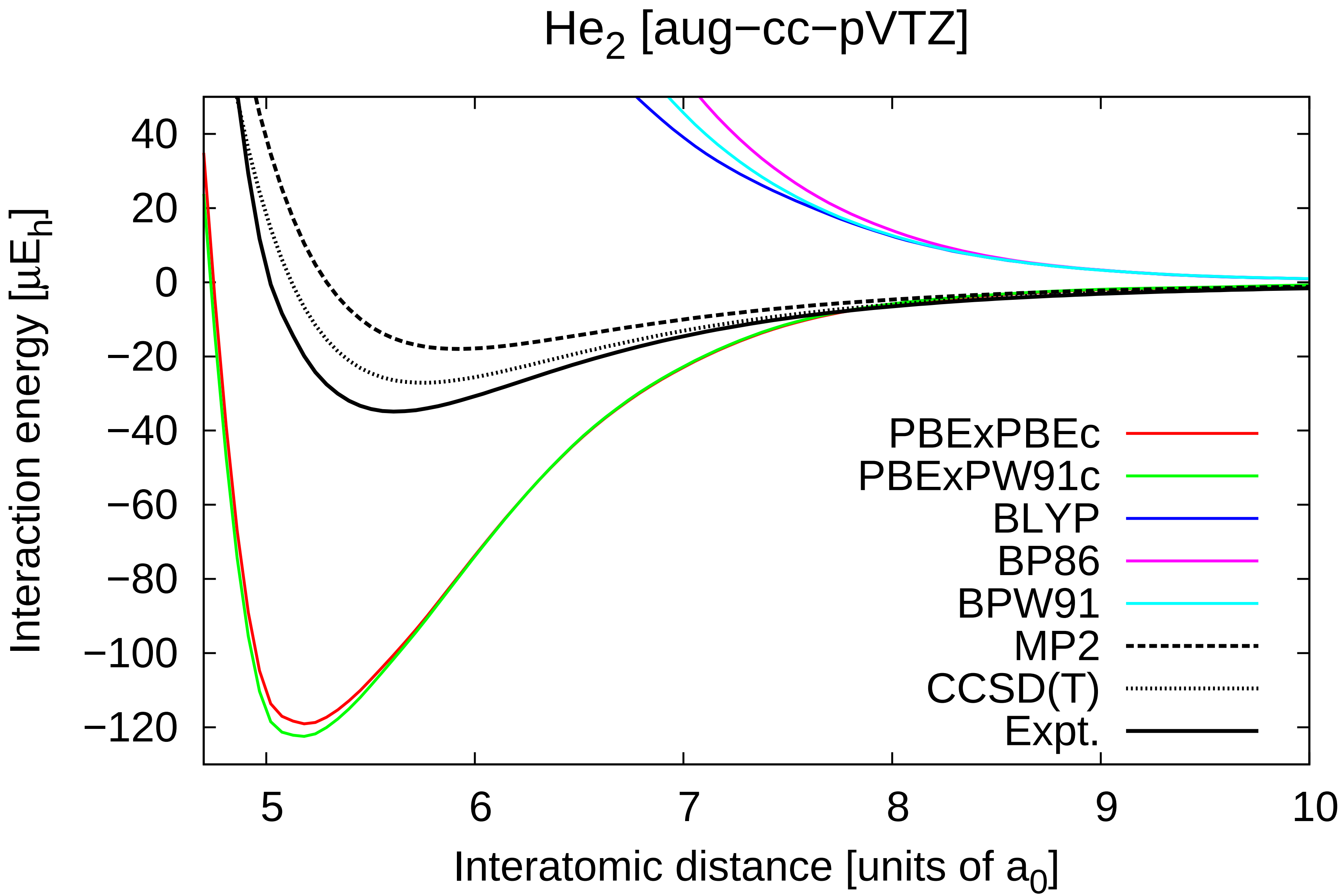
EXERCISE

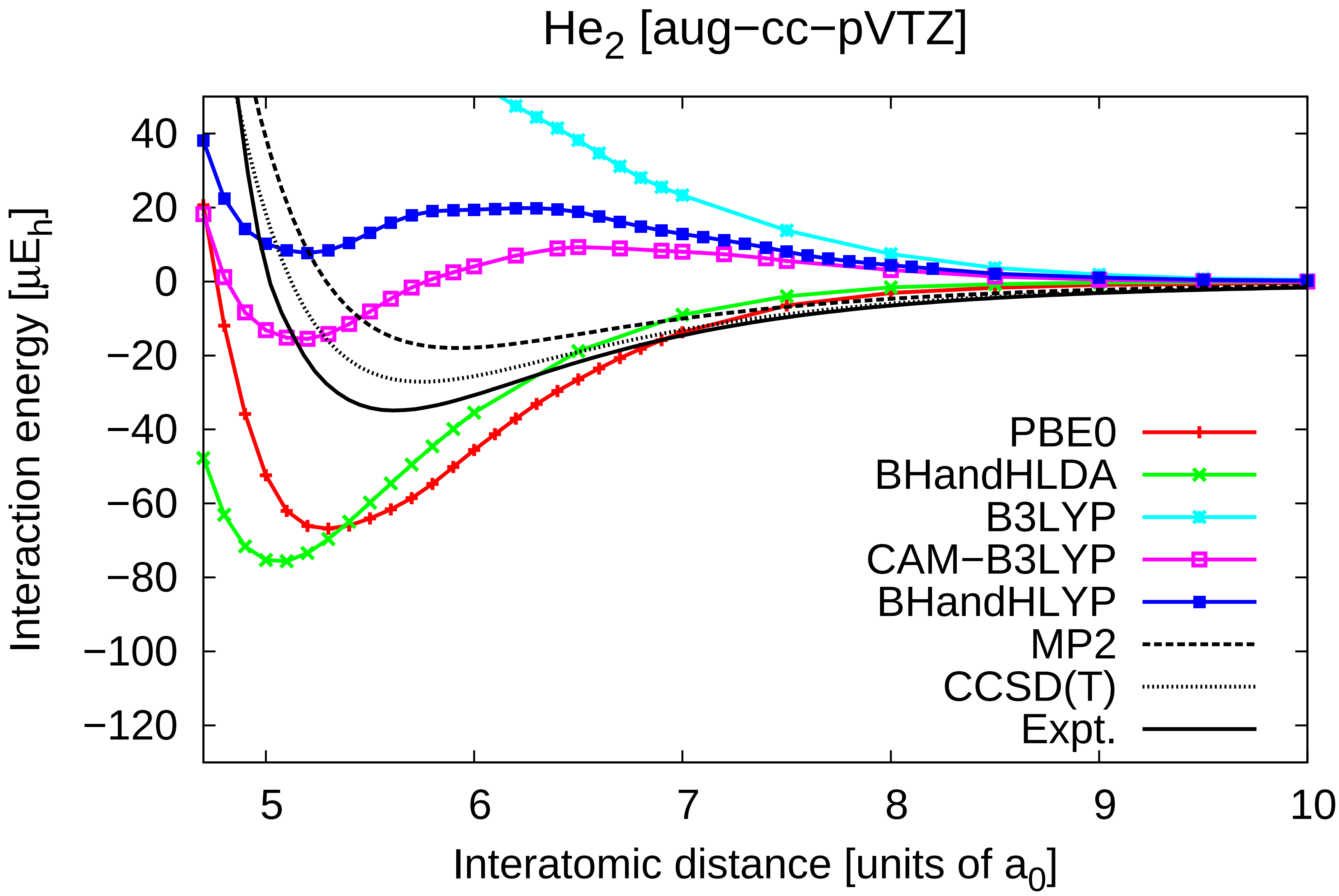
Show that, if we want these LDAs to fulfill the exact *scaling relations*, then we should have $\alpha = \frac{5}{3}$ and $\beta = \frac{4}{3}$. With $A = \frac{3}{10}(3\pi^2)^{2/3}$ and $B = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$ we recover the non-interacting kinetic (so-called Thomas–Fermi) and exchange energies of a *uniform electron gas* with density n, respectively.

- LDA for the correlation energy: $E_{\mathrm{c}}[n] \approx E_{\mathrm{c}}^{\mathrm{LDA}}[n] = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{c}}\big(n(\mathbf{r})\big)n(\mathbf{r})$.


H_2 [$1^1\Sigma_g^+$, aug−cc−pVQZ]
Energy [E_h]
−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 a_0]
FCI
HF
LDA
PBE
B3LYP
CAM−B3LYP


He2 [aug−cc−pVTZ]
LDA
MP2
CCSD(T)
Expt.
Interaction energy [μEh]
40
20
0
−20
−40
−60
−80
−100
5
6
7
8
9
10
Interatomic distance [units of a0]


He$_2$ [aug−cc−pVTZ]
Interaction energy [μE$_h$]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBExPBEc
PBExPW91c
BLYP
BP86
BPW91
MP2
CCSD(T)
Expt.


He2 [aug−cc−pVTZ]
Interaction energy [μEh]
Interatomic distance [units of a0]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
PBE0
BHandHLDA
B3LYP
CAM−B3LYP
BHandHLYP
MP2
CCSD(T)
Expt.