Multi-configurational density functional theory by decomposition of the electron-electron interaction into long-range and short-range contributions

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Kohn-Sham DFT

Kohn-Sham (KS) scheme

$$E = \min_{\mathbf{\Phi}} \left\{ \langle \mathbf{\Phi} | \hat{T} + \hat{V}_{ne} | \mathbf{\Phi} \rangle + E_{\mathrm{H}}[n_{\mathbf{\Phi}}] + E_{xc}[n_{\mathbf{\Phi}}] \right\}$$

$\mathbf{\Phi}$: **single-determinant** wave function

Approximations for exchange-correlation functional $E_{xc}[n]$: LDA, GGA, ...

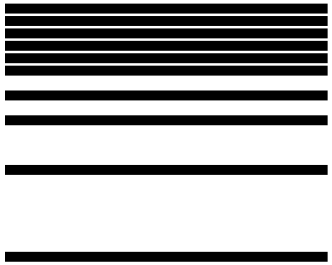
Performance of usual approximations for $E_{xc}[n]$

- interactions at **short interelectronic distances**: **well described**
- interactions due to energetic **near-degeneracies**: **not well described**

KS DFT: near-degeneracy problem (e.g., atoms/molecules)

KS system

$\hat{W}_{ee} = 0$

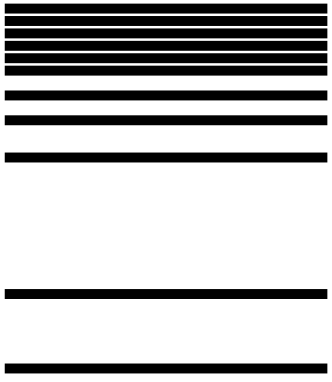


E_{KS}

Φ

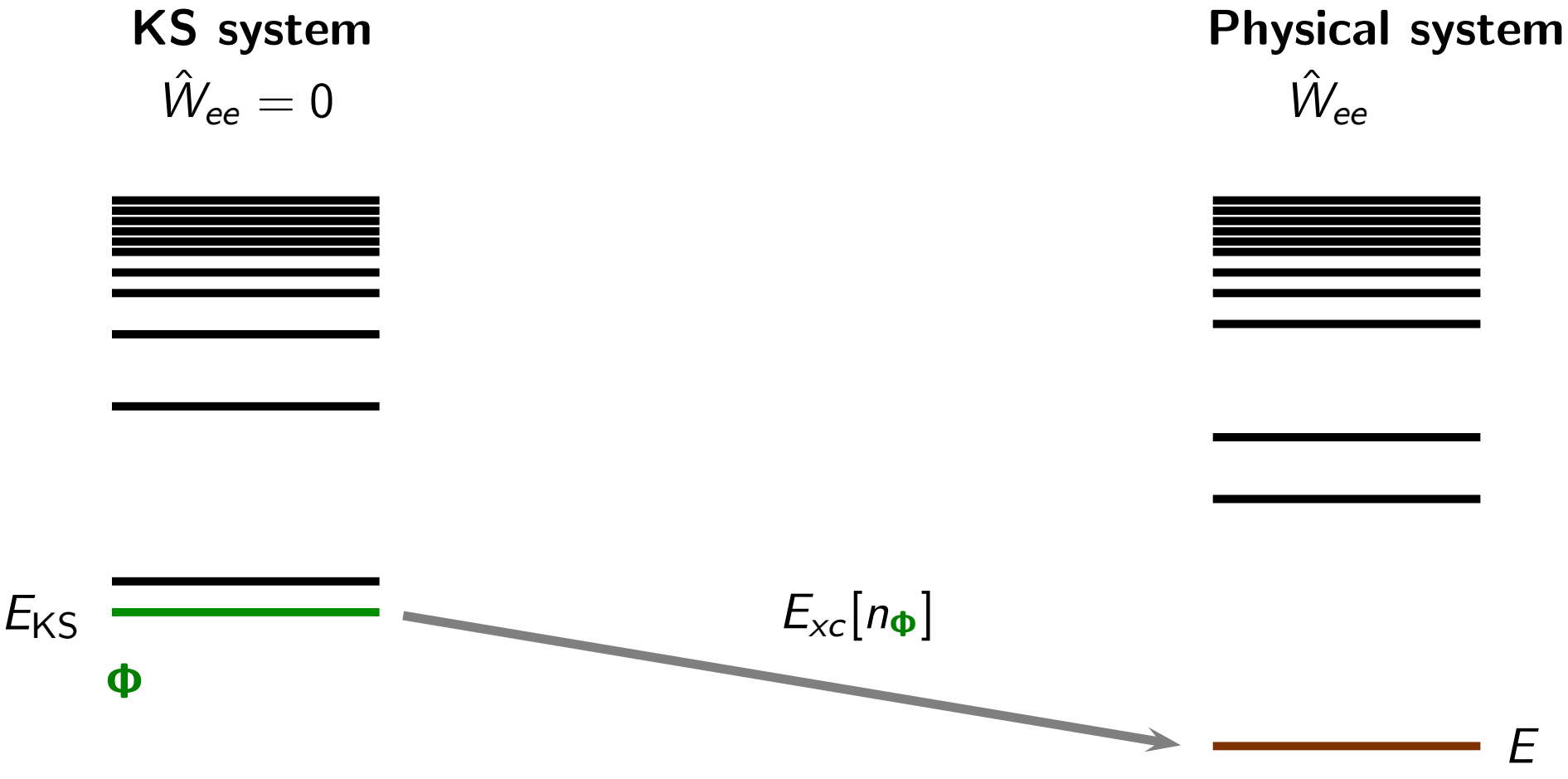
Physical system

$\hat{W}_{ee}$



E

KS DFT: near-degeneracy problem (e.g., atoms/molecules)



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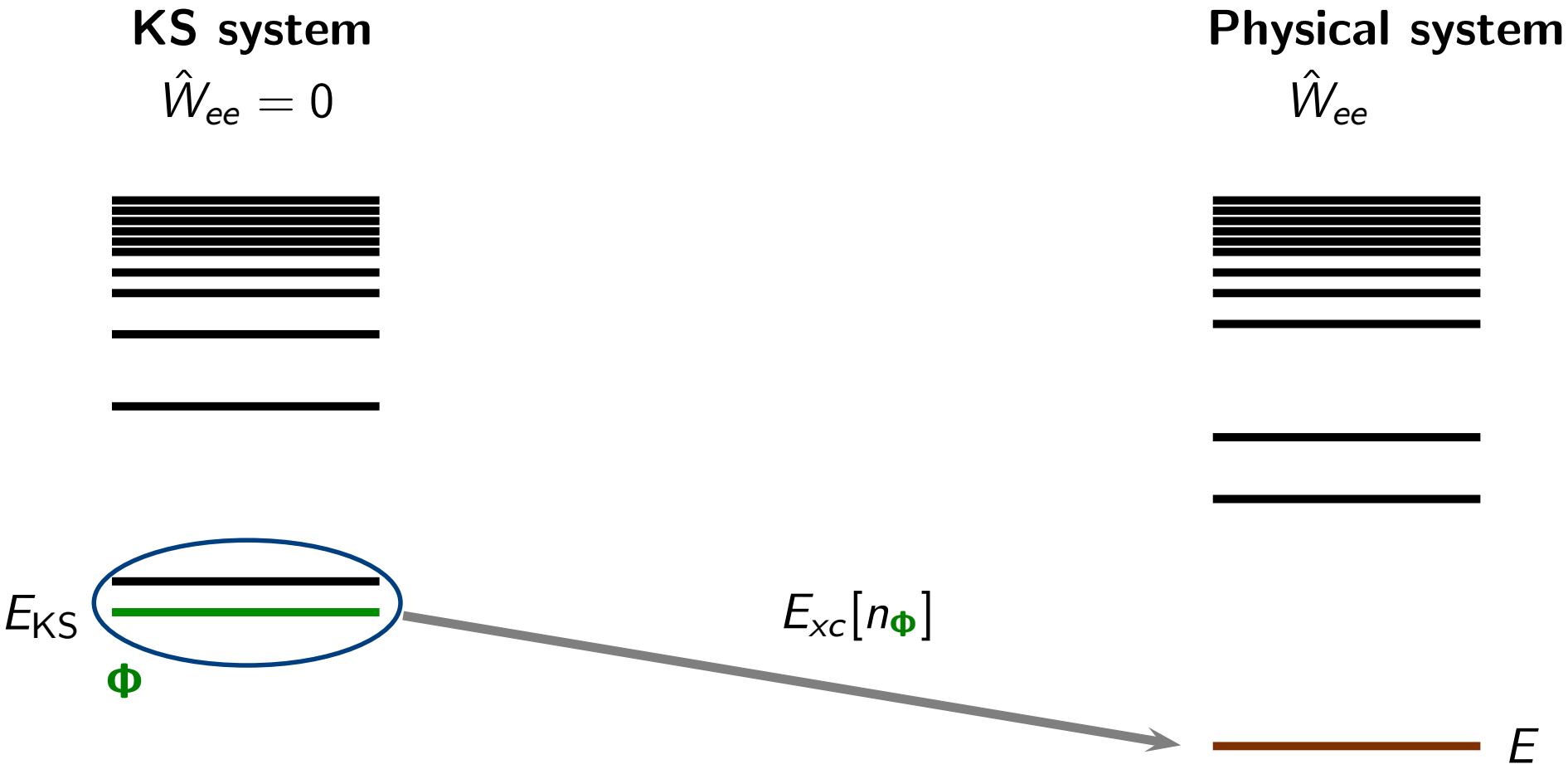


Near-degeneracy $\Longrightarrow$ **usual approximations for** $E_{xc}[n]$ **are inaccurate**

Examples: Be atom, diatomic molecule at dissociation, ...

How to deal with near-degeneracy in DFT?

Some approaches

- Artificial breaking of spatial or spin symmetry:

  Restricted Kohn-Sham (RKS) $\longrightarrow$ *Unrestricted* Kohn-Sham (UKS)

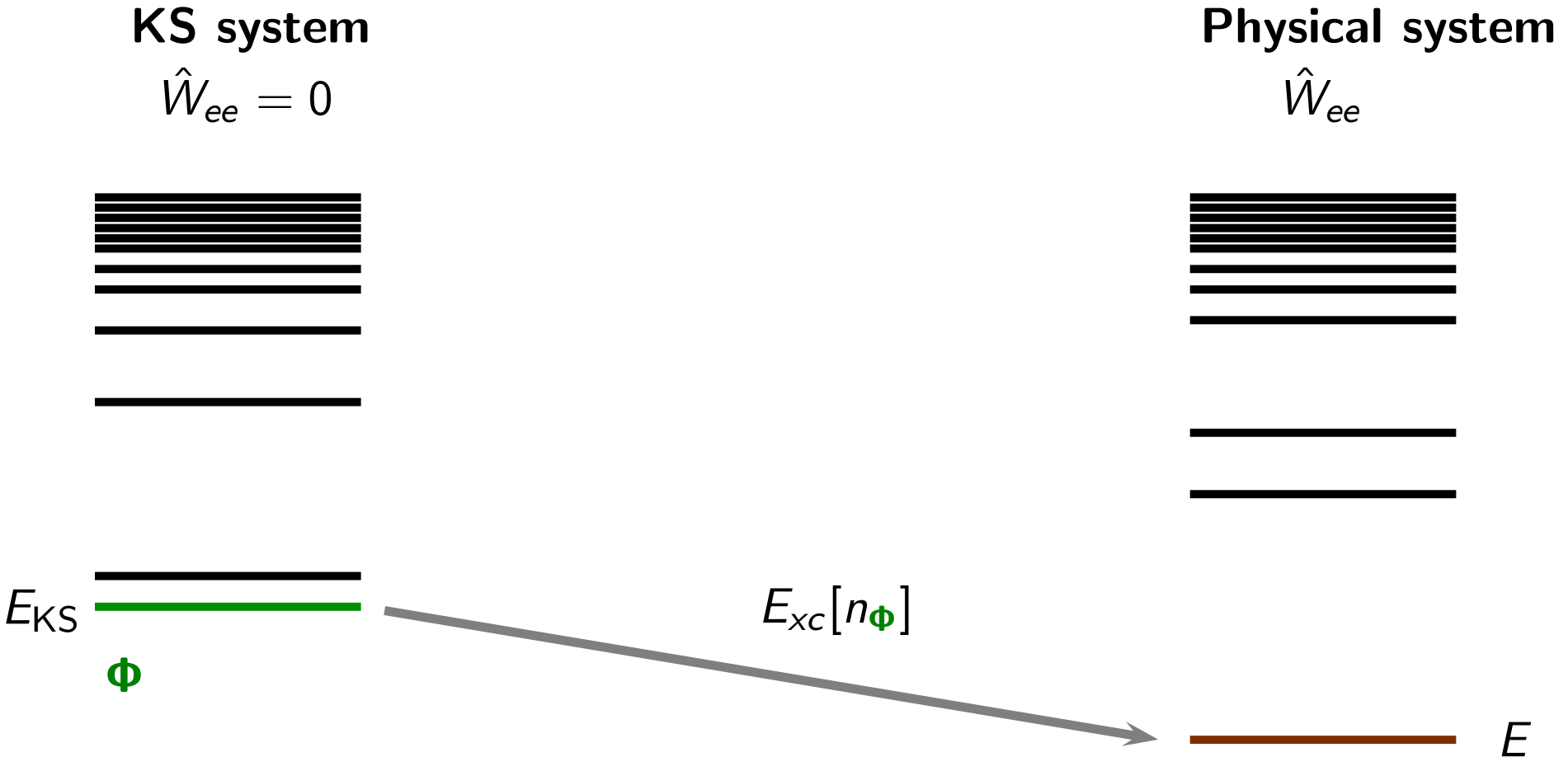
- Pure state $\longrightarrow$ Ensemble of states

  $\Longrightarrow$ fractional orbital occupation numbers

- Standard multi-configurational wave function calculation, completed by a density functional

- **Long-range/short-range decomposition** (Andreas Savin)

Multi-configurational DFT: the idea



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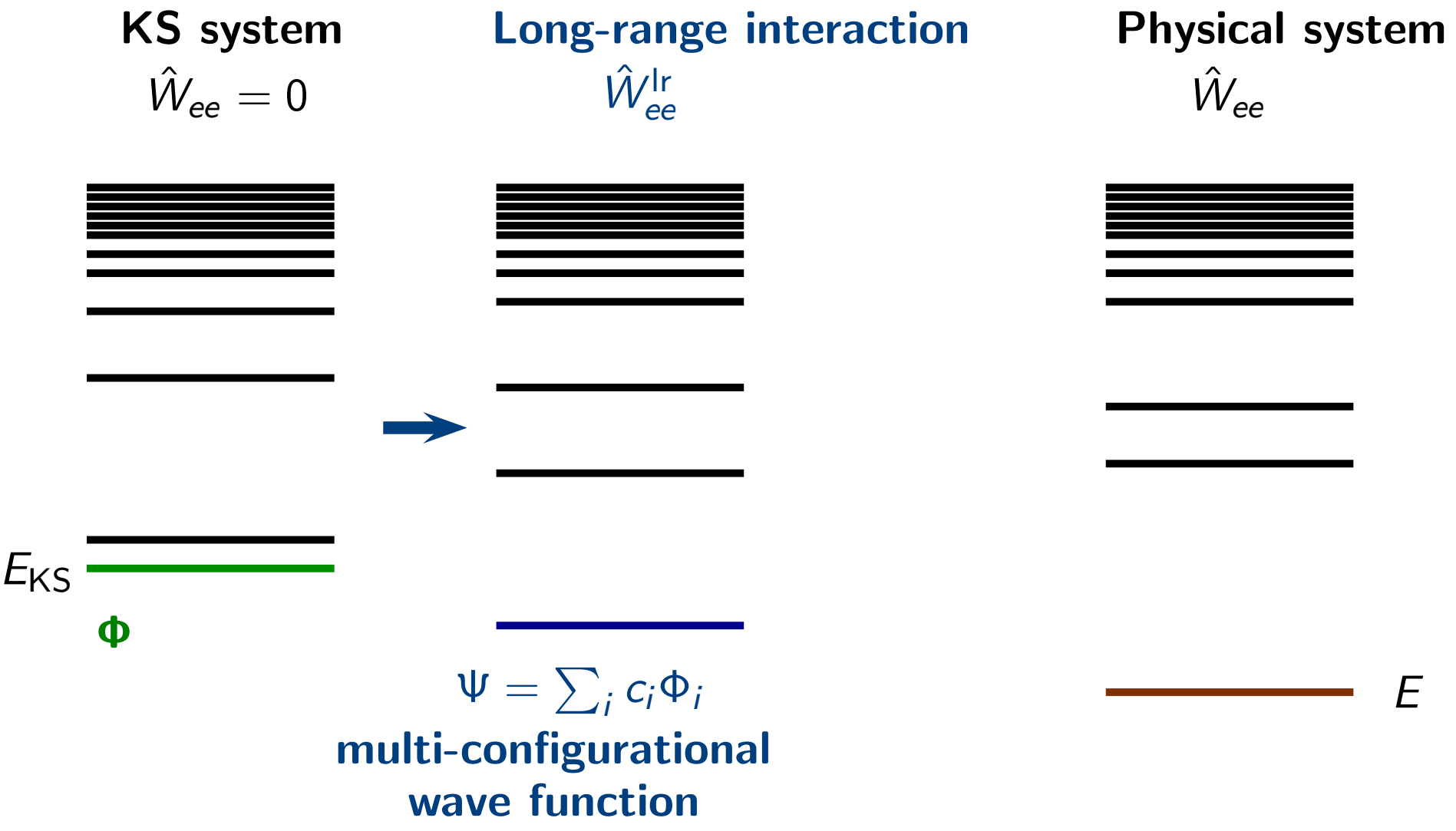

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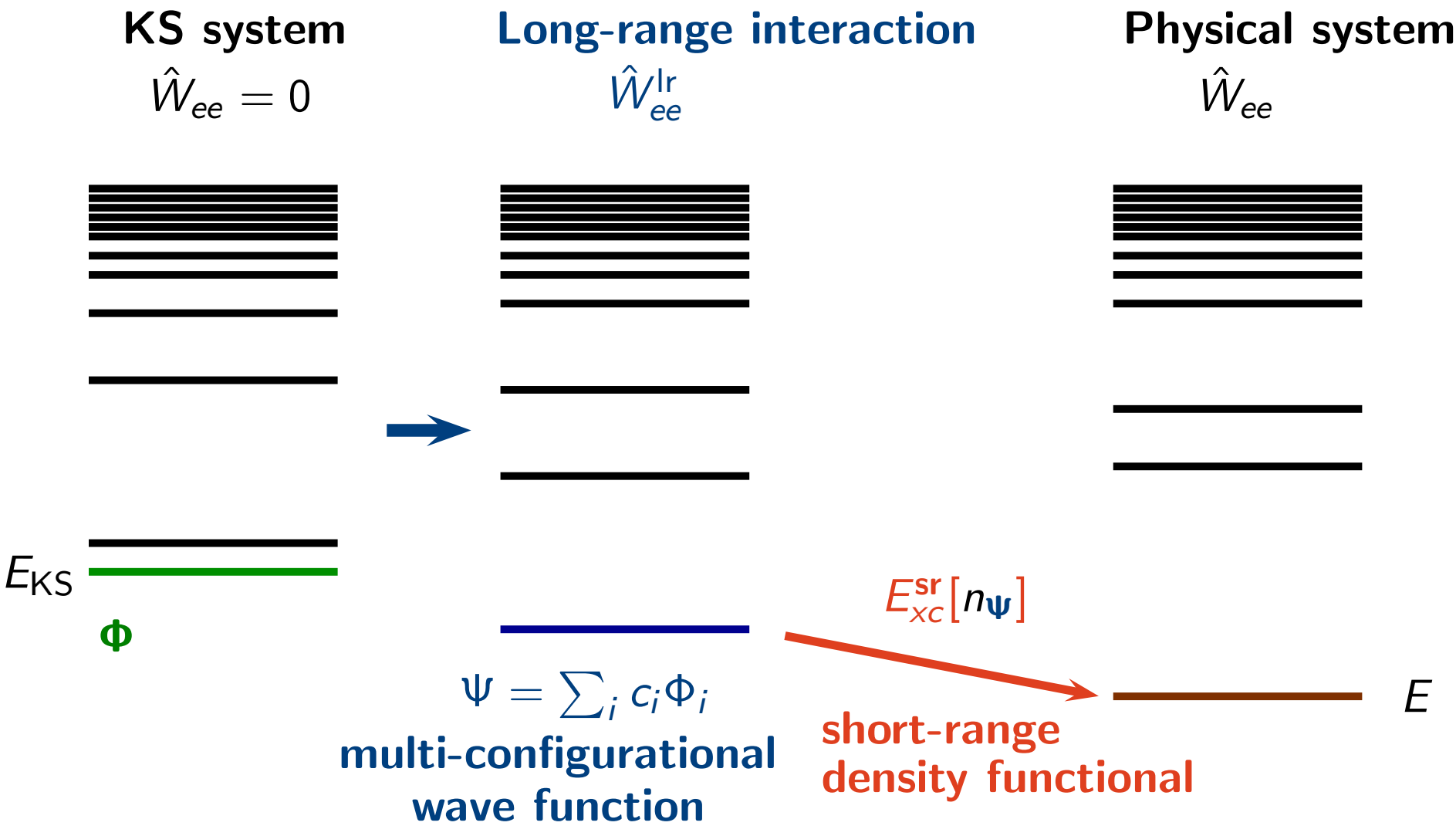
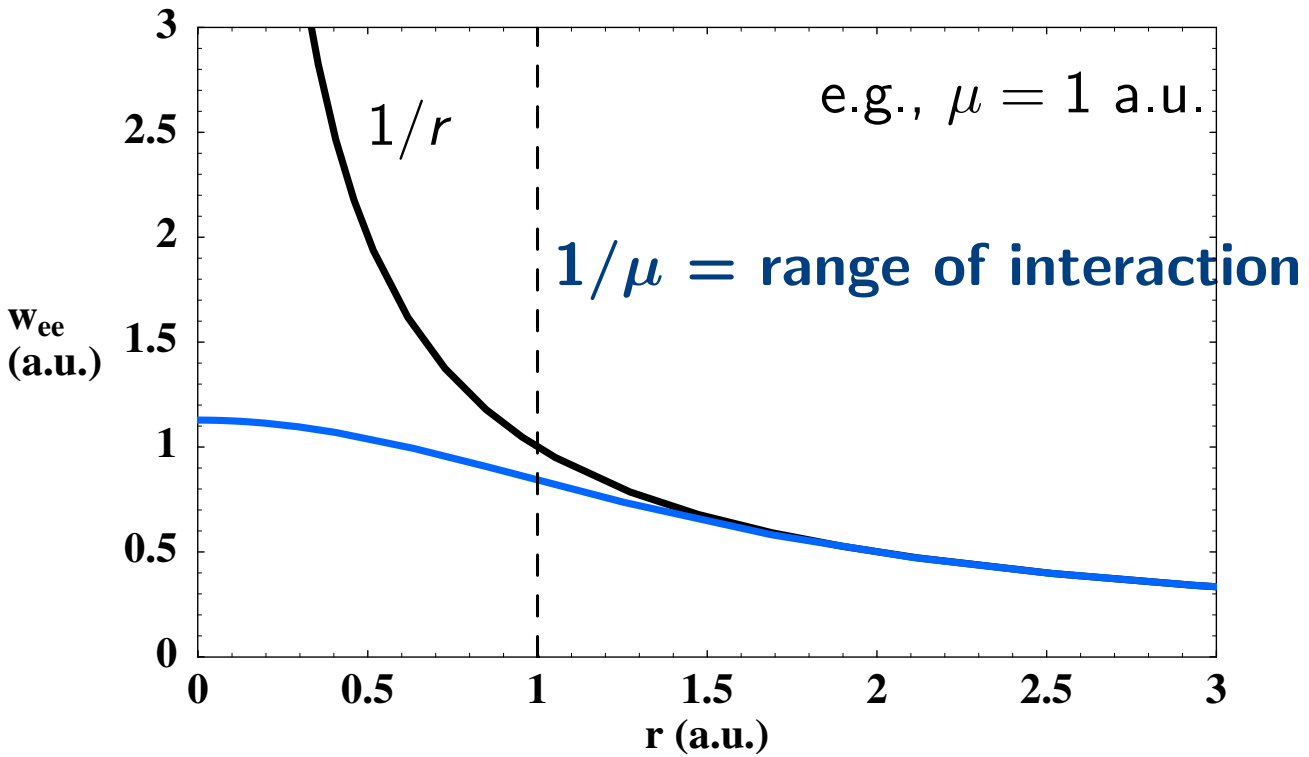


Long-range electron-electron interaction

Possible definition using the error function:

$$w_{ee}^{\mathrm{lr},\mu}(r) = \frac{\mathrm{erf}(\mu r)}{r}$$



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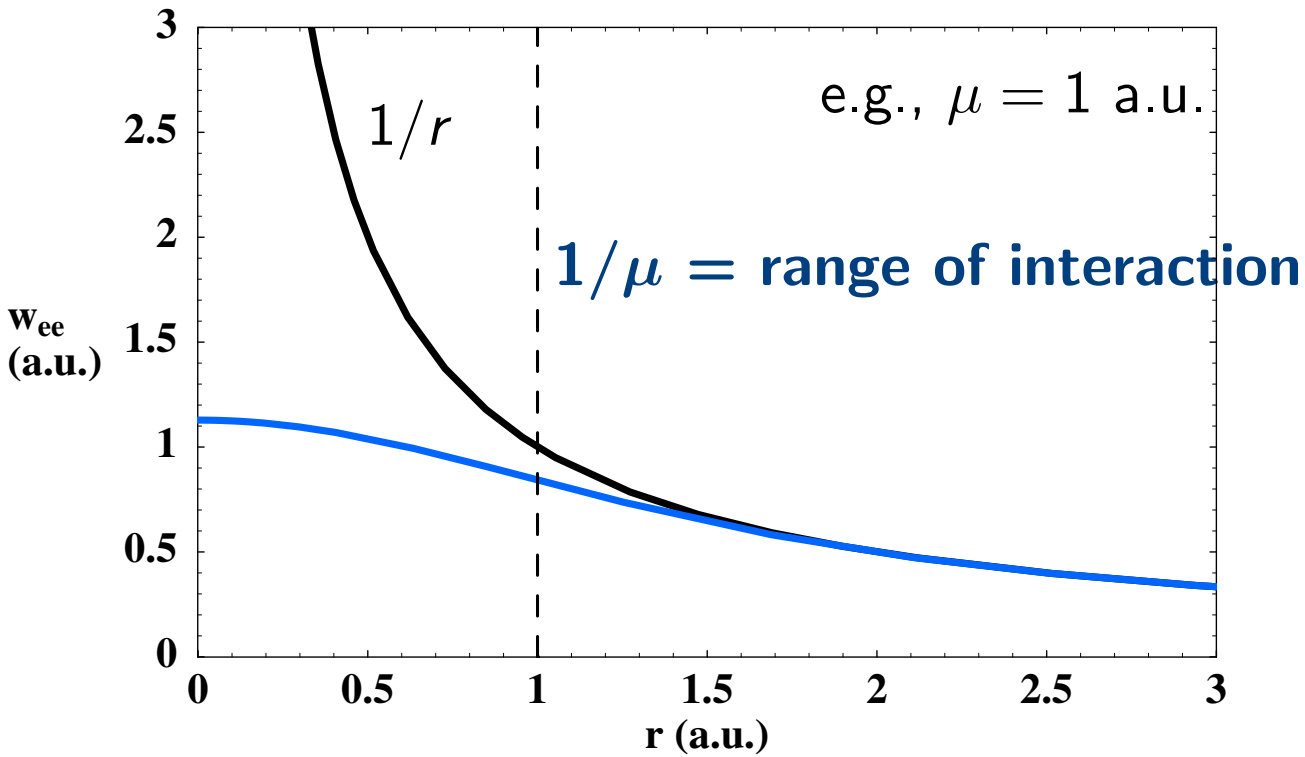

Limiting cases: $w_{ee}^{\mathrm{lr},\mu=0}(r) = 0$ and $w_{ee}^{\mathrm{lr},\mu\to\infty}(r) = \frac{1}{r}$

Multi-configurational DFT

Multi-determinantal extension of the Kohn-Sham scheme

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

$\boldsymbol{\Psi} = \sum_{\mathbf{i}} \mathbf{c_i} \boldsymbol{\Phi_i}$: **multi-determinantal** wave function

Multi-configurational DFT

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$\Psi = \sum_i c_i \Phi_i$: **multi-determinantal** wave function

- **In principle: exact**
- Limiting cases:
  $\mu = 0 \implies$ KS DFT
  $\mu \to \infty \implies$ Standard wave function methods
- **In practice: approximations** are necessary for Ψ and $E_{xc}^{\mathrm{sr},\mu}[n]$
- E.g., Ψ = MCSCF wave function $\implies$ **"MCSCF+DFT" method**

Short-range **exchange** energy: **LDA approximation**

$$E_{x,\mathrm{LDA}}^{\mathrm{sr},\mu}[n] = \int n(\mathbf{r})\, \varepsilon_{x,\mathbf{unif}}^{\mathrm{sr},\mu}(n(\mathbf{r}))d\mathbf{r}$$

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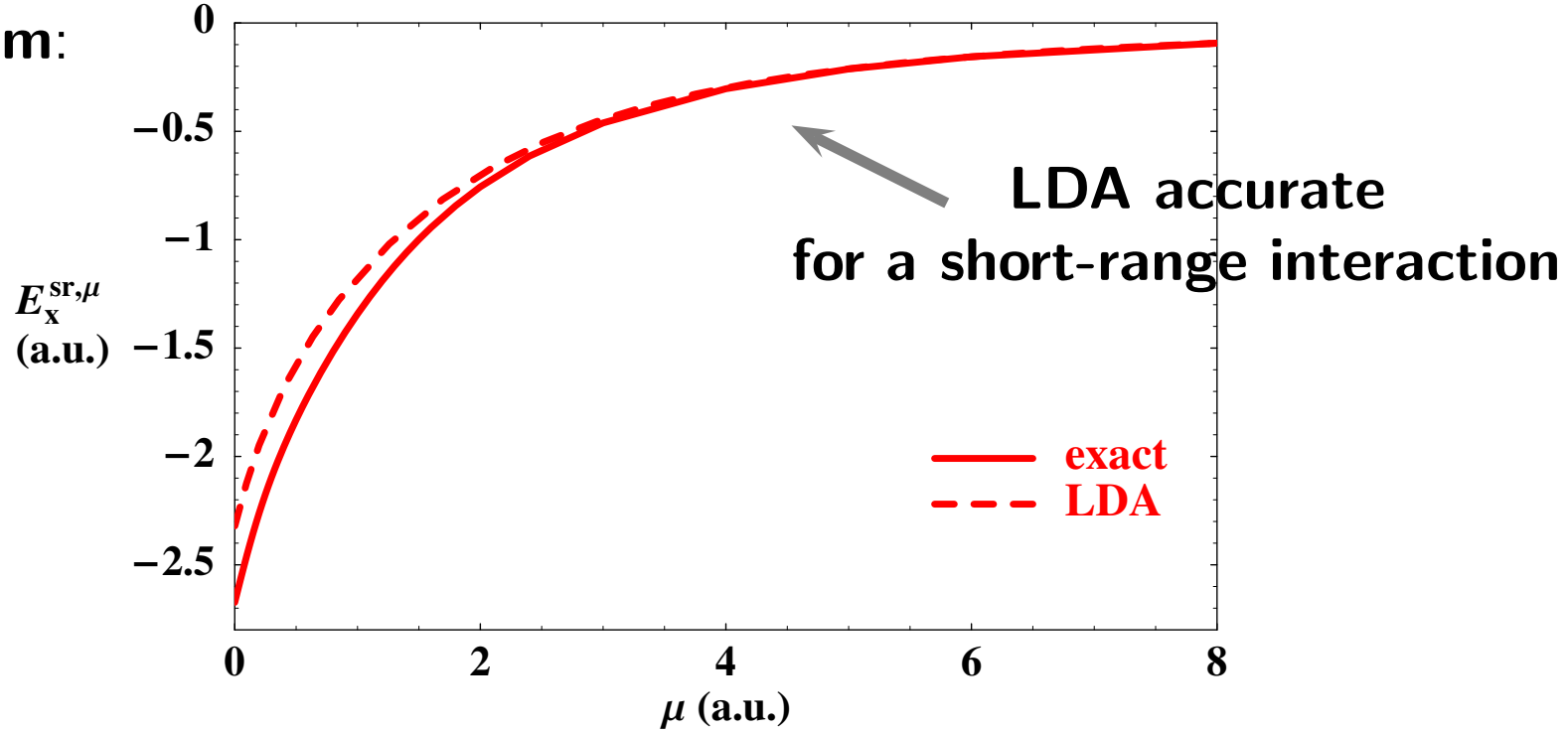
For **Be atom**:



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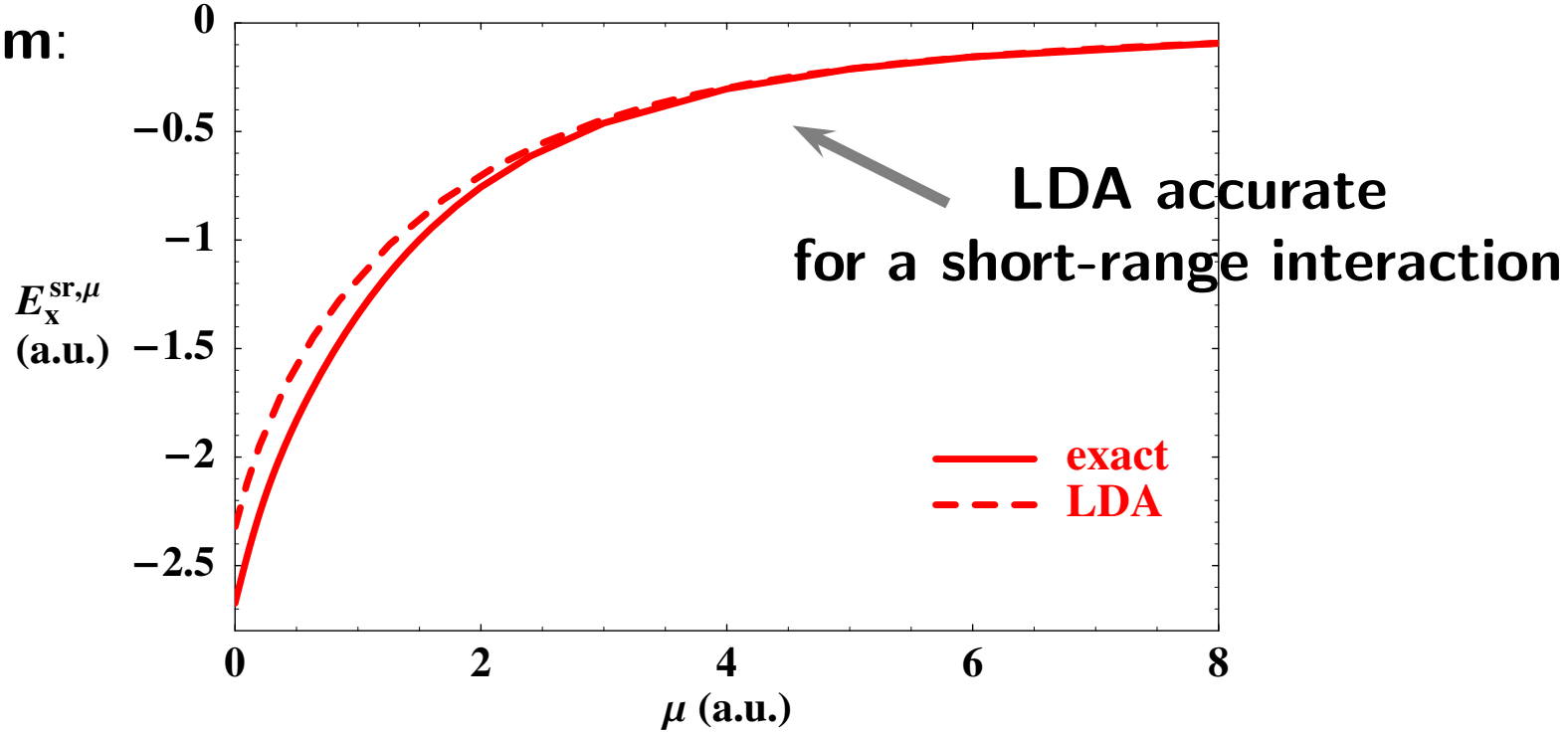

Asymptotic expansion for $\mu \longrightarrow \infty$:

$$E_x^{\mathrm{sr},\mu} = -\frac{A_1}{\mu^2}\int n(\mathbf{r})^2 d\mathbf{r} + \frac{A_2}{\mu^4}\int n(\mathbf{r})\left(\frac{|\nabla n(\mathbf{r})|^2}{2n(\mathbf{r})} + 4\tau(\mathbf{r})\right) d\mathbf{r} + \cdots$$

Short-range **correlation** energy: **LDA approximation**

$$E_{c,\mathrm{LDA}}^{\mathrm{sr},\mu}[n] = \int n(\mathbf{r})\, \varepsilon_{c,\mathbf{unif}}^{\mathrm{sr},\mu}(n(\mathbf{r}))\, d\mathbf{r}$$

Short-range **correlation** energy: **LDA approximation**

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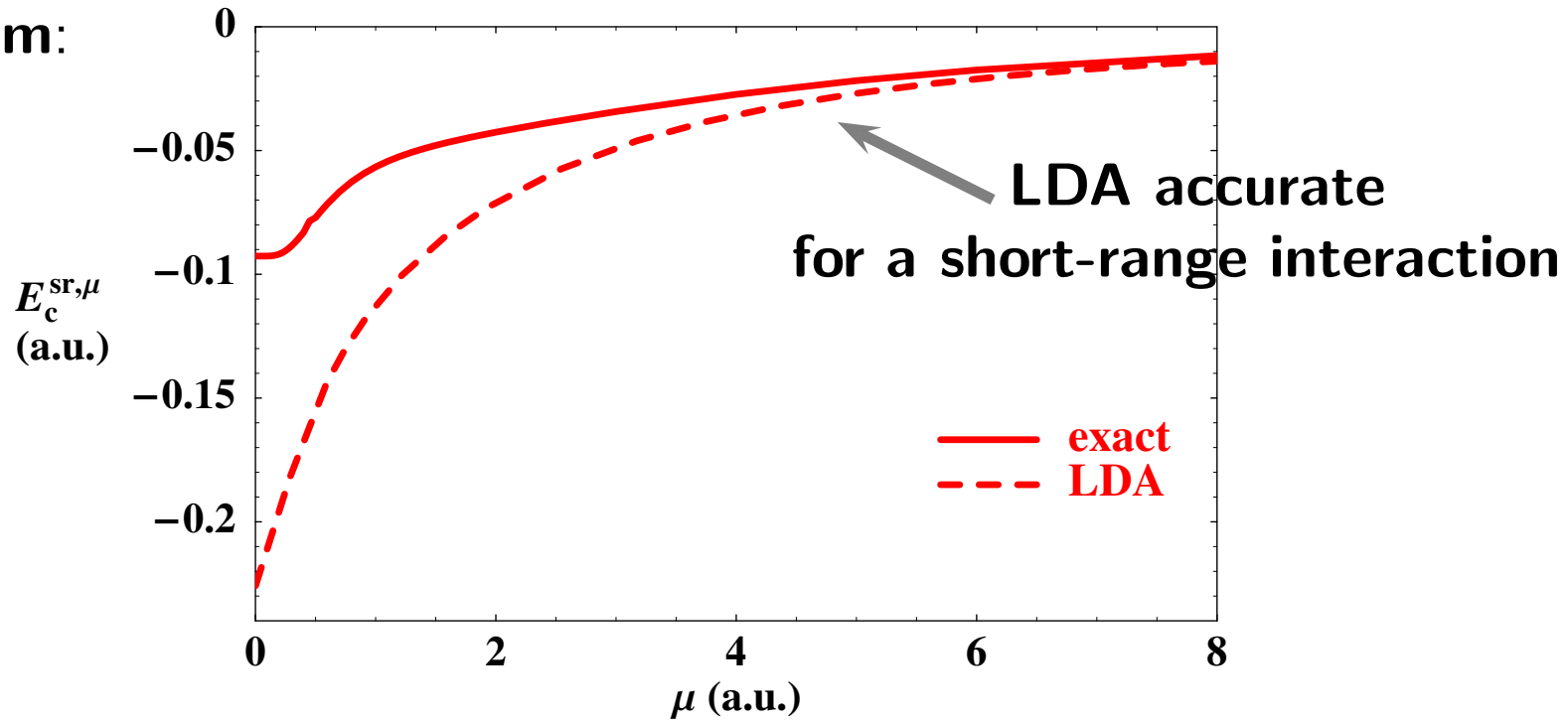

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$$E_{c,\mathrm{LDA}}^{\mathrm{sr},\mu}[n] = \int n(\mathbf{r})\, \varepsilon_{c,\mathbf{unif}}^{\mathrm{sr},\mu}(n(\mathbf{r}))d\mathbf{r}$$

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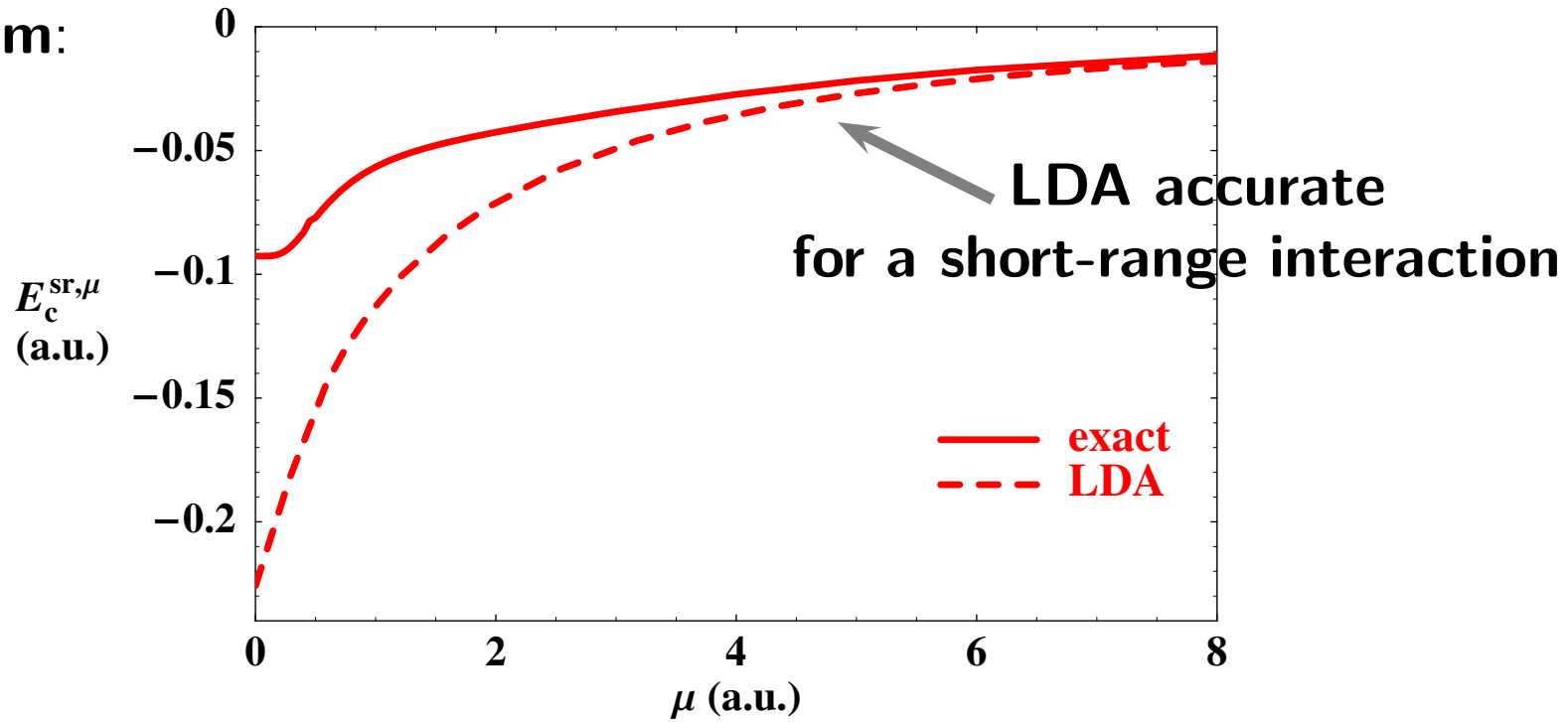


Asymptotic expansion for $\mu \longrightarrow \infty$:

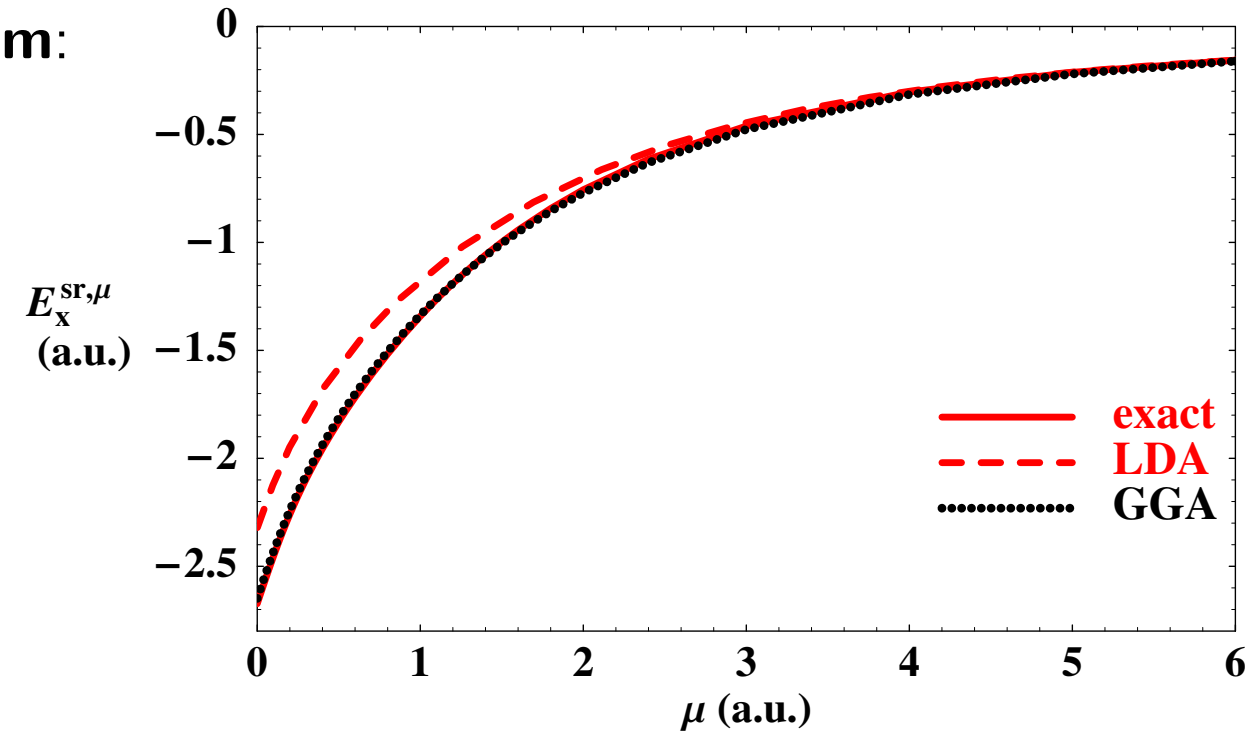
$$E_c^{\mathrm{sr},\mu} = \frac{B_1}{\mu^2}\int n_{2,c}(\mathbf{r},\mathbf{r})d\mathbf{r} + \frac{B_2}{\mu^3}\int n_2(\mathbf{r},\mathbf{r})d\mathbf{r} + \cdots$$

Short-range **exchange** energy: **GGA approximation**

Short-range GGA functional of Heyd, Scuseria and Ernzerhof (2003) based on the PBE exchange hole:

$$\varepsilon_{x,\mathrm{GGA}}^{\mathrm{sr},\mu}(n) = \frac{1}{2}\int n_{x,\mathrm{PBE}}(n, |\nabla n|, r_{12})\, w_{ee}^{\mathrm{sr},\mu}(r_{12})\, d\mathbf{r}_{12}$$

For **Be atom**:



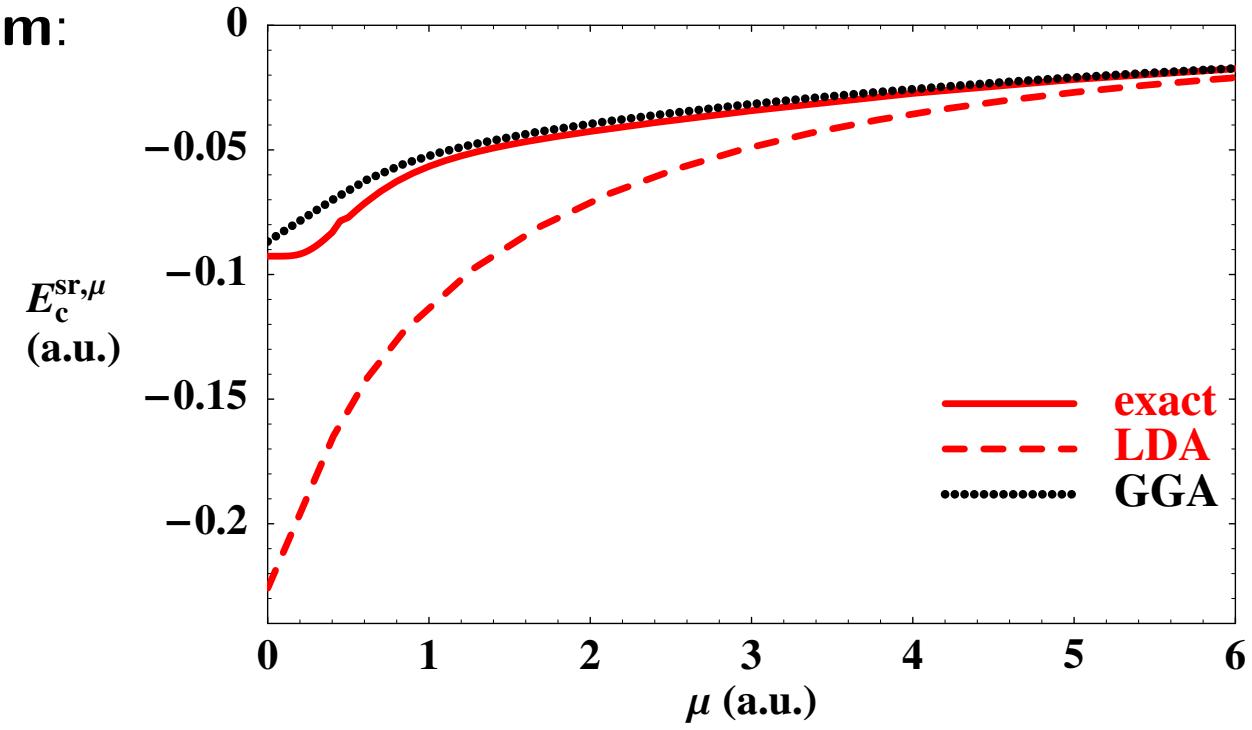
$\Longrightarrow$ **GGA describes well a longer range of interaction**

Short-range **correlation** energy: **GGA approximation**

Interpolation between PBE at $\mu = 0$ and expansion of LDA for $\mu \longrightarrow \infty$:

$$\varepsilon_{c,\mathrm{GGA}}^{\mathrm{sr},\mu}(n,|\nabla n|) = \frac{\varepsilon_{c,\mathrm{PBE}}(n,|\nabla n|)}{1 + d_1(n)\mu + d_2(n)\mu^2}$$

For **Be atom**:



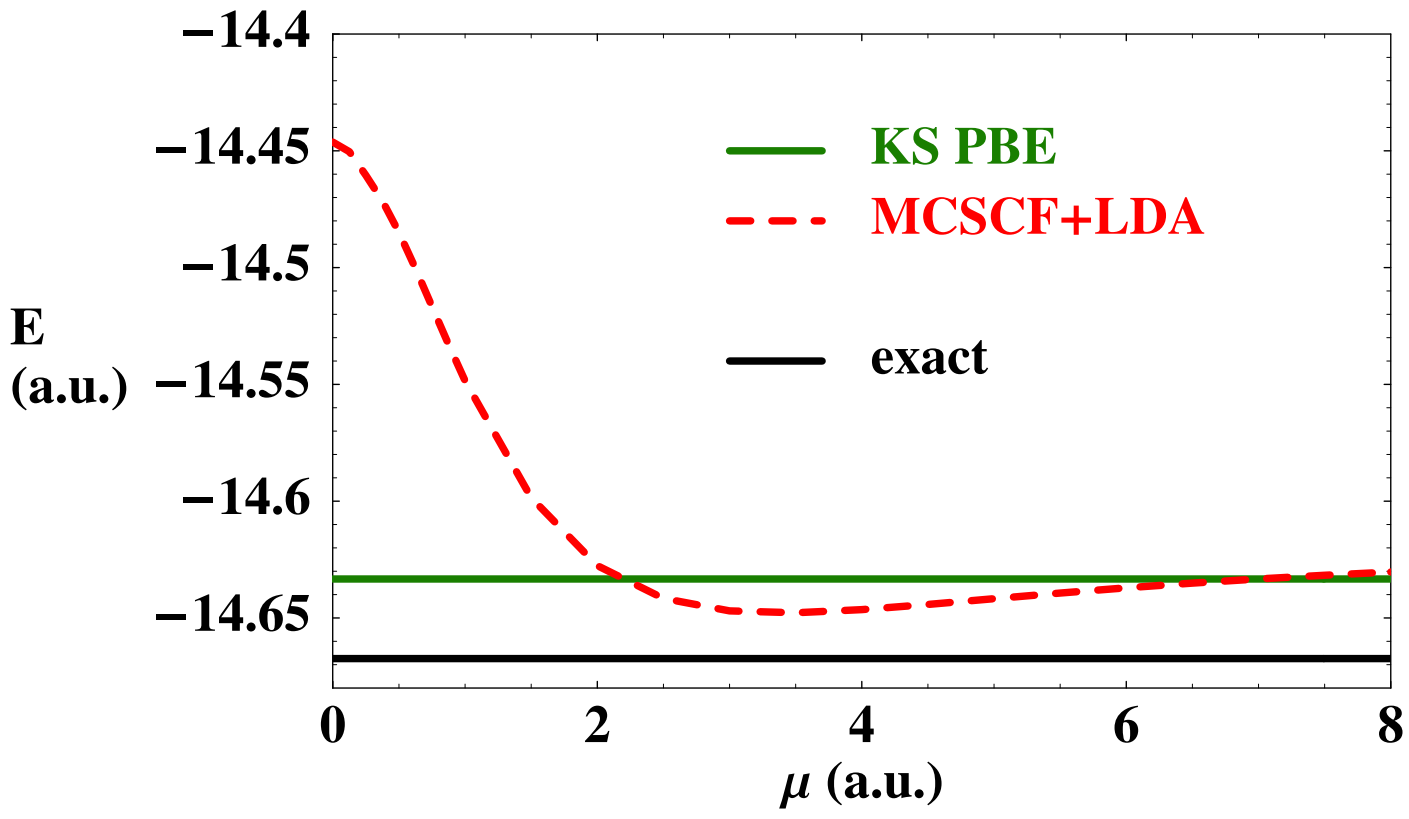
$\Longrightarrow$ **GGA describes well a longer range of interaction**

MCSCF+DFT: Be atom

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

MCSCF ($1s2s$, $1s2p$)

LDA, GGA



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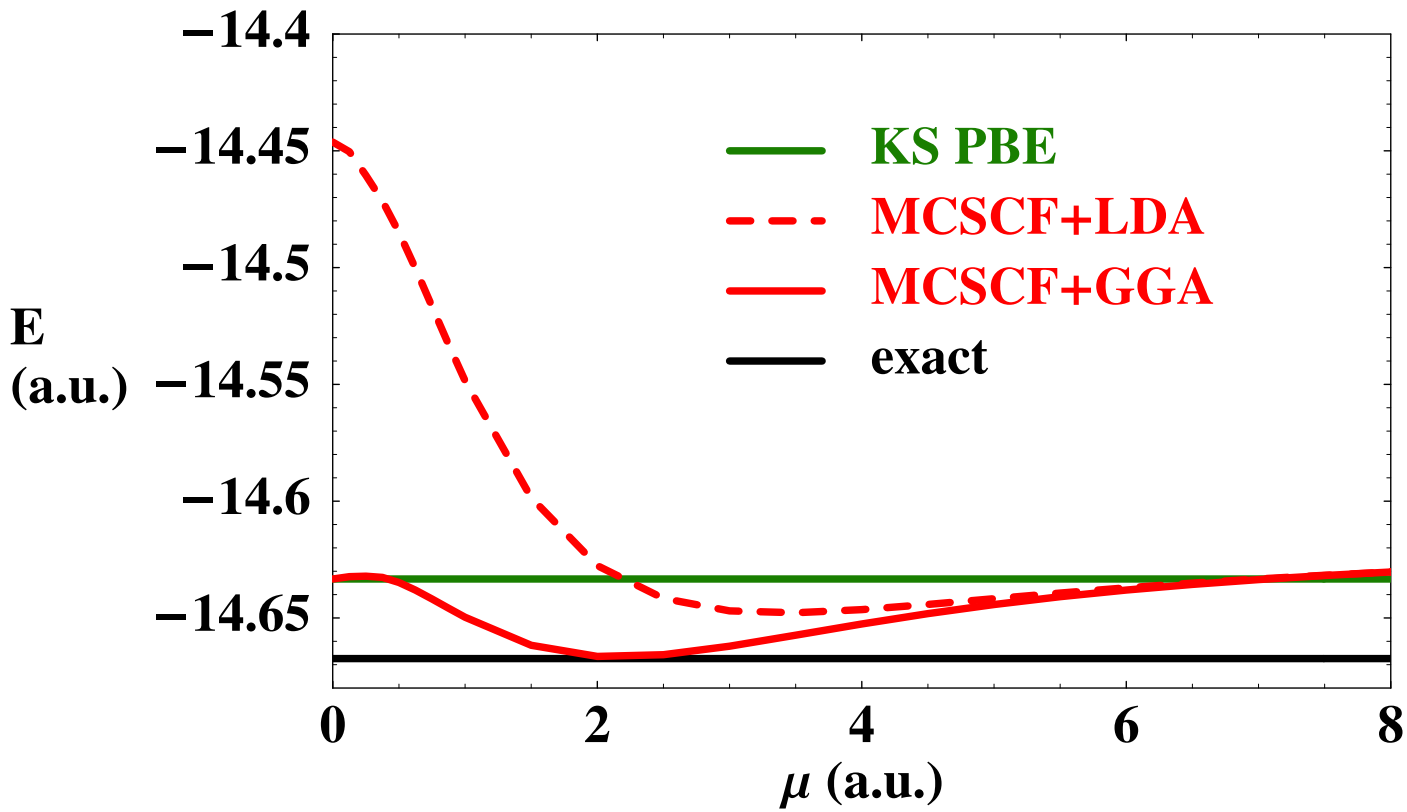
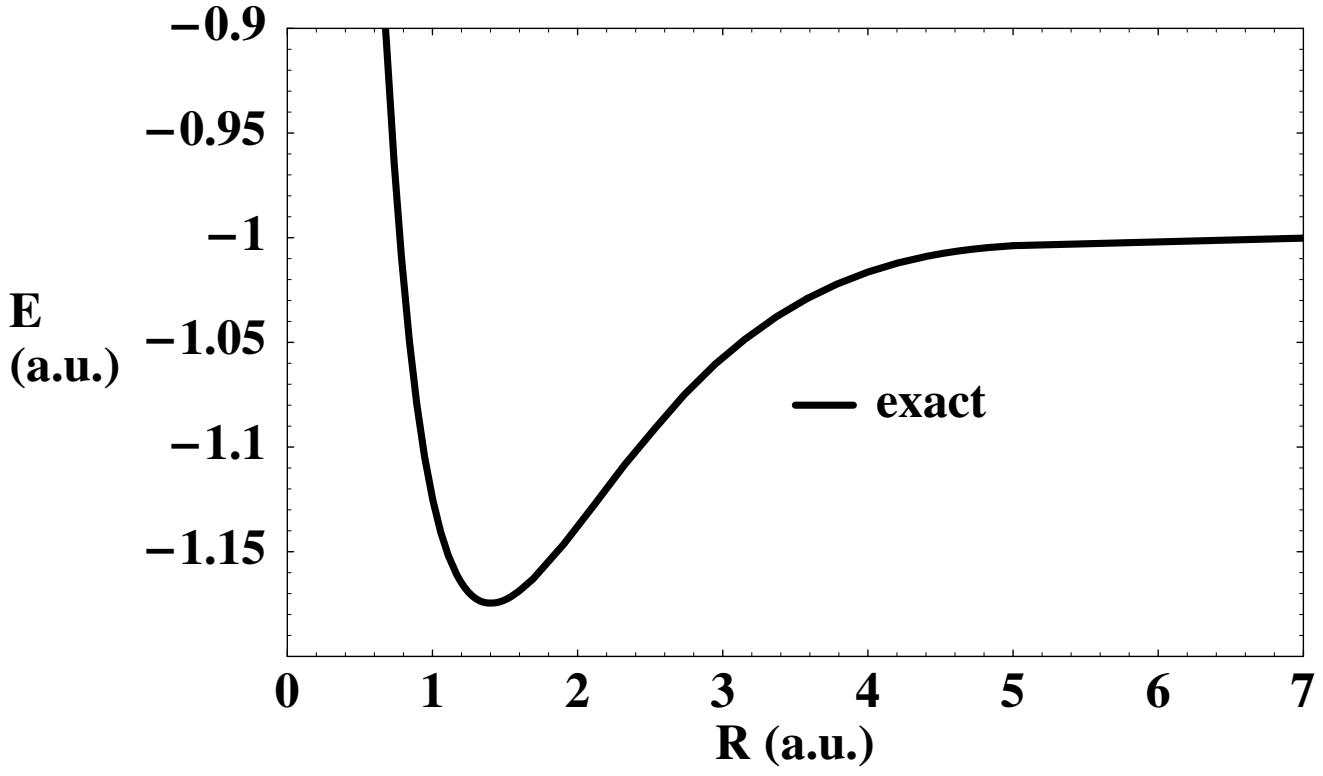
LDA, GGA



$\Longrightarrow$ **At intermediate μ, MCSCF+DFT is more accurate than RKS DFT and MCSCF**

MCSCF+DFT: dissociation of H_2

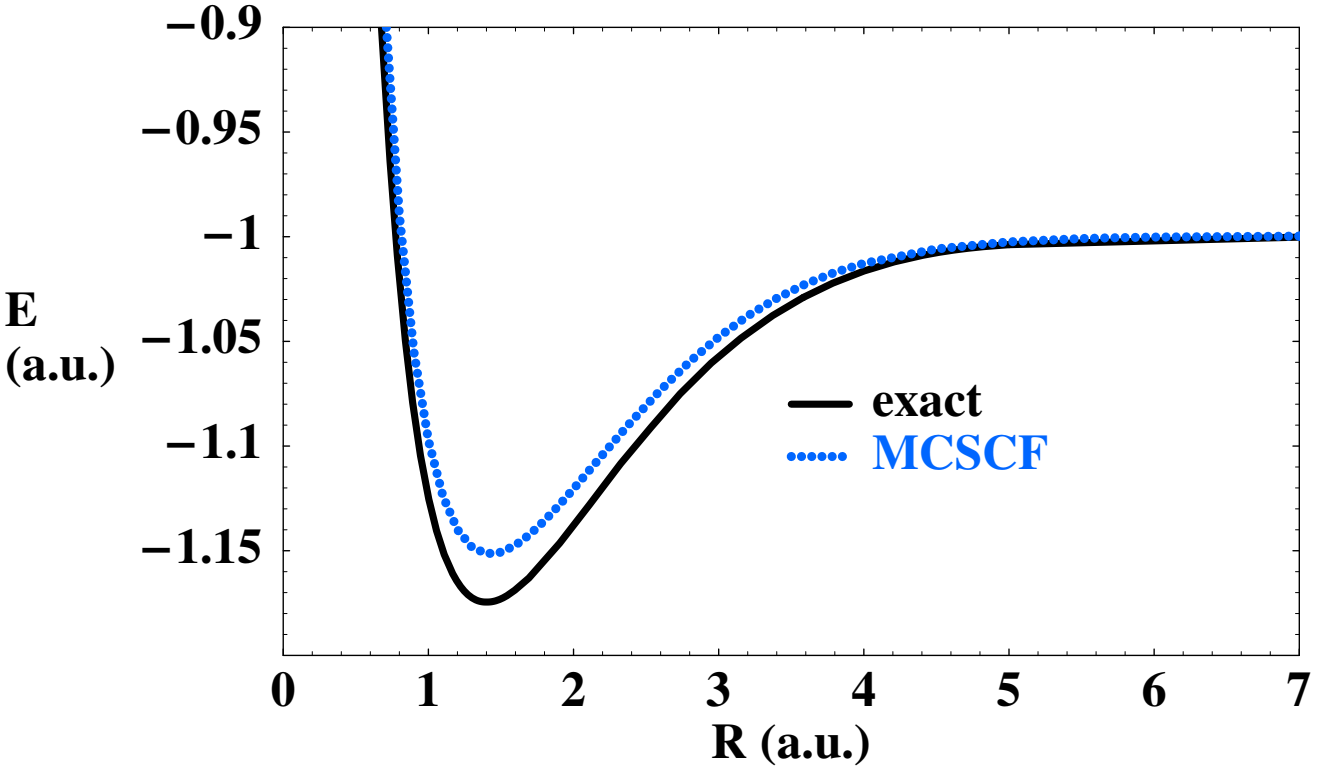
MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.
D_e (eV)	**4.8**

MCSCF+DFT: dissociation of H_2

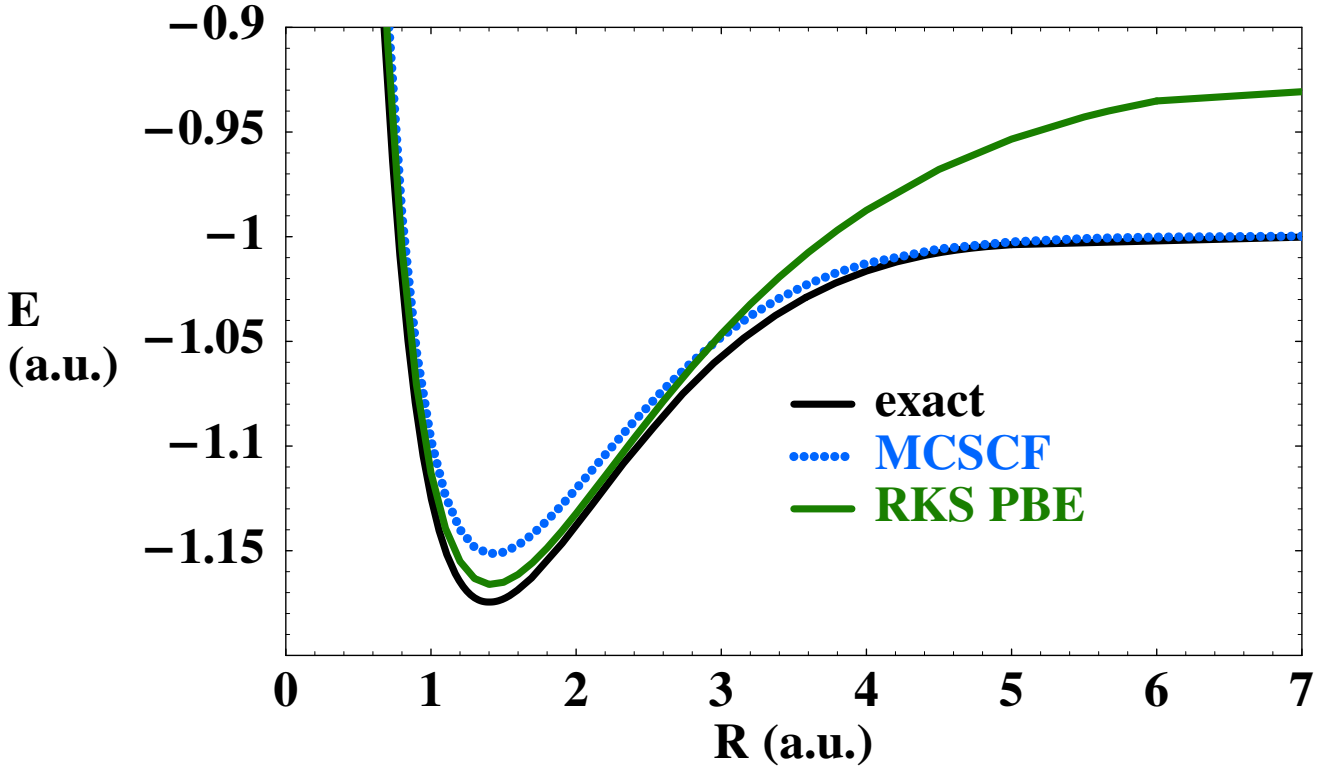
MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	MCSCF
D_e (eV)	**4.8**	4.1

MCSCF+DFT: dissociation of H_2

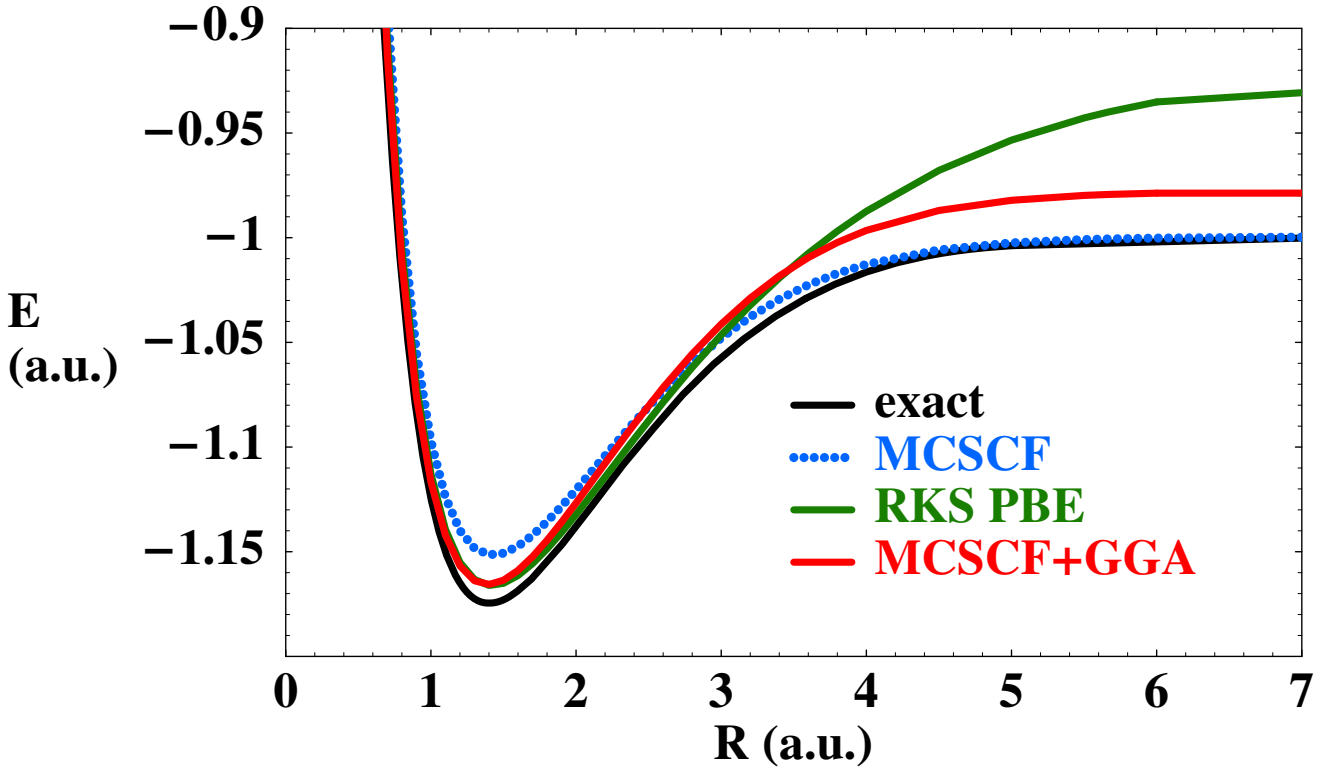
MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	MCSCF	RKS PBE
D_e (eV)	**4.8**	4.1	6.8

MCSCF+DFT: dissociation of H_2

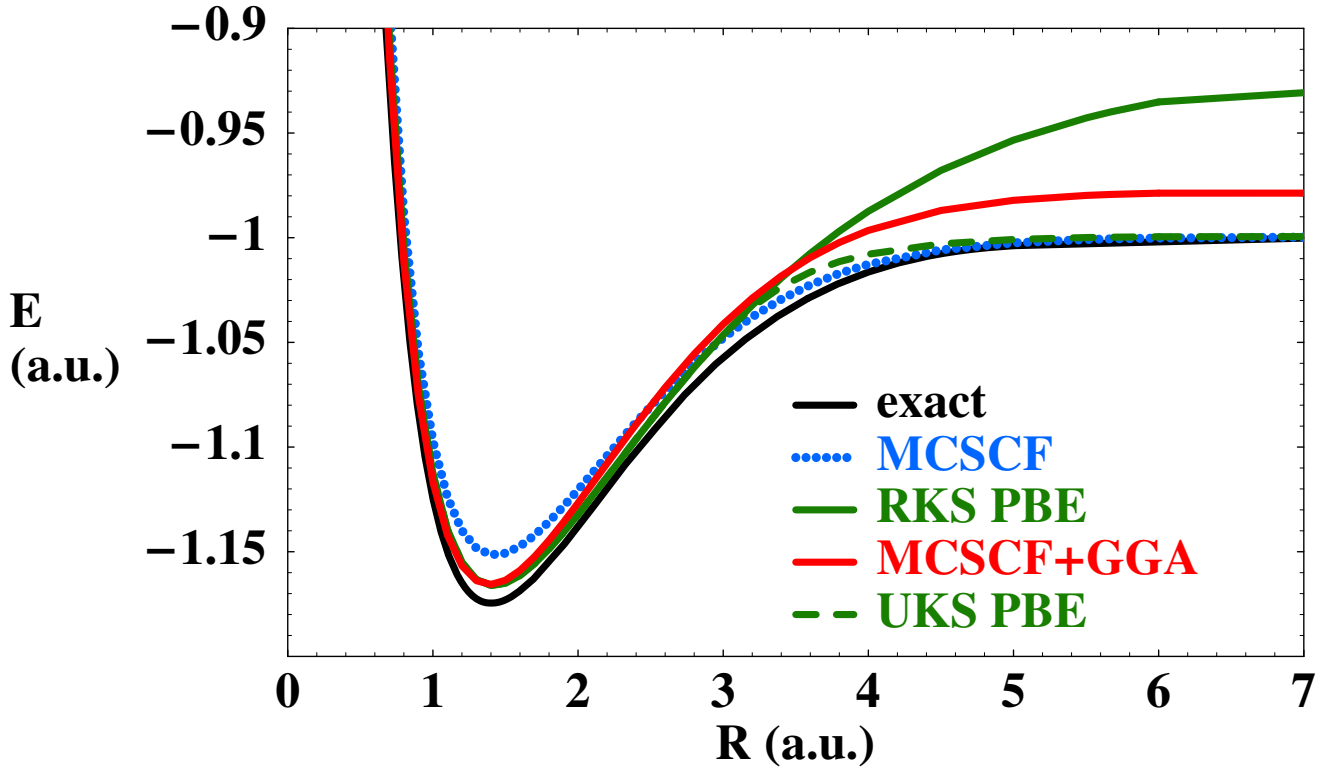
MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	MCSCF	RKS PBE	**MCSCF+GGA**
D_e (eV)	**4.8**	4.1	6.8	**5.1**

MCSCF+DFT: dissociation of H_2

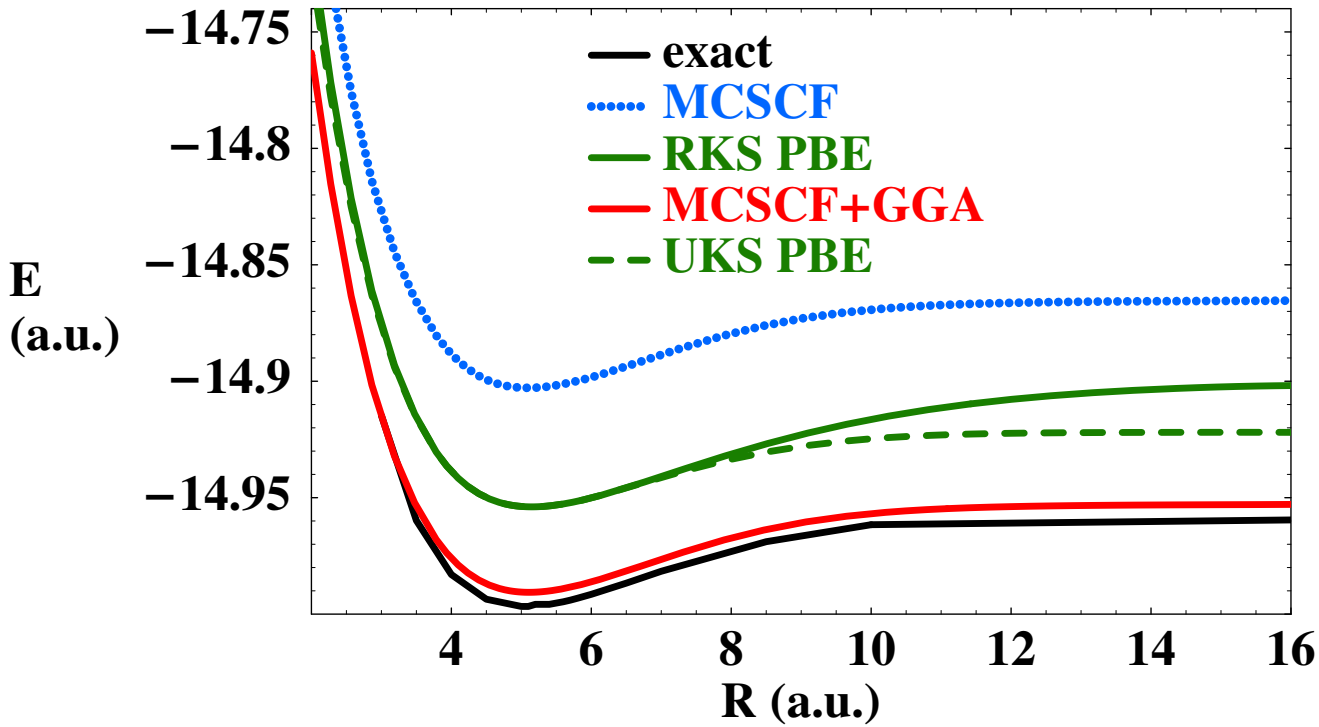
MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	MCSCF	RKS PBE	**MCSCF+GGA**	UKS PBE
D_e (eV)	**4.8**	4.1	6.8	**5.1**	4.5

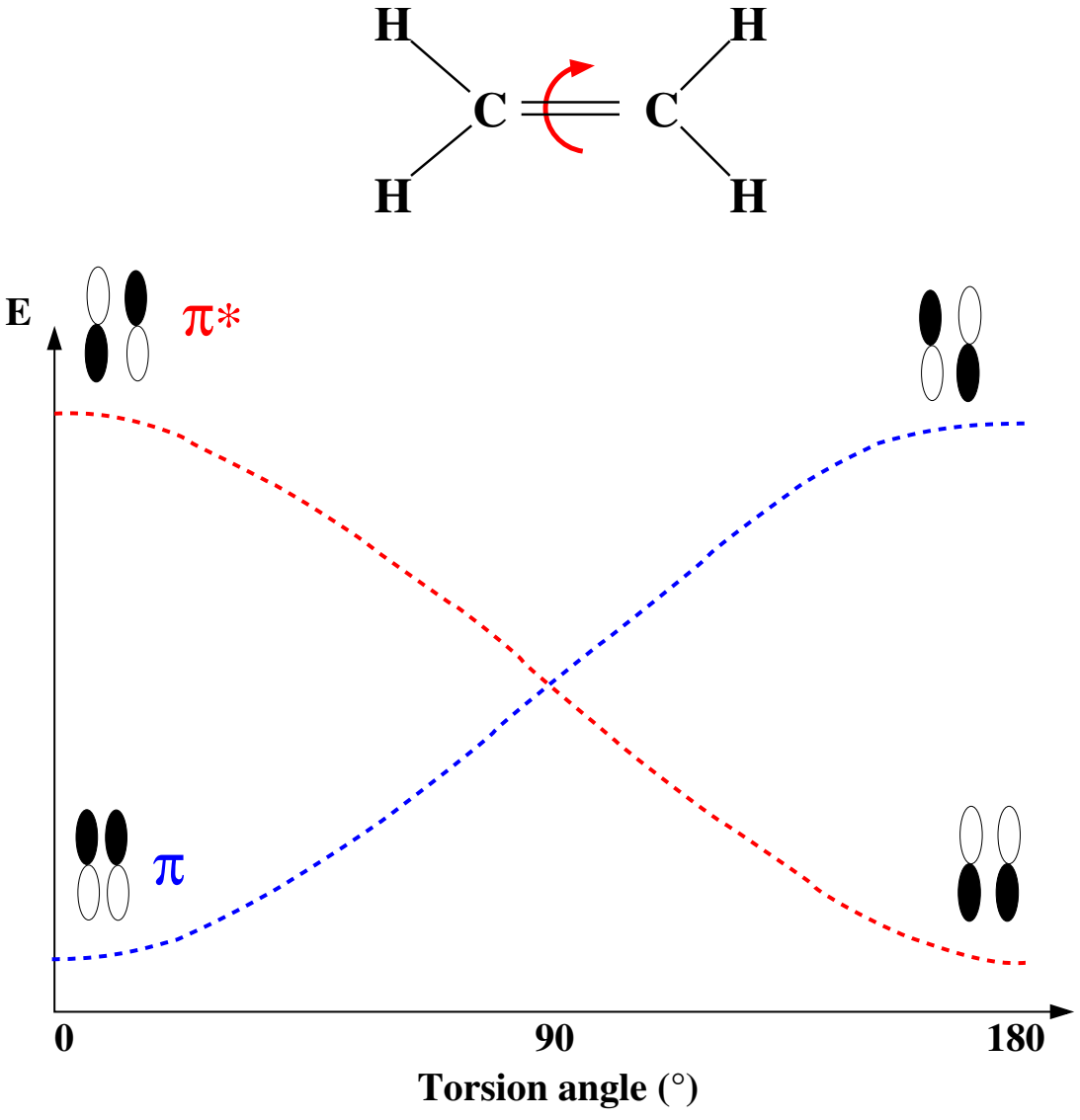
MCSCF+DFT: dissociation of Li_2

MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	MCSCF	RKS PBE	**MCSCF+GGA**	UKS PBE
D_e (eV)	**1.1**	1.0	1.5	**1.0**	0.9

MCSCF+DFT: avoided crossing in the torsion of ethylene



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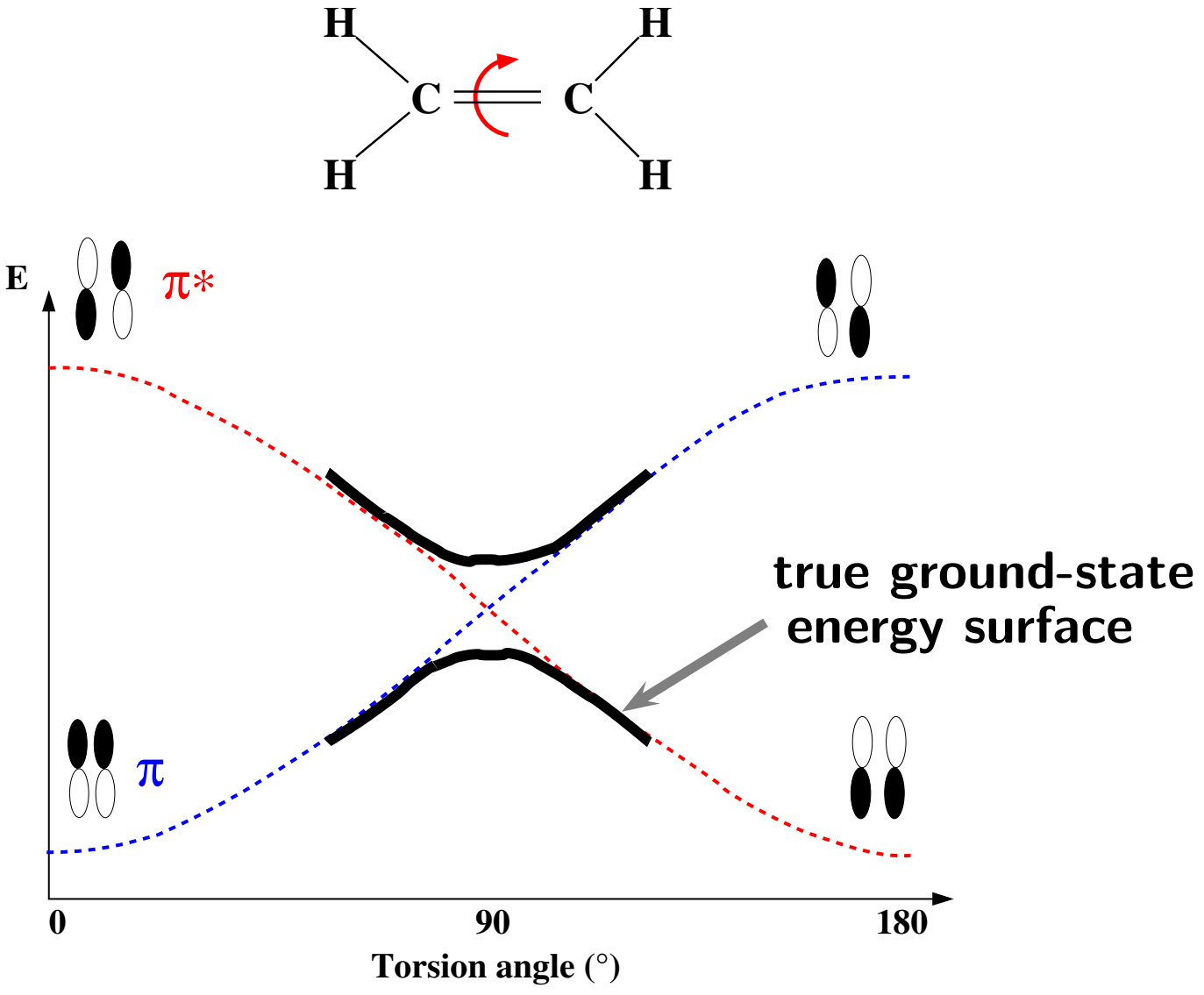
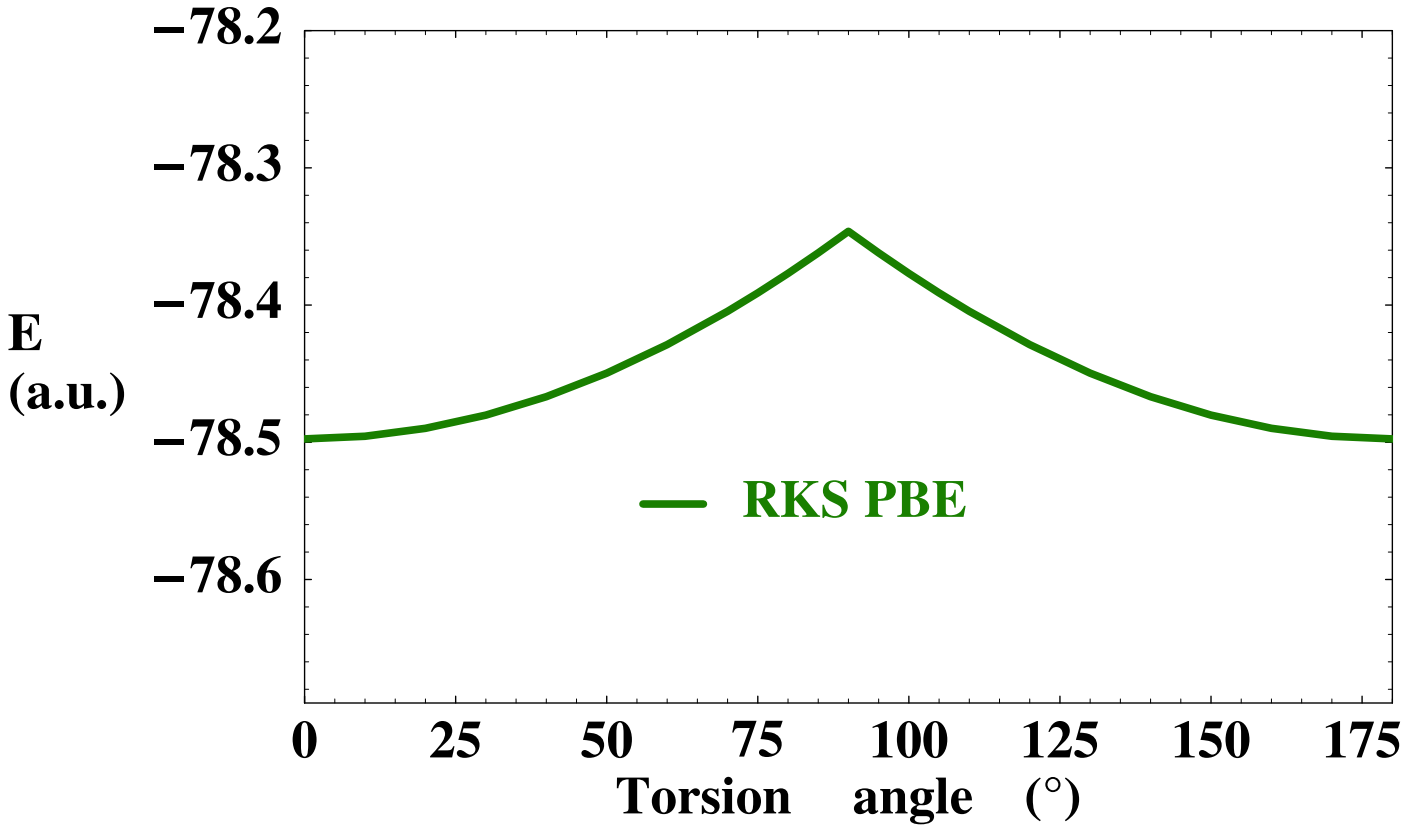


MCSCF+DFT: avoided crossing in the torsion of ethylene

MCSCF+GGA with $\mu = 1$ a.u.:



	Exp.	RKS PBE
barrier (kcal/mol)	**65.0**	91.3

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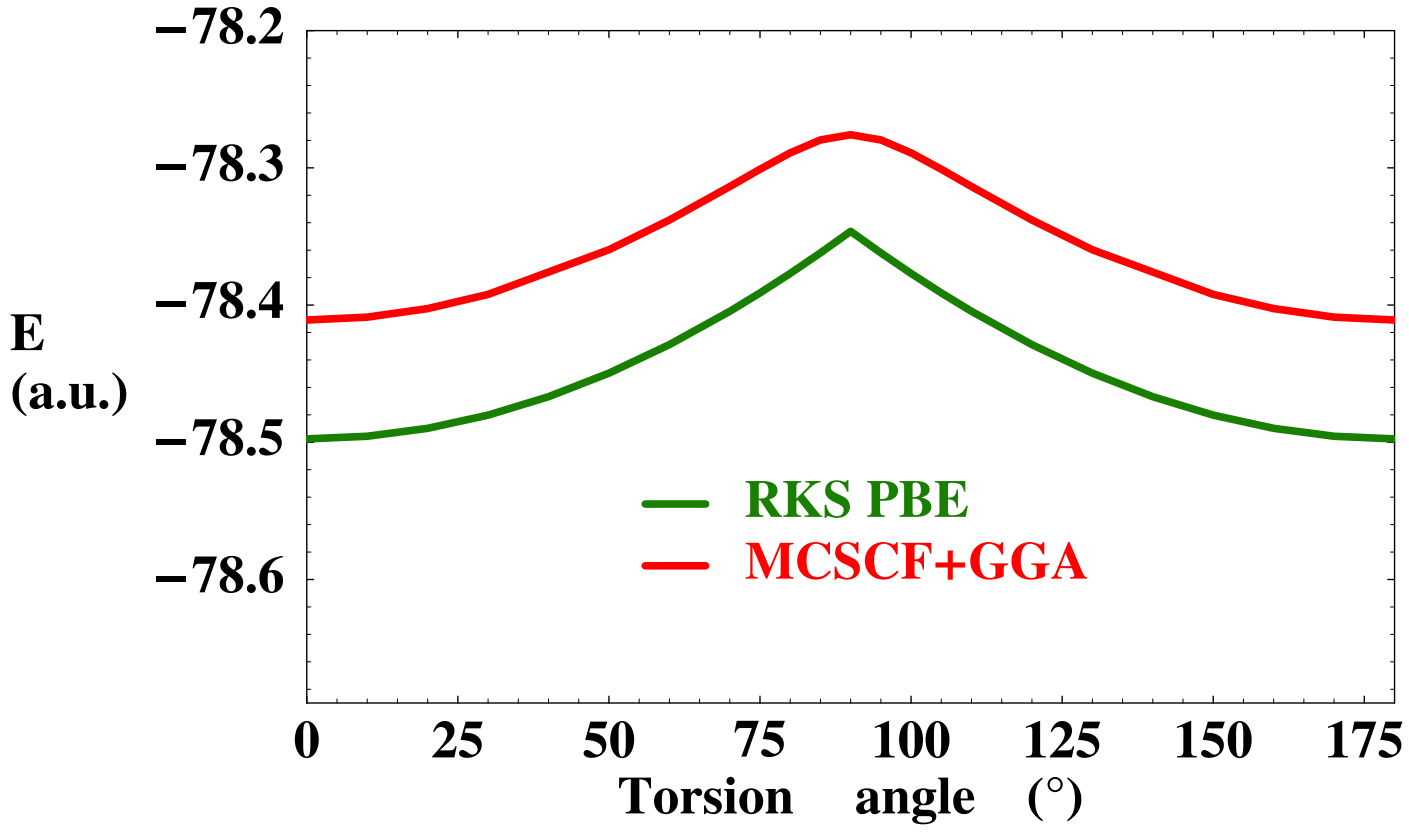

	Exp.	RKS PBE	**MCSCF+GGA**
barrier (kcal/mol)	**65.0**	91.3	**79.7**

Conclusions and perspectives

Summary

- **Near-degeneracy $\Longrightarrow$ RKS DFT** with usual functionals **inaccurate**
- **Multi-configurational DFT**: MCSCF calculation with a long-range interaction + short-range density functional
- **Short-range LDA and GGA approximations** are more **accurate** than their Coulombic analogues
- Some energy calculations on simple atomic and molecular systems: **MCSCF+GGA improves on MCSCF and RKS GGA**

For references, see **www.lct.jussieu.fr/toulouse/**

Conclusions and perspectives

On-going work on MCSCF+DFT

- Improve treatment of open-shell systems
- Exact short-range exchange + very accurate short-range correlation via pair density

On-going related works in collaboration

- MCSCF+DFT: linear response theory, relativistic effects (H. J. Aa. Jensen, Odense, Denmark)
- Coupled-Cluster+DFT (H. Stoll, Stuttgart, Germany)
- MP2+DFT, RPA+DFT for van der Waals (J. G. Ángyán, Nancy, France)

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