Density-functional approximations

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M1 course: Modelling 1

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 $s[n](\mathbf{r}) = \dfrac{\delta S[n]}{\delta n(\mathbf{r})} + \dfrac{S[n] - \int \mathrm{d}\mathbf{r}\; \dfrac{\delta S[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\int \mathrm{d}\mathbf{r}\; n(\mathbf{r})} := \dfrac{\delta S[n]}{\delta n(\mathbf{r})} + C_{\mathrm{LZ}}[n]$ ← 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 *(will be solved during "Modelling 2" exercise sessions)*

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

Standard density-functional approximations (DFAs)

Local and semi-local functionals

$$E_{\mathrm{xc}}[n] \approx \int d\mathbf{r}\, \varepsilon_{\mathrm{xc}}\big(n(\mathbf{r})\big) \times n(\mathbf{r})$$

LDA *(uniform electron gas)*

*S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (8): 1200–1211 (**1980**).*

$$E_{\mathrm{xc}}[n] \approx \int d\mathbf{r}\, \varepsilon_{\mathrm{xc}}\big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\big) \times n(\mathbf{r})$$

$$\vdots$$

Generalized gradient approximations (GGAs):

LYP, PBE, …

*C. **L**ee, W. **Y**ang, and R. G. **P**arr. Phys. Rev. B, 57:785, (**1988**).*

*J. P. **P**erdew, K. **B**urke, M. **E**rnzerhof, Phys. Rev. Lett., 77, 3865 (**1996**).*

Hybrid functionals

Hartree-Fock-like exchange energy *(evaluated with KS orbitals)*

$$E_{\mathrm{xc}}[n] \approx \alpha E_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + (1-\alpha)E_{\mathrm{x}}^{\mathrm{DFA}}[n_\Phi] + E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi]$$

B3LYP

*A. D. **B**ecke, J. Chem. Phys. 98, 1372 (**1993**).*

$$E_{\mathrm{xc}}[n] \approx E_{\mathrm{x}}^{\mathrm{lr,HF}}[\Phi] + E_{\mathrm{x}}^{\mathrm{sr,DFA}}[n_\Phi] + E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi]$$

$$\vdots$$

$$\hat{W}_{\mathrm{ee}} = \hat{W}_{\mathrm{ee}}^{\mathrm{lr}} + \hat{W}_{\mathrm{ee}}^{\mathrm{sr}}$$

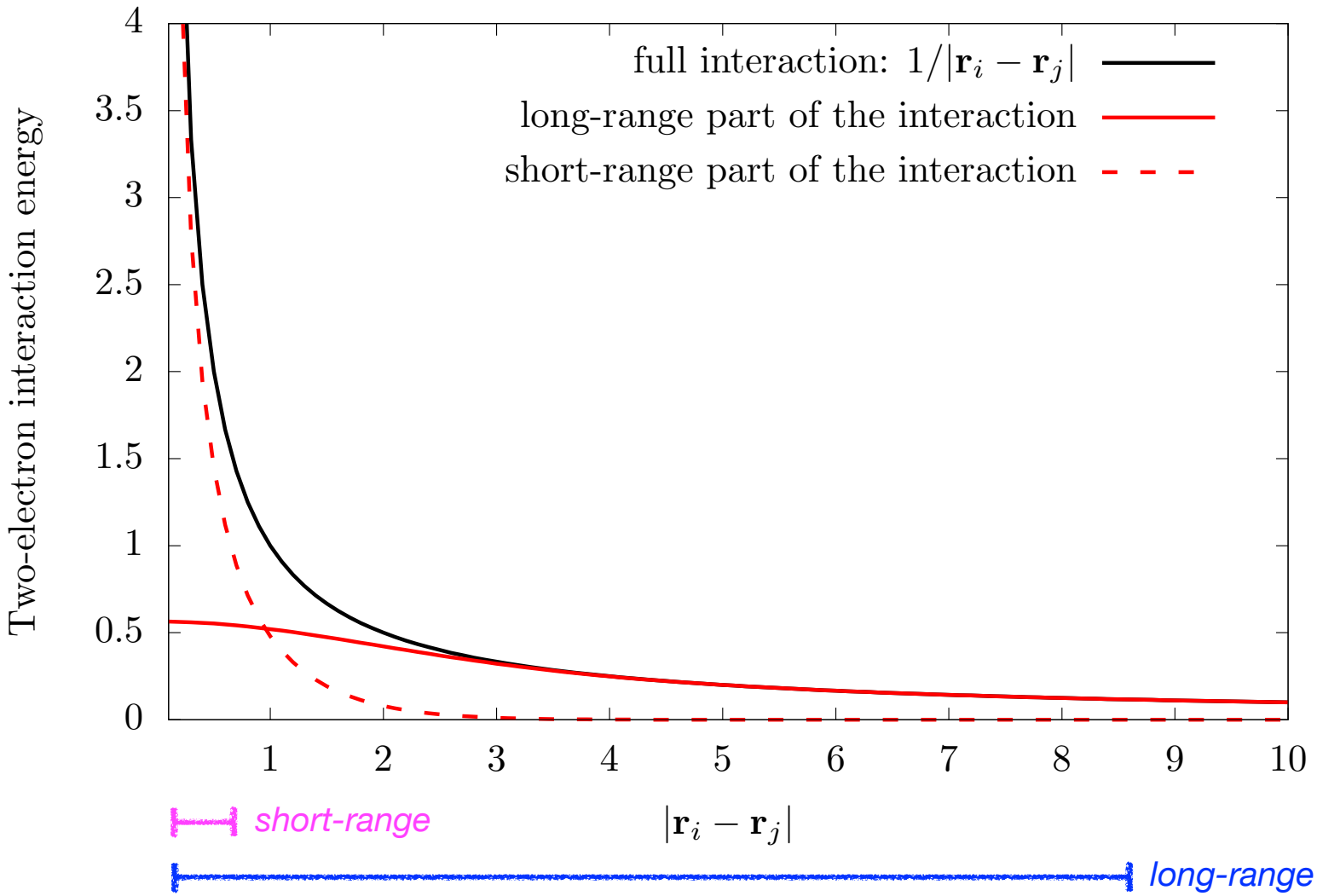
Long-range short-range

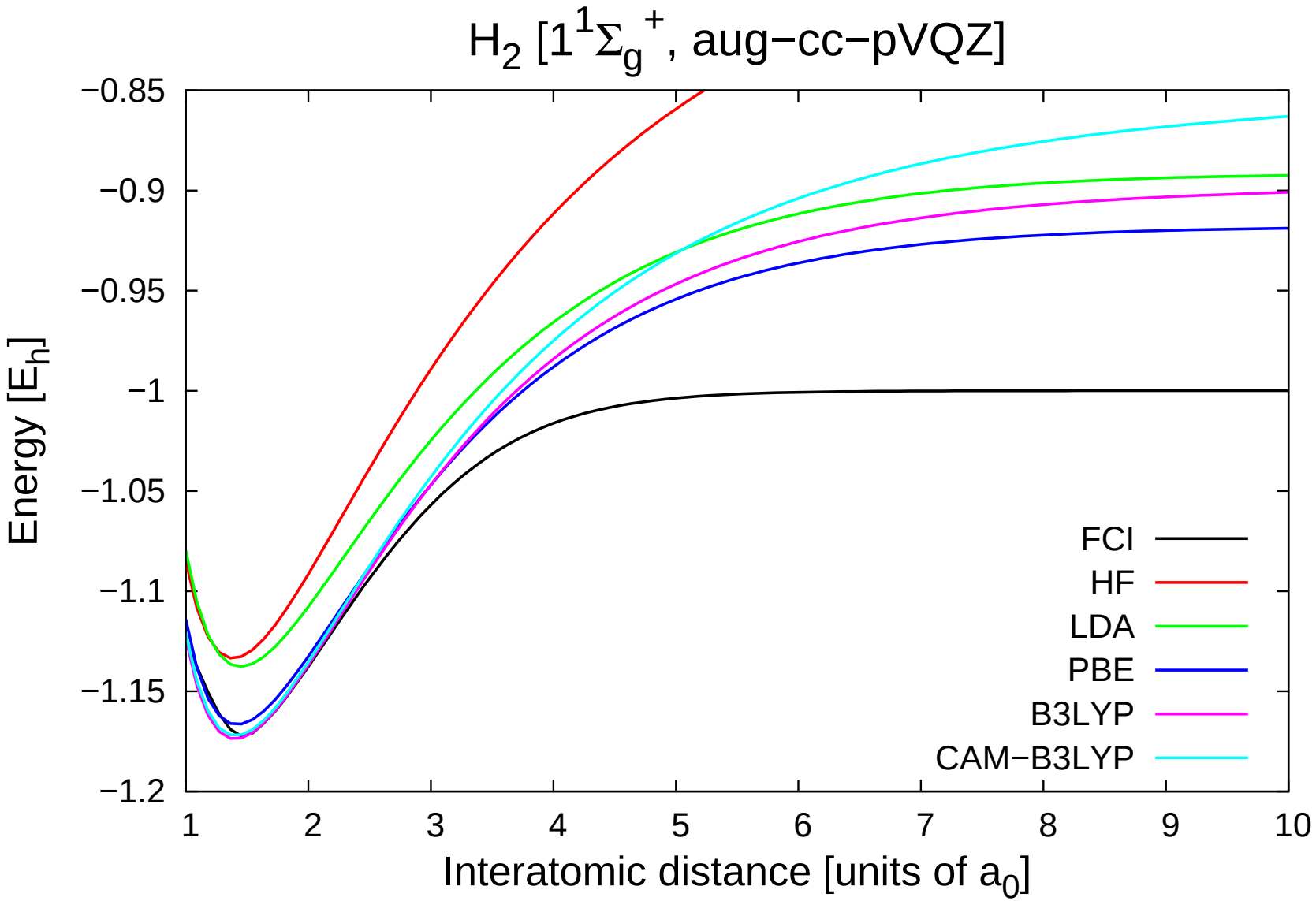
Range-separated hybrids

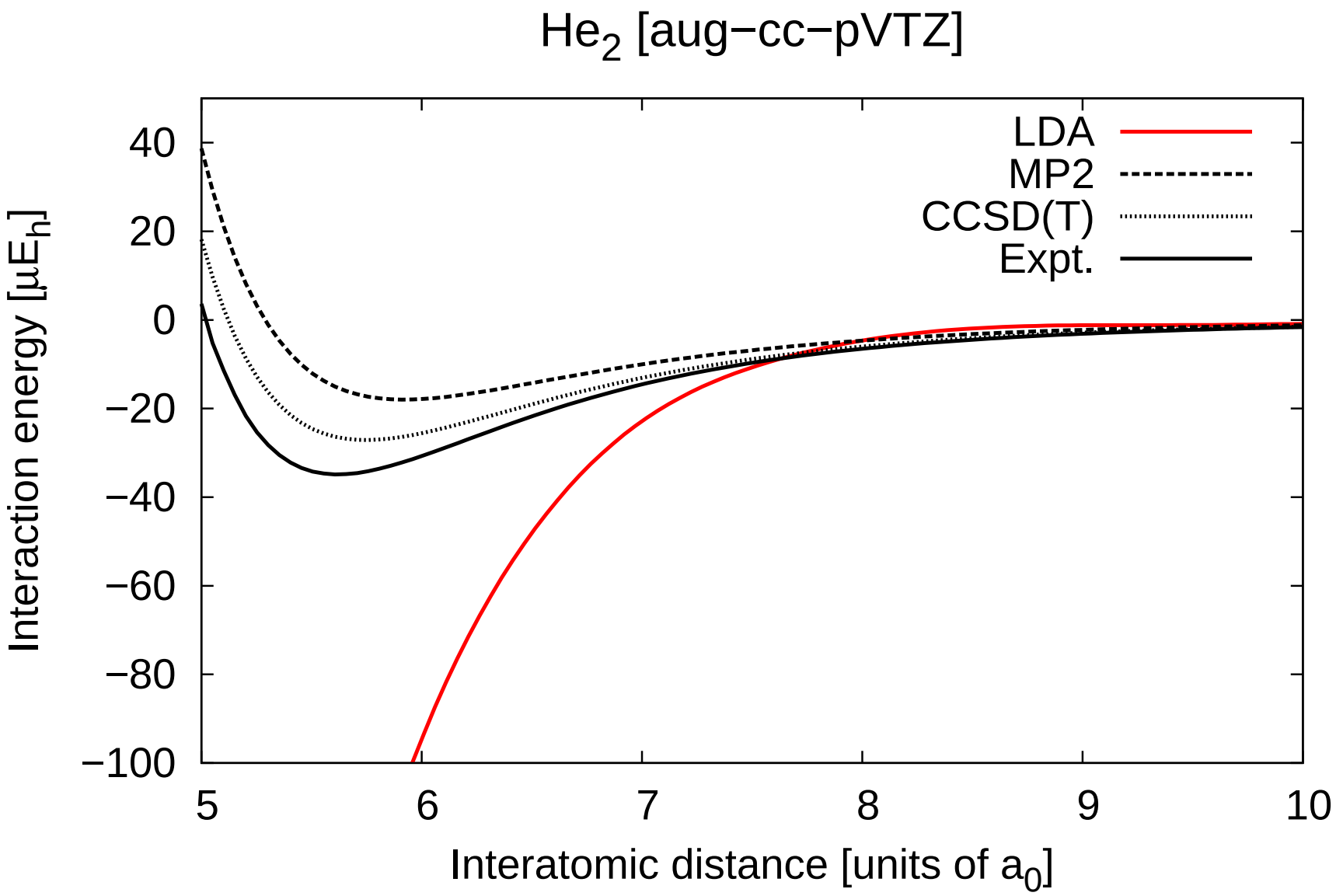
CAM-B3LYP

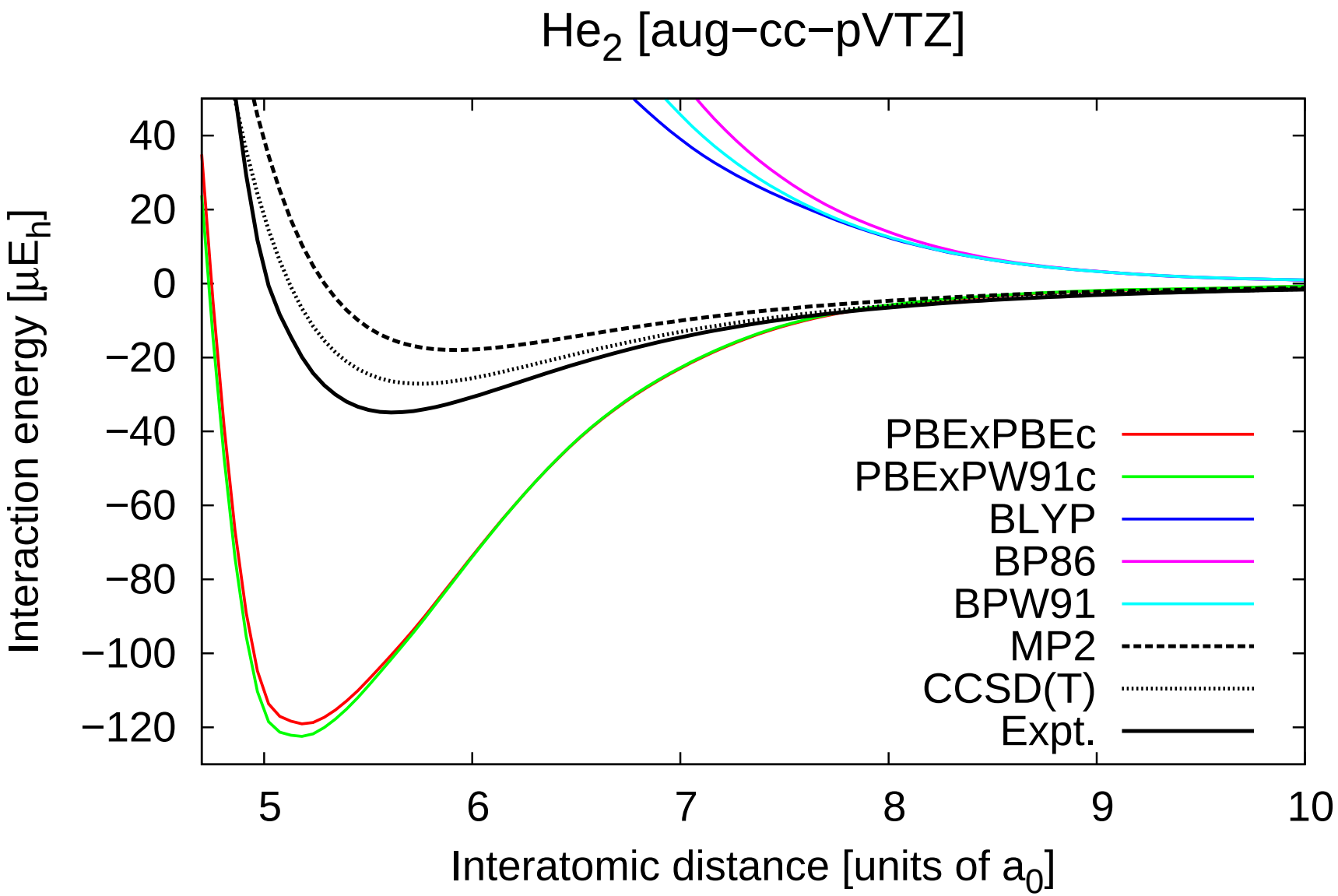
*Yanai, T.; Tew, D. P.; Handy, N. C., Chem. Phys. Lett., 393, 51-57 (**2004**).*

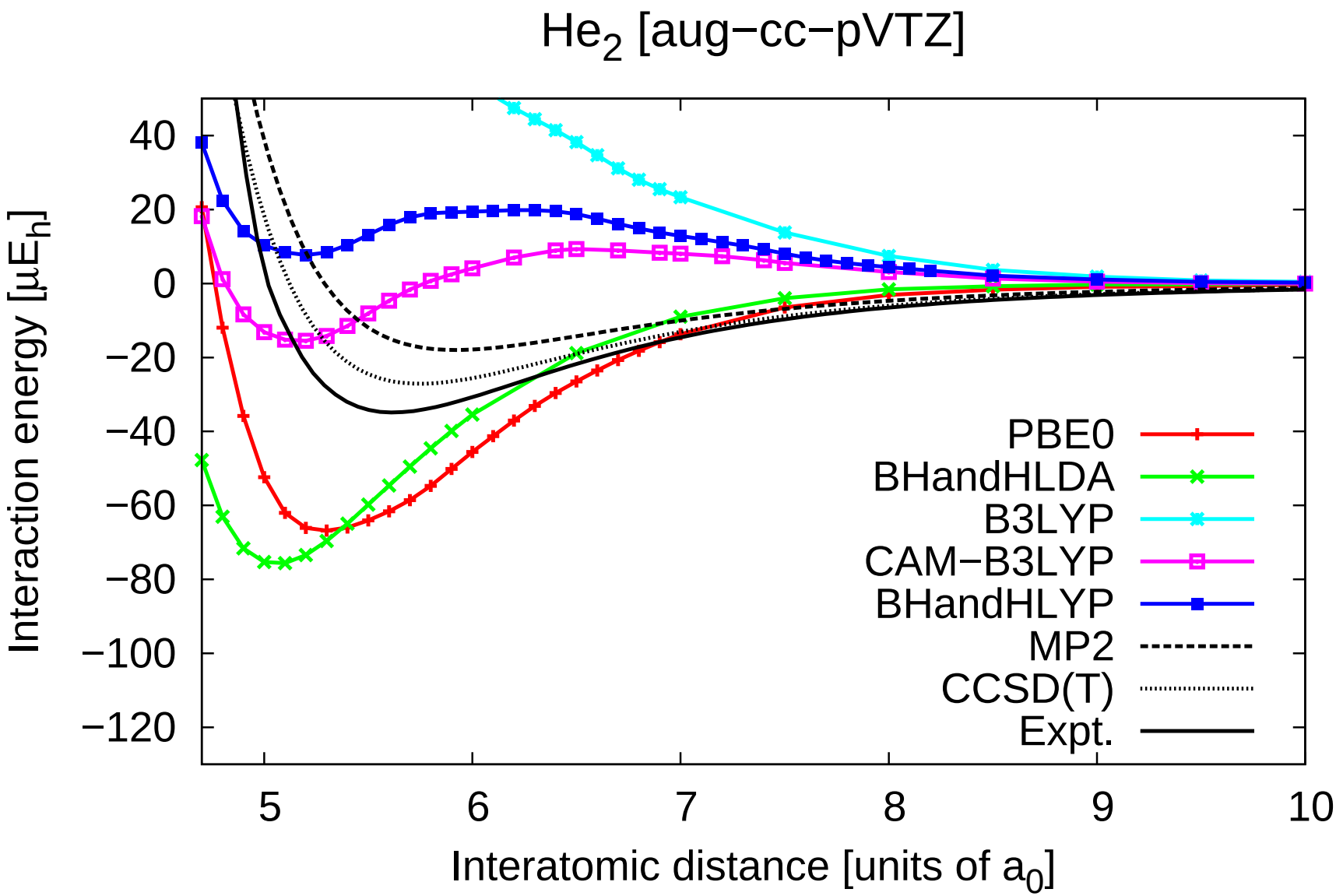
(arbitrary) range separation of the electronic repulsion




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


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]


He2 [aug−cc−pVTZ]
Interaction energy [μEh]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a0]
PBExPBEc
PBExPW91c
BLYP
BP86
BPW91
MP2
CCSD(T)
Expt.


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

PCCP

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DFT exchange: sharing perspectives on the workhorse of quantum chemistry and materials science

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In this paper, the history, present status, and future of density-functional theory (DFT) is informally reviewed and discussed by 70 workers in the field, including molecular scientists, materials scientists, method developers and practitioners. The format of the paper is that of a roundtable discussion, in which the participants express and exchange views on DFT in the form of 302 individual contributions, formulated as responses to a preset list of 26 questions. Supported by a bibliography of 777 entries, the paper represents a broad snapshot of DFT, anno 2022.