Getting beyond density functional approximations by using lessons from density functional theory

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Basic idea: models and corrections they provide

1. Solve the Schrödinger equation for one or several model Hamiltonians (to desired accuracy).
2. Use exact conditions and information provided by the model to construct corrections.

Comparison

- "Complete basis set" (CBS) extrapolation
- ...

Basic idea: choice

1. Remove the singularity from the potential of the interaction between electrons and solve the Schrödinger equation.
2. Correct to recover results for Coulomb interaction:
    - Density functionals
    - Extrapolation
    - Exact conditions on the wave function: Generalized coalescence conditions

Frame

- Non-relativistic electronic Schrödinger equation
- $N = 2$ electrons †
- Harmonium (Schrödinger equation separable) †

† In this presentation.

Overview

- Constructing models (removing the singularity)
- Correcting the model error
    - Density functionals
    - Extrapolation
    - Generalized coalescence conditions

Removing the singularity

- Choice of a modified interaction
- Specific case of harmonium
- How to add the missing term

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Motivation for model interaction

- Need for a coupling operator, not necessarily long-range
    - Near-degeneracy, entanglement
- $A \dots B$ [134]: structure of density matrices for $\mathrm{r}_A \in \Omega_A, \mathrm{r} \in \Omega_B$

$$\gamma(\mathrm{r}_A, \mathrm{r}_B) \neq \sum_i \omega_i \gamma_i(\mathrm{r}_A, \mathrm{r}_B) \tag{1}$$

$$P_2(\mathrm{r}_A, \mathrm{r}_B) \neq \sum_i \omega_i P_{2,i}(\mathrm{r}_A, \mathrm{r}_B) \tag{2}$$

- Long-range techniques $\neq$ short-range techniques/physics
    - Multipolar expansion, dispersion vs. Coulomb cusp related
- Faster convergence when no singularity is present
    - in 1- and N-particle basis set size
    - tensor product decomposition of $1/r$

B. N. Khoromskij, W. Hackbusch

$$\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty d\alpha\, e^{-\alpha^2 r^2} \approx \sum_i a_i e^{-\alpha_i^2 r^2}$$

needs ≈24 terms; for $w(\mu \approx 0.5 \dots 1)$, 2-3 are needed.

Short-range description accessible

- electron repulsion "universal" (behind density functional approximations?)
- Darboux's principle (1878)
  One may derive an asymptotic expansion in degree j for the coefficients a_j of a series solely from knowledge of the singularities of the function $f(z)$ that the series represents.

J. P. Boyd, Acta Appl. Math. 56, 1 (1999).

Specific choice for eliminating the singularity in the Coulomb interaction: Ewald decomposition

$$w(|\mathrm{r}_1 - \mathrm{r}_2|, \mu) = \frac{\mathrm{erf}(\mu|\mathrm{r}_1 - \mathrm{r}_2|)}{|\mathrm{r}_1 - \mathrm{r}_2|}$$

Ewald decomposition, D. Ceperley, [59]

$$w(r = 0, \mu) = \frac{2}{\sqrt{\pi}}\mu$$

$$w(r \to \infty, \mu) \to \frac{1}{r}$$

$$w(r, \mu = 0) = 0$$

$$w(r, \mu = \infty) = 1/r$$

Another choice for a non-singular interaction

Calculations in finite basis sets (Gaussian, plane wave, . . .) introduce a cutoff in the interaction

E. Giner, ..., J. Toulouse, [186,192]

Removing the singularity

- Choice of a modified interaction: $w = \mathrm{erf}(\mu r)/r$
- Specific case of harmonium
- How to add the missing term

Removing the singularity

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The harmonium hamiltonian

$$H_{harm}(\mu) = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}\omega^2(r_1^2 + r_2^2) + w(|\mathrm{r}_1 - \mathrm{r}_2|, \mu)$$

Change of variables

$$\begin{aligned} \mathrm{R} &= (\mathrm{r}_1 + \mathrm{r}_2)/2 \\ \mathrm{r} &= \mathrm{r}_1 - \mathrm{r}_2 \end{aligned}$$

yields $H_{harm}(\mu) = H_R + H_r(\mu)$,

$$\begin{aligned} H_R &= -\frac{1}{4}\nabla_R^2 + \omega^2 R^2 \\ H_r(\mu) &= -\nabla_r^2 + \frac{1}{4}\omega^2 r^2 + w(r, \mu) \end{aligned}$$

The Schrödinger equation for harmonium

$$H_R \Psi_R = E_R \Psi_R$$

as 3D harmonic oscillator.

$$H_r(\mu)\Psi_r(\mu) = E(\mu)\Psi_r(\mu)$$

solved with

$$\Psi_r = \psi(r) Y_{\ell,m}(\Omega_r)$$

Radial (1D) Schrödinger eqn.,

$$H(\mu)\psi(r,\ell,\mu) = E(\mu)\psi(r,\ell,\mu).$$

where

$$H(\mu) = -\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} + \frac{1}{4}\omega^2 r^2 + w(r,\mu)$$

Harmonium $\omega = 1/2$

Ground state:

$$E(\mu = \infty) = 5/4$$

$$\psi(r, \ell = 0, \mu = \infty) \propto e^{-\frac{1}{4}\omega r^2}(1 + \frac{1}{2}r)$$

$$E(\mu = 0) = 3/4$$

$$\psi(r, \ell = 0, \mu = 0) \propto e^{-\frac{1}{4}\omega r^2}$$

$$E(\mu_1) < E(\mu_2), \;\; \mu_1 < \mu_2$$

The Pauli principle

For interchange of r_1 with r_2,

- no sign change in R,
- no sign change in r, for even ℓ * (sign change through spin function, singlets)
- sign change, for odd ℓ (triplets)

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*Kutzelnigg, Morgan 1992

Removing the singularity

- Choice of a modified interaction
- Specific case of harmonium: 1D radial equation
- How to add the missing term

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Adiabatic connection, general

$$H(\lambda,\mu) = H(\mu) + \lambda\left(H - H(\mu)\right)$$

Schrödinger equation:

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

First-order perturbation theory (Hellmann-Feynman theorem, P. Güttinger):

$$\partial_\lambda E(\lambda,\mu) = \langle\Psi(\lambda,\mu)|\partial_\lambda H(\lambda,\mu)|\Psi(\lambda,\mu)\rangle$$

Adiabatic connection:

$$E = E(\lambda=0,\mu) + \int_0^1 d\lambda\,\langle\Psi(\lambda,\mu)|\partial_\lambda H(\lambda,\mu)|\Psi(\lambda,\mu)\rangle$$

Correction to $E(\mu) = E(\lambda=0,\mu)$:

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

Adiabatic connection, for harmonium, $N = 2$

$$H - H(\mu) = \bar{w}(r,\mu) = \frac{1}{r} - \frac{\mathrm{erf}(\mu r)}{r} = \frac{\mathrm{erfc}(\mu r)}{r}$$

- $\bar{w}$ is short-ranged (for “large” μ).
- $\bar{w}$ has a Coulomb singularity.
- $v(\mathrm{r}_1) + v(\mathrm{r}_2)$ is chosen not to change.

$$\partial_\lambda E(\lambda,\mu) = \int_0^\infty dr\, 4\pi\, r^2\, \frac{\mathrm{erfc}(\mu r)}{r}\, |\psi(r,\ell,\lambda,\mu)|^2$$

Adiabatic connection:

$$\bar{E}(\mu) = \int_0^1 d\lambda \int_0^\infty 4\pi r^2 dr\, \bar{w}(r,\mu)\, |\psi(r,\ell,\lambda,\mu)|^2$$

Remarks on the adiabatic connection

- $\Psi(\lambda \neq 0, \mu)$ in $\langle \Psi(\lambda, \mu) | \partial_\lambda H(\lambda, \mu) | \Psi(\lambda, \mu) \rangle$ is unknown, as Schrödinger equation solved only for $\lambda = 0$.
- When $H - H(\mu)$ modifies only the interaction between electrons, integration over all variables except r performed first: one still has an integral over λ and r.
- Kinetic energy for $\lambda > 0$ not needed.
- Direct connection to fluctuation-dissipation theorem, RPA, etc.

Removing the singularity. Summary

- Choice of a modified interaction
- Specific case of harmonium
- How to add the missing term: adiabatic connection over $\lambda \bar{w}$, short-range operator – singularity present

Removing the singularity

Procedure:

- Choose a model long-range interaction (μ in $\mathrm{erf}(\mu r)/r$).
- Solve the Schrödinger equation (harmonium, radial equation).
- Use the adiabatic connection to correct:

$$E = E(\lambda = 0, \mu) + \int_0^1 d\lambda \, \langle \Psi(\lambda, \mu) | \partial_\lambda H(\lambda, \mu) | \Psi(\lambda, \mu) \rangle$$

How?

Basic idea: choice

1. Remove the singularity from the potential of the interaction between electrons and solve the Schrödinger equation.
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    - Density functionals
    - Extrapolation
    - Exact conditions on the wave function: Generalized coalescence conditions

Density functional correction

Hohenberg-Kohn Theorem valid for $w(r,\mu)$

$$F(\rho,w)=\sup_v\left(E(v,w)-\int_{\mathbb{R}^3}d\mathrm{r}\rho(\mathrm{r})v(\mathrm{r})\right)$$

$$E(v,w)=\inf_\Psi\langle\Psi|T+\sum_{i=1,N}v(\mathrm{r}_i)+\sum_{1\leq i<j\leq N}w(|\mathrm{r}_i-\mathrm{r}_j|)|\Psi\rangle$$

Lieb, 1983

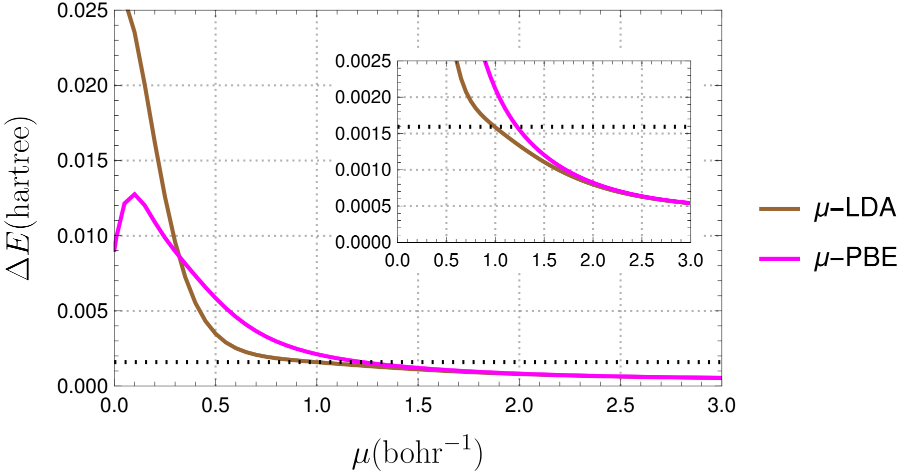
- Kohn-Sham treats explicitly $w=0$ problem, and obtains with a density functional the correction for the $w=1/r$ system.
- Here, we consider $w(r,\mu)$ instead of $w(r,\mu=0)=0$, [52].
- $v(r)\rightarrow v(r,\mu)$, only for density functional correction, in principle, to yield ρ.
- Ground state theory.
- Variational, in principle.

Producing density functional approximations

Local density approximation: transfer from the uniform electron gas,

- for correction of $E(\mu)$: μ-LDA, μ-PBE
- only for [exchange and] correlation

Larger errors as range extends (μ decreases)



Density functional correction. Summary

Density functional approximations can be constructed (μ-LDA, etc.)
Not clear what to do for small μ (longer range).

Extrapolation

FLEIM

Forward Looking Empirical Interpolation Method [202] †

- Use several models $E(\mu_i), \quad i = 0, \dots, M$
    - M can be increased, but should be kept small.

      Keep the number of accurate calculations small.
    - μ_i choosen among values smaller than some freely chosen μ.

      Cost is expected to decrease with μ; e.g., multipolar expansion possible.
- Choose basis functions $\chi_k(\mu)$ able to describe $\bar{E}(\mu)$.
- Select M such basis functions (using only basis set knowledge).
- Solve

$$E = E(\mu_i) + \sum_{k=1}^{M} c_k \chi_k(\mu_i) \quad i = 1, .., M+1$$

for E.

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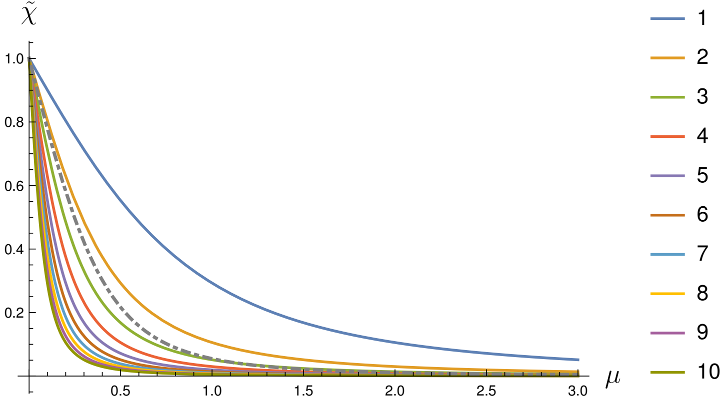
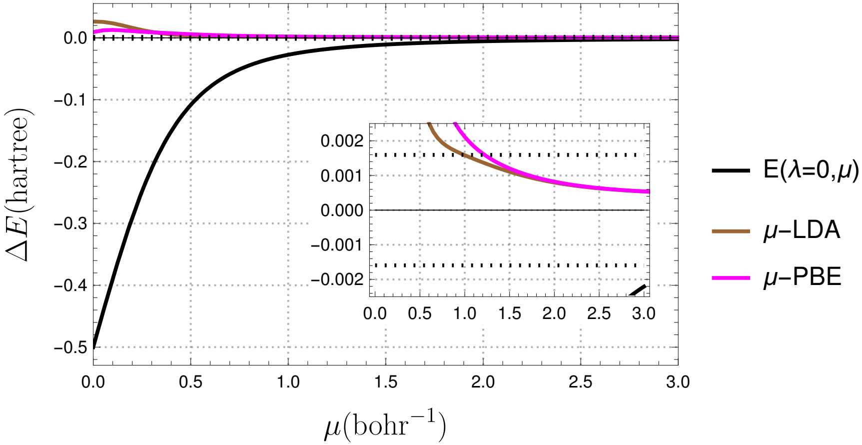
† Variant of EIM, Barrault, Maday, Nguyen, Patera, Compt. Rend. Math., **339, 667 (2004)**

Choice of basis

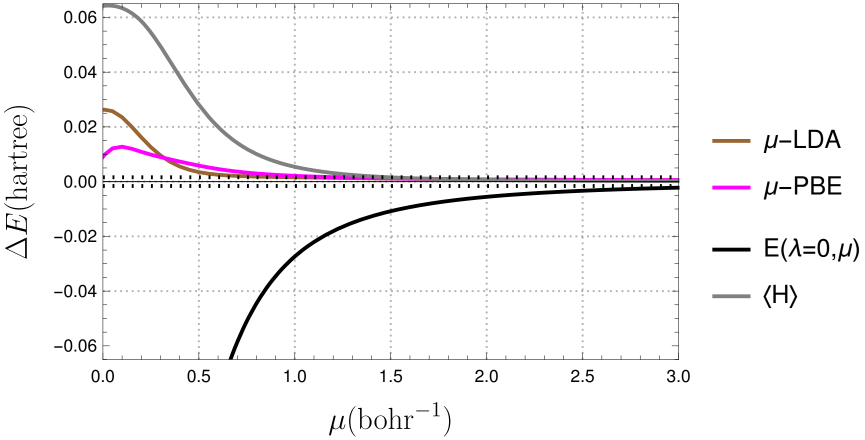
$$\chi_k(\mu) = 1 - \frac{k\mu}{\sqrt{1+(k\mu)^2}}$$



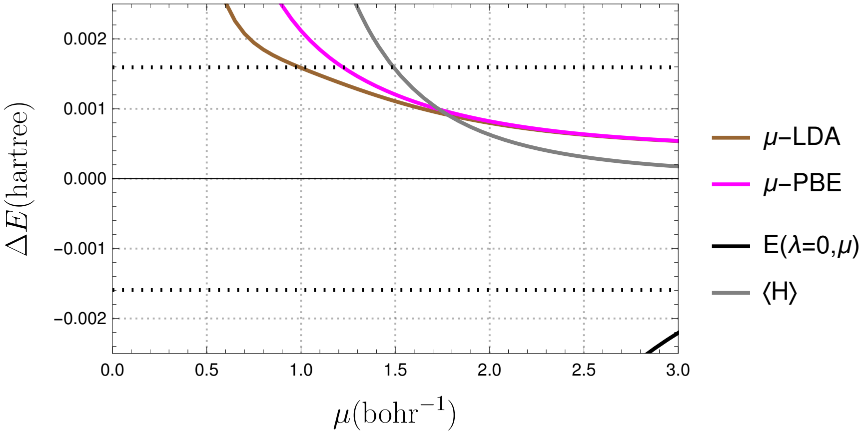
Low quality of model



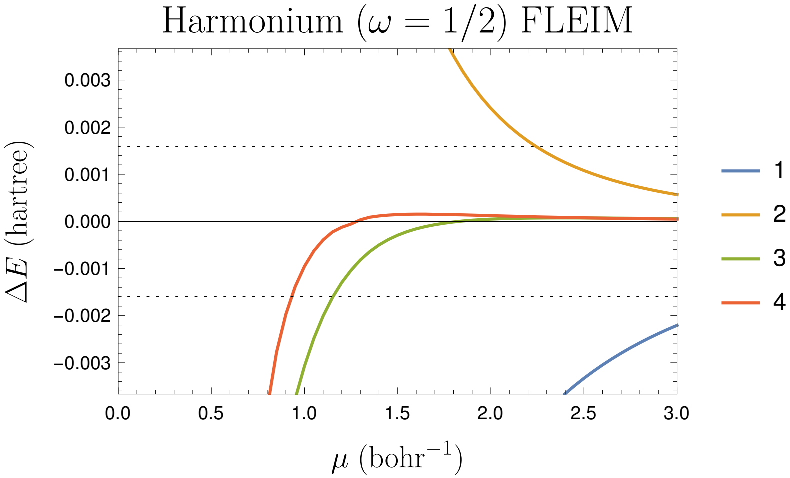
$\langle H \rangle$



$\langle H\rangle$



Errors


Harmonium ($\omega = 1/2$) FLEIM
ΔE (hartree)
0.003
0.002
0.001
0.000
−0.001
−0.002
−0.003
0.0
0.5
1.0
1.5
2.0
2.5
3.0
μ (bohr^{-1})
1
2
3
4

Extrapolation: Summary

- FLEIM works, but needs a few points
- “Wall” at small μ

Generalized coalescence conditions

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

. . .

Coalescence conditions

Kato cusp condition: Change $\mathrm{r}_1, \mathrm{r}_2$ to R, r.

$$H = -\partial_r^2 - \frac{2}{r}\partial_r + \frac{\ell(\ell+1)}{2r^2} + \frac{1}{r} + \ldots$$

$$\frac{H\psi}{\psi} = E$$

for all r, also for $r \to 0$. For $r \to 0$,

$$\psi(r,\ell) = r^\ell \sum_{k=0} c_k r^k$$

Generalized:

$$\frac{H^n\psi}{\psi} = E^n$$

imposed for test function

Generalized coalescence conditions for the separable Schrödinger equation

$$v(r) + w(r) = \sum_{k=-1} \alpha_k r^k$$

$$\psi(r,\ell) = r^\ell \sum_{k=0} c_k r^k$$

$$-2c_1 + \alpha_{-1} c_0 = 0 \tag{3}$$

$$-n(n+1)\, c_n + \sum_{k=-1}^{n-2} \alpha_k c_{n-k-2} + (\alpha_0 - E) c_{n-2} = 0,\ n = 2, 3, \ldots \tag{4}$$

- Generalization to non-separable case exists.
- They do not specify c_0 (normalization); yield only c_k/c_0
- c_k depend on λ, μ.

Perturbation of the exact solution, $\mu \to \infty$

- Change of variables ($r \to 0, \mu \to \infty$)

$$H(\lambda,\mu) = T(r) + \frac{\mathrm{erf}(\mu r)}{r} + \lambda \frac{\mathrm{erf}(\mu r)}{r} = \mu^2 \left(T(x) + \frac{1}{\mu} \left(\frac{\mathrm{erf}(x)}{x} + \lambda \frac{\mathrm{erf}(x)}{x} \right) \right)$$

$$T(x) + \frac{1}{\mu} \left(\frac{\mathrm{erf}(x)}{x} + \lambda \frac{\mathrm{erf}(x)}{x} \right) \approx 0$$

- $\psi(r,\ell,\lambda,\mu)$ is explicit (erf, etc.), to order $1/\mu$, up to normalization factor.
- In particular,

$$\psi(r,\ell,\lambda,\mu) = \psi(r=0,\ell) \left(1 + \mu^{-1} \frac{1-\lambda}{(2\ell+1)\sqrt{\pi}} + \dots \right) \sum_{k=0} \frac{c_k}{c_0} r^k$$

leaves unknown prefactor $\psi(r=0,\ell)$ independent of λ, μ.

Obtaining the prefactor $|\psi(r=0,\ell)|$

- Short-range operator $\mathfrak{w}(\mathfrak{r})$ explores ψ for short-range only.
- Choice: $\mathfrak{w}(\mathfrak{r}) = \bar{w}(r,\mu) = \mathrm{erfc}(\mu r)/r$, as also in

$$\langle\psi(\mu)|H|\psi(\mu)\rangle = \langle\psi(\mu)|H(\lambda=0,\mu)|\psi(\mu)\rangle + \langle\psi(\mu)|\bar{w}|\psi(\mu)\rangle$$

- $\psi(r,\ell,\lambda=0,\mu)$ supposed known from $H(\mu)\psi(\mu) = E(\mu)\psi(\mu)$.

$$\int_0^\infty dr\, 4\pi r^2 |\psi(r,\ell,\lambda=0,\mu)|^2 \mathfrak{w}(r) = |\psi(\ell,r=0)|^2 \int_0^\infty dr 4\pi r^2 \left|\frac{\psi(r,\ell,\lambda=0,\mu)}{\psi(r=0,\ell)}\right|^2 \mathfrak{w}(r)$$

- To get $|\psi(\lambda=0)|^2$, use for the r.h.s. the expression for large μ,

$$\mathcal{I}(\lambda,\mu,K) = \int_0^\infty dr\, 4\pi r^2 \left| \left(1+\mu^{-1}\frac{1-\lambda}{(2\ell+1)\sqrt{\pi}}\right) \sum_{k=0}^{K} \frac{c_k}{c_0} r^k \right|^2 \bar{w}(r,\mu)$$

- Analytical expression for $\mathcal{I}$ through

$$\int_0^\infty dr\, 4\pi r^2\, r^k \frac{\mathrm{erfc}(\mu r)}{r} = \frac{4\sqrt{\pi}}{k+2}\Gamma\left(\frac{k+3}{2}\right)\mu^{-(k+2)}$$

Obtaining the correction to the energy $\bar{E}(\mu)$

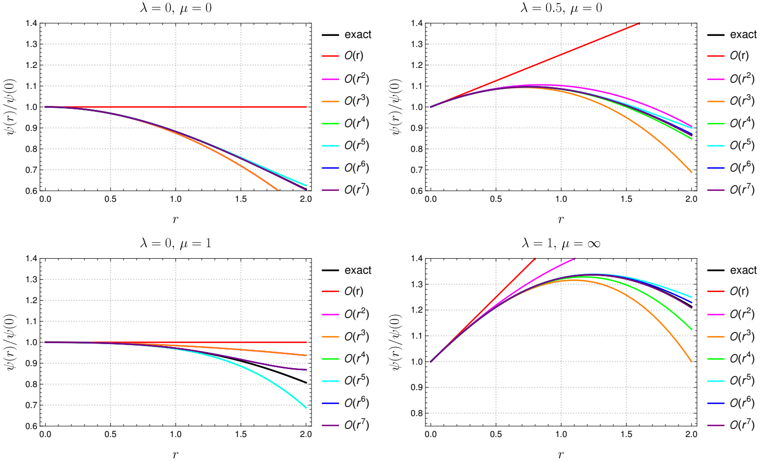
The adiabatic connection,

$$\bar{E}(\mu) = \int_0^1 d\lambda \int_0^\infty 4\pi r^2 dr\, \bar{w}(r,\mu)\,|\psi(r,\ell,\lambda,\mu)|^2$$

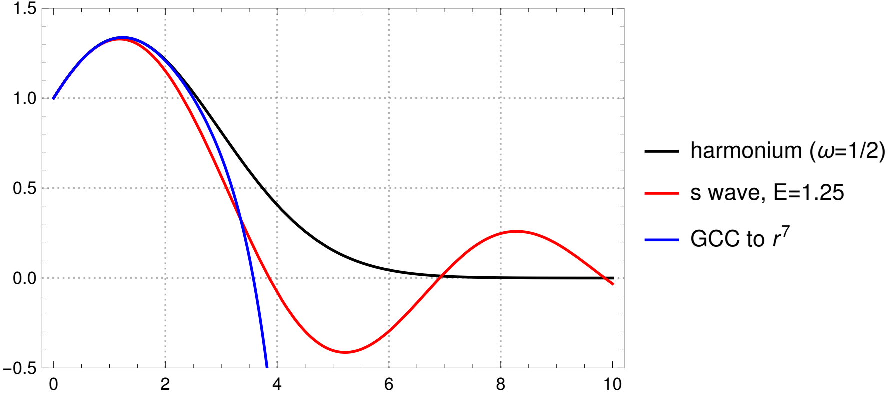
for $\mu \to \infty$,

$$\bar{E}(\lambda=0,\mu) \approx \frac{\langle \psi(\lambda=0,\mu)|\bar{w}|\psi(\lambda=0,\mu)\rangle}{\mathcal{I}(\lambda=0,\mu,K)} \int_0^1 d\lambda\, \mathcal{I}(\lambda,\mu,K)$$

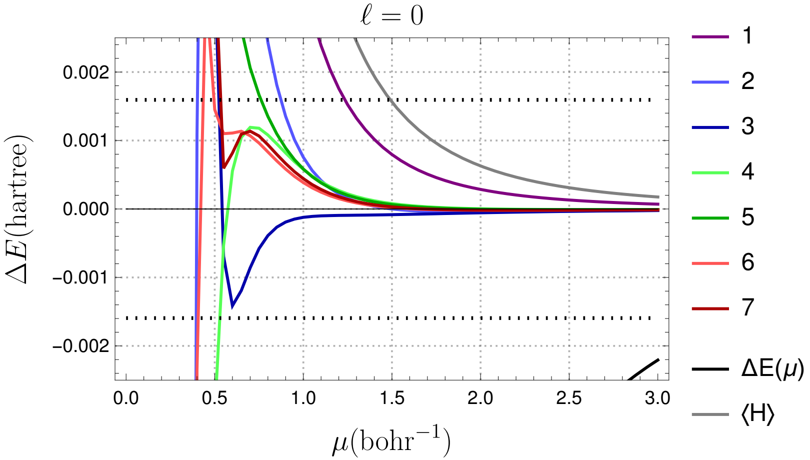
ψ for "small" *r*



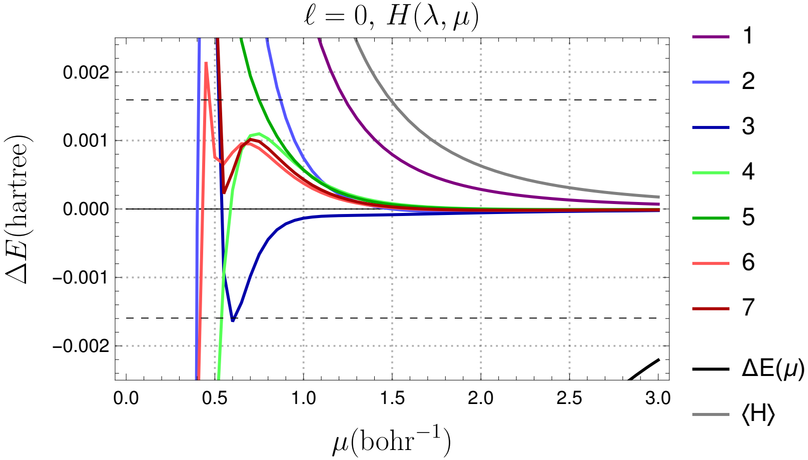
Sensitivity to external potential (ω)



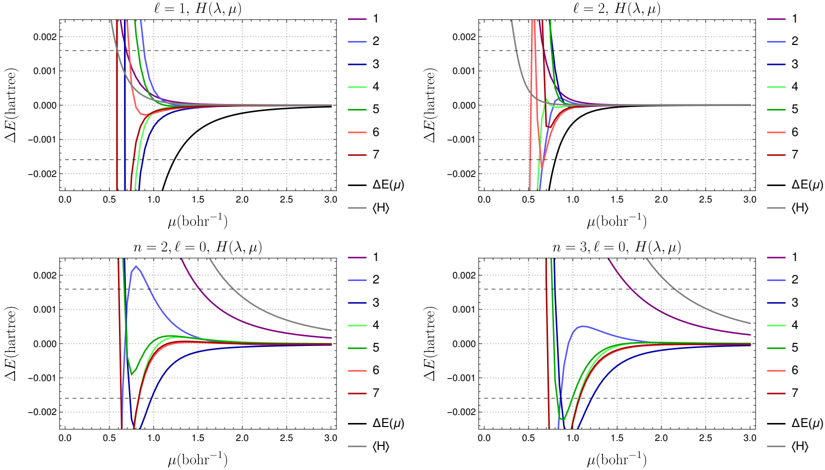
Using the “unknown” exact energy



Using $E(\lambda,\mu) \approx E(\mu) + \lambda\langle\psi(\lambda=0,\mu)|\bar{w}(\mu)|\psi(\lambda=0,\mu)\rangle$



Excited states using $E(\lambda, \mu) \approx \langle H(\lambda, \mu) \rangle$



Generalized coalescence conditions.Summary

- Only one model system
- Model system partially interacting: “wall” when interaction starts having long-range character
- Improvement over $\langle H \rangle$
- Improvement over using Kato cusp condition only

Present status and perspective

Present status and perspective

Topic	Present	To explore
Relationship with DFT	global	local[1]
Model interaction	$\mathrm{erf}(\mu r)/r$	basis set dependent[2], etc.
Basis (extrapolation)	satisfactory	improvement
Basis (GCC[3])	r^k	?
Applicability GCC[3]	harmonium	arbitrary systems[4]
Mathematical foundation	for chemists	for mathematicians
The "wall" (small μ)	exists	eliminated?

[1] Size-consistency

[2] Projection, localization / optimized effective potential

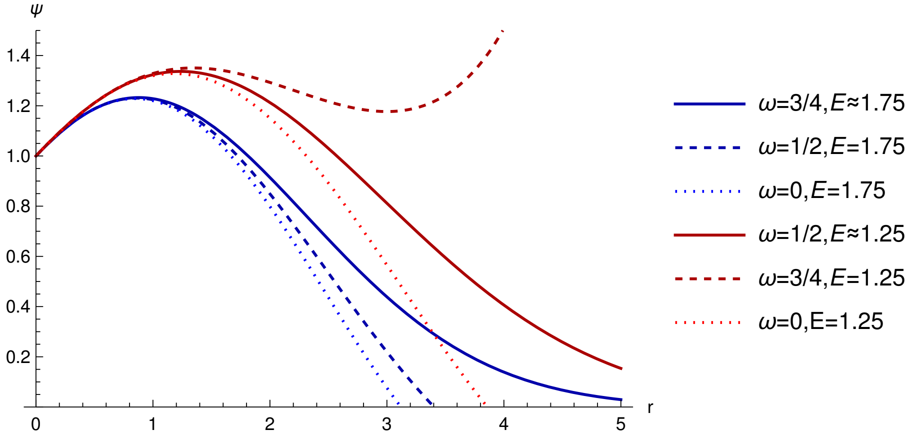
[3] Generalized coalescence conditions

[4] Algorithms

Supplementary information

Short-range description "universal"

$$\left(-\nabla_r^2 + \frac{1}{4}\omega^2 r^2 + 1/r - E\right)\psi(r) = 0, \quad \psi(0) = 1, \ \psi'(0) = 1/2$$



A natural choice for a non-singular interaction

Almost all calculations are done in a basis set.
Project the Coulomb operator $(1/r)$ onto this basis set with projection operator $P_{\mathcal{B}}$:

$$w = \int_{S^2} d\Omega_r \, P_{\mathcal{B}} \, \frac{1}{r} \, P_{\mathcal{B}}$$

w is non-singular.
w is non-local.
Localization possible as for one-particle optimized effective potential.
One can associate a μ-value to it.

E. Giner, ..., J. Toulouse, [186,192]

For plane waves

$$\int_{\mathbb{R}^3} d\mathrm{r}_1 \int_{\mathbb{R}^3} d\mathrm{r}_2 \, e^{i\mathrm{p}\mathrm{r}_1} e^{i\mathrm{q}\mathrm{r}_2} \frac{1}{|\mathrm{r}_1 - \mathrm{r}_2|} \propto \delta(\mathrm{p}+\mathrm{q}) \frac{1}{|\mathrm{p}-\mathrm{q}|^2}$$

Similar to a cutoff in $|\mathrm{p}-\mathrm{q}|$. $\mathrm{erf}(\mu r)/r$ is a smooth cutoff.