A spherical p-method for full-potential electronic structure problems

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Kohn-Sham density functional theory

We consider an isolated closed-shell molecular system in full-potential Kohn-Sham density functional theory (DFT) at temperature zero. Given M nuclei of charges $\{Z_k\}_{k=1}^M$ at positions $\{X_k\}_{k=1}^M$ with $N_e = 2N$ electrons, the critical point condition for the Kohn-Sham density functional E^{KS} is equivalent to a non-linear eigenvalue problem (in Hartree units):
Find lowest N eigenpairs $(\varepsilon_i, \psi_i)_{i=1}^N \subset \mathbb{R} \times H_0^1(\Omega)$, $(\psi_i, \psi_j) = \delta_{ij}$

$$\frac{1}{2}\int_\Omega \nabla\phi \cdot \nabla\psi_i dx + \int_\Omega V_{\text{eff}}\ \phi\psi_i\ dx = \varepsilon_i (\phi, \psi_i)_{L^2(\Omega)} \qquad (1)$$

with the self-consistency requirement $\rho(x) = 2\sum_{i=1}^N |\psi_i(x)|^2$, where

$$V_{\text{eff}}(x) = \sum_{k=1}^M \frac{Z_k}{|x - X_k|} + \int_\Omega \frac{\rho(x')}{|x - x'|} dx' + v_{xc}[\rho].$$

Major difficulty in practical calculations: Resolution of the Coulomb singularity induced by the singular nuclear potentials $Z_k/|x - X_k|$.

A recent development was the suggestion of hp-finite element method (FEM) with local a priori geometric refinement in the vicinity of the nuclei, which was shown to yield exponential convergence [1]. Unfortunately, such an approach suffers from the introduction of a large number of degrees of freedom that accumulate at the nuclei. In this work, we propose to replace the geometric refinements near the nuclei in favour of a locally adapted discretization to obtain a pure p-method.

Mortar sphere-p-FEM

Motivation: Electronic orbitals exhibit cusp singularity at nucleus X_k and with spherical coordinates $(r, \Theta) \in \mathbb{R} \times S^2$ for distance vector $x - X_k$ the local expansion [3]

$$\psi_i(x) = \sum_{\ell=1}^\infty r^\ell \sum_{0\le j\le \ell} c_{k,\ell} Y_j(\Theta)\ , \qquad (2)$$

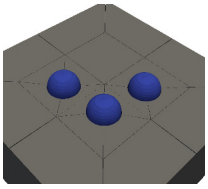
where $Y_j \in \mathcal{Y}_j := \{Y \in C^\infty(S^2) | -\Delta_{S^2} Y = j(j+1)Y\}$, the eigenspace of spherical harmonics for the eigenvalue j.

This implies $H^s([0, R] \times S^2)$-regularity to any order $s \in \mathbb{R}_+$ [2].

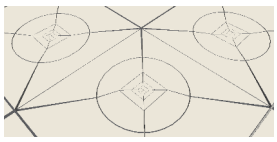
Inspired by a descendant of the augmented plane wave method in [2], we propose a

mortar sphere-p-FEM

→ decomposition of Ω into disjoint atomic spheres $\{C_k\}$ and intermediate domain D
→ spherical p-method on every atomic sphere C_k
→ p-FEM discretization on curved hexahedral elements in intermediate domain D
→ Weakly continuous matching of basis functions at interfaces ∂C_i by mortar coupling



Mesh for H_2O with domain decomposition



hp-adaptive FEM mesh for H_2O

Spherical p-method: tensor product of radial polynomials with spherical harmonics

$$S^p(C_k) = P_p(0, R) \otimes \bigoplus_{0\le j\le p} \mathcal{Y}_j$$

Approximation properties of $S^p(C_k)$ for electronic orbital type singularities (2) (*cf.* [2])

$$\inf_{v_p \in S^p(C_i)} \|u - v_p\|_{H^1([0,R]\times S^2)} \le C_s p^{-(s-1)} \|u\|_{H^s([0,R]\times S^2)} \qquad (3)$$

p-FEM in intermediate domain: H^1-conforming FEM on a curved hexahedral mesh T

$$S^p(D, T) = \{u \in H^1(D) |\ u \circ F_K \in P_p(0, 1)^{\otimes 3}\ \forall K \in T\}$$

with analogous spectral approximation properties as (3) in $H^s(D)$.

Mortar coupling: Continuity of ψ_i over interface $\Gamma_k = \partial C_k$ approximated by weakly vanishing jump condition on the traces with discrete space $M^p(\Gamma_k) \subset H^{-1/2}(\Gamma_k)$

$$V_p = \left\{v \in \bigoplus_{k=1}^M S^p(C_k) \oplus S^p(D, T) \middle| \int_{\Gamma_k} [v] w dS = 0\ \forall w \in M^p(\Gamma_k), \forall k\right\} (4)$$

Theorem: Super-algebraic p-convergence of discrete ε_i^p and ψ_i^p for V_p-discretized non-conforming version of linearized (ρ fixed) asymptotic eigenvalue problem (1).

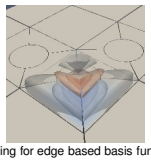
Construction of a basis for the mortar space

For each FE basis function b in $S^p(D, t)$ non-vanishing on a *single* interface Γ_k an extension into the ball C_k is computed by

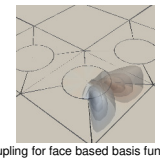
① Representing the trace of b on Γ_k in the basis of the trace space $TS^p(D, T, \Gamma_k)$ → coefficients C_{D,Γ_k}.
② Selecting a set of functions in $S^p(C_k)$ whose traces form a basis of $TS^p(C_k)$.
③ Computing coefficients of weakly continuous continuation of b into C_k relative to functions chosen in step ② by resolving the mortaring condition (4):

$$S_{M^p(\Gamma_k), TS^p(C_k,\Gamma_k)} c_{C_k,\Gamma_k} = S_{M^p(\Gamma_k), TS^p(D,T,\Gamma_k)} c_{D,\Gamma_k} \qquad (5)$$

with the overlap matrices $S_{M^p(\Gamma_k), TS^p(C_k,\Gamma_k)}$ and $S_{M^p(\Gamma_k), TS^p(D,T,\Gamma_k)}$.
④ Lifting each local interface basis function into the interior of C_k.



Coupling for edge based basis function.



Coupling for face based basis function.

High-order finite element quadrature must be used at the numerical evaluation of overlap integrals in (5) to obtain machine precision without sacrificing performance.

Asymptotic study of the Kohn-Sham problem

① Galerkin discretization and solution of the non-linear problem

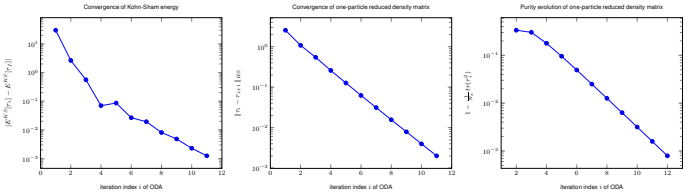
- Minimization of the non-linear Kohn-Sham energy functional by the optimal damping algorithm [4]: iterative steepest descent for extension of Kohn-Sham model to mixed states,

in (mixed) state τ find $\arg\inf_\sigma \frac{d}{dt} E^{KS}[(1-t)\tau + t\sigma]\big|_{t=0} = \langle H_{\rho_\tau}\rangle_\sigma - \langle H_{\rho_\tau}\rangle_\tau$.

- Requires the solution of a generalized eigenvalue problem corresponding to a linearized form of (1) with relaxed self-consistency in every step. This is achieved by a transform to a standard eigenvalue problem by a Cholesky-factorization of the shifted Hamiltonian and subsequent Lanczos iteration for the largest eigenvalues.
- The Hartree potential can be obtained by solving Poisson's equation.
- For the exchange-correlation energy we used the local density approximation (LDA) with Dirac's formula for the exchange in the homogeneous electron gas.

② Results for the non-linear Kohn-Sham problem

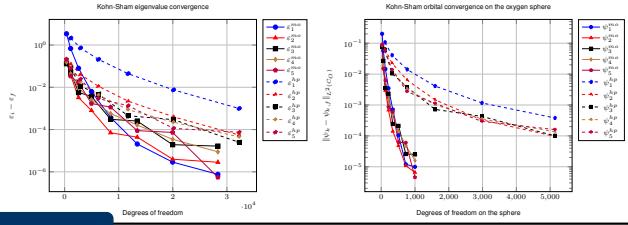
Optimal damping iteration for H_2O molecule with fixed mortar sphere-p-FEM Galerkin discretization $V_{p=7}$ using electronic orbitals for isolated nuclear potential as initial state



Purity converges to 1, i.e. iterate is asymptotically a standard Kohn-Sham solution.

③ Linearized asymptotic Kohn-Sham eigenvalue problem: mortar sphere-p-FEM vs. hp-FEM

Comparison of discrete eigenpair convergence for linearized Kohn-Sham eigenvalue problem (1) on H_2O with ρ fixed from solution of non-linear problem in previous section and reference solution computed using $V_{p=10}$ (38772 DoFs).
→ exponential convergence for both discretizations
→ mortar sphere-p-FEM is more efficient than hp-FEM in terms of precision per DoF



References

[1] Yvon Maday. h–p finite element approximation for full-potential electronic structure calculations. *Chinese Annals of Mathematics, Series B*, 35(1):1–24, 2014.
[2] H. Chen and R. Schneider. Numerical analysis of augmented plane waves methods for full-potential electronic structure calculations. *Preprint 116, DFG-SPP 1324*, 2012.
[3] Heinz-Jürgen Flad, Reinhold Schneider, and Bert-Wolfgang Schulze. Asymptotic regularity of solutions to Hartree–Fock equations with Coulomb potential. *Mathematical Methods in the Applied Sciences*, 31(18):2172–2201, 2008.
[4] Eric Cancès. Self-consistent field algorithms for Kohn–Sham models with fractional occupation numbers. *The Journal of Chemical Physics*, 114(24):10616–10622, 2001.
[5] Website of the numerical C++ library Concepts, `http://www.tu-berlin.de/?concepts`, 2015.