$h-P$ discontinuous Galerkin methods for electronic structure calculation

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We analyse some models used in quantum chemistry for electronic structure computations and we provide some convergence results for the $h-P$ discontinuous Galerkin method on a model problem (Gross-Pitaevskii). We prove the exponential convergence of the approximation to the exact solution and analyze the asymptotics of the solution near its singularities to provide an *a priori* optimized approximation space.
In many real world problems in quantum chemistry, we are mainly concerned with the computation of the *ground state energy* of a system. We consider non linear eigenvalue problems of the form

$$\mathcal{F}u = \lambda u \tag{1}$$

where $\mathcal{F}$ is a self adjoint elliptic operator (depending on u) containing a potential V with singularities in a set of isolated points $\mathcal{C}$.
The solutions to (1) belong to the *countably normed Sobolev space*

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

Since the solution is not regular in the "classical" (Sobolev) sense, the speed of convergence of widely used real space methods (such as the finite element (FE) or the spectral element (SE) methods) is bounded by the regularity of the solution. $h-P$ finite elements methods exploit the structure of the space (2) and provide approximations that are *exponentially convergent* to the solution under a certain hypothesis on the weighted L^2 norms of the derivatives.
Due to the above mentioned characteristics of the models of interest, we consider as a model problem the *Gross-Pitaevkii equation* which for a given domain Ω is written in variational form as

$$ {}_{X'}\langle A^u v, w\rangle_X = \int_\Omega \nabla u \cdot \nabla v + \int_\Omega V uv + \int_\Omega u^2 vw = \lambda(u,v) \tag{3}$$

for $X = H^1(\Omega)$. The analysis applied to this problem can be generalized to some electronic structure models, and it should be the basis for the extension to more complex models such as those mentioned above.
The analysis of the convergence of the numerical solution to the exact solution of (3) is composed of multiple steps. Firstly, we derive some estimates on the regularity of the solution: we find that

$$u \in \mathcal{A}_\gamma(\Omega,\mathcal{C}) = \{v \in \mathcal{K}^{\infty,\gamma}(\Omega,\mathcal{C}) : |v|_{\mathcal{K}^{k,\gamma}} \leq CA^k k!,\ \forall k\}.$$

Secondly, we prove that the discontinuous approximation is converging to the exact solution. Exploiting the results obtained in the linear case [1] and treating the nonlinearity similarly to [2], we prove that

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

Finally, by employing a Mellin transform of the equation, we obtain an asymptotic development of the solution near $\mathcal{C}$. We can therefore optimize the mesh grading parameters and the polynomial order slope using information that we derive on the eigenfunction.

Références

[1] P. F. Antonietti, A. Buffa, and I. Perugia. Discontinuous Galerkin approximation of the Laplace eigenproblem. *Computer Methods in Applied Mechanics and Engineering*, 195(25-28):3483–3503, 2006.

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