Interpolation and extrapolation methods in quantum chemistry

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Overview

- Explaining the title
- Numerical examples (variants)

Explaining the title

- Interpolation and extrapolation
- in quantum chemistry

Interpolation and extrapolation

Interpolation and extrapolation

$$f(x) \approx \sum_{i=0}^{M_0} c_i \chi_i(x)$$

- $\chi_i(x)$ "appropriately" chosen, often x^i,
- $f^{(n)}(x)$, $n = 0, 1, \ldots$ in some points x_k, $k = 0, 1, \ldots$ determine the c_i.

Nomenclature

- Interpolation if $x \in (\min\{x_0, x_1, \ldots\}, \max\{x_0, x_1, \ldots\})$
- Extrapolation if $x \notin (\min\{x_0, x_1, \ldots\}, \max\{x_0, x_1, \ldots\})$

Subset of basis set expansion methods

Here, E is expanded in a basis, not Ψ.

Variants of interpolation

- Hermite interpolation
- Lagrange interpolation
- Taylor series and perturbation theory
- Quadrature

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  Known : $f(x_0), f'(x_k)$: integrand
- Taylor series and perturbation theory
  Known : $k = 0$

Practical considerations

- How many points x_k are needed?
  If evaluation of $f(x_k)$ expensive, their number should be small.
- How many derivatives are needed?
  Computing $f^{(n)}(x_k)$ may be cheaper than computing $f(x \neq x_k)$; $n = 1$!
- How are the points to be chosen?
  Cost may differ for different x.
- How to choose the basis functions?
  With the correct basis function, $\chi(x) \propto f(x)$, only one point is needed, but providing a small number of good basis functions can be difficult.

In quantum chemistry

In quantum chemistry

$$H\,\Psi = E\,\Psi$$

Notations

- $H = T + V + W$,
- $T = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2$,
- $V = \sum_i^N v(\mathbf{r}_i)$,
- $W = \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

Remarks

$$H(\alpha) = H + \alpha\, A$$

Property (A): $\left.\frac{d\,E(\alpha)}{d\,\alpha}\right|_{\alpha=0}$

Emphasis on E

Beyond quantum chemistry?

- As for eigenvector continuation *, the main idea is to bring in exploit information from related systems.
- In quantum chemistry, electron-electron interaction is the main culprit.
- The challenge is to reduce the computational effort. The path taken here is to consider simplified Hamiltonians.
- To obtain the physically significant results, some formally exact information about the physical system is introduced. †

Not discussed

- Valence Bend
- Non-orthogonal Configuration Interaction

*Frame, He, Ipsen, Lee, Lee, Rrapaj, *PRL* **121**, 032501 (2018)

† "Perturbing the exact solution"

Models

We are interested in some system ("assumed reality", "exact"), but only some models (characterized by numbers μ_i are easily accessible numerically.
Models are supposed to be solved with sufficient accuracy.
Correction to approximate the exact result by extrapolation.

Example: Complete Basis Set extrapolation (CBS)

- Exact: "complete basis set"
- Coulomb potential: in a calculation with the basis set truncated at an angular quantum number $L \gg 0$, the correlation energy error is dominated by a term proportional to $1/L^3$

  Kutzelnigg, Morgan *J. Chem. Phys.* **96**, 4484 (1992)
- $E \approx a + b\,L^{-3}$: a, b obtained from calculations with different L.
- Extension for "well-chosen" basis sets where $x_k = L$ is replaced by another number.

Models in this presentation

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

Notations

- $H(\lambda,\mu) = T + V + W(\mu) + \lambda\bar{W}(\mu)$,
- T, V unchanged (risky?)
- $W = \sum_{i<j}^{N} w(|\mathbf{r}_i - \mathbf{r}_j|, \mu)$,
- $\bar{W} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - w(|\mathbf{r}_i - \mathbf{r}_j|, \mu)$,
- μ defines a model, typically: $w(r, \mu = 0) = 0$, $w(r, \mu = \infty) = 1/r$,
- λ permits connection to exact system, $\lambda = 1$; alternatively through $\mu \to \infty$.
- λ as argument omitted: $\lambda = 0$ (model).
- μ as argument omitted: $\lambda = 1$, or $\mu = \infty$ (exact).

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

Evidently, not physical interaction. Range separation [59]:

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

Limiting cases

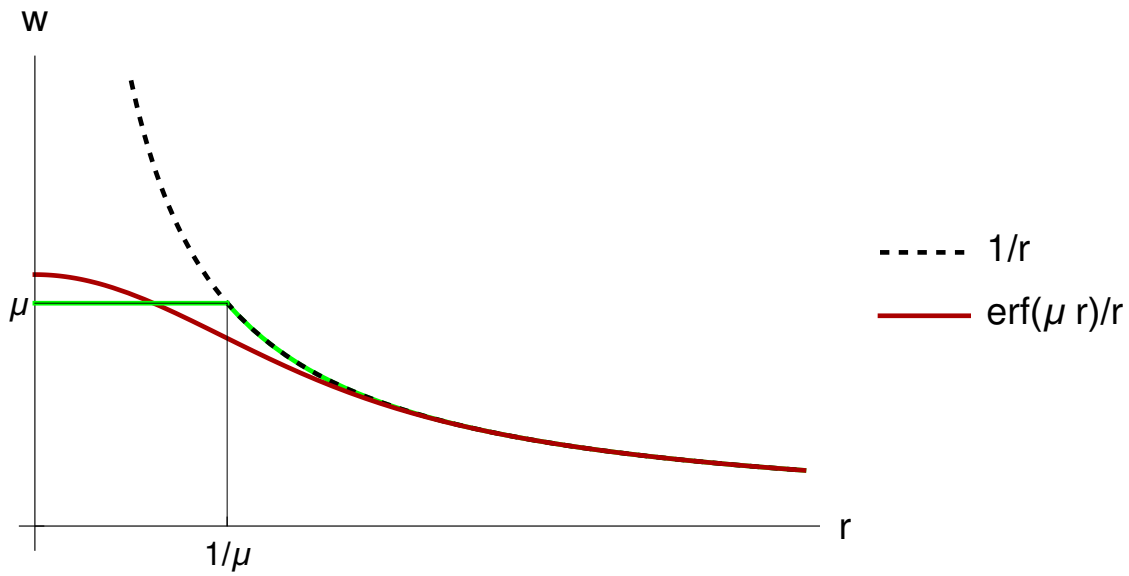
- non-interacting system: $\mu = 0$
- physical system: $\mu = \infty$

Alternatives

For example, Yukawa interaction [52]

$$\frac{1}{r} = \underbrace{\frac{1 - e^{-\mu r}}{r}}_{w(r,\mu)} + \underbrace{\frac{e^{-\mu r}}{r}}_{\bar{w}(r,\mu)}$$

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



- μ: model chosen
- $w(r,\mu)$: long ranged
- $\bar{w}(r,\mu) = 1/r - w(r,\mu)$: short ranged
- correlated wave function for $\mu > 0$
- models with small μ are supposed to be more easily accessible

Motivation for the choice of $w(r, \mu)$

- $w(r, \mu) = \frac{\mathrm{erf}(\mu r)}{r}$ better for correlated calculations using common basis sets.
  - Description with finite basis sets easier to achieve:

$$\frac{\mathrm{erf}(\mu r)}{r} = (2\pi)^{-3} \int_{\mathbb{R}^3} d\,\mathbf{k} \frac{4\pi}{k^2} e^{-\frac{k^2}{4\mu^2}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

    $e^{-\frac{k^2}{4\mu^2}}$ is a smooth cutoff; components of plane waves with large k projected out; best when $\mu \to 0$.
  - Singularity not present in $w(r, \mu < \infty)$
- Missing part (short-range interaction) "universal", i.e., $v(\mathbf{r})$-independent
  - Physical argument: when $|\mathbf{r}_i - \mathbf{r}_j| \to 0$, singularity becomes dominant, $v(\mathbf{r})$ does not matter
  - Mathematical argument: Kato cusp condition and generalizations
  - Experience: with density functional theory

Practical considerations

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

to be solved [150].

- How many points μ_k are needed for a good interpolation?
  Evaluation of $E(\mu_k)$ is expensive: should be kept to a minimum.
- How many derivatives are needed?
  Computing $E^{(1)}(\mu_k) = \langle \Psi(\mu_k) | \bar{W} | \Psi(\mu_k) \rangle$ is cheaper than computing $E(\mu \neq \mu_k)$.
- How are the points to be chosen?
  Cost increases with μ.
- How to choose the basis functions?
  We know that for $\mu \to \infty$, $E(\mu) + c\mu^{-2} \to \infty$. $\mu^{-k}, k \geq 2$ basis, for large μ.

Numerical examples

System: harmonium

for $N = 2$ electrons (for numerical examples).

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{2}\omega^2\left(\mathbf{r}_1^2 + \mathbf{r}_2^2\right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

is separable with $\mathbf{R} = (\mathbf{r}_1 - \mathbf{r}_2)/2, \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$:

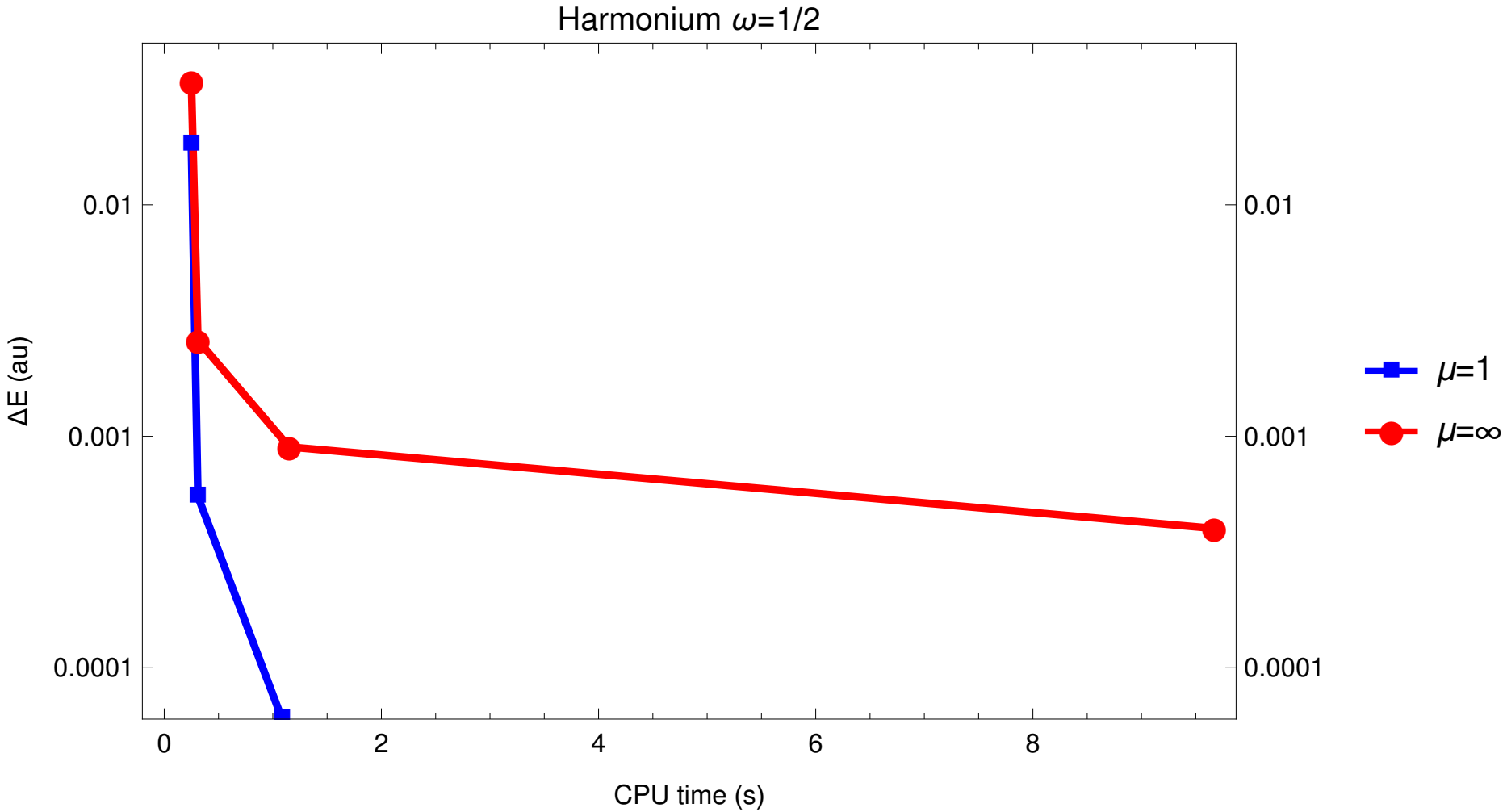
$$\left(-\frac{1}{4}\nabla_{\mathbf{R}}^2 + \omega^2\mathbf{R}^2\right)\Psi_{\mathbf{R}} = E_{\mathbf{R}}\Psi_{\mathbf{R}}$$

$$\left(-\nabla_{\mathbf{r}}^2 + \frac{1}{4}\omega^2\mathbf{r}^2 + \frac{1}{r}\right)\Psi_{\mathbf{r}} = E_{\mathbf{r}}\Psi_{\mathbf{r}}$$

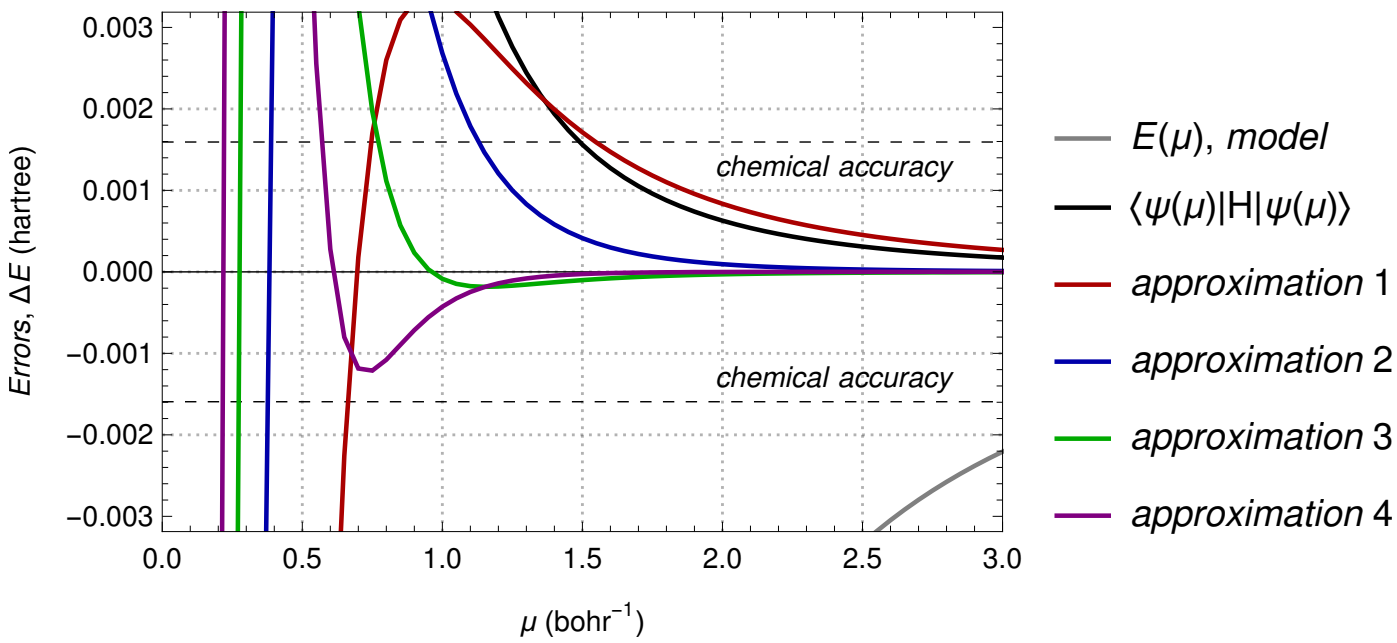
$$\Psi_{\mathbf{r}} = \psi(r)Y_{\ell m}(\Omega)$$

- gives 1D differential equation,
- is analytically solvable for certain values of ω
- generalized to $1/r \to w(r, \mu)$ (erfonium, Karwowski).

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



How to read the plots (for energy errors)



- Energy errors for several models with several corrections
- Chemical accuracy $= 1$ kcal/mol Pople, *Rev. Mod. Phys.*, **71**, 1267 (1999)
- For comparison, errors of $E(\mu)$ and of $\langle \Psi(\mu)|H|\Psi(\mu)\rangle$
- Approximations constructed to be correct for large μ;
  wall around $\mu \approx 0.5$

Corrections using up to $E(\mu), E^{(1)}(\mu), \ldots, E^{(n)}(\mu)$ [150]

$$E \approx E(\mu) + \sum_{k=2}^{n+1} c_k \mu^{-k}$$

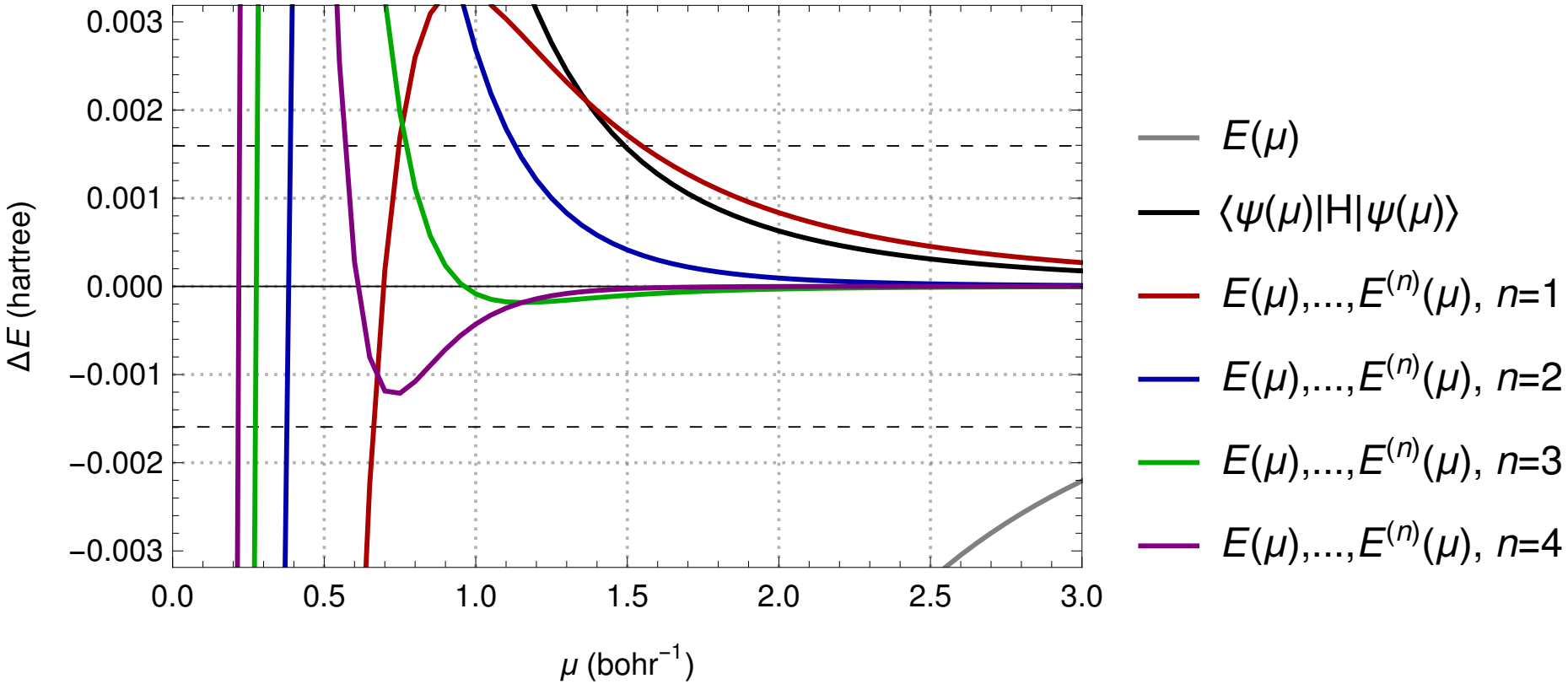
$$0 \approx E^{(1)}(\mu) + \sum_{k=2}^{n+1} c_k (-k) \mu^{-k-1}$$

$$0 \approx E^{(2)}(\mu) + \sum_{k=2}^{n+1} c_k (-k)(-k-1) \mu^{-k-2}$$

$\ldots$

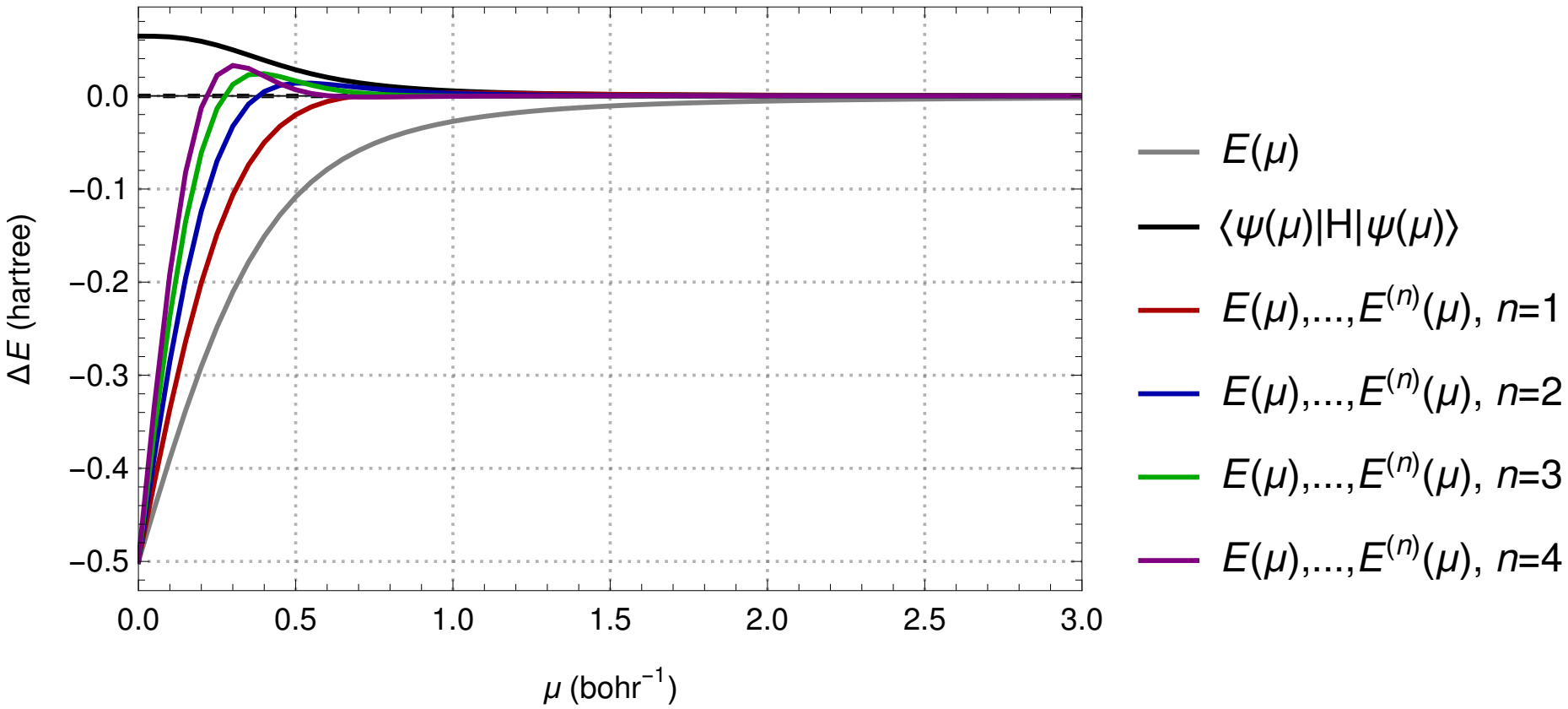
- Solved by $\approx \to =$
- $k \geq 2$: exact result (dimensional)
- Known: μ, $E(\mu), E^{(1)}(\mu), \ldots$
- Unknown: E, c_k; only E needed.

Corrections using up to $E(\mu), E^{(1)}(\mu), \ldots, E^{(n)}(\mu)$



- Increase in n brings improvement for large μ, worsening starts around $\mu = 1$, wall around $\mu = 0.5$.
- $n = 1$ close to $\langle H \rangle$ (large μ): both first-order perturbation theory

Origin of the wall. V independent of μ?



How to improve V? DFT?

Origin of the wall. μ^{-k} as basis?

- The basis functions $\chi_k(\mu) = \mu^{-k}$ diverge at $\mu = 0$
- Many basis sets that don't diverge at $\mu = 0$ can be chosen, e.g.,

$$\chi_k(\mu) = 1 - k\,\mu(1 + k^2\mu^2)^{-1/2}$$

  satisfy
  - $\chi_k(\mu \to \infty) \propto \mu^{-2}$
  - $\chi_k(\mu = 0) = 1$
- How to choose the best small set?

Choosing basis sets functions from a large set using EIM

EIM: Empirical Interpolation Method (magic points)

Maday, Nguyen, Patera, Pau, *Comm. Pure Appl. Analysis*, **8**, 383 (2009)

FLEIM: Forward Looking EIM

Polack, Maday, AS [204] .

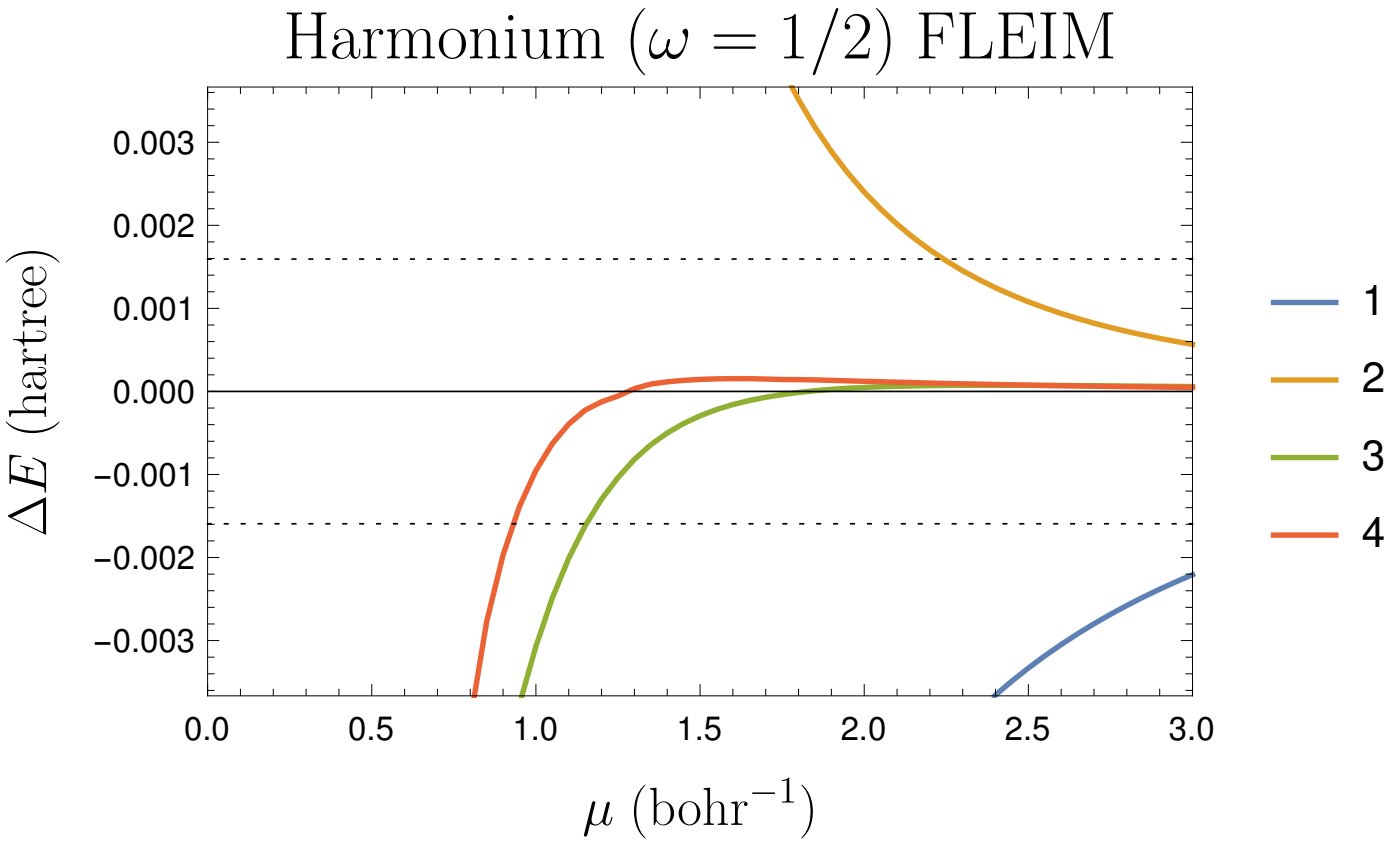
A greedy method to produce basis sets of increasing size without using the knowledge of the function to interpolate.

Algorithm

1. Choose a large basis set, $L = \{\chi_1, \chi_2, \dots\}$.
2. Select a small subset of basis functions, $S \subset L$.
3. Produce approximants of the basis functions not in S by interpolation; the "worst" is χ_j.
4. Enlarge S by including χ_j, $S := S \cup \chi_j$.
5. Iterate from 3.

FLEIM

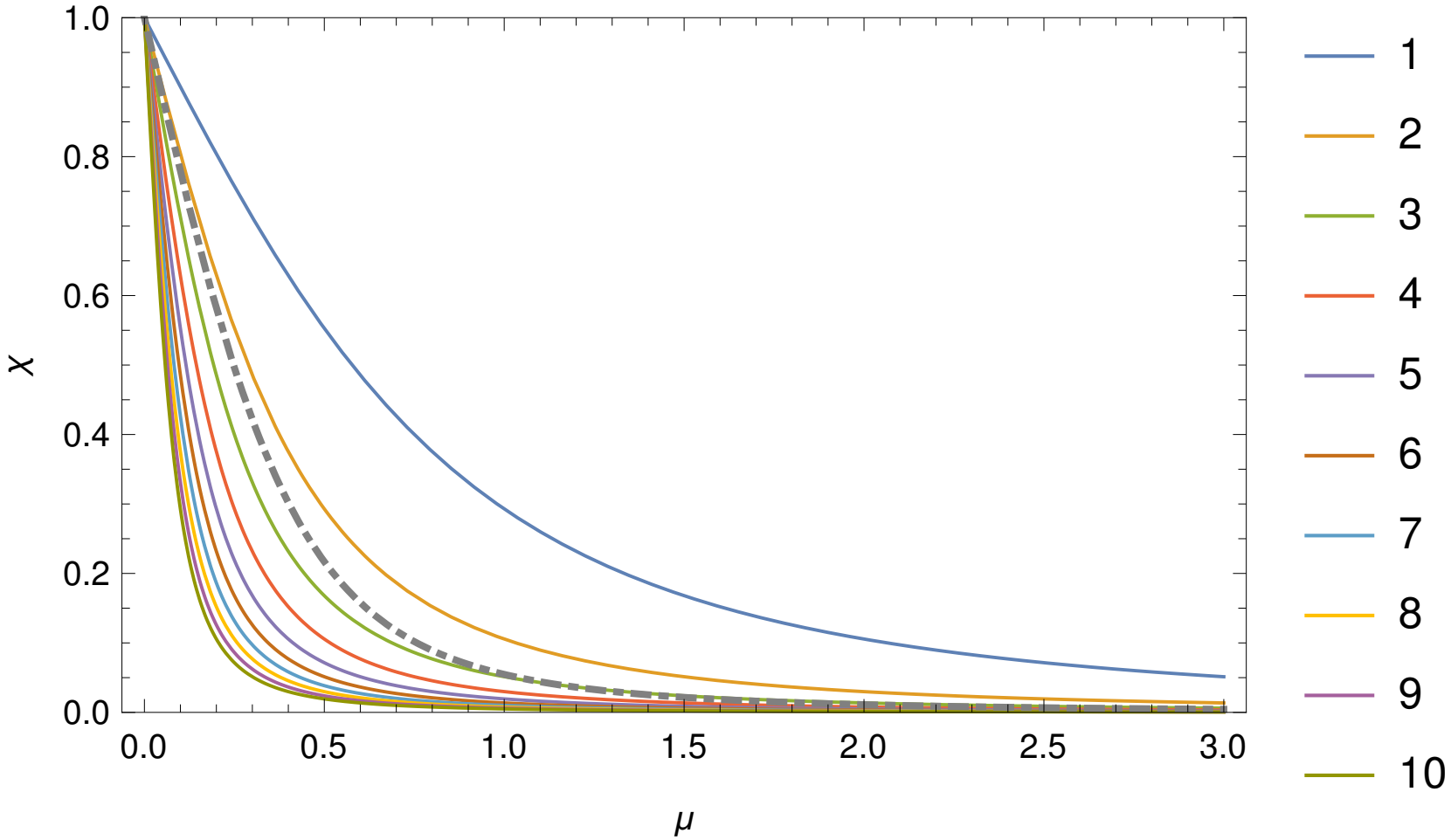
Lagrange interpolation variant, using points $\leq \mu$



Polack, Maday, AS [204]

Accuracy increases with number of points; wall remains.

Wall due to basis set expansion?



$E(\mu) \propto \chi_2(\mu)$ for small μ, $E(\mu) \propto \chi_3(\mu)$ for large μ: not by $\sum_m c_m \chi_m(\mu)$.

Eigenvector continuation

Frame, He, Ipsen, Lee, Lee, Rrapaj, *PRL* **121**, 032501 (2018)

Related eigenfunctions are used

$$\Psi \approx c_1 \Psi(\mu_1) + c_2 \Psi(\mu_2)$$

$$\mathbb{H}\mathbb{C} = \mathbb{S}\mathbb{C}E$$

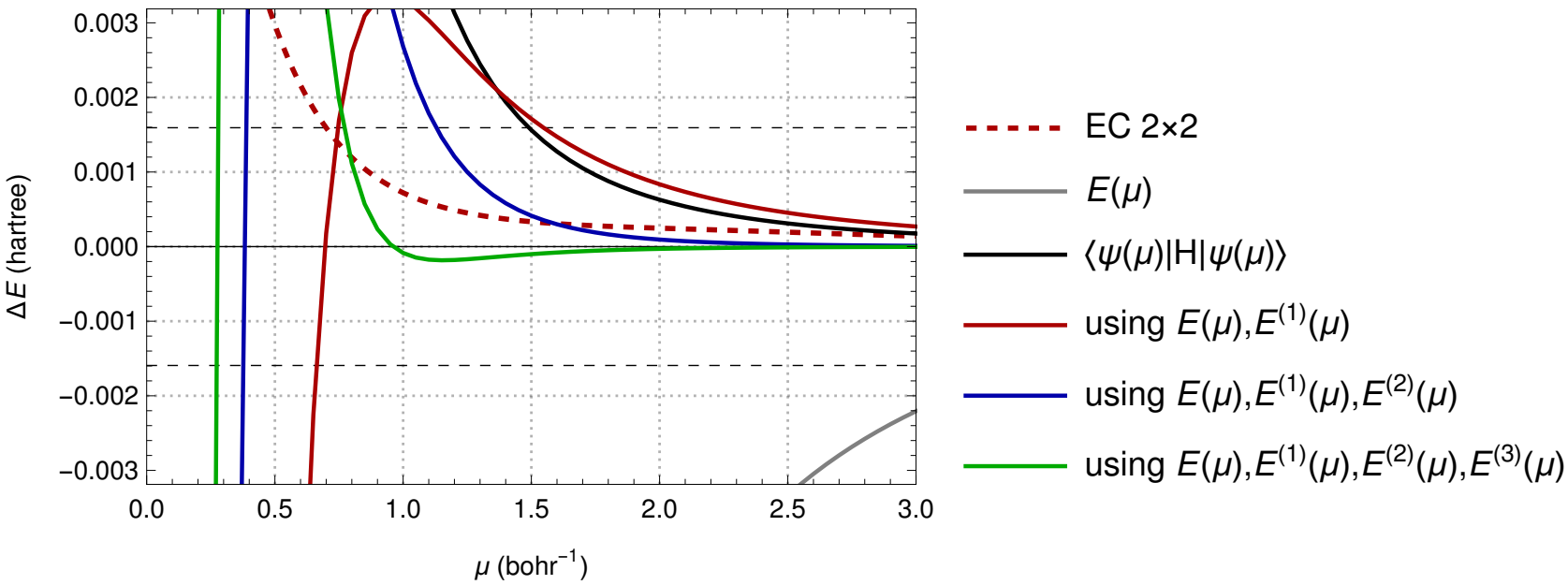
$$\mathbb{H} = \begin{pmatrix} \langle \Psi(\mu_1)|H|\Psi(\mu_1)\rangle & \langle \Psi(\mu_1)|H|\Psi(\mu_2)\rangle \\ \langle \Psi(\mu_2)|H|\Psi(\mu_1)\rangle & \langle \Psi(\mu_2)|H|\Psi(\mu_2)\rangle \end{pmatrix}$$

$$\mathbb{S} = \begin{pmatrix} \langle \Psi(\mu_1)|\Psi(\mu_1) & \langle \Psi(\mu_1)|\Psi(\mu_2) \\ \langle \Psi(\mu_2)|\Psi(\mu_1) & \langle \Psi(\mu_2)|\Psi(\mu_2) \end{pmatrix}$$

Example (not used below): hydrogenic atoms as basis for H

- Excited states of $Z = 1 + \epsilon$ as basis: error $\propto \epsilon^2$
- Eigenvector continuation, $Z = 1 + \epsilon$ and $Z = 1 + a\,\epsilon$: error $\propto a^2\epsilon^4$

Eigenvector continuation



- $\mu_1 < \mu_2 = \mu$; μ_1 optimized.
- 2 by 2 matrix; larger matrices did not significantly improve the range of μ that give errors within chemical accuracy.
- EC range is larger than that obtained using low derivatives.
- EC is probably cheaper than using $E^{(4)}$, and is variational (much better at $\mu = 0$.

Reducing the number of model systems: GCC

- Why?
  - Computing $E(\mu)$ is expensive.
  - Cost of $E^{(n)}(\mu)$ increases fast with $n > 1$.
- How?
  - Adiabatic connection
  - Generalized coalescence conditions (GCC): behavior of the wave function when electrons are at short distances

Adiabatic connection

$$f(b) = f(a) + \int_a^b dx\ f'(x)$$

$$H(\lambda, \mu) = H(\lambda = 0, \mu) + \lambda \bar{W}(\mu)$$

$$E = E(\lambda = 0, \mu) + \int_0^1 d\lambda\, \langle \Psi(\lambda, \mu) | \bar{W} | \Psi(\lambda, \mu) \rangle$$

- Problem: knowledge of $\Psi(\lambda > 0, \mu)$
- Approach: $\bar{W}$ is short-range; only short-range part of $\Psi(\lambda, \mu)$ is needed.

Cusp conditions (behavior of Ψ for $|\mathbf{r}_i - \mathbf{r}_j| \to 0$)

Singularity of the Coulomb interaction $\to$ cusp in the exact wave function

Kato, *Commun. Pure Appl. Math.*, **10**, 151 (1957).

Generalized Coalescence Conditions (GCC) from

$$H^n \Psi = E^n \Psi$$

Kurokawa, Nakashima, Nakatsuji, *Adv. Quantum Chem.*, **73**, 59 (2016).

...

Karwowski, AS [201]

Adiabatic connection using GCC for harmonium (1D)

$$\psi_\ell \approx \psi_{\ell,K}(r,\lambda,\mu) = r^\ell \sum_{k=0}^{K} \frac{c_k}{c_0} r^k$$

$$c_1/c_0 = \lambda/(2\ell+2), \ldots$$

Higher order terms explicit, dependent on ℓ, E, λ, μ known [201].

$$E \approx E(\lambda=0,\mu) + |c_0|^2 \int_0^1 d\lambda \int_0^\infty r^2 dr \, |\psi_{\ell,K}(r,\lambda,\mu)|^2 \, \bar{w}(r,\mu)$$

Remarks

- r^k in $|\psi_\ell|^2$ gives leading term $\propto \mu^{-k-2}$ for $\mu \to \infty$; validity range.
  Analogy to basis set expansion: coefficients fixed by GCC, not interpolation.
- c_0 needed (normalization, not short-range); obtained from

$$\langle \Psi(\mu) | \bar{W}(\mu) | \Psi(\mu) \rangle \approx |c_0|^2 \int_0^\infty r^2 dr \, |\psi_{\ell,K}(r,\lambda=0,\mu)|^2 \, \bar{w}(r,\mu)$$

[150]

Asymptotic behavior ($\mu \to \infty$) for adiabatic connection

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

where

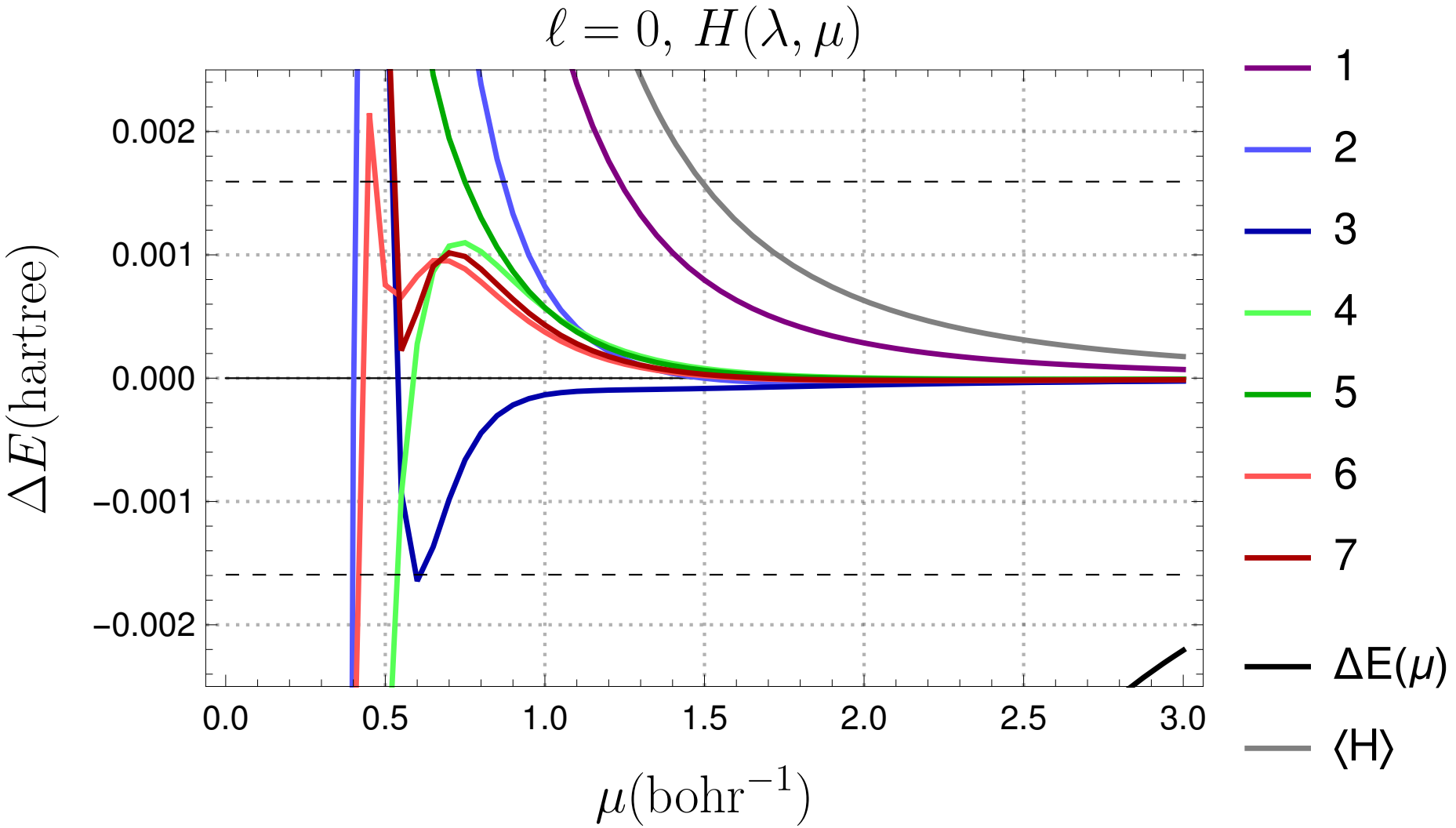
$$\alpha(\mu) = \frac{\int_0^1 d\lambda \int_0^\infty r^2 dr\, |\psi_{\ell,K}(r,\lambda,\mu)|^2\, \bar{w}(r,\mu)}{\int_0^\infty r^2 dr\, |\psi_{\ell,K}(r,\lambda=0,\mu)|^2\, \bar{w}(r,\mu)}$$

and c_k/c_0 are explicitely given in terms of ℓ, μ, λ, E. Good approximation for E in the expression of c_k/c_0: $\langle\Psi(\mu)|H|\Psi(\mu)\rangle$ (self-consistency possible, but not significant). AS, Karwowksi [205]

Computational effort for approximating E

comparable to that for $\langle\Psi(\mu)|H|\Psi(\mu)\rangle$.

Adiabatic connection for the GCC expansion, $\psi_{\ell,K}$

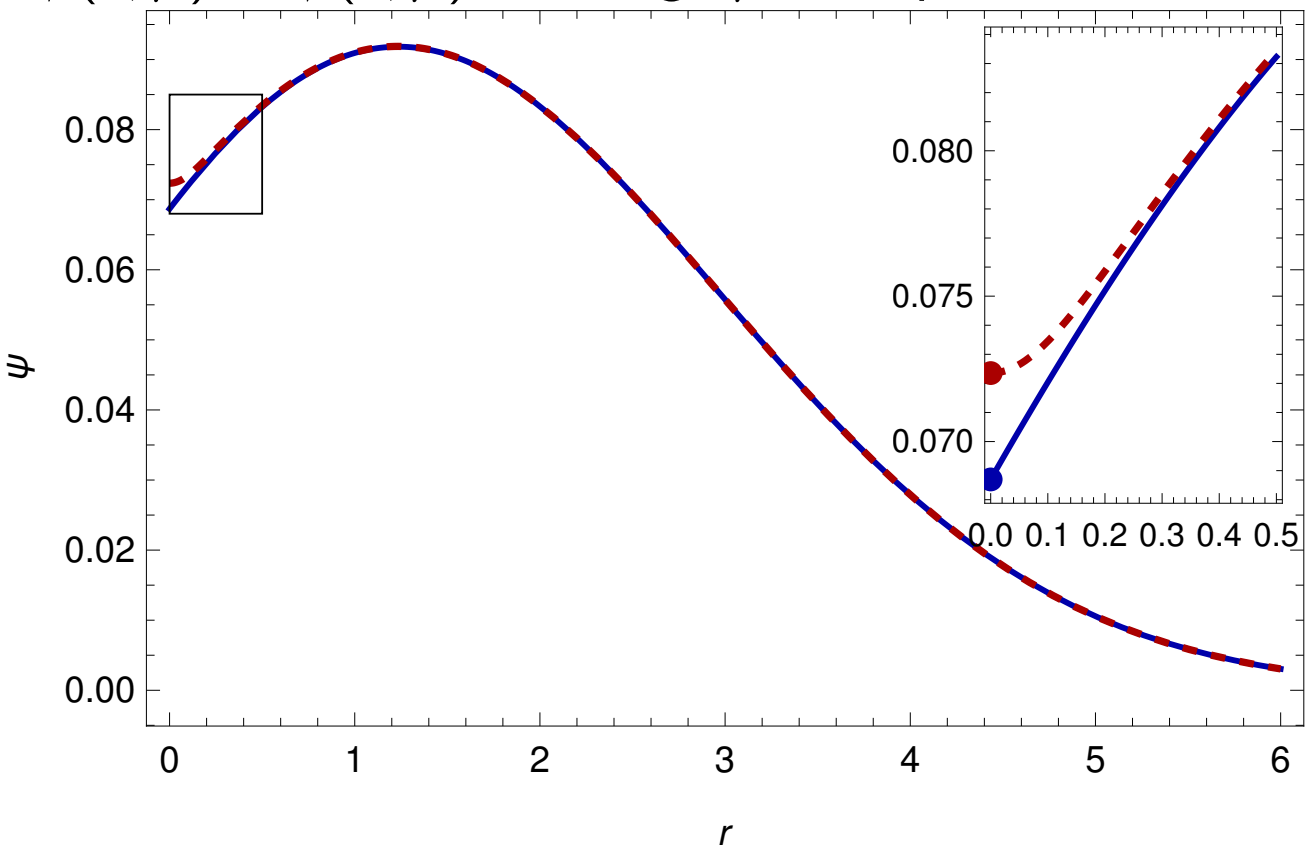


Wall not eliminated

Reducing the number of model systems: Perturbation theory

Gori-Giorgi, AS [118]

$\psi(r,\mu) \approx \psi(r,\mu)$, for large μ, except for small r.



Asymptotic PT1

- Derivation
  - First-order problem in $1/\mu$ has analytical solution, $\psi_{\ell,asy}(r,\lambda,\mu)$,
  - integration constant fixed by merging into $\mu=\infty$ solution.

Gori-Giorgi, AS [118]

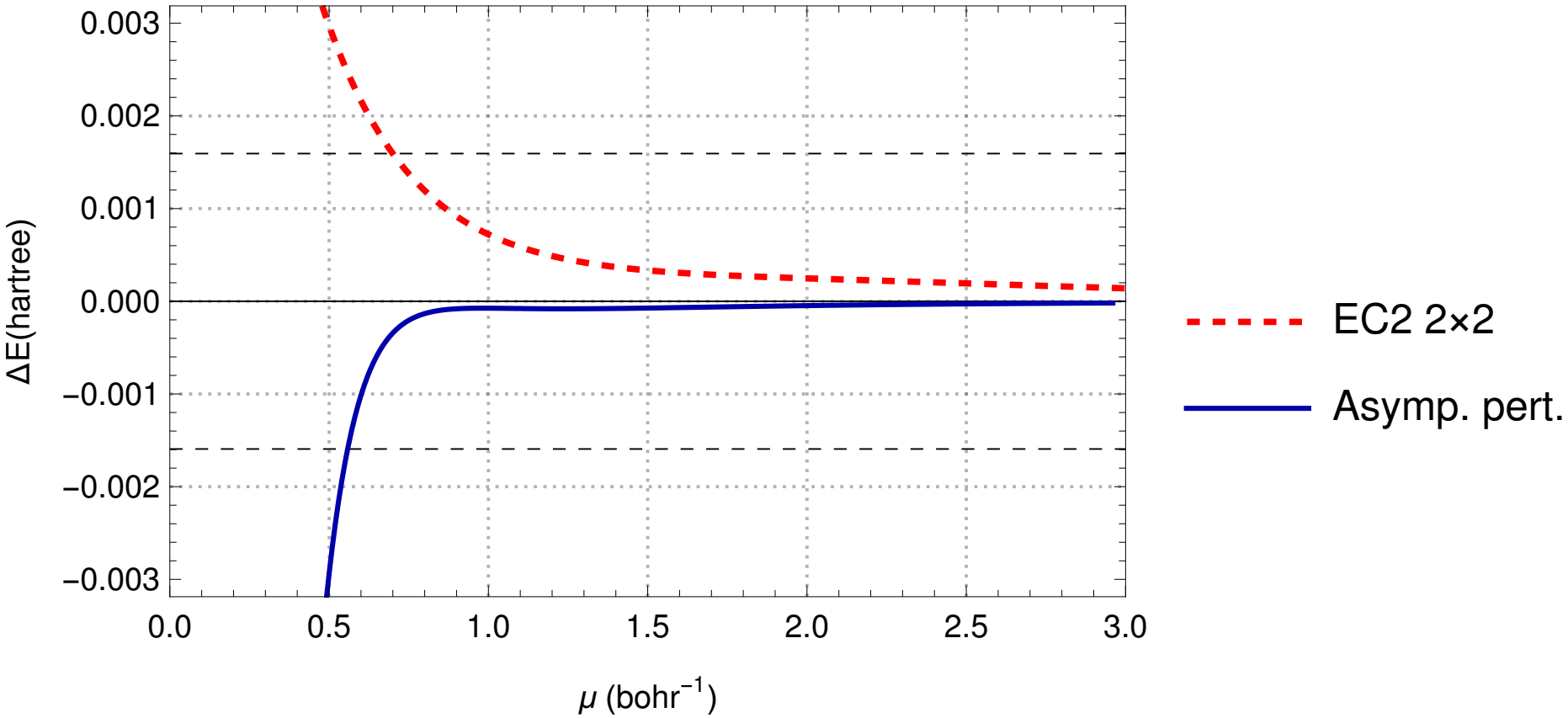
- Energy expression (as before)

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

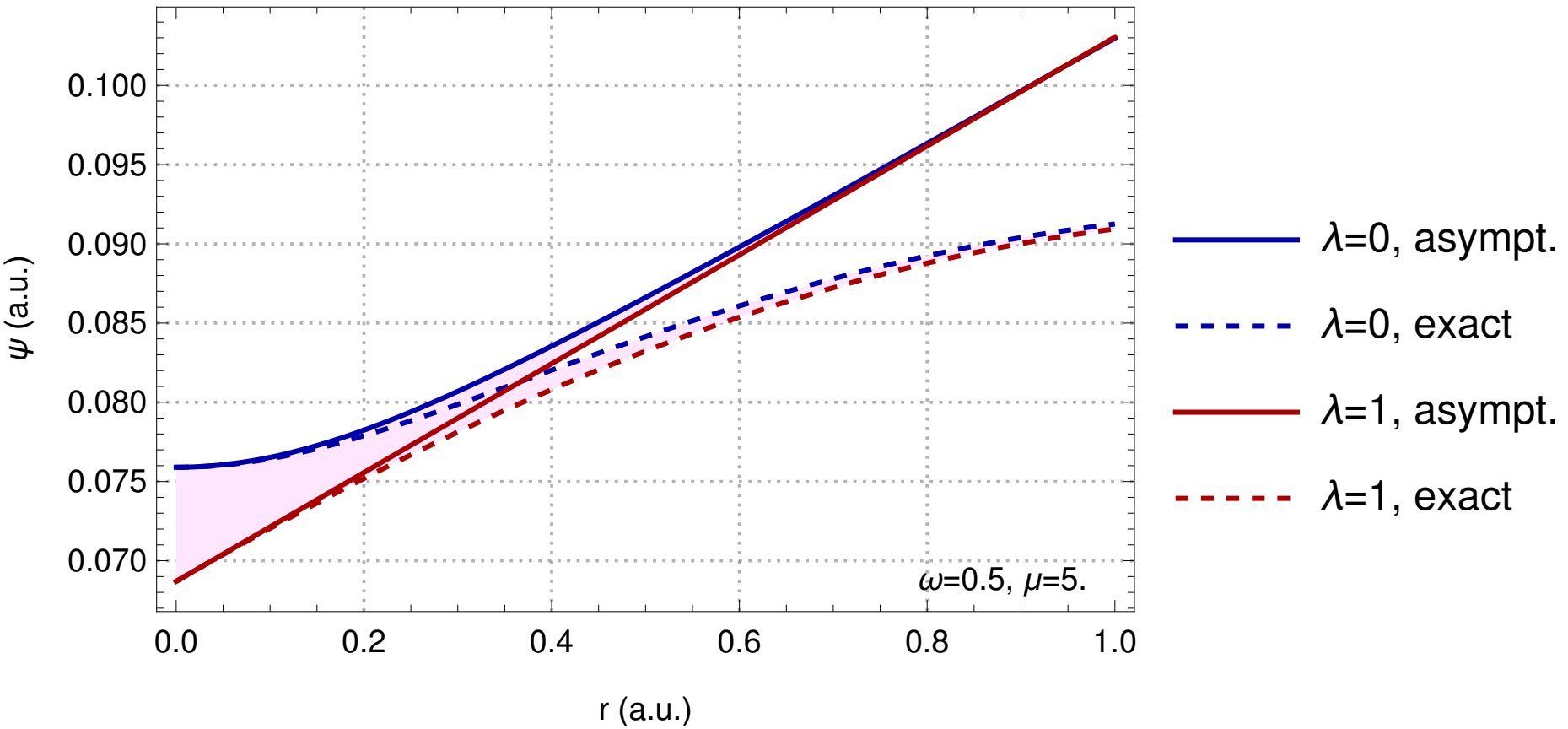
where

$$\alpha(\mu) = \frac{\int_0^1 d\lambda \int_0^\infty r^2 dr\, |\psi_{\ell,asy}(r,\lambda,\mu)|^2\, \bar{w}(r,\mu)}{\int_0^\infty r^2 dr\, |\psi_{\ell,asy}(r,\lambda=0,\mu)|^2\, \bar{w}(r,\mu)}$$

Asymptotic PT1 result



A hidden error compensation at larger r when integrals are considered



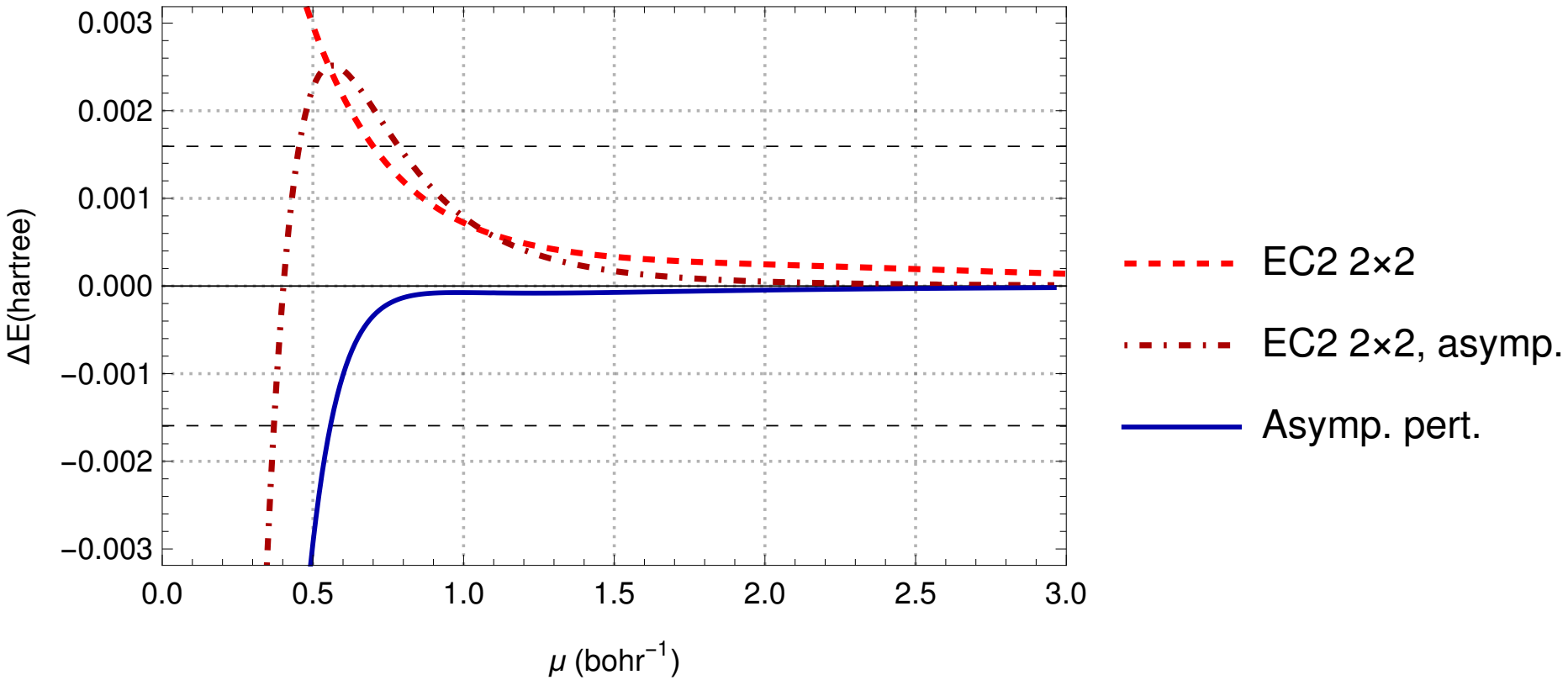
Asymptotic eigenvector continuation

Asymptotic EC: information from a single μ

Reduce 2×2 EC to 1 point by using asymptotic PT1 form of ψ_ℓ.
Tricks:

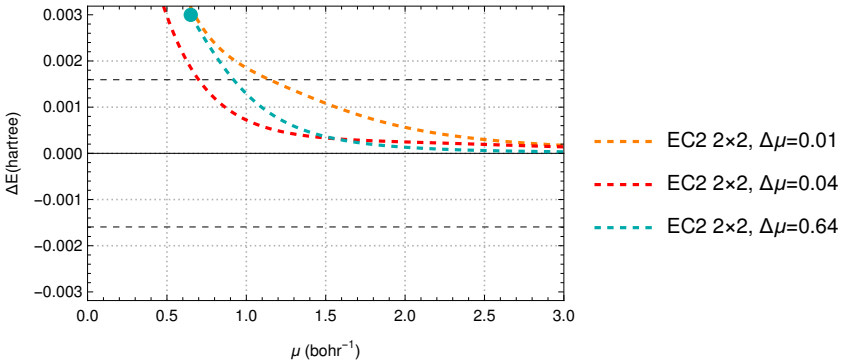
- $H = H(\mu) + \bar{W}(\mu)$
- $\partial_\mu E(\mu) = \langle \Psi(\mu) | \partial_\mu W(\mu) | \Psi(\mu) \rangle$; $\partial_\mu W(\mu)$ is also short-ranged.
- Decompose matrix elements into terms containing short range operators, and terms depending on μ_1 only. This can be done both for $\mathbb{H}$ and the overlap.
- Use exact results for μ_1.
- Use asymptotic formulas for terms containing μ_2 and short range operators.

Asymptotic EC result

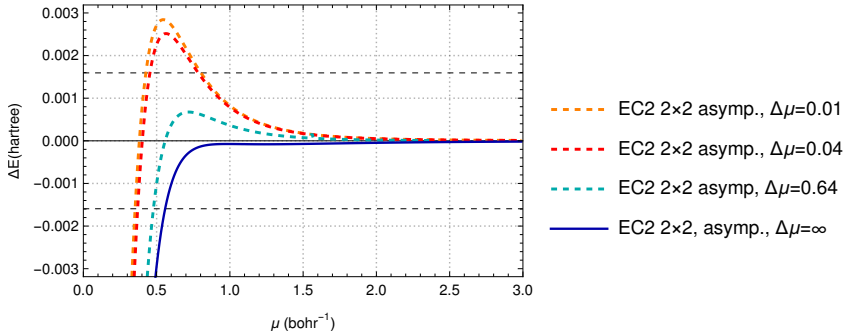


Effect of $\Delta\mu = \mu_2 - \mu_1$ on EC

Eigenvector continuation



Asymptotic approximation to EC



Remarks:

- EC curves start at μ_2, as $\Psi(\mu_2 > \mu_1)$ needed
- Asymptotic EC curves start at ∞, as only $\Psi(\mu_1)$ is needed.
- Asymptotic EC curve for $\Delta\mu = \infty$ = asymptotic PT1.
- EC curve for $\Delta\mu = \infty$ starts at $\mu_2 = \infty$.

Improving small μ results

Taylor's method with integral remainder

$$f(x) = f \sum_{k=0}^{K} \frac{1}{k!}(x-a)^k f^{(k)}(x) + \int_a^x dt\, \frac{1}{K!}(x-t)^K f^{(K+1)}(t)$$

Proof: integration by parts

$$E(\lambda = 1) = E(\lambda = 0) + \sum_{k=0}^{K} \frac{1}{k!} E^{(k)}(0) + \int_0^1 dt\, \frac{1}{K!}(1-t)^K E^{(K+1)}(t)$$

Taylor's method with integral remainder: special cases

- Perturbation theory

$$E(\lambda=1) = \underbrace{E(\lambda=0) + \sum_{k=1}^{K} \frac{1}{k!} E^{(k)}(\lambda=0)}_{\text{Perturbation theory to order } K} + \int_0^1 dt\, \frac{1}{K!}(1-t)^K E^{(K+1)}(t)$$

- Adiabatic connection in DFT: $K=0$

$$E(\lambda=1) = \underbrace{E(\lambda=0)}_{\text{model}} + \underbrace{\int_0^1 dt\, E^{(1)}(t)}_{\text{correction to model}}$$

- Adiabatic connection to order K?

$$E(\lambda=1) = \underbrace{E(\lambda=0) + \sum_{k=0}^{K} \frac{1}{k!} E^{(k)}(0)}_{\text{Perturbation theory to order } K} + \underbrace{\int_0^1 dt\, \frac{1}{K!}(1-t)^K E^{(K+1)}(t)}_{\text{correction to model}}$$

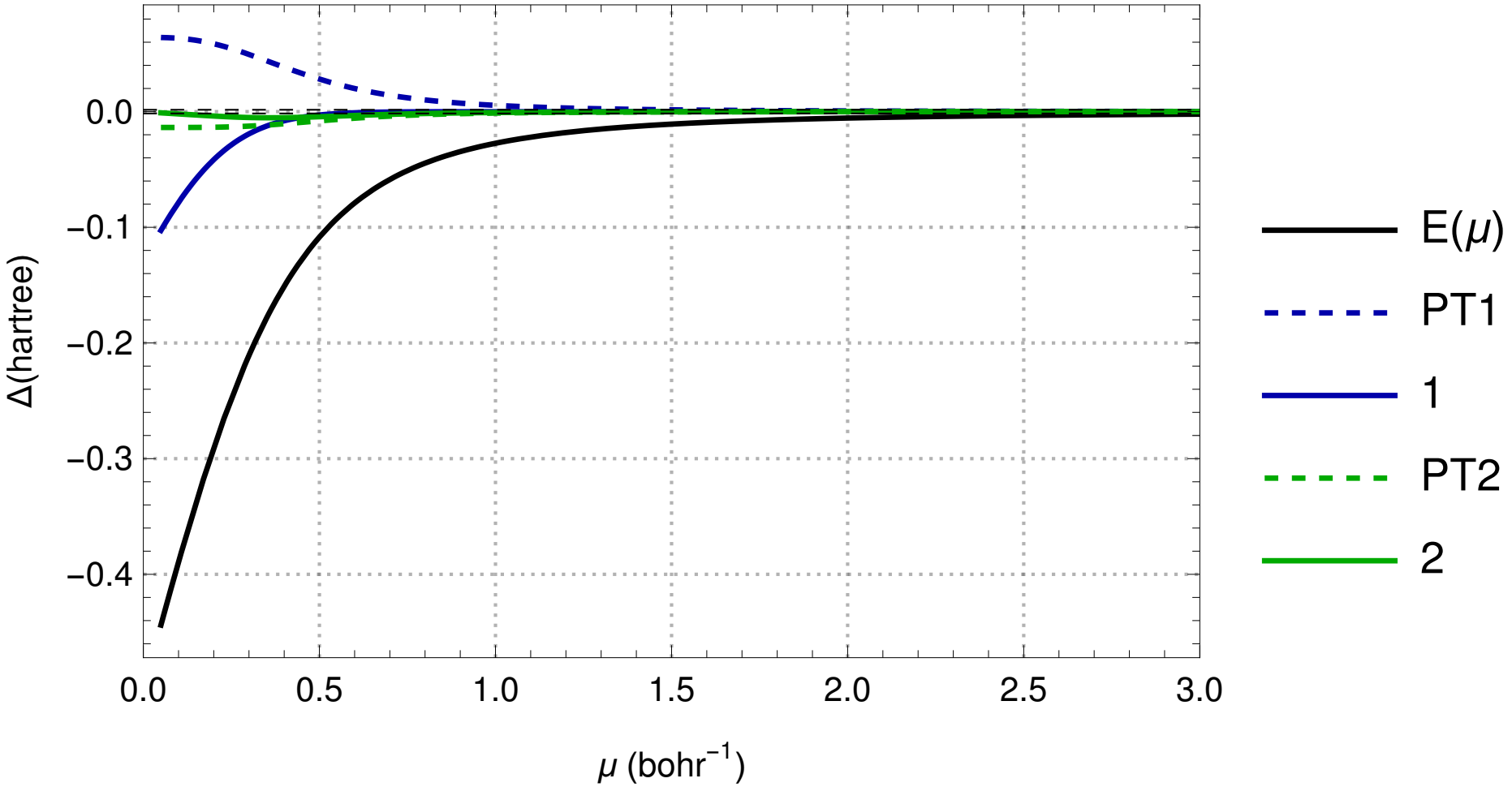
Working formula

In perturbation theory to order K, replace $E^{(K)}$ by $\alpha^{(K)}(\mu)\, E^{(K)}$

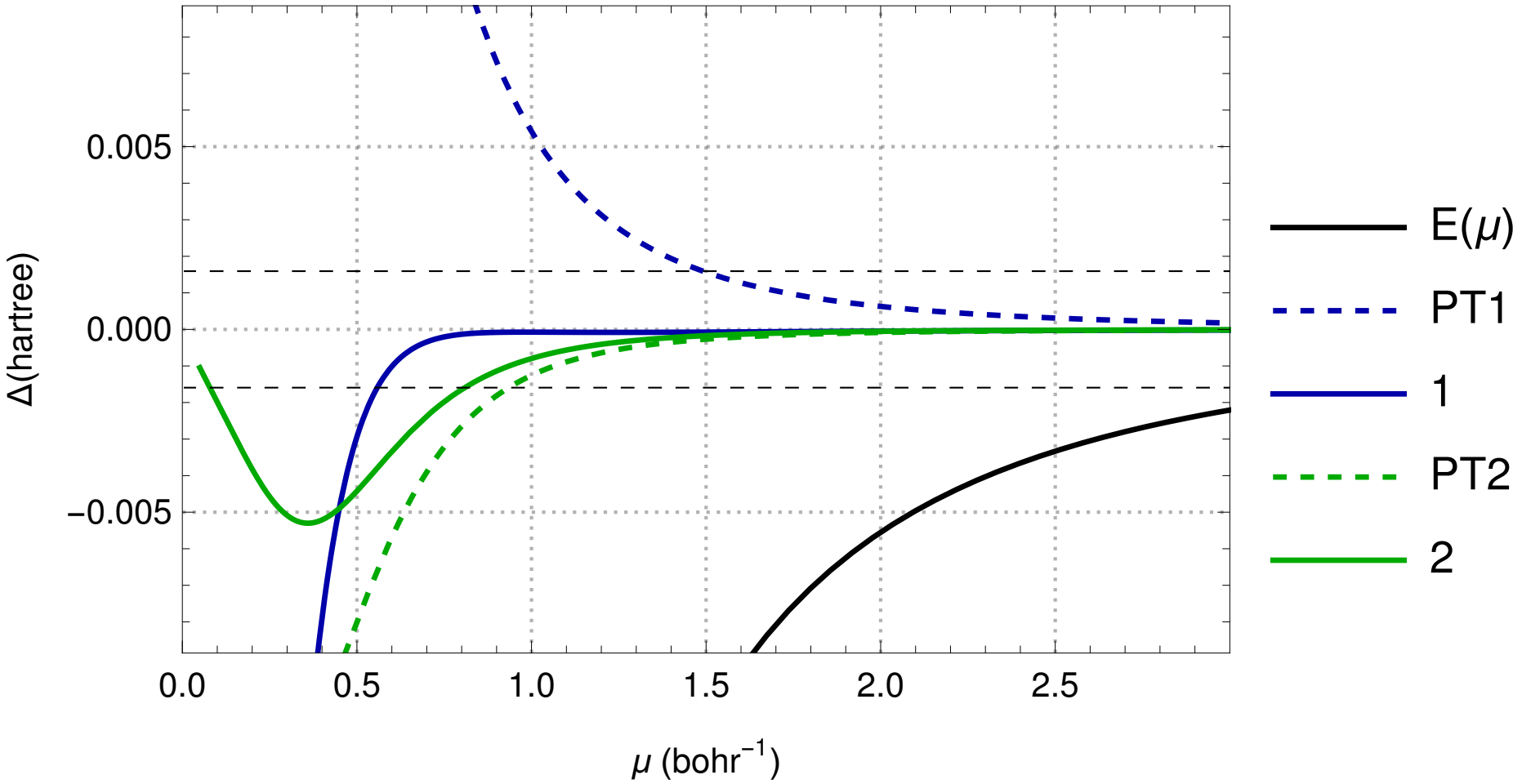
$$\alpha^{(K)}(\mu) = \frac{\int_0^1 d\lambda \frac{1}{(K-1)!}(1-\lambda)^{K-1} \int_0^\infty dr\, r^2\, \partial_\lambda^{K-1} |\psi_{\ell,asy}(r,\lambda,\mu)|^2 \bar{w}(r,\mu)}{\int_0^\infty dr\, r^2 \left(\partial_\lambda^{K-1} |\psi_{\ell,asy}(r,\lambda,\mu)|^2\right)_{\lambda=0} \bar{w}(r,\mu)}$$

$\alpha^{(K)}(\mu)$: analytic expression, no empirical parameters.

Results for harmonium, $\omega = 1/2$



Results for harmonium, $\omega = 1/2$, zoomed in.



Summary

Summary

- Knowledge of behavior of models with long-range interaction can be effectively corrected by different techniques: interpolation, adiabatic connection, eigenvector continuation.
- Up to now corrections to the non-nteracting 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.

Appendix

Generalized Coalescence Conditions

For $r = |\mathbf{r}_1 - \mathbf{r}_2| \to 0$,

$$\mathcal{W} = \sum_i v(\mathbf{r}_i) + \sum_{i<j} w(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$\mathcal{W}(r, \dots) = \sum_{k=-1}^{\infty} w_k(\dots) r^k$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_{k=0}^{\infty} r^k c_k(\dots)$$

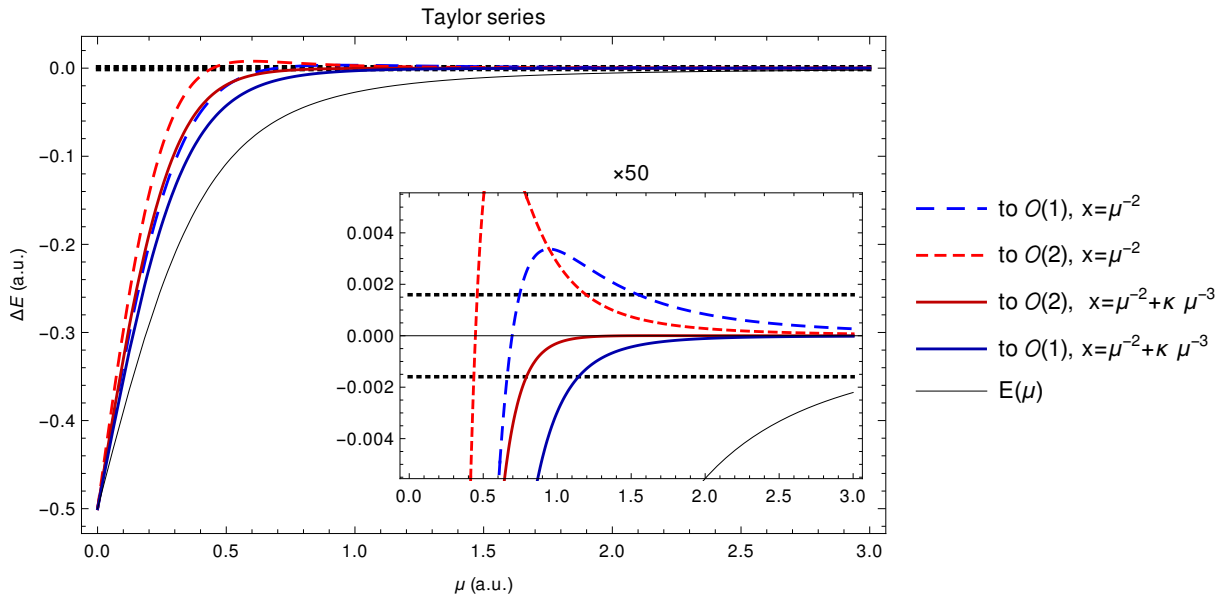
$$T(\mathbf{r}_1, \mathbf{r}_2, \dots) = -\partial_r^2 + \mathcal{T}(\dots)$$

$$\begin{aligned} -2c_1 + w_{-1}c_0 &= 0 \\ -6c_2 + w_{-1}c_1 + \left(\widehat{\mathcal{T}}(\dots) + w_0 - E\right) c_0 &= 0 \\ \dots & \end{aligned}$$

Taylor series

Using $x(\mu)$ such that x monotonously approaches 0 as $\mu \to \infty$, e.g., $x(\mu) = \mu^{-2}$ ‡,

$$E(x=0) = E(x) - x\,E^{(1)}(x) + \frac{1}{2}x^2 E^{(2)}(x) + \ldots$$

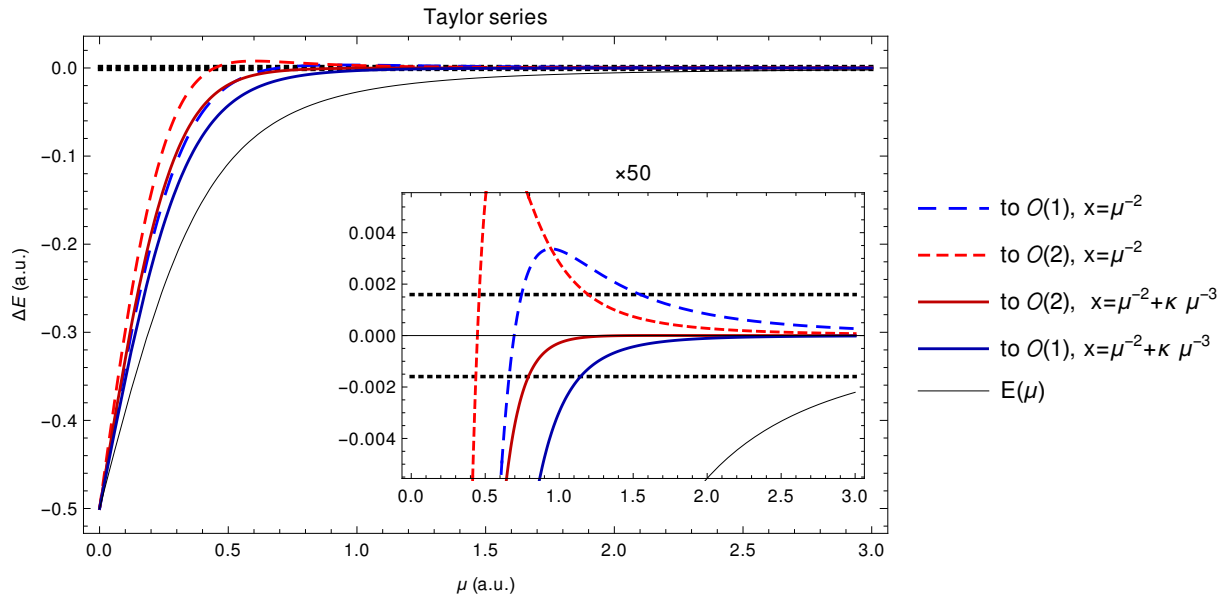


‡Derived from the exact analytical behavior of $E(\mu \to \infty)$

Taylor series

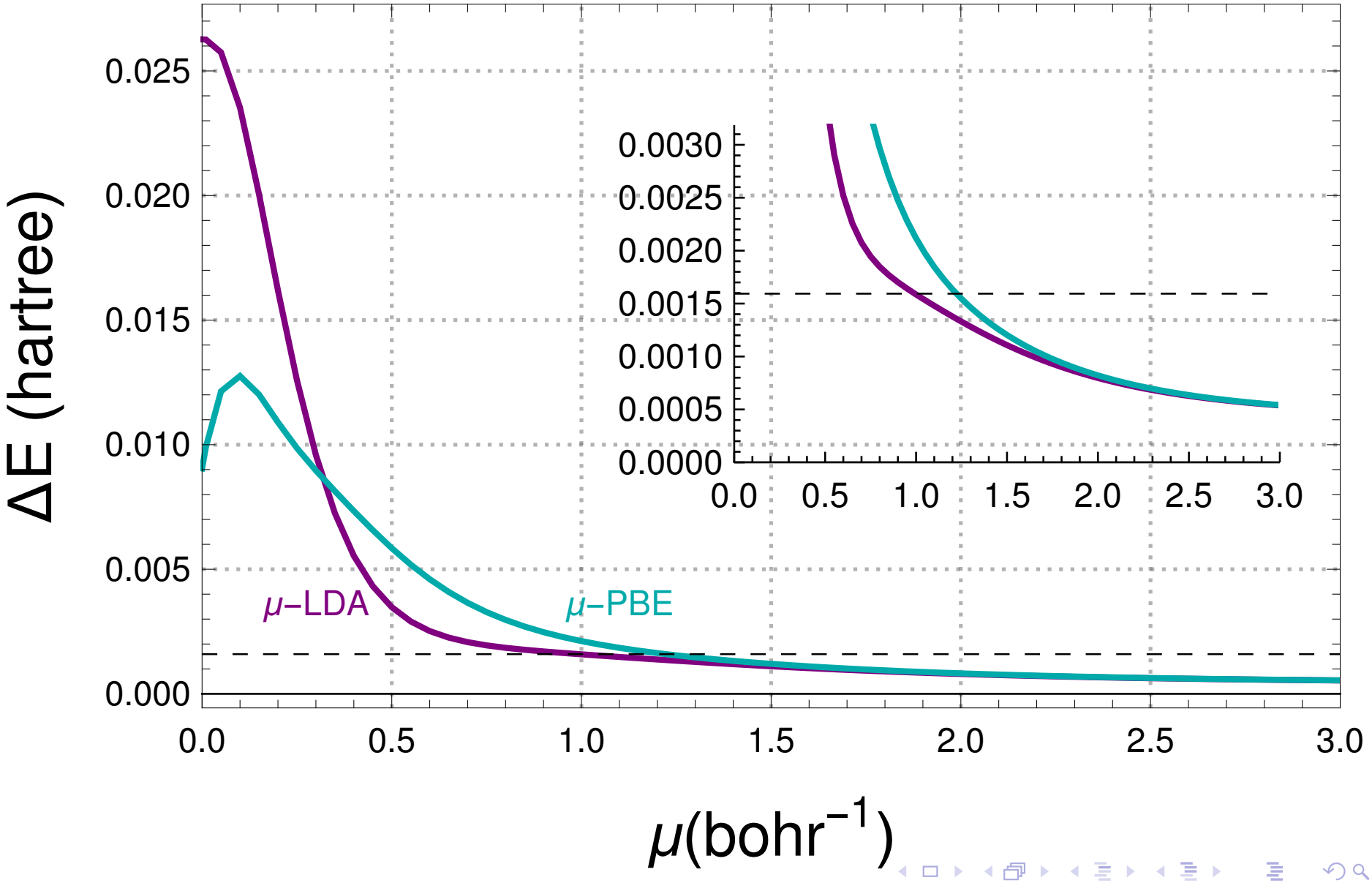
Using $x(\mu)$ such that x monotonously approaches 0 as $\mu \to \infty$, e.g., $x(\mu) = \mu^{-2} + \kappa\mu^{-3}$ §,

$$E(x=0) = E(x) - x\,E^{(1)}(x) + \frac{1}{2}x^2 E^{(2)}(x) + \ldots$$



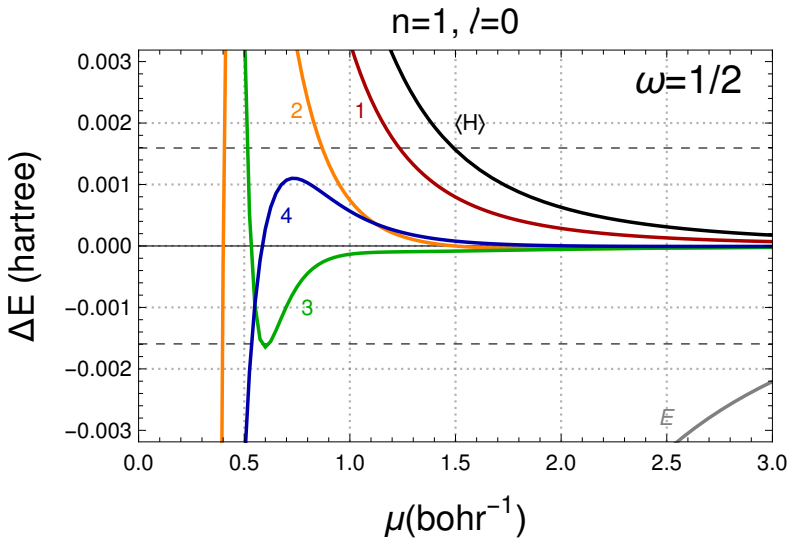
§Derived from the exact analytical behavior of $E(\mu \to \infty)$ including the knowledge of the Kato cusp condition, Gori-Giorgi, AS [118]

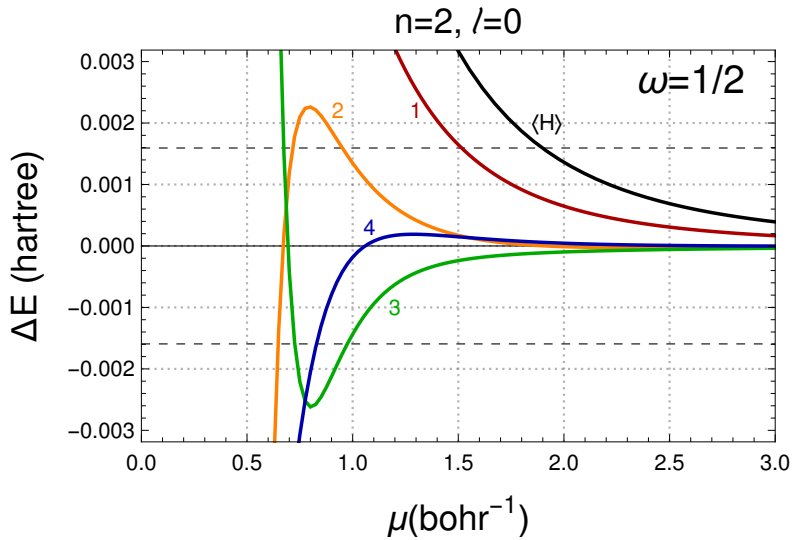
μ-LDA and μ-PBE errors for harmonium $\omega = 1/2$

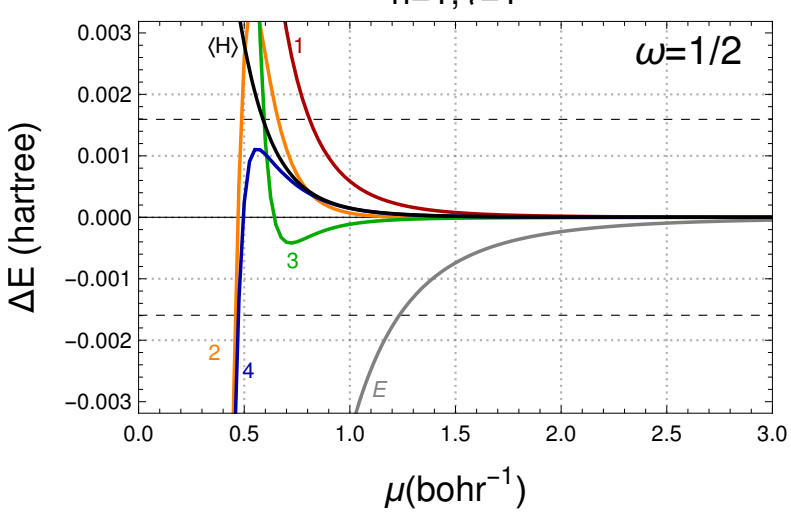


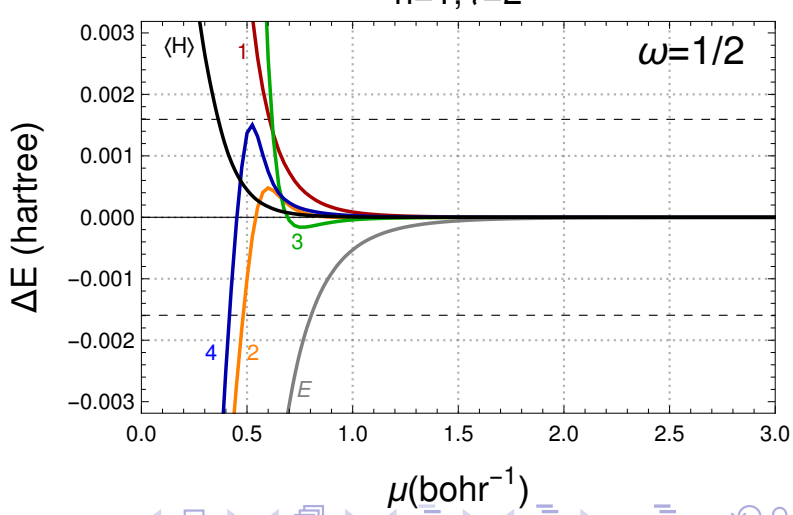
Ground state and excited states with GCC

AS, Karwowski[205]



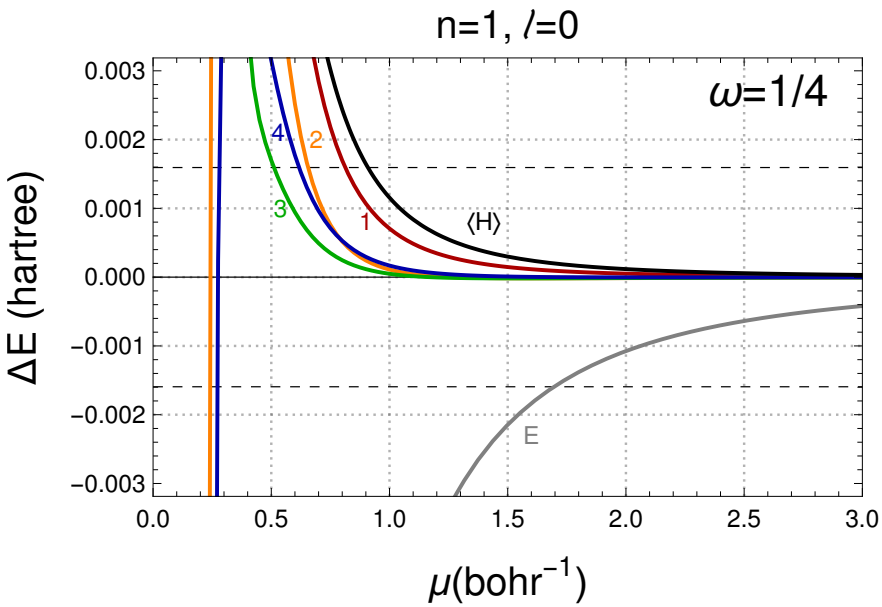


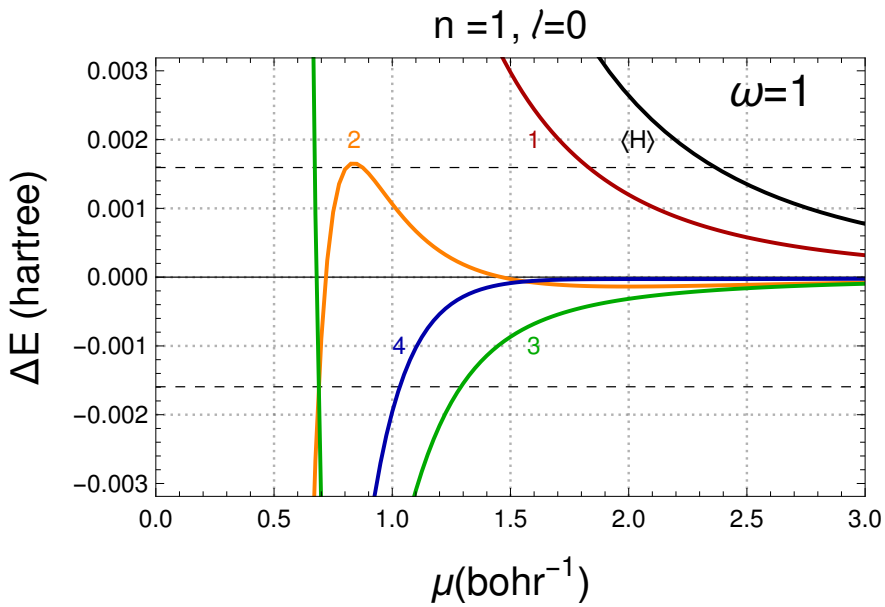




Effect of changing the system using GCC

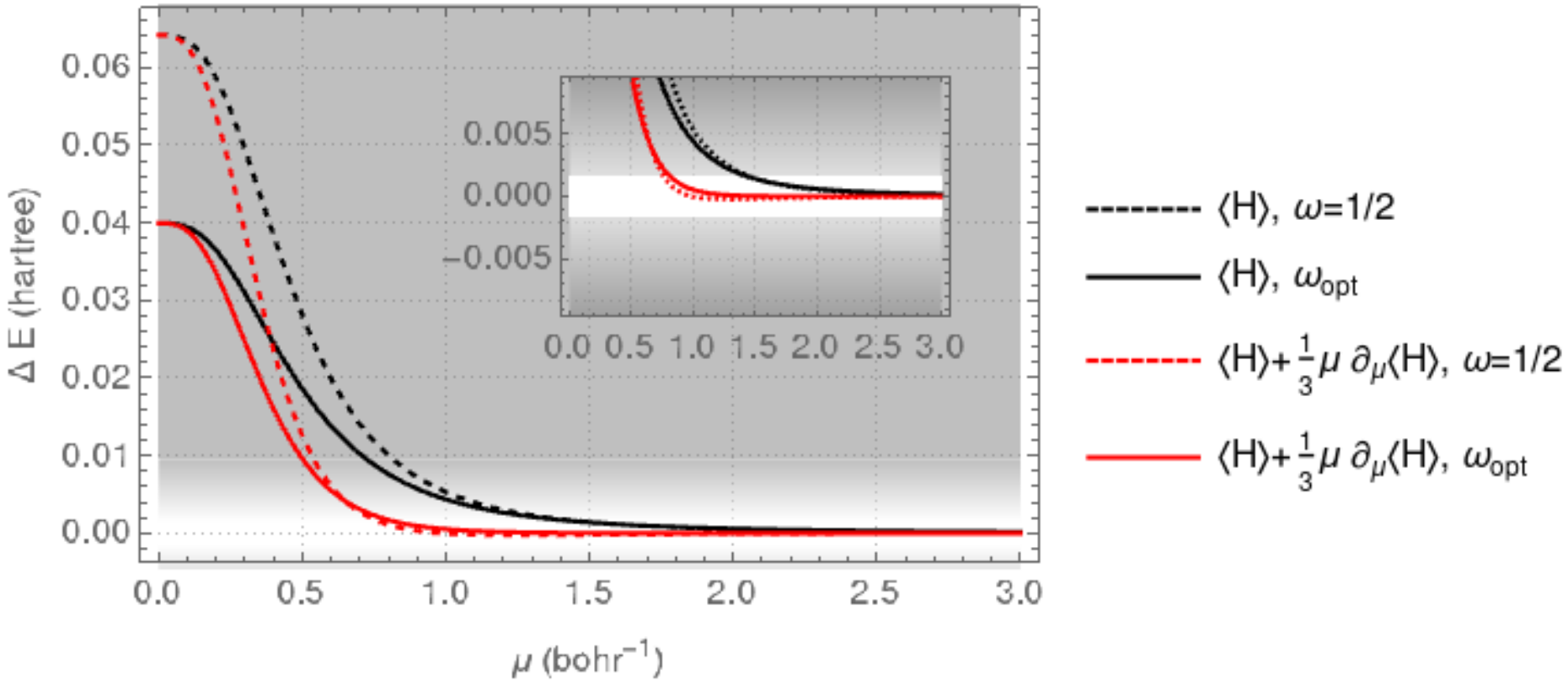
AS, Karwowski[205]





Effect of changing the potential

[205]



Constructing $\mathbb{H}$

$$I(\mu_1,\mu_2,\mu_3) = \int_0^\infty r^2 dr\, \psi_\ell(r,\lambda=0,\mu_1)\, \bar{w}(r,\mu_2)\psi_\ell(r,\lambda=0,\mu_3)$$

$$\zeta(\mu_1) = \langle\Psi(\mu_1)|\bar{W}(\mu_1)|\Psi(\mu_2)\rangle / I(\mu_1,\mu_1,\mu_1)$$

$$E(\mu_2) = E(\mu_1) + \int_{\mu_1}^{\mu_2} d\mu\, \langle\Psi(\mu)|\partial_\mu W(\mu)|\Psi(\mu)\rangle$$

$$\approx E(\mu_1) + \zeta(\mu_1) \int_{\mu_1}^{\mu_2} d\mu \int_0^\infty r^2 dr\, |\psi_\ell(r,\lambda=0,\mu)|^2\, \partial_\mu w(r,\mu)$$

$$\langle\Psi(\mu_1)|H|\Psi(\mu_2)\rangle = \langle\Psi(\mu_1)|H(\mu_1) + \bar{W}(\mu_1)|\Psi(\mu_2)\rangle$$

$$\approx E(\mu_1) + \zeta(\mu_1) I(\mu_1,\mu_1,\mu_2)$$

$$\langle\Psi(\mu_2)|H|\Psi(\mu_2)\rangle = \langle\Psi(\mu_1)|H(\mu_2) + \bar{W}(\mu_1)|\Psi(\mu_2)\rangle$$

$$\approx E(\mu_2) + \zeta(\mu_1) I(\mu_2,\mu_2,\mu_2)$$

Constructing $\mathbb{S}$

$$\langle \Psi(\mu_1)|H(\mu_1) + \bar{W}(\mu_1)|\Psi(\mu_2)\rangle = \langle \Psi(\mu_1)|H(\mu_2) + \bar{W}(\mu_2)|\Psi(\mu_2)\rangle$$

$$(E(\mu_1) - E(\mu_2))\,\langle \Psi(\mu_1)|\Psi(\mu_2)\rangle = \langle \Psi(\mu_1)|\bar{W}(\mu_2) - \bar{W}(\mu_1)|\Psi(\mu_2)\rangle$$