h-P discontinuous Galerkin finite element method for electronic structure calculations

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We combine results from

- Numerical approximation of elliptic problems in non smooth domains
- Approximation of non linear eigenvalue problems

and apply them to the models used in quantum chemistry.

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1. Motivation: models for electronic structure calculations
2. Convergence, regularity
3. Asymptotics of the solution and design of an optimal h-P space from a priori estimates.

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Motivation: the Schrödinger equation

The Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

is set in a $1 + 3(N + M)$ dimensional space for a system of N electrons and M nuclei. It is therefore hard to approach computationally, even for systems of moderately small size.

A first approximation (Born-Oppenheimer) consists in considering the nuclei as fixed particles, thus calculating only electronic wavefunctions.

Many methods have been proposed for the approximation of the electronic wavefunctions: among them

- Hartree-Fock (and post Hartree-Fock) methods,
- methods based on density functional theory (Kohn-Sham local density approximation, ...).

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Motivation: the Hartree-Fock approximation

$$I^{\mathrm{HF}} = \inf\left\{ E^{\mathrm{HF}}(\varphi_1, \ldots, \varphi_N),\ \varphi_i \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \varphi_i \varphi_j = \delta_{ij} \right\}$$

$$E^{\mathrm{HF}} = \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \varphi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V + \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\Phi(x)\rho_\Phi(y)}{|x-y|} dxdy - \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\tau_\Phi(x,y)|^2}{|x-y|} dxdy$$

where

$$\tau_\Phi(x,y) = \sum_{i=1}^{N} \varphi_i(x)\varphi_i(y) \qquad \rho_\Phi(x) = \tau_\Phi(x,x)$$

It can be shown that

$$\varphi_i = \underset{\varphi}{\operatorname{argmin}} \left\{ \langle \mathcal{F}\varphi, \varphi \rangle,\ \varphi \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} |\varphi|^2 \le 1,\ \int_{\mathbb{R}^3} \varphi_i \varphi_j = 0,\ \forall j \neq i \right\},$$

where $\mathcal{F}$ is the self adjoint operator

$$\mathcal{F}\psi = -\frac{1}{2}\Delta\psi + V\psi + \left(\rho_\Phi \star \frac{1}{|x|} \right) \psi - \int_{\mathbb{R}^3} \frac{\tau_\Phi(x,y)}{|x-y|} \psi(y) dy.$$

We therefore have the eigenvalue problem

$$\mathcal{F}\varphi_i = \varepsilon_i \varphi_i \qquad i = 1, \ldots, N$$

[Flad et al., 2008] showed that around the origin the solutions belong to (a subset of) the countably normed spaces

$$\mathcal{K}^{\infty,\gamma} = \left\{ u \in \mathcal{D}' :\ |x|^{|\alpha|-\gamma} \partial^\alpha u \in L^2,\ |\alpha| = s,\ \forall s \in \mathbb{N} \right\}.$$

Classic finite element and spectral approximations

The eigenfunctions are thus not regular in the Sobolev spaces $H^k(\Omega) = W^{k,2}(\Omega)$, but share features with the solution of e.g. problems in non convex polygonal domains or fraction elliptic problems.

The convergence speed of "classic" finite element and spectral methods is bounded by the regularity of the solution in Sobolev spaces.

Classic finite element and spectral methods

If $u \in H^{s+1}(\Omega)$, the following approximation results hold:

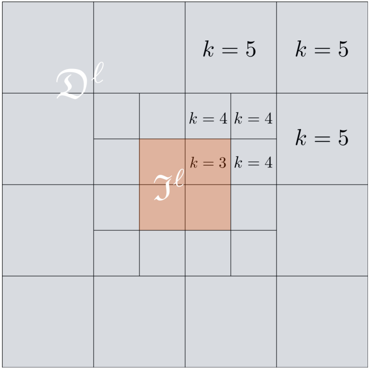
- for finite element methods of degree $r \leq s$ and element size h:

$$\|u - u_h\|_{H^1(\Omega)} \lesssim h^r |u|_{H^{r+1}(\Omega)};$$

- for spectral methods of degree p:

$$\|u - u_\delta\|_{H^1(\Omega)} \lesssim p^{-s} \|u\|_{H^{s+1}(\Omega)};$$

The discontinuous h-P finite elements method



Finite element space:

$$X_\delta = \{v \in L^2(\Omega) : v_{|_S} \in \mathbb{Q}_{k_S}(S), \forall S \in \mathcal{T}\}.$$

The mesh is geometrically refined by a factor σ towards the center (where the singularity lies), while the polynomial degree usually decreases with a slope s.

Graded mesh, uniform slope:
At the refinement step ℓ, the elements in $\mathcal{I}^\ell$ will have edges of length σ^ℓ, while in the outermost element the polynomial degree will be $k_0 + \lfloor s\ell \rfloor$

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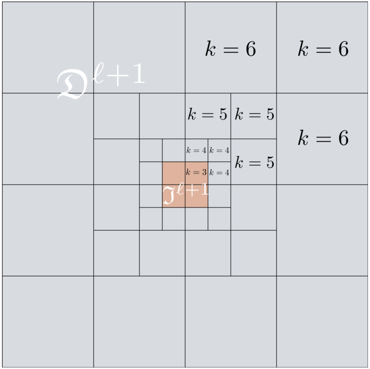

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The discontinuous approach

We consider the bilinear form associated with the Laplace operator

$$d(u,v) = (\nabla u, \nabla v)_\Omega,$$

defined over $X \times X$ (with e.g. $X = H_0^1(\Omega)$) and define a bilinear form over $X_\delta \times X_\delta$

$$d_\delta(u_\delta, v_\delta) = \sum_{S\in\mathcal{T}} (\nabla u_\delta, \nabla v_\delta)_S - \underbrace{\sum_{e\in\mathcal{E}} (\{\!\{\nabla u_\delta\}\!\}, [\![v_\delta]\!])_e}_{\text{consistency}} - \underbrace{\sum_{e\in\mathcal{E}} (\{\!\{\nabla v_\delta\}\!\}, [\![u_\delta]\!])_e}_{\text{adjoint consistency}}$$

$$+ \underbrace{\sum_{e\in\mathcal{E}} \alpha \frac{k_e^2}{h_e} ([\![u_\delta]\!], [\![v_\delta]\!])_e}_{\text{stability}}.$$

The set $\mathcal{E}$ is the set of all $d-1$ dimensional inter-element boundaries, while $\{\!\{\cdot\}\!\}$ and $[\![\cdot]\!]$ are average and jump operators respectively.

Approximation results in the discontinuous h-P space

Let $X = \mathcal{K}^{\infty,\gamma}(\Omega, \mathcal{C}) \cap H^1(\Omega)$. We introduce the space $X(\delta) = X + X_\delta$ and the norms

$$\|u\|_{\mathrm{DG}}^2 = \sum_{S\in\mathcal{T}} \|\nabla u\|_S^2 + \sum_{e\in\mathcal{E}} \frac{N_e^2}{h_e} \|[\![u]\!]\|_e^2$$

$$|||u|||_{\mathrm{DG}}^2 = \|u\|_{\mathrm{DG}}^2 + \sum_{K\in\mathfrak{D}^\ell} \sum_{e\in\mathcal{E}_K} \frac{h_e}{k_e^2} \|\nabla u\|_e^2 + \sum_{K\in\mathfrak{I}^\ell} \sum_{e\in\mathcal{E}_K} k_e^2 |e|^{-1} h_e \|\nabla u\|_{L^1(e)}^2$$

We now consider the space

$$\mathcal{A}_\gamma = \left\{ v \in \mathcal{K}^{\infty,\gamma}(\Omega, \mathcal{C}),\ |u|_{\mathcal{K}^{k,\gamma}} \le CA^k k! \right\}$$

with $|v|_{\mathcal{K}^{k,\gamma}}^2 = \sum_{|\alpha|=k} \|r^{k-\gamma}\partial^\alpha v\|^2$, r distance from the nearest singularity in $\mathcal{C}$. [Schötzau et al., 2013] showed that for a function $u \in \mathcal{A}_\gamma$ and a space X_δ with N degrees of freedom,

$$\inf_{v_\delta \in X_\delta} |||u - v_\delta|||_{\mathrm{DG}} \lesssim \exp(-bN^{1/(d+1)}).$$

The Gross-Pitaevskii equation

In a periodic domain $\Omega = (\mathbb{R}/L)^d$ we consider the problem of minimizing the energy

$$E(v) = \underbrace{\frac{1}{2}\int_\Omega |\nabla v|^2}_{d(v,v)} + \frac{1}{2}\int_\Omega V v^2 + \frac{1}{2}\int_\Omega F(v^2)$$

under the constraint $\|v\| = 1$. The unique minimizer u satisfies for $\lambda \in \mathbb{R}$

$$_{X'}\langle A^u u - \lambda u, v\rangle_X = 0 \quad \forall v \in X$$

where

$$_{X'}\langle A^u v, w\rangle_X = d(u,v) + \int_\Omega V u v + \int_\Omega F'(u^2) v w.$$

The discrete counterparts are

$$\langle A_\delta^{u_\delta} u_\delta - \lambda_\delta u_\delta, v_\delta\rangle = 0 \quad \forall v_\delta \in X_\delta$$

$$\langle A_\delta^{u_\delta} v_\delta, w_\delta\rangle = d_\delta(v_\delta, w_\delta) + \int_\Omega V v_\delta w_\delta + \int_\Omega F'(u_\delta^2) v_\delta w_\delta.$$

Regularity

We may prove the following result for the problem under consideration:

Regularity of the solution

Let us suppose for the sake of simplicity that $f(u^2) = u^2$. Then, if $u \in X$ is the solution to the eigenvalue problem for a potential $V \in A_\gamma(\Omega, \mathcal{C})$,

$$u \in A_\gamma(\Omega, \mathcal{C}).$$

Note that singular potentials are allowed, and those give rise to solutions with cusp-like singularities.

Sketch of the proof:

- $\|r^{|\alpha|+2}\partial^{\alpha+\beta}u\| \leq \|r^{|\alpha|+2}\partial^{\alpha}\Delta u\| + \left\|\left[r^{|\alpha|+2}, \Delta\right]\partial^\alpha u\right\| + \left\|\left[\partial^\beta, r^{|\alpha|+2}\right]\partial^\alpha u\right\|$, with $|\beta| = 2$.
- Equation on the first term, then bounds on the three terms. □

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Convergence

Convergence of the approximation

Let (u, λ) be the solution to the eigenvalue problem and let $(u_\delta, \lambda_\delta)$ be the h-P discontinuous approximations. Then, under proper hypotheses on F,

$$\|u - u_\delta\|_{\mathrm{DG}} \leq C \inf_{v_\delta \in X_\delta} \|\|u - v_\delta\|\|_{\mathrm{DG}}$$

and

$$|\lambda_\delta - \lambda| \leq C \left(\|u - u_\delta\|_{\mathrm{DG}}^2 + \|u - u_\delta\|_{L^2} \right).$$

Similar results have been obtained in [Cancès et al., 2010] in the simpler case of a continuous approximation. The main difference for this case stems from the fact that the approximation is not conforming, i.e., $X_\delta \not\subset X$, thus $\lambda_\delta \not\geq \lambda$.

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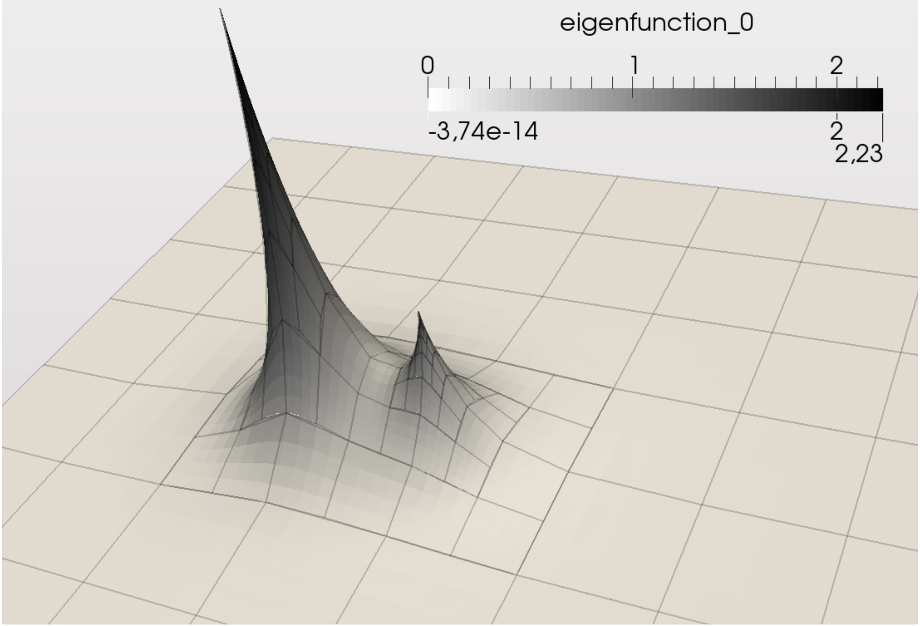
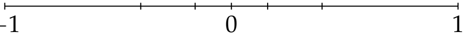
Results visualized

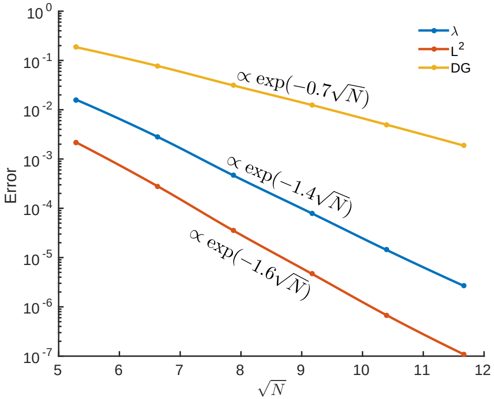


Numerical experiments

In the one dimensional case, with periodic domain $\Omega = [-1, 1]/2\mathbb{Z}$ and the singularity at the center, with potential $V(x) = -|x|^{-3/4}$,



we get the convergence results



Asymptotics of the solution: iterative scheme

We consider the iterative scheme

$$-\Delta u_{n+1} - \frac{1}{|x|^{\gamma}} u_{n+1} + u_n^2 u_{n+1} - bP_{u_n} u_{n+1} = \lambda_{n+1} u_{n+1}$$

where

- $\gamma > 0$ such that $|x|^{-\gamma} \in L^1(\Omega)$,
- P_{u_n} is the projector on u_n,
- $b > 0$ is a shift parameter that enforces the convergence.

We can prove that

- $\|u_n\|_{H^1(\Omega)}$ is bounded, and
- $\sum_{n \in \mathbf{N}} \|u_{n+1} - u_n\|$ is bounded.

Therefore, u_n converges towards a solution of the nonlinear Gross-Pitaevskii equation, with $f(u^2) = u^2$.

Asymptotics of the solution: Mellin transform

We consider the eigenvalue problem

$$-\Delta u_{n+1} - \frac{1}{|x|^\gamma} u_{n+1} + u_n^2 u_{n+1} - bP_{u_n} u_{n+1} = \lambda_{n+1} u_{n+1}.$$

Using the Mellin transform

$$\hat{u}(z) = (\mathcal{M}u)(z) = \int_0^\infty r^{z-1} u(r) dr \qquad \left(\mathcal{M}^{-1}\hat{u}\right)(r) = \int_{\Re z = \beta} r^{-z} \hat{u}(z) dz$$

and an hypothesis on u_n, we get (dropping the subscript $\cdot_{n+1}$)

$$z(z+1)\hat{u}(z) \simeq \hat{u}(z+2-\gamma) + \lambda \hat{u}(z+2) + \sum_{j \in \mathbf{N}} \sum_{k=0}^{\lfloor j/2 \rfloor} a_{jk} \hat{u}(z+2+j-k\gamma).$$

The opposites of the poles of the Mellin transform are the exponents of the asymptotic expansion: for $x \to 0$

$$u \sim C + x + x^{2-\gamma} + \dots$$

One dimensional error analysis

[Gui and Babuska, 1985] showed that for $u \sim x^\alpha$ $(x \to 0)$, given a scaling factor σ and a polynomial increase s

$$\|u - \Pi(u)\| \simeq C(\sigma) \left(\sum_{i=2}^{m} \frac{\sigma^{(2\alpha-1)(1-i)} r^{2(1+s(i-1))}}{(1+s(i-1))^{2\alpha}} \right)^{1/2},$$

where one part is bigger in the element at the singularity and the other tends to be bigger in outer elements.

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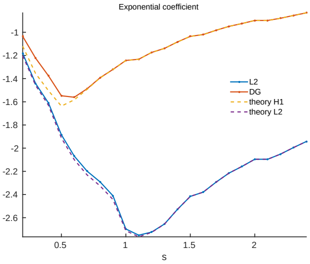


Since $u'(x) \sim x^{\alpha-1}$, we can prove (and show numerically) that the speed of convergence of the two norms of the approximation error reach their minima for different values of the parameters.

Slope optimization

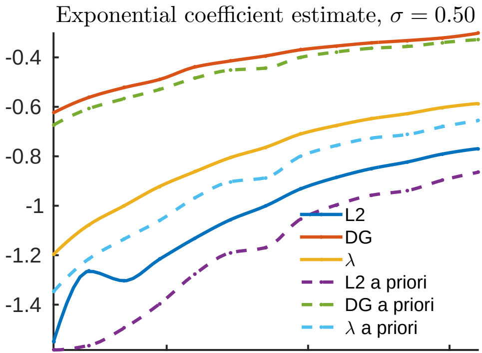
Back to Gross-Pitaevskii:

$$-\Delta u - \frac{1}{|x|^\gamma} u + u^3 = \lambda u.$$

We consider the behaviour of the "exponential coefficient" κ in

$$\|u - u_\delta\| \lesssim \exp\left(\kappa\sqrt{N}\right)$$

with respect to the slope s.



Slope optimization: different potentials

Behaviour for different values of γ in

$$-\Delta u - \frac{1}{|x|^\gamma} u + u^3 = \lambda u.$$

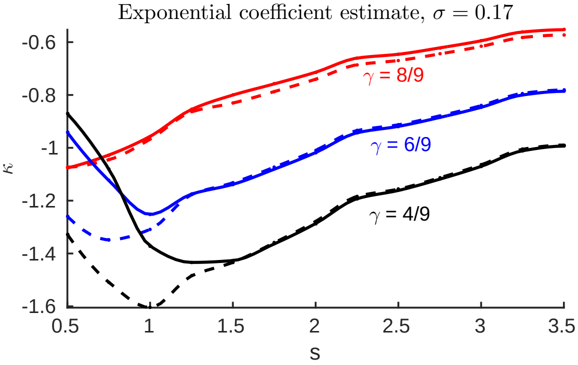


Figure: κ for the DG norm of the error. Dashed line: theory; continuous line: numerical results.

Conclusions and perspectives

- The approximate eigenfunctions and eigenvalues converge with exponential speed to the exact solution.

- The analysis may be applied to the Gross-Pitaevskii and the Thomas-Fermi-von Weizsäcker models, but should be extended to more complex models.

- Given the asymptotics of the solution to the problem considered, the mesh and finite dimensional space can be optimized *a priori* and estimates for the convergence speed can be derived, mainly where the error near the singularity is bigger.

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Thank you for your attention

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