Are density functional approximations following density functional theory?

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Outline

- Preliminaries
  Setting the frame
- Density functional approximations (DFAs)
  Reminding some basic notions
- Constructing an alternative

Preliminaries

The question asked

Can density functional quality results be obtained differently?

The context

- *Assumed reality*: electronic Schrödinger equation

$$H\Psi = E\Psi$$

$$H = T + V + W$$

  - T: kinetic energy
  - $V = \sum_i^N v(\mathbf{r}_i)$: one-particle (electron-nuclei, "external") potential
  - $W = \sum_{i<j} w(|\mathbf{r}_i - \mathbf{r}_j|)$: two particle (Coulomb) potential

The context

- *Assumed reality*: electronic Schrödinger equation

$$H\Psi = E\Psi$$

- *Model*: $E(\mu)$, e.g., Schrödinger equation

$$H(\mu)\Psi(\mu) = E(\mu)\Psi(\mu)$$

Conventions

- μ characterizes model,
- "Cost" increases with μ
- $w(r, \mu = 0) = 0$
- $w(r, \mu = \infty) = 1/|\mathbf{r}_i - \mathbf{r}_j|$.

Correction needed

$$E = E(\mu) + \bar{E}(\mu)$$

Models

Models should be "cheap".

Mean-field, e.g., Kohn-Sham model

- $V \to V_{\text{mean-field}}$
- $W \to 0$

Alternative

- V unchanged

  (for now)
- $W \to W(\mu)$

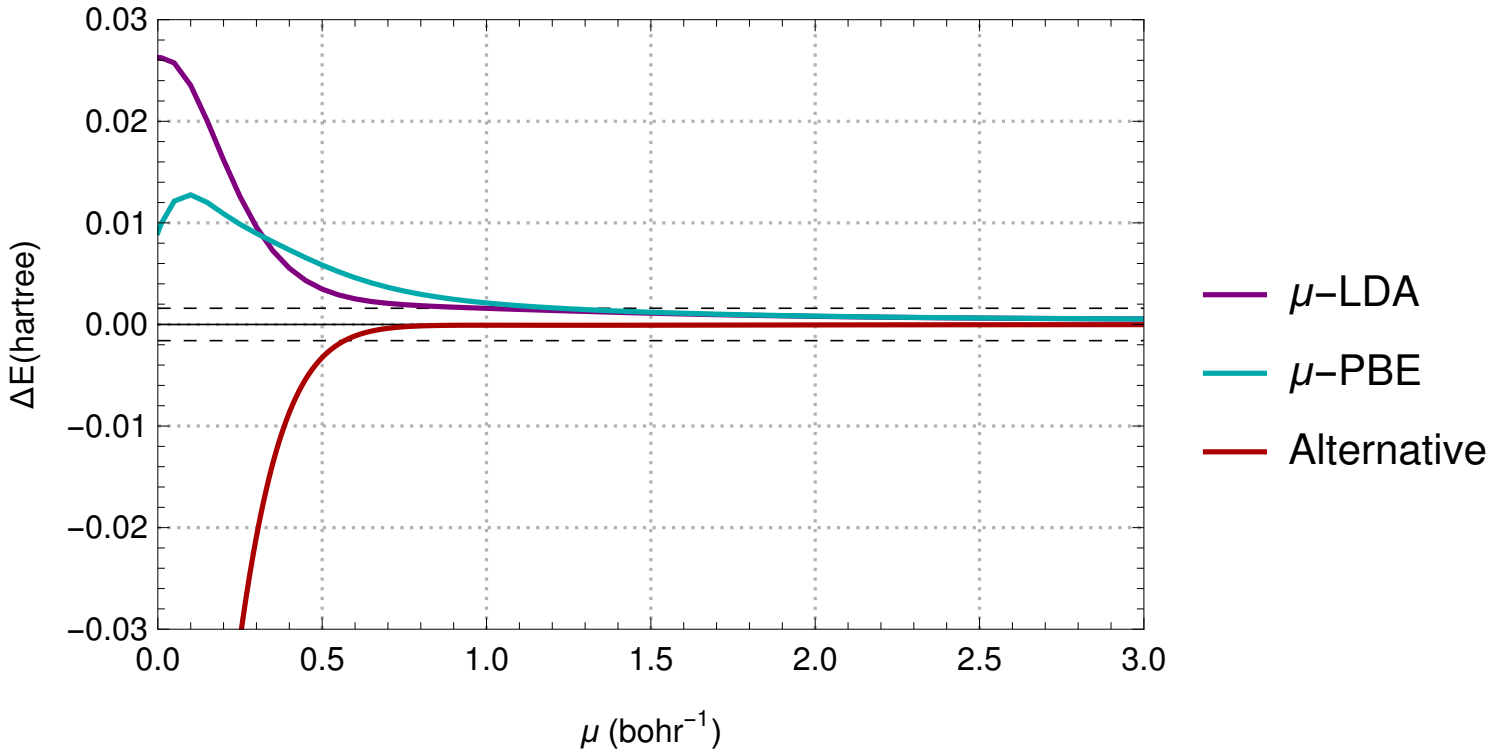
  More expensive; keep μ small.

Corrections

Correction should be "cheap", too.

- Computed from the electron density,
  DFAs: density functional approximations, based upon density functional theory (DFT)
- Based on known exact properties of the wave function.
  Alternative $\neq$ CI, CC, ..., but rather following ideas present in the construction of DFAs.
  Different from DFAs, because
  - Hohenberg-Kohn theorem not used,
  - no restriction to the ground state
  - ...

Preliminaries. Summary



- μ: different models (cost increases with μ)
- ΔE: errors of the models
- μ-LDA, μ-PBE: density functional approximations
- Alternative: not using a density functional
- Chemical accuracy between dashed lines (± 1 kcal/mol).

Density functional approximations

DFT and DFAs

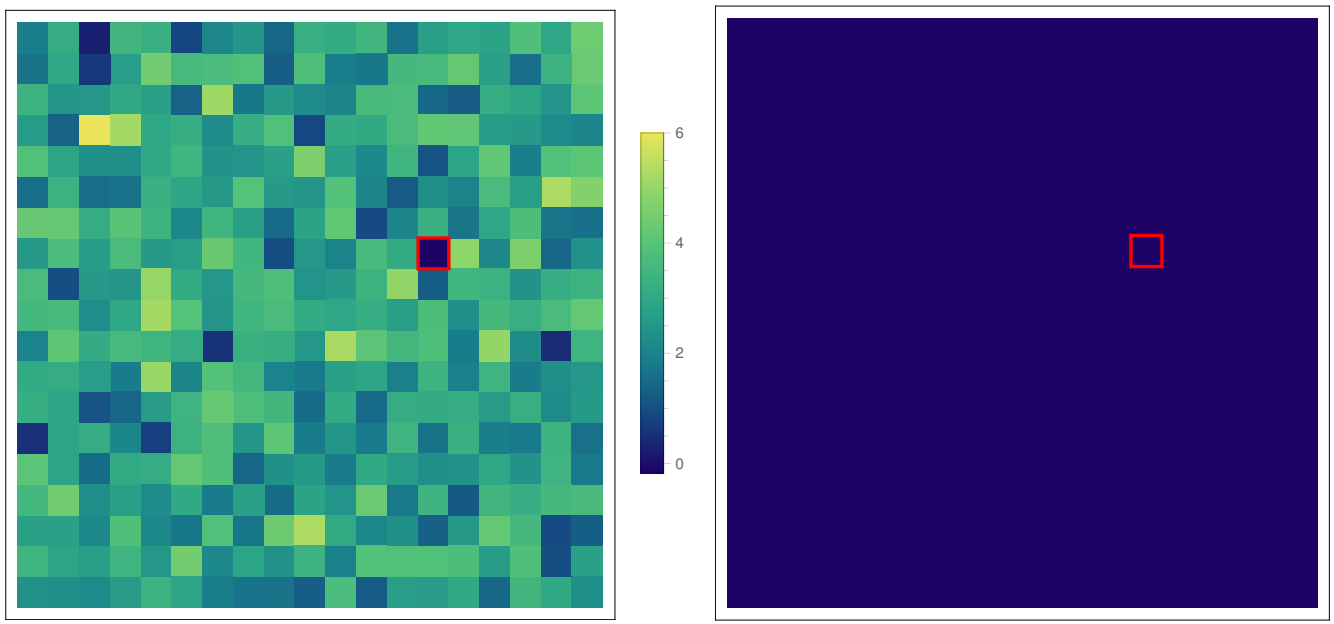
- There is Density Functional Theory (DFT)
  Hohenberg-Kohn theorem, scaling properties of density functionals, ...
- There are Density Functional Approximations (DFAs)
  Cheap expressions for calculating $\bar{E}$ using the density

Local density approximation (LDA)

Transfer from the uniform electron gas

Actual density *

Assumed density * (LDA)



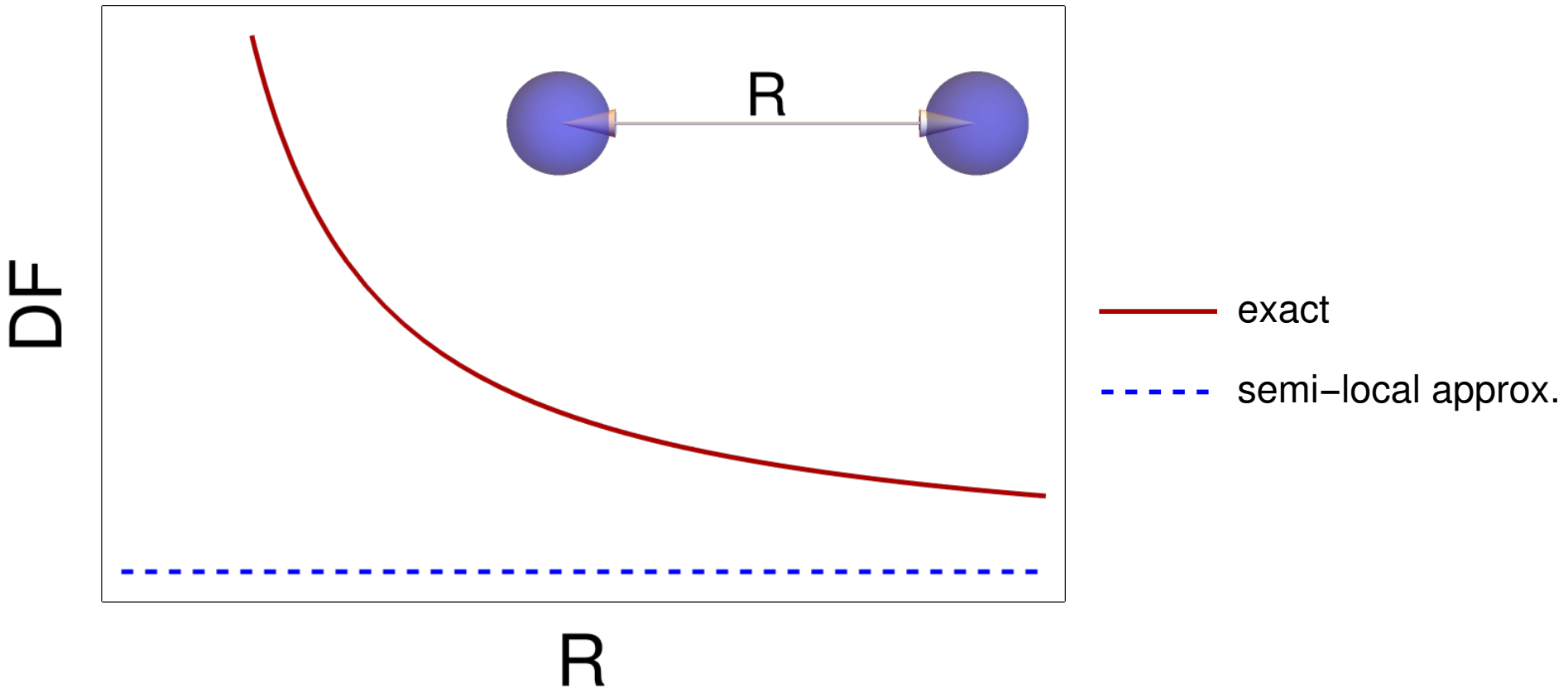
*Density: average number of electrons per volume element

Limitations of the density functional approach?

- Using not the density, $\rho(\mathbf{r})$, but the partial densities $\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})$.
  Why?
- Hohenberg-Kohn theorem: for the ground state.
  What about the excited states? Time-dependent DFT? What DFAs? For ground state of different symmetries? How about the dependence on the external potential?
- (Semi-)local approximations.
  How far can they go?

How far can semi-local approximations go?

Example of long-range interaction between spatially separated charge distributions



No problem for short-range interactions

Constructing a convenient model: range separation

$$w(r) = 1/r = w(r,\mu) + \bar{w}(r,\mu)$$

- $w(r,\mu)$: long-ranged, appears within the model
- $\bar{w}(r,\mu)$: short-ranged, treated by correction

Price to pay

Long-range correlation explicit (multi-determinant wave function)

Choice of $w(r,\mu)$ and $\bar{w}(r,\mu)$: range separation

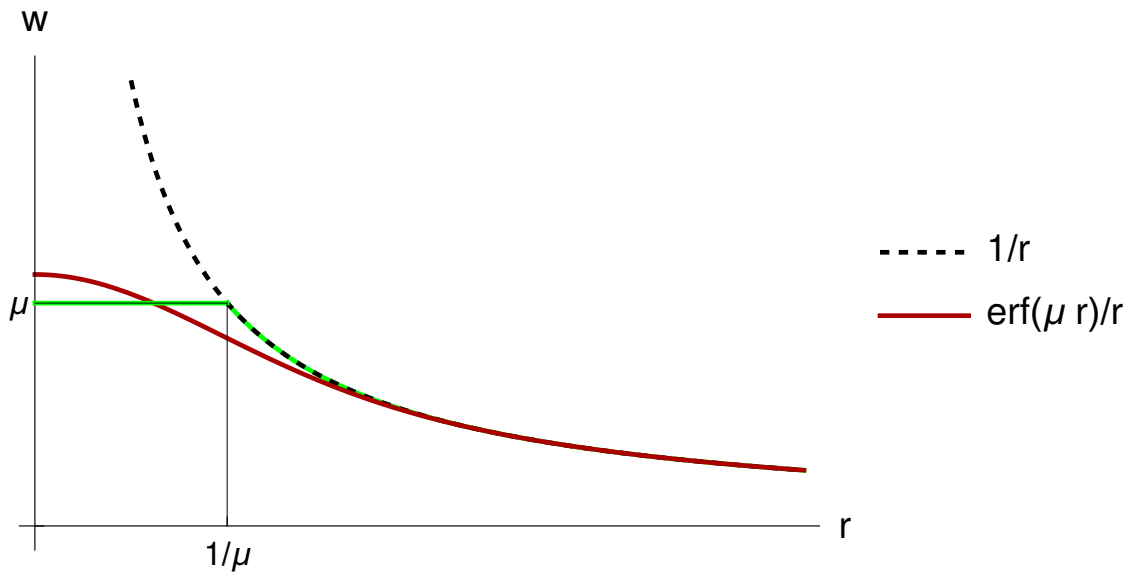
$$\frac{1}{r} = \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{w(r,\mu)} + \underbrace{\frac{\mathrm{erfc}(\mu r)}{r}}_{\bar{w}(r,\mu)}$$

[59]

Limiting cases for model

- non-interacting system: $\mu = 0$
  $\mathrm{erf}(0) = 0$
- physical system: $\mu = \infty$
  $\mathrm{erf}(\infty) = 1$

$w(r,\mu) = \mathrm{erf}(\mu r)/r$



- μ: model chosen,
- $w(r,\mu)$: long ranged,
- $\bar{w}(r,\mu) = 1/r, -w(r,\mu)$: short ranged,
- $w(r,\mu=\infty) = 1/r$ (Coulomb, physical system),
- $w(r,\mu=0) = 0$: (non-interacting model).

System: harmonium (erfonium)

Karwowski, AS [208]

- $N = 2$ electrons
- Spherical symmetry
- $v(r) = \frac{1}{2}\omega^2 r^2$

  If not otherwise specififed, $\omega = 1/2$ a.u.

Separability of variables

$w(r, \mu)$ shows up only in a 1D Schrödinger equation

$$\left[-\left(\partial_r^2 + \frac{2}{r}\partial_r \right) + \frac{\ell(\ell+1)}{r^2} + \frac{1}{4}\omega^2 r^2 + w(r,\mu) \right] \psi(r,\mu) = E(\mu)\psi(r,\mu)$$

$E(\mu), \psi(\mu)$ also depend on quantum numbers n, ℓ, m.

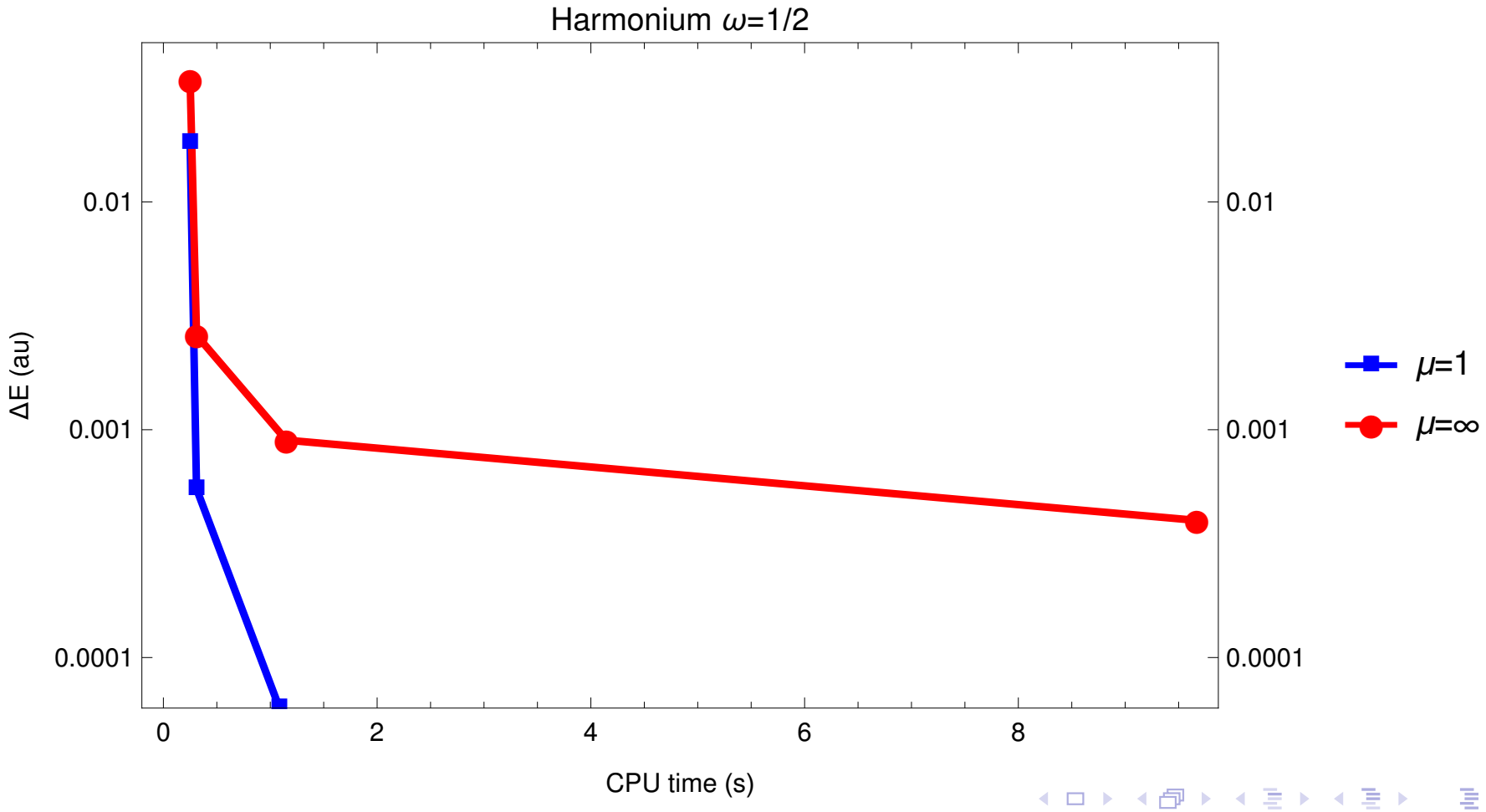
Equation easy to solve numerically to desired accuracy – approximations can be checked reliably

Is the model (small μ) cheaper?

Example: $\omega = 1/2$, $\mu = 1$ vs. $\mu = \infty$ (exact).

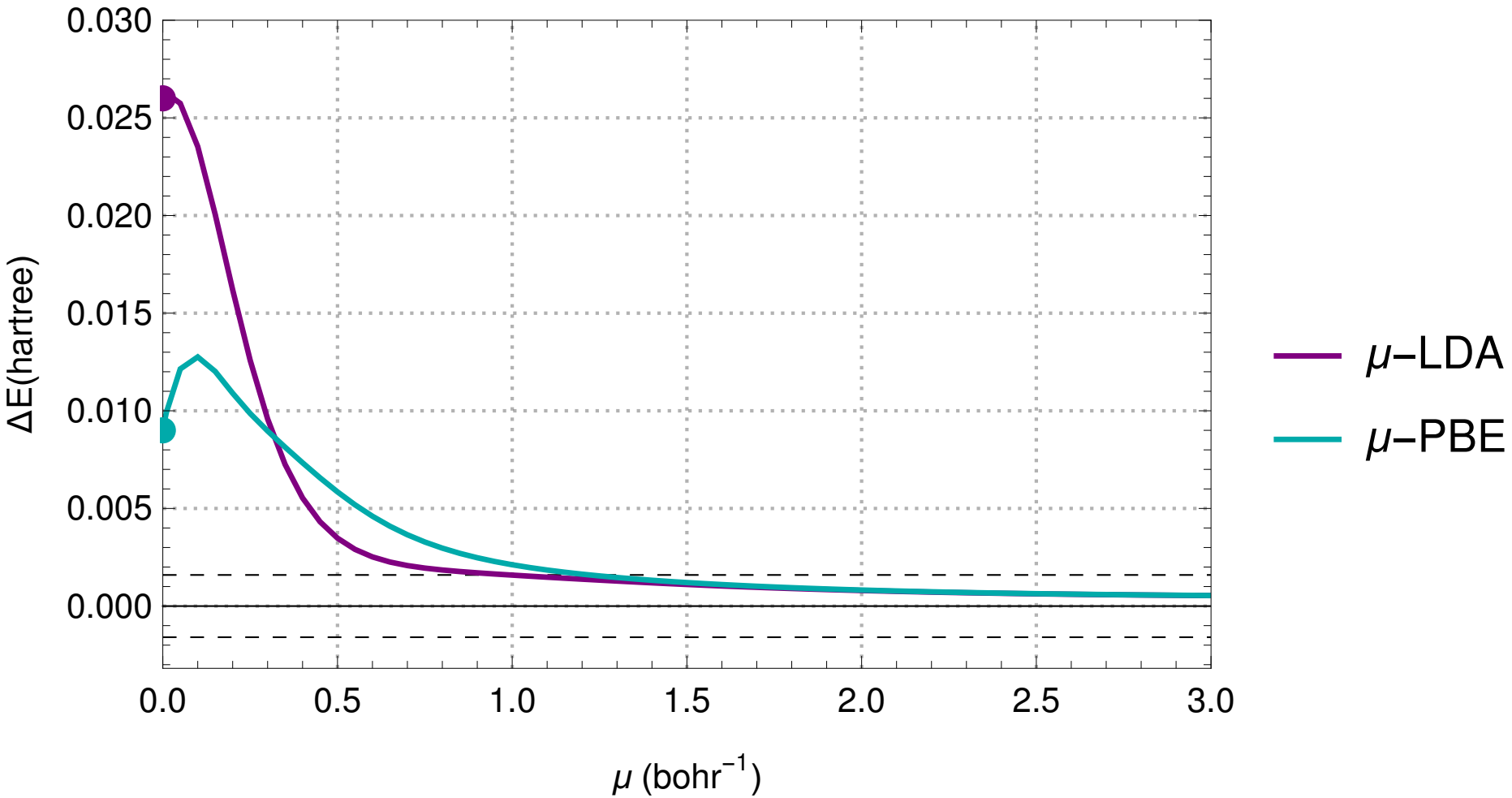
AS [206]

Convergence w.r.t. basis set size: maximal $L = 0, 1, 2, \ldots$



DFAs for harmonium (erfonium)

AS[192]



DFAs. Summary

- DFAs work well for larger μ.
- How to improve for $\mu \to 0$?

Alternatives for $\bar{E}(\mu)$

Basic trick: basis set expansion

AS[150]

$$\bar{E}(\mu) \approx \sum_{m=1}^{M} c_m \chi_m(\mu)$$

Important issues

- How to choose the basis functions?
- How to determine the unknowns, E, c_m?
- How to reduce the number of models?
- How to use only information from "cheap" models (small μ)?

How to choose the basis functions?

AS[150]; Polack, Maday, AS [205]; Karwowski, AS [206], ...

- Decay of $\bar{E}(\mu)$;
  e.g., $\propto \mu^{-k}$.
- Short-range behavior of the wave function when it approaches the exact solution (because correction affects contribution from the short-range part)
  e.g., $\langle \Psi(\mu) | \bar{W}(\mu) | \Psi(\mu) \rangle$ needs only short-range part of $\Psi(\mu)^2$.

How to determine the unknowns?

- Information from model system(s):

$$E^{(k)}(\mu_1), E^{(k)}(\mu_2), \ldots \text{ with } k = 0, 1, \ldots .$$

Keyword: Interpolation (Lagrange, Hermite, Taylor series, quadrature, ...)

- Information about the wave function

Generalized coalescence conditions (GCC): Kato cusp condition, ...)

Kato, *Commun. Pure Appl. Math.*, **10**, 151 (1957); Kurokawa, Nakashima, Nakatsuji, *Adv. Quantum Chem.*, **73**, 59 (2016); Karwowski, AS [201], ...

Perturbation theory around the exact solution

Gori-Giorgi, AS[118]

How to reduce the number of models?

All formulas below use information from a single model (first order perturbation theory in the model, $E^{(1)}(\mu)$.

Ab initio corrections

$$E \approx E(\mu) + \alpha(\mu)\langle\Psi(\mu)|\bar{W}(\mu)|\Psi(\mu)\rangle$$

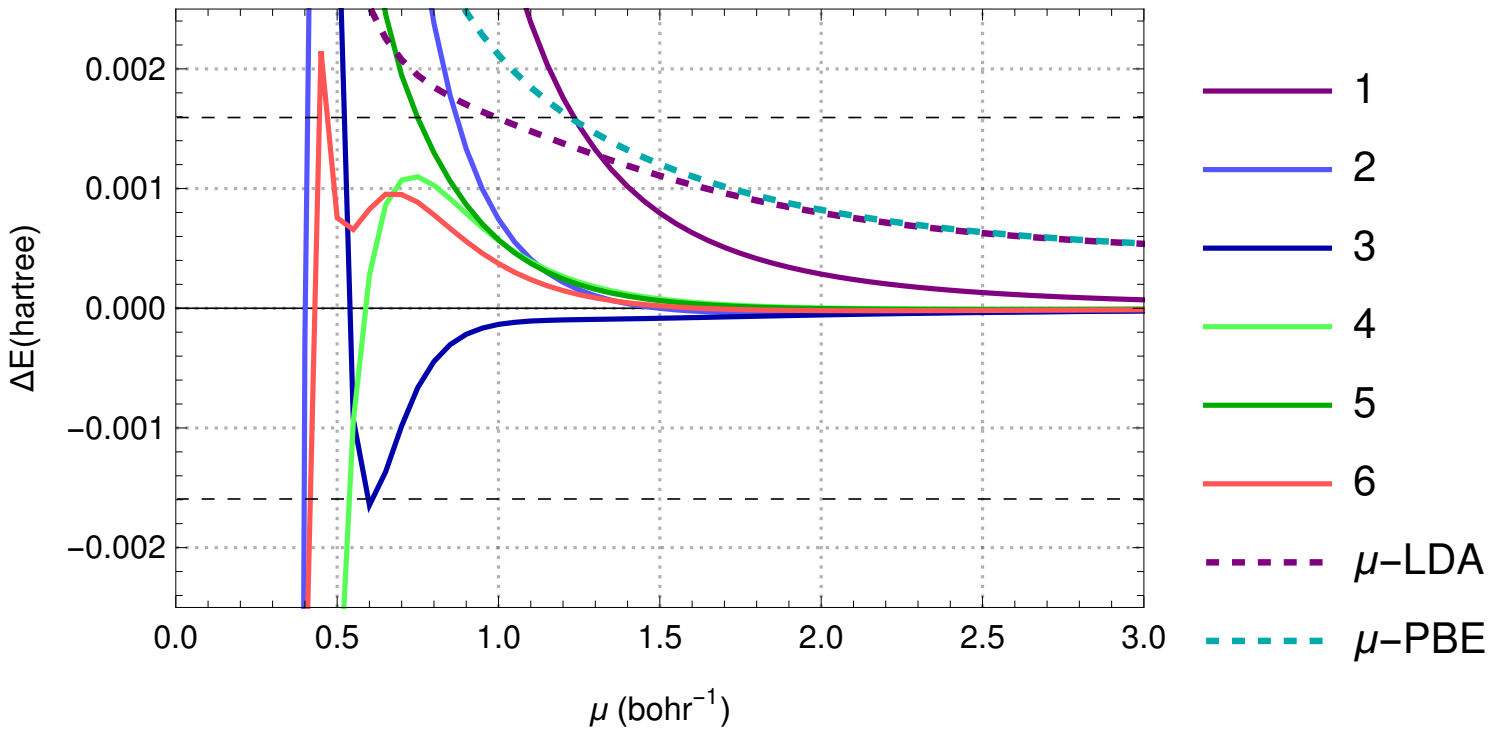
$\alpha(\mu)$ derived from theory: exploiting the GCC to order K

Adiabatic connection for the GCC expansion

$\alpha(\mu)$ exploiting the GCC to order K

Karwowski, AS[201]

$$E \approx E(\mu) + \alpha(\mu)\langle\Psi(\mu)|\bar{W}(\mu)|\Psi(\mu)\rangle$$

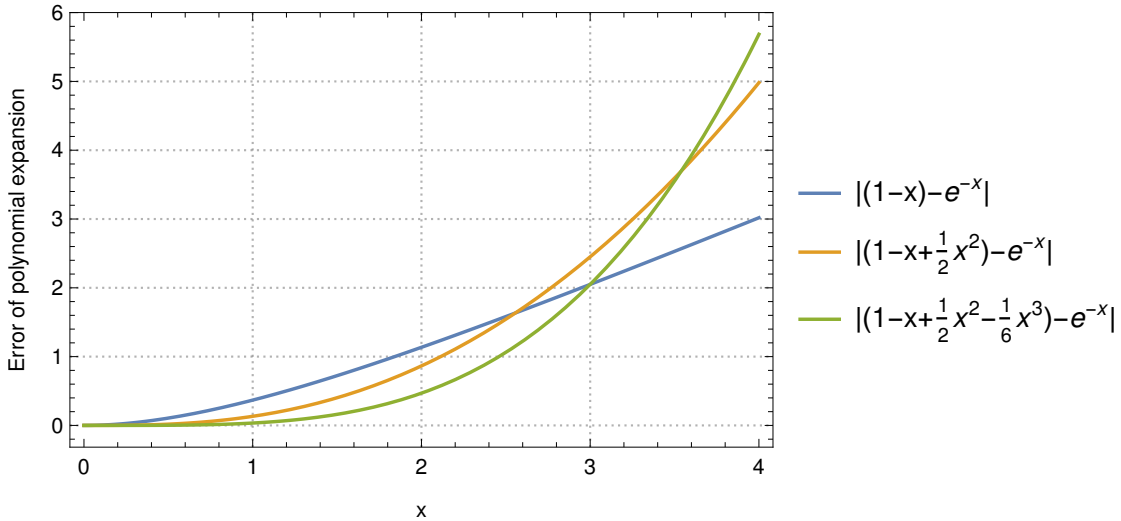


Wall around $\mu \approx 0.5$ bohr^{-1}

Origin of the *wall*?

- $E = E(\mu) + \bar{E}(\mu)$
  - $E(\mu)$: accurate
  - $\bar{E}(\mu)$: estimated
- $\bar{E}(\mu)$ GCC comparable to (even more accurate than) DFAs for large μ
- Small μ remain problematic (as for DFAs)

Analogy: errors in Taylor series



Away from polynomial expansion?

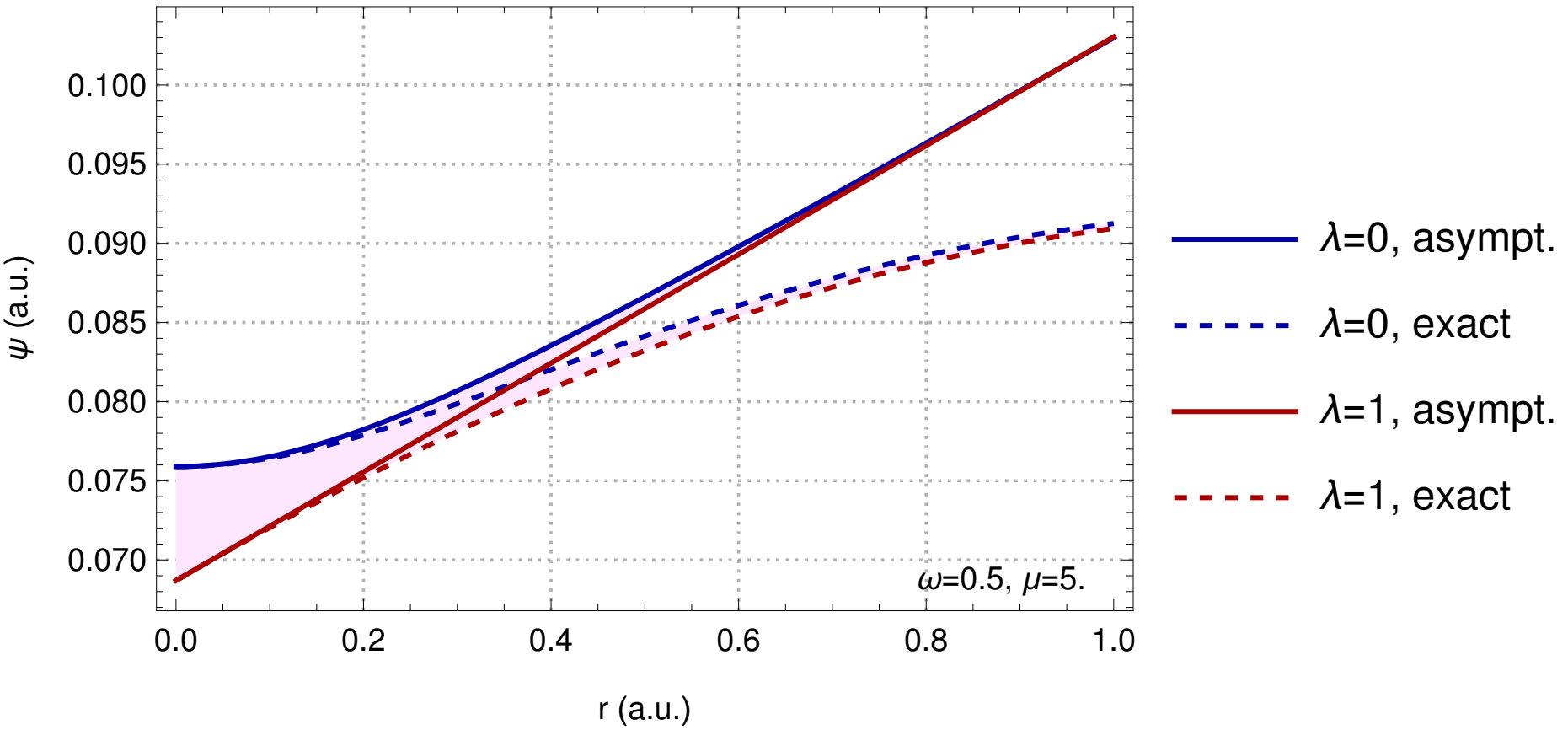
Ab initio corrections

$$E \approx E(\mu) + \beta(\mu)\langle\Psi(\mu)|\bar{W}(\mu)|\Psi(\mu)\rangle$$

$\beta(\mu)$ derived from theory: exploiting the behavior of $\Psi(\mu \to \infty)$

Behavior of Ψ(large μ)

Gori-Giorgi, AS[118]

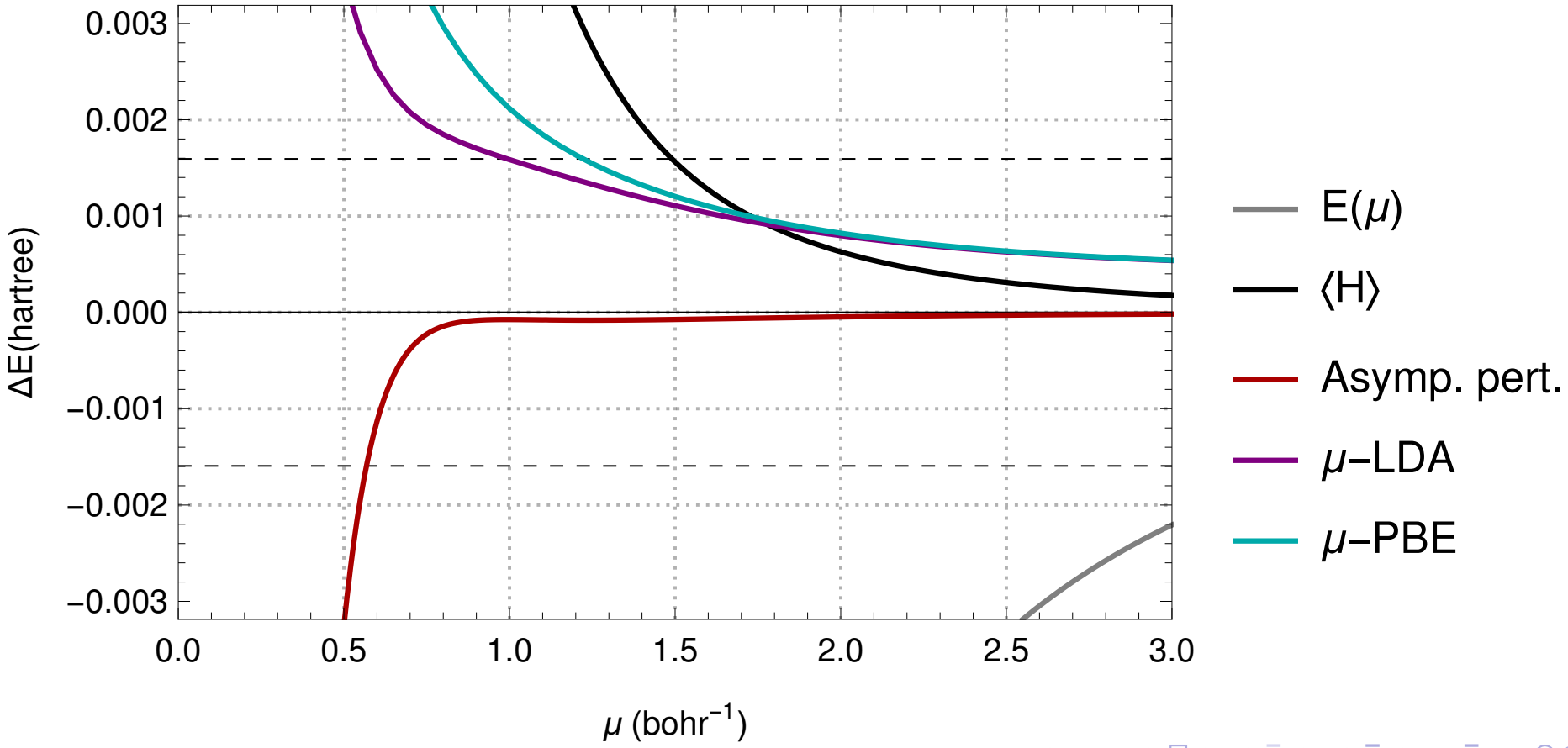


A hidden error compensation

Asymptotic PT1 result

AS[192]

$$E \approx E(\mu) + \beta(\mu)\langle\Psi(\mu)|\bar{W}(\mu)|\Psi(\mu)\rangle$$



Can the model be cheaper?

For now, μ decreased but gong to second order perturbation theory in the model.

Ab initio corrections

Correcting the model with PT2 *

$$E \approx E(\mu) + E^{(1)}(\mu) + \gamma(\mu) E^{(2)}(\mu)$$

$\gamma(\mu)$ derived from theory: exploiting the behavior of $\Psi(\mu \to \infty)$

*Before, only $E^{(1)} = \langle \Psi(\mu) | \bar{W}(\mu) | \Psi(\mu) \rangle$ was used

Correcting the model with PT2

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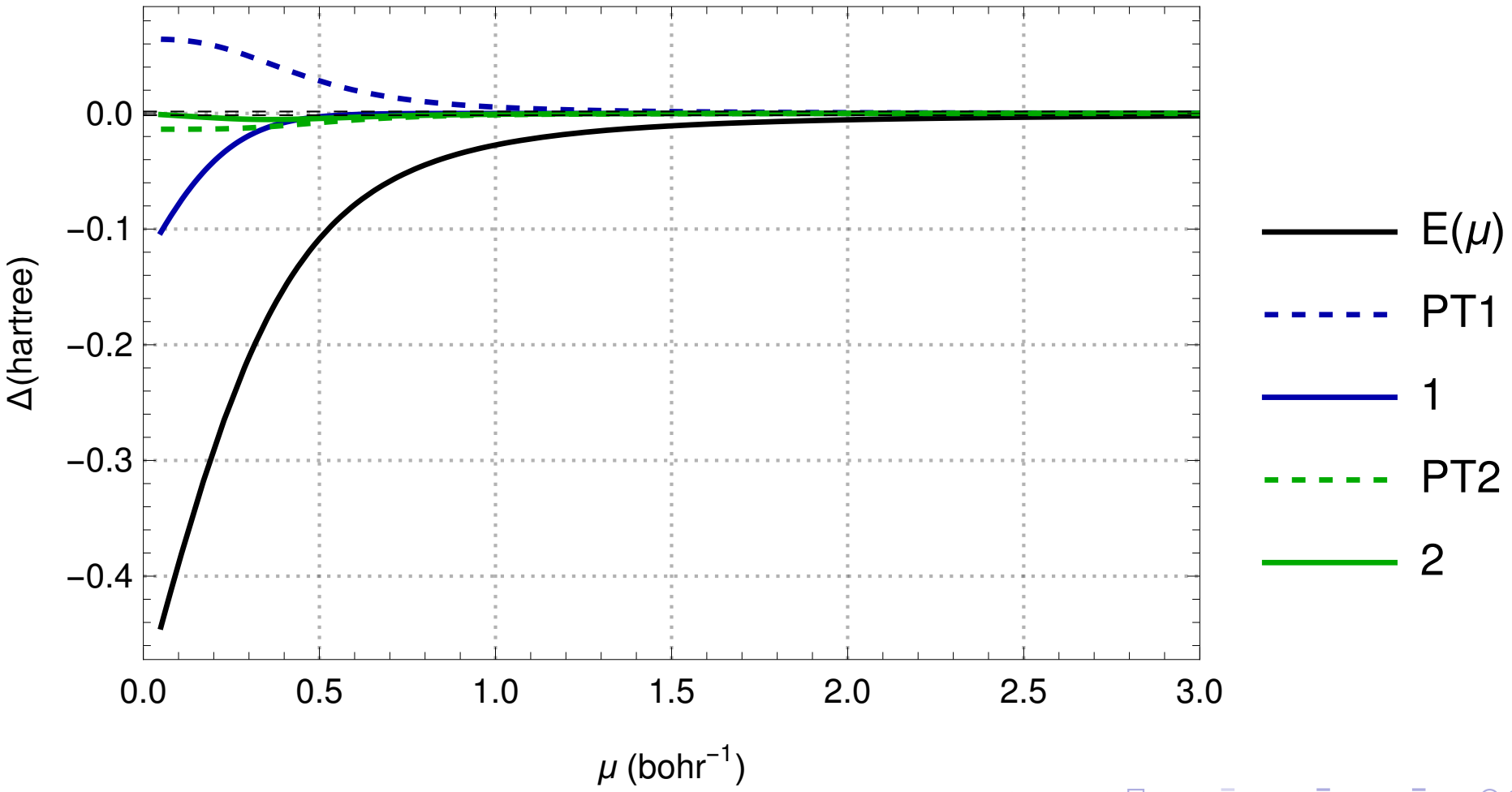

Correcting the model with PT2

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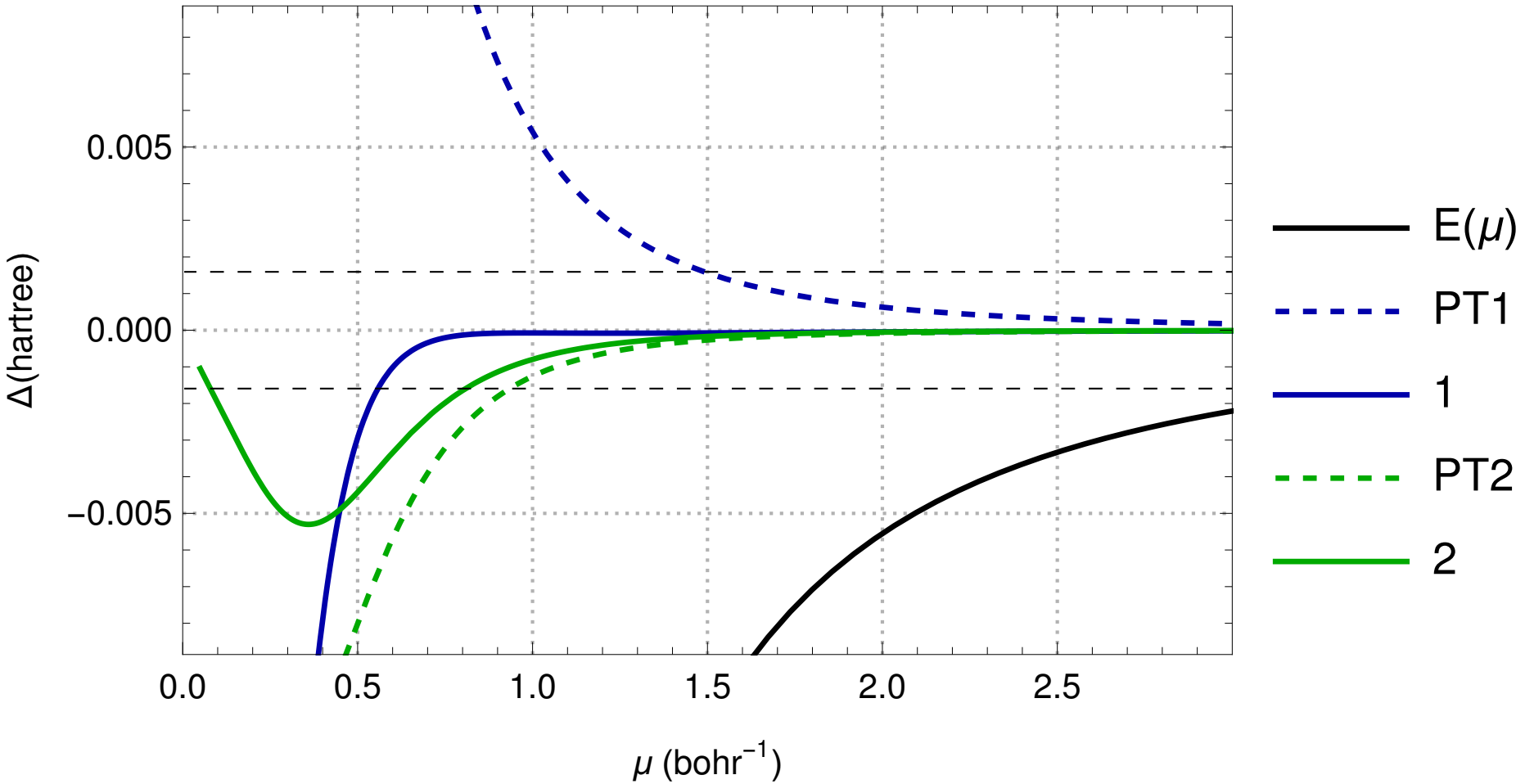

Summary

Summary

- Knowledge of behavior of models with long-range interaction can be effectively corrected by taking advantage of the behavior of the wave function at small distance between electrons and adiabatic connection.
- Up to now corrections to the non-interacting model were not possible with the same accuracy. One can get closer starting from low-order perturbation theory.
- No restriction to ground state.
- Asymptotic error estimates are possible by comparing different orders.