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ABSTRACT: In electronic structure calculations using Density Functional Theory (DFT) within the Kohn-Sham (KS) scheme, near-degeneracy correlation effects are generally not properly described by the current approximate energy functionals. In fact, whereas the KS scheme is based on a non-interacting reference system having a single determinant as wave-function, near-degeneracy requires the explicit consideration of several determinants. This can be achieved by introducing long-range electron-electron interactions into the reference system. The multi-determinantal reference wave-function obtained in this way is then combined with a density functional approximation for the remaining short-range correlation effects. Compared to previous studies, we propose in this work a more efficient separation of long-range and short-range interactions improving the accuracy of the method.

Introduction

Electronic correlation is generally treated by:

DFT

- based on the Kohn-Sham (KS) fictitious non-interacting system
- no systematic improvement
- near-degeneracy is not explicitly treated
- local correlation effects are well treated

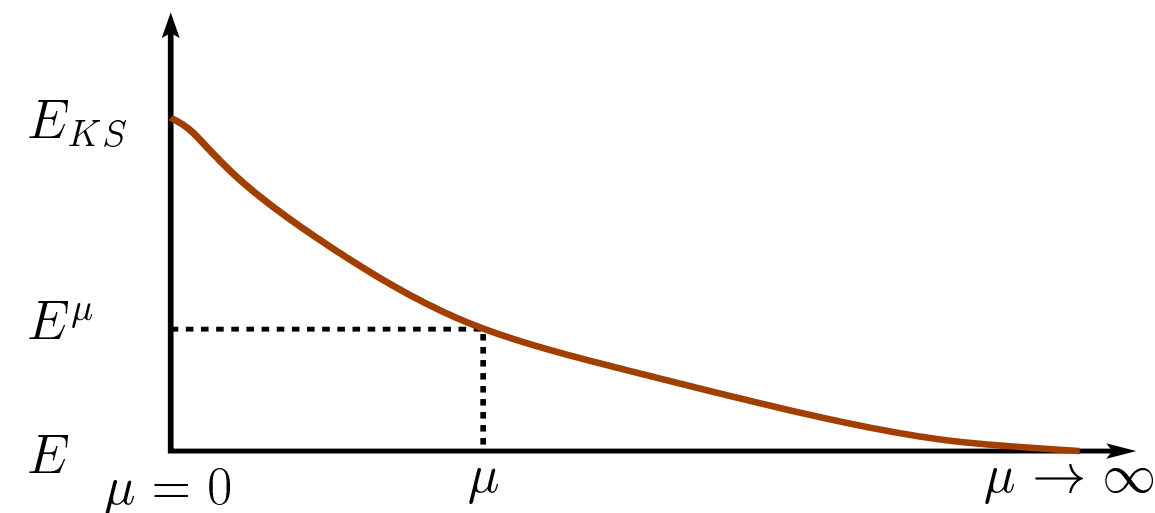
Wave-Function methods

- based directly on the physical system
- systematic improvement
- near-degeneracy is easily treated
- a long expansion of determinants is needed to treat local correlation

These two approaches can be combined via the **adiabatic connection procedure** to take advantage of both of them.

Adiabatic connection

Adiabatic connections [1] connect the KS system to the physical system by **continuously switching on the electron-electron interaction** \hat{V}_{ee}^μ according to a parameter μ varying, e.g., from 0 to ∞ :



At $\mu = 0$, KS non-interacting system:

$$(\hat{T} + \hat{V}_{KS})|\Phi\rangle = E_{KS}|\Phi\rangle \quad (1)$$

At $\mu \rightarrow \infty$, physical interacting system:

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ne})|\Psi\rangle = E|\Psi\rangle \quad (2)$$

At intermediate μ , **partially interacting system**:

$$(\hat{T} + \hat{V}_{ee}^\mu + \hat{V}_{ne})|\Psi^\mu\rangle = E^\mu|\Psi^\mu\rangle \quad (3)$$

where $\hat{V}^\mu = \sum_i v^\mu(\mathbf{r}_i)$ is the local external potential ensuring that the density n remains equal to the physical one.

Generalized Kohn-Sham scheme

The standard Kohn-Sham scheme of DFT consists in treating explicitly only the KS non-interacting system ($\mu = 0$) and adding a functional correction to recover the physical system ($\mu \rightarrow \infty$).

Instead, we can use the partially interacting system at intermediate μ (equation 3) as the reference system.

The ground-state electronic energy of the physical system can indeed be expressed with the ground-state wave-function of the partially interacting system Ψ^μ as

$$E = \langle \Psi^\mu | \hat{T} + \hat{V}_{ee}^\mu + \hat{V}_{ne} | \Psi^\mu \rangle + \bar{F}^\mu[n_{\Psi^\mu}] \quad (4)$$

where $\bar{F}^\mu[n]$ is the required density functional correction incorporating the part of the interaction not included in the reference system.

Whereas the reference wave-function in the standard KS scheme is a single determinant, the reference wave-function Ψ^μ in this generalized scheme is a multi-determinantal wave-function, which can naturally incorporate near-degeneracy correlation effects.

In practice, the Generalized Kohn-Sham scheme consists in solving a fictitious partially interacting system (equation 3) by standard wave-function methods (MCSHF, CI) and then adding a remaining correction through a functional $\bar{F}^\mu[n]$ (equation 4).

The method constitutes a rigorous intermediate between the standard one-determinant DFT ($\mu = 0$)

$$E = \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + \bar{F}^{\mu=0}[n_\Phi] \quad (5)$$

and the traditional multi-determinantal wave-function formulation of the electronic problem ($\mu \rightarrow \infty$)

$$E = \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} | \Psi \rangle \quad (6)$$

The mixing of both approaches is controlled with the parameter μ which sets the proportion of electron-electron interaction treated by wave-function methods and by density functional approximations.

Long-range/short-range separation

The modified electron-electron interaction $\hat{V}_{ee}^\mu = \sum_{i<j} v_{ee}^\mu(r_{ij})$ is chosen so as to incorporate the long-range part of the interaction.

Therefore, the wave-function Ψ^μ of the effective system (3), incorporating only long-range interactions, is expected to be well approximated by an expansion into a few determinants corresponding to near-degeneracy effects, whereas local approximations for the functional $\bar{F}^\mu[n]$, describing only the remaining short-range correlation, are expected to be accurate.

Two forms of long-range interaction $v_{ee}^\mu(r)$ have been tested:

erf: $\frac{\text{erf}(\mu r)}{r}$ [2, 3]

erfgau: $\frac{\text{erf}(\mu r)}{r} - \frac{2\tilde{\mu}}{\sqrt{\pi}} e^{-\frac{1}{3}\tilde{\mu}^2 r^2}$

with $\tilde{\mu} \approx 3\mu$ so that μ corresponds to an inverse cut-off radius in both cases.

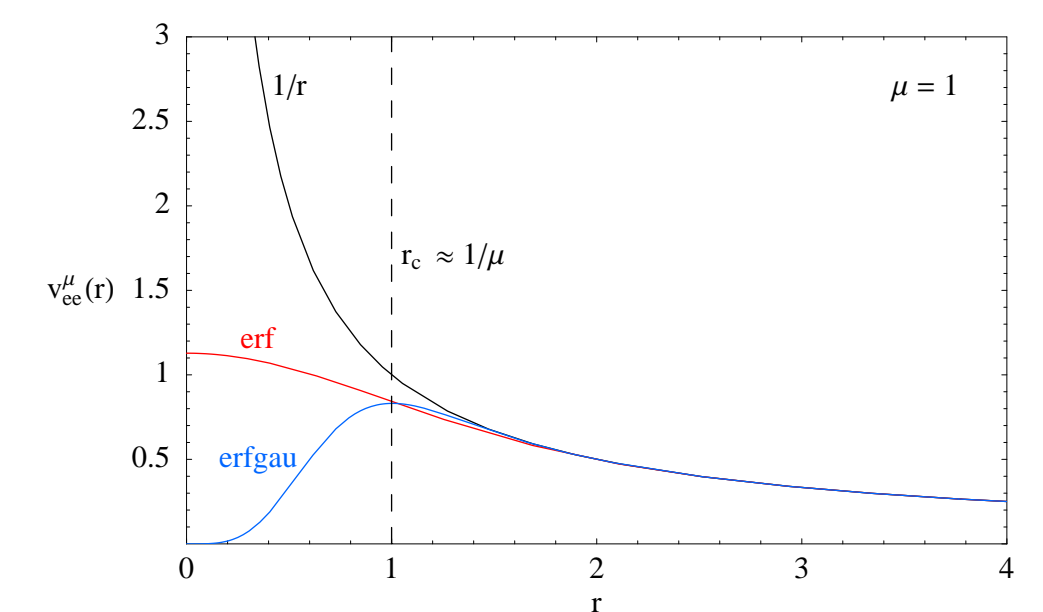


Figure 1: Coulomb and long-range interactions.

Short-range interactions are better removed in **erfgau**.

Short-range functional

The short-range functional $\bar{F}^\mu[n]$ is decomposed as

$$\bar{F}^\mu[n] = \bar{U}^\mu[n] + \bar{E}_{xc}^\mu[n] \quad (7)$$

where $\bar{U}^\mu[n]$ is the short-range Hartree energy and $\bar{E}_{xc}^\mu[n]$ is the remaining unknown short-range exchange-correlation functional.

The **Local Density Approximation** (LDA) is used for $\bar{E}_{xc}^\mu[n]$

$$\bar{E}_{xc}^\mu[n] = \int n(\mathbf{r}) \bar{\varepsilon}_{xc}^\mu(n(\mathbf{r})) d\mathbf{r} \quad (8)$$

where $\bar{\varepsilon}_{xc}^\mu(n)$ are taken from the uniform electron gas with modified interaction.

While the exchange energy density $\bar{\varepsilon}_x^\mu(n)$ can be calculated analytically, the correlation energy density $\bar{\varepsilon}_c^\mu(n)$ is obtained from a fit of Coupled-Cluster RPA [4] or FHNC [5] data, incorporating theoretical conditions.

Accurate reference calculations

For several atoms, the potentials $v^\mu(\mathbf{r})$ keeping the density constant along adiabatic connections, appearing in the definition of the partially interacting systems (equation 3), are accurately computed for the **erf** [6] and **erfgau** interactions by a maximization procedure.

It is then possible to compute accurate short-range exchange and correlation energies, e.g. for He and Be, along the adiabatic connections and assess the accuracy of the LDA approximation.

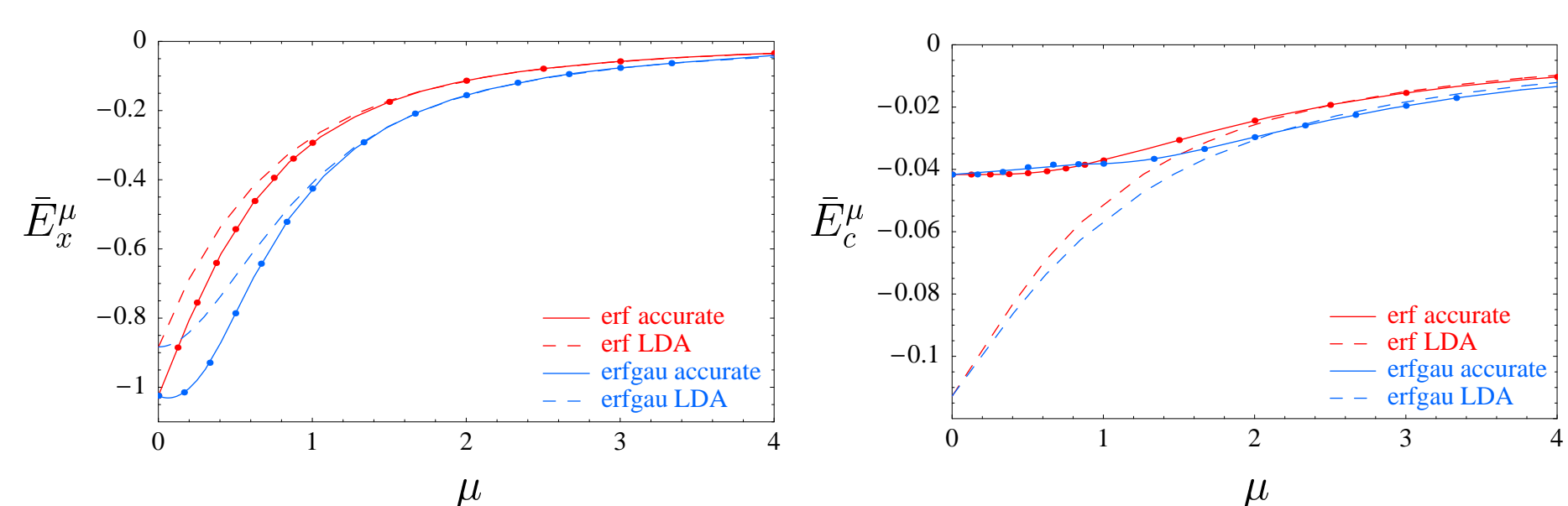


Figure 2: Exchange energy of He along adiabatic connections.

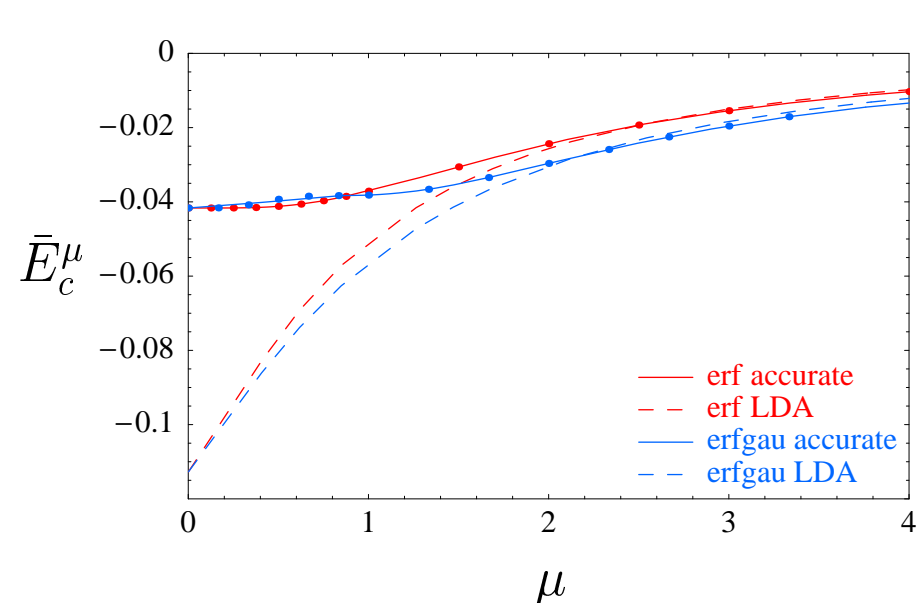


Figure 3: Correlation energy of He along adiabatic connections.

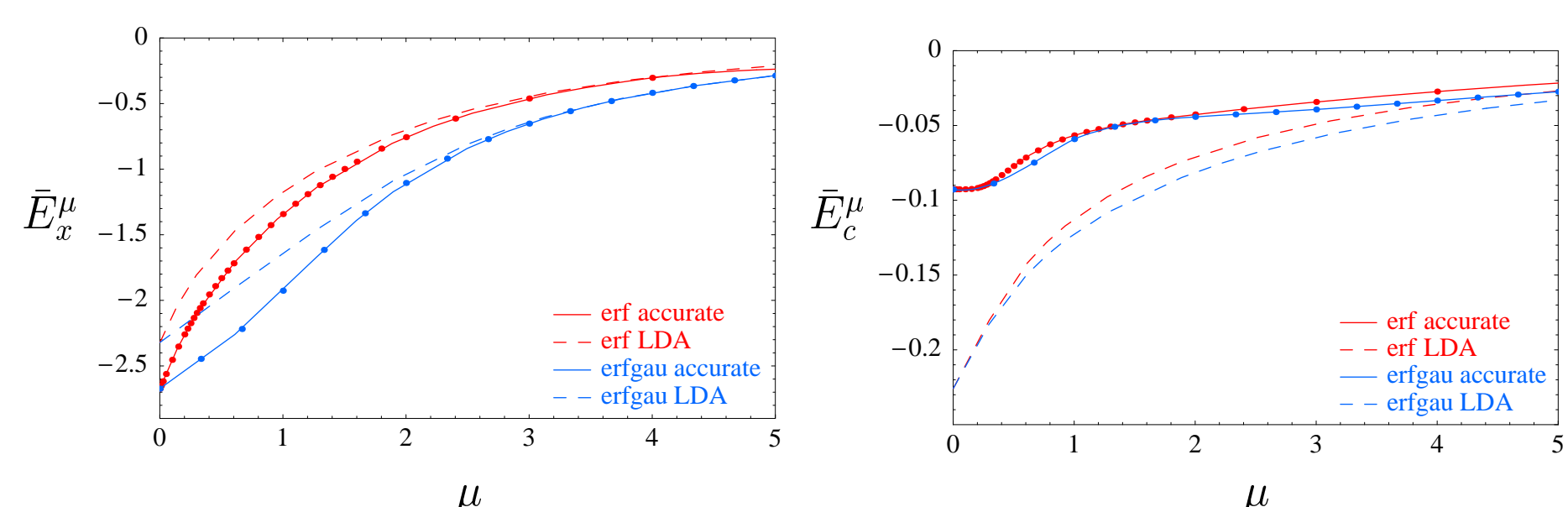


Figure 4: Exchange energy of Be along adiabatic connections.

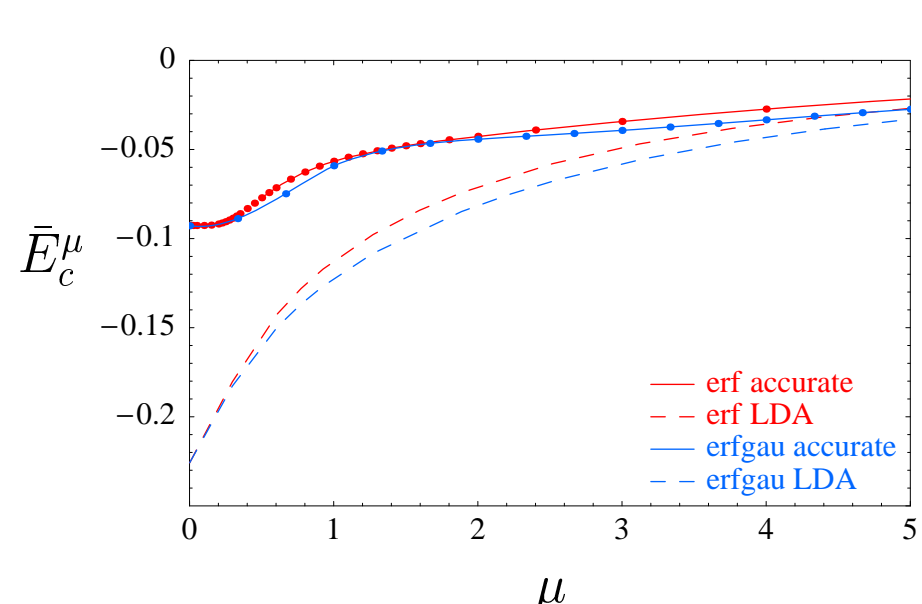


Figure 5: Correlation energy of Be along adiabatic connections.

For both exchange and correlation:

- The LDA approximation becomes more accurate on increasing of μ .
- Compared to **erf**, the LDA functional for **erfgau** reaches the accurate curve at a higher energy (in absolute value).

Applications

Two-electron integrals with modified interactions as well as corresponding LDA short-range functionals have been implemented into Molpro 2002 [7].

The method is applied on He and Be where the effective Hamiltonian (3) is solved with the CI program of Molpro for increasingly configuration spaces.

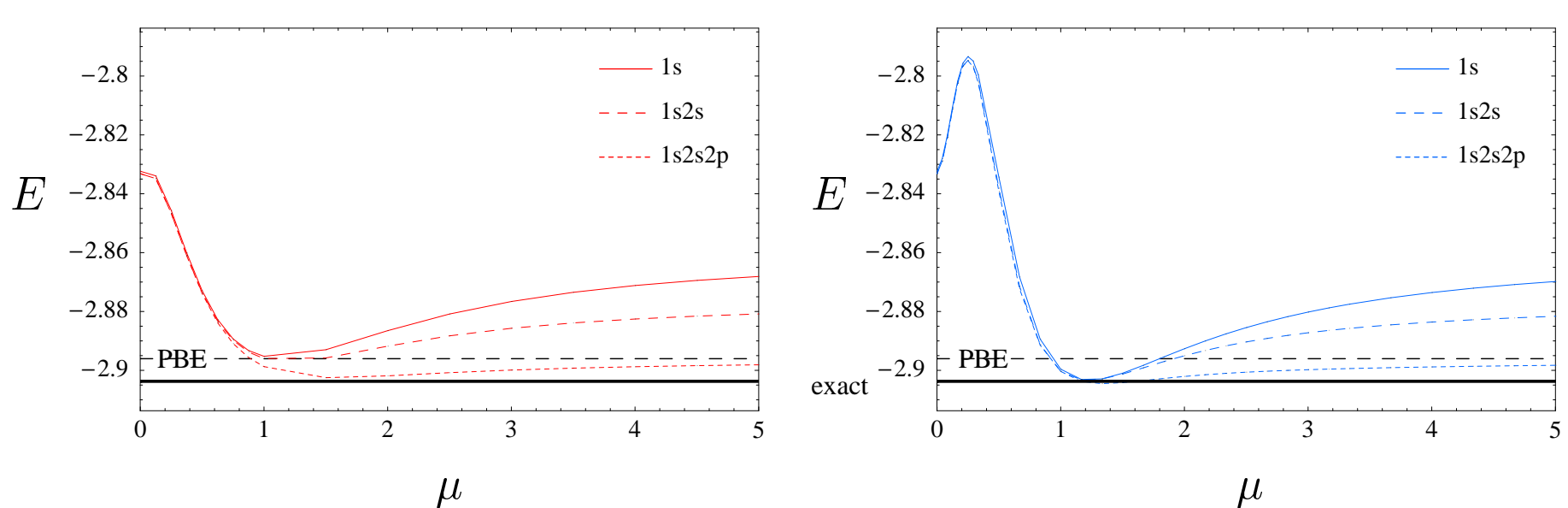


Figure 6: Total CI+DFT energy of He with erf interaction.

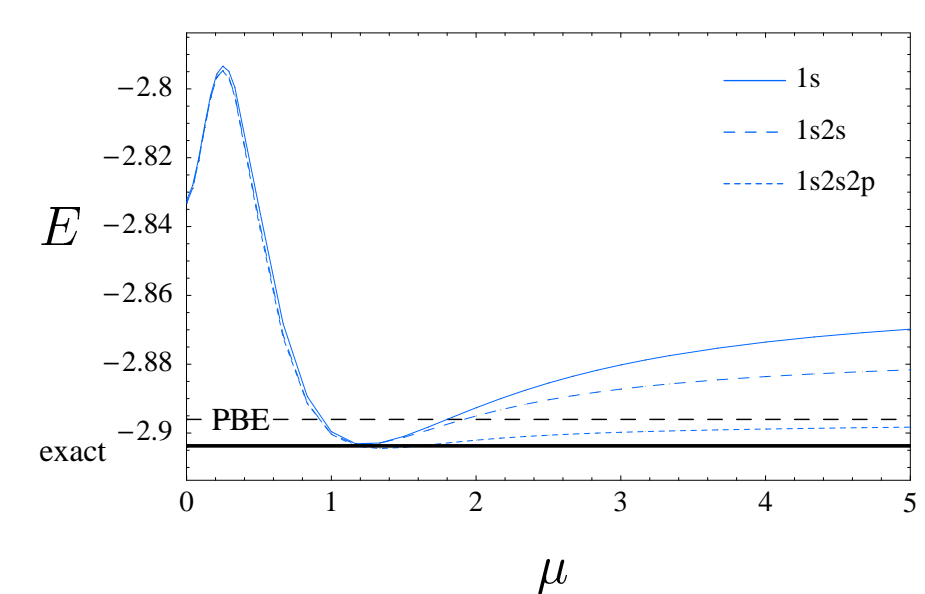


Figure 7: Total CI+DFT energy of He with erfgau interaction.

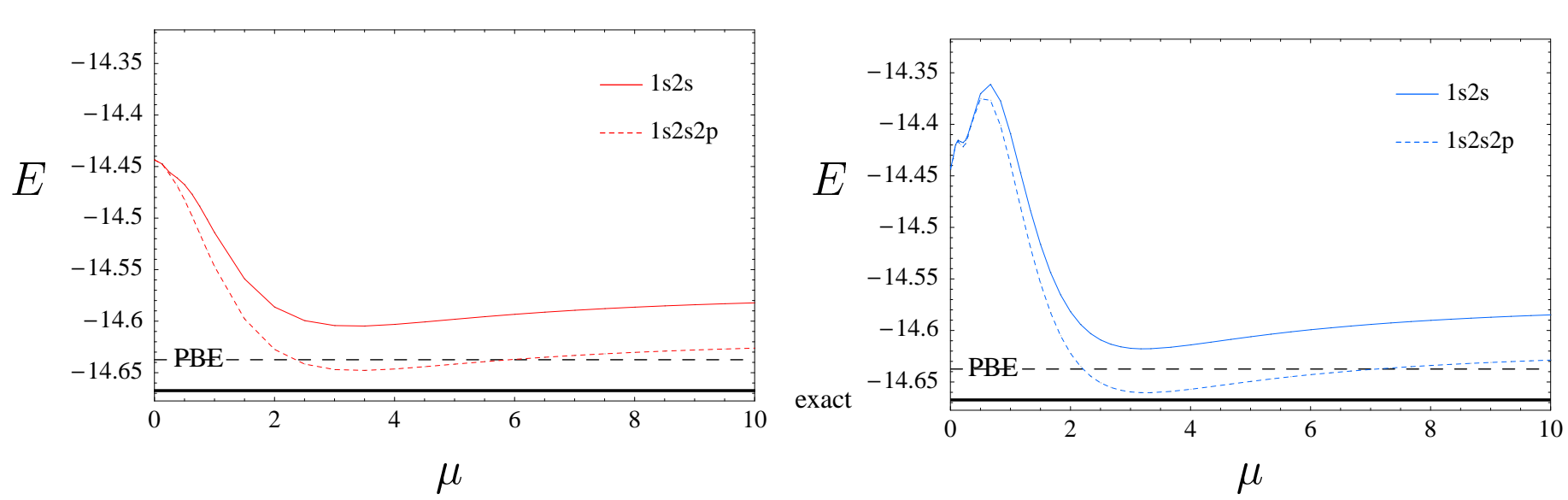


Figure 8: Total CI+DFT energy of Be with erf interaction.

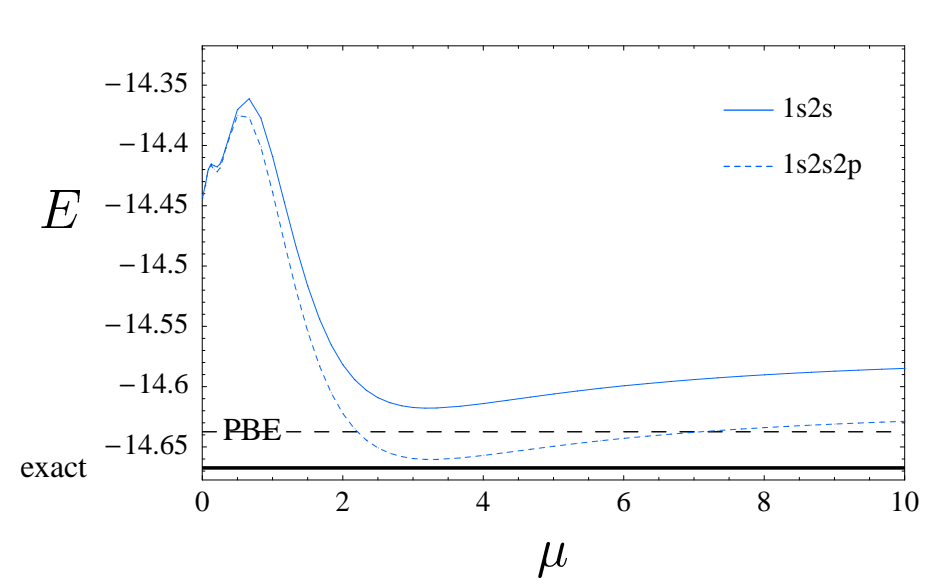


Figure 9: Total CI+DFT energy of Be with erfgau interaction.

- There is an optimal μ for which the method is more accurate than standard DFT ($\mu = 0$) and wave-function treatments ($\mu \rightarrow \infty$).
- Inclusion of more than one configuration in the reference wave-function is important for Be where near-degeneracy effects are strong.
- At the optimal μ , **erfgau** is more accurate than **erf**.

Conclusions and perspectives

- We have proposed a method which rigorously combines a multi-determinant wave-function incorporating near-degeneracy effects with a density functional for the remaining local correlation effects.
- This combination is based on the separation of correlation effects into long-range and short-range interactions.
- In practice, the parameter μ controls the mixing between wave-function and DFT.
- At optimal μ , the method takes advantage of both approaches and leads to accurate ground-state total atomic energies.
- Compared to **erf**, the long-range/short-range separation is better realized with **erfgau** and leads to better total energies at the optimal μ , validating the strategy of long-range/short-range separation.
- The short-range functionals can be improved (inclusion of gradients of the density,...)
- Other forms of modified electron-electron interactions can be tested.

References

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