High-Order, Adaptive Methods for Atomic Structure Calculations

Ondřej Čertík[1,2], John E. Pask[1], Pavel Solin[2]   [1] Lawrence Livermore National Laboratory, [2] University of Nevada, Reno

Abstract

We compare several high-order **finite element (FE)** methods for solving the radial Schrödinger and Dirac equations, in particular, spectral FEM (uniform-p-FEM), p-FEM, h-FEM, and hp-FEM. All methods provide a robust way of calculating all eigenstates to machine precision. They differ in the rate of convergence and whether a good initial mesh is needed or not, as well as providing robust error control.

Motivation

The need for an efficient solution to the radial Dirac equation arises in the calculation of the **equation of state (EOS) and opacity of materials under extreme conditions**.

These calculations often rely on self-consistent average-atom codes to compute the atomic structure for a representative atom in a plasma. For plasmas at low densities and high temperatures, a very large number of Rydberg states are accessible, often requiring the calculation of principal quantum numbers of 100 or higher.

This poses a challenge for the existing average-atom models, since they have difficulty in **resolving all the bound states** just below the continuum, and accurately computing the wave-function of high-principal-quantum-number states near the nucleus.

High-Order Methods

Finite element (FE) methods [2] partition the problem domain into subdomains called "elements", and represent the desired solution as a linear combination of piecewise polynomials defined within each element; wherein h characterizes the element size and p, the polynomial order.

- h-FEM increases accuracy by decreasing h
- p-FEM increases accuracy by increasing p
- hp-FEM increases accuracy by refining both h and p simultaneously

Polynomial and strictly local basis → robust and naturally parallel method for solution of large-scale PDE problems, as in electronic structure [3].
hp-FEM has many favorable properties: exponential convergence, automatic adaptivity (no a priori knowledge needed), any geometry and boundary conditions, and systematic error control.

Schrödinger Equation

Radial Schrödinger equation:

$$(-\tfrac{1}{2}\rho^2 R')' + (\rho^2 V + \tfrac{1}{2}l(l+1))R = \epsilon\rho^2 R$$

Weak formulation:

$$\int \tfrac{1}{2}\rho^2 R'v' + (\rho^2 V + \tfrac{1}{2}l(l+1))Rv\,d\rho - \tfrac{1}{2}[\rho^2 R'v]_0^a =$$

$$= \epsilon\int \rho^2 Rv\,d\rho$$

Discretization in an FE basis produces a generalized eigenvalue problem of the form $Ax = \lambda Bx$. Setting boundary term $\tfrac{1}{2}[\rho^2 R'(\rho)v(\rho)]_0^a = 0$ imposes $R'(a) = 0$ but no restriction on R at $\rho = 0$, due to vanishing of ρ^2. We impose $R(a) = 0$ by restricting the FE basis and allow the natural BC at $\rho = 0$: we solve for $R(0)$ directly (note that in general $R(0) \neq 0$).

Dirac Equation

Radial Dirac equations:

$$-\hbar c\left(\frac{d}{d\rho} - \frac{\kappa}{\rho}\right)Q + (V + mc^2 - W)P = 0$$

$$+\hbar c\left(\frac{d}{d\rho} + \frac{\kappa}{\rho}\right)P + (V - mc^2 - W)Q = 0$$

Weak formulation:

$$\int PVv_1\,d\rho - \hbar cQ'v_1 + \hbar c\frac{\kappa}{\rho}Qv_1\,d\rho = \epsilon\int Pv_1\,d\rho$$

$$\int \hbar cP'v_2 + \hbar c\frac{\kappa}{\rho}Pv_2 + (V-2mc^2)Qv_2\,d\rho = \epsilon\int Qv_2\,d\rho$$

Correspondence between the radial Schrödinger and Dirac equation is:

$$\rho^2 R^2(\rho) = P^2(\rho) + Q^2(\rho)$$

References

[1] Z. Romanowski: Application of h-adaptive, high order finite element method to solve radial Schrödinger equation, Molecular Physics, 107: 13, 1339–1348 (2009).

[2] P. Solin, K. Segeth, I Dolezel: Higher-Order Finite Element methods, Chapman & Hall/CRC Press (July 2003).

[3] J.E. Pask and P.A. Sterne: Finite element methods in ab initio electronic structure calculations, Modelling Simul. Mater. Sci. Eng. 13, R71 (2005).

## Hydrogen Atom (3 lowest states of Schrödinger equation for $Z = 1$)

Comparison of uniform-p-FEM, h-FEM (Romanowski [1]), p-FEM (two different meshes) and hp-FEM:
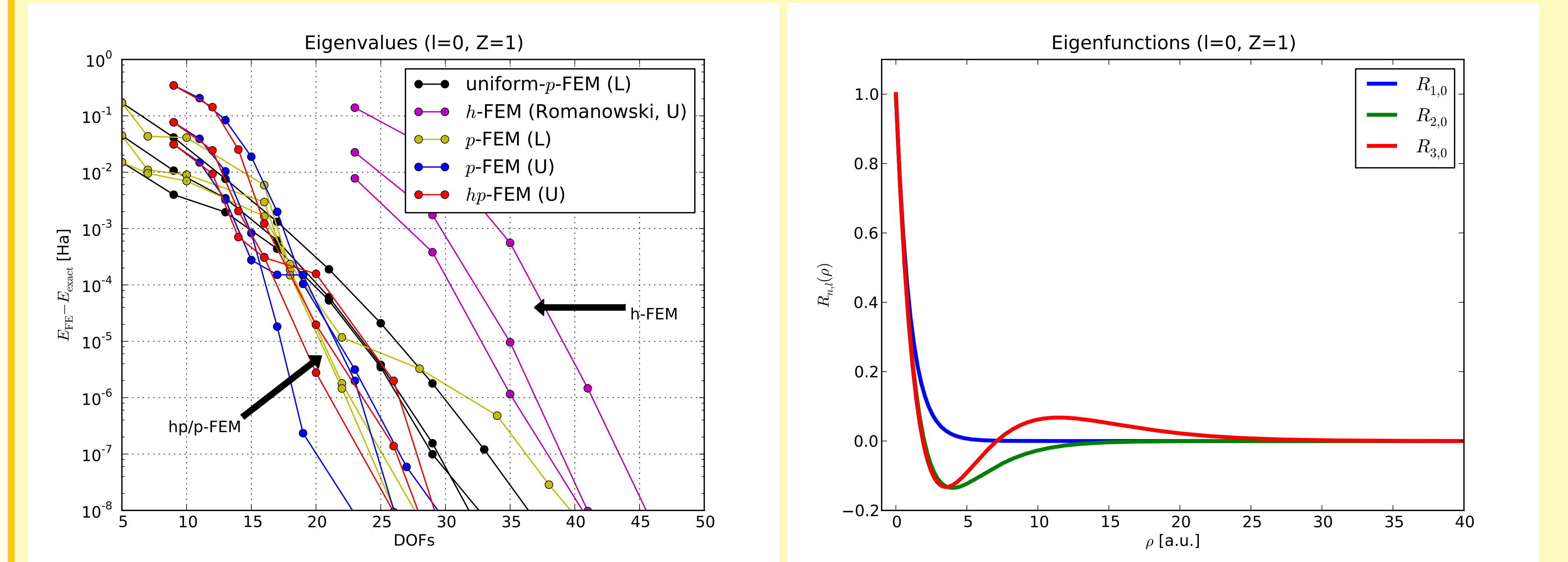
(L) starts from logarithmic initial mesh, (U) starts from uniform initial mesh. Computational domain is $[0, 100\,\text{a.u.}]$.

Silver Atom (50 lowest states of Schrödinger equation for $Z = 47$)

Comparison of uniform-p-FEM (two different meshes), p-FEM and hp-FEM (domain $[0, 150\,\text{a.u.}]$):
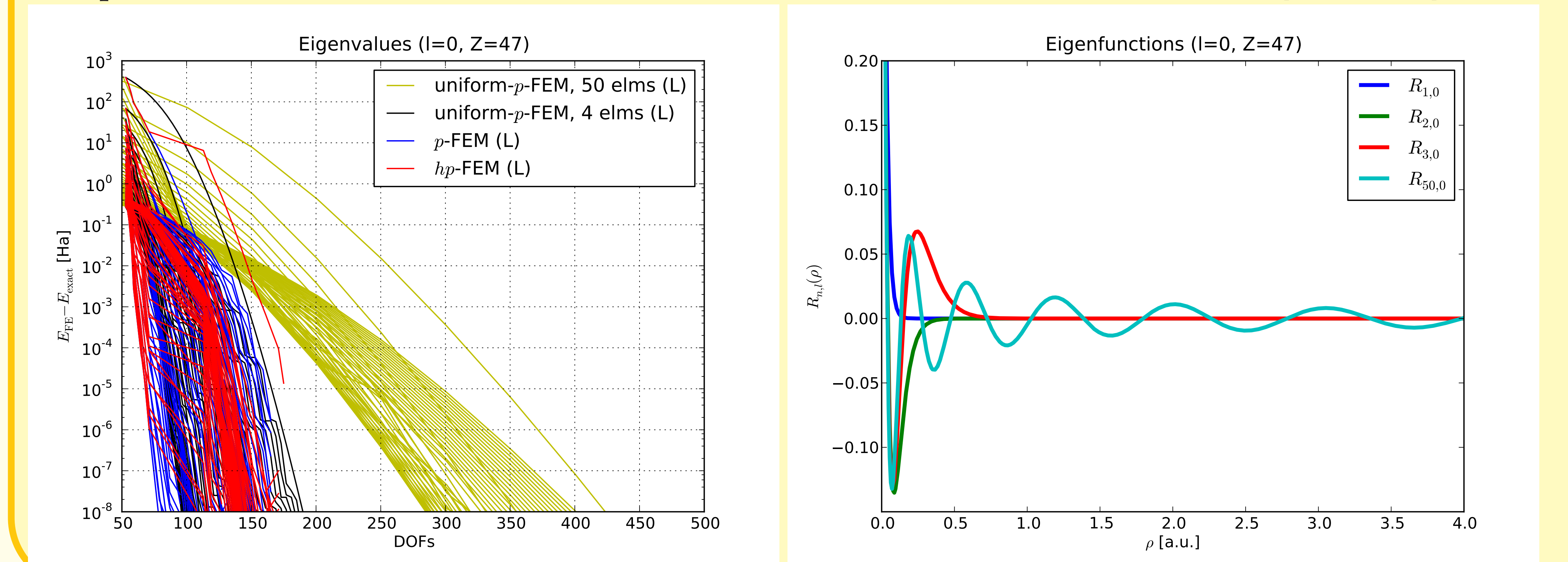
Conclusions

- High-order adaptive FE methods provide a **robust, variational alternative** to conventional shooting methods, finding all desired states simultaneously, with accuracy and orthogonality approaching machine precision.

- High-order p-FEM and hp-FEM are **superior to h-FEM in atomic structure context**.

- hp-FEM is the method of choice when little or no a priori information is available; however, in atomic-structure context, much is known → high-order p-FEM can be superior in practice (due to practical constraints on hp-FEM mesh — further research is needed).

- **Future**: extend present Schrödinger formulations to Dirac equation and self-consistent calculations.

Meshes for Error $< 10^{-6}\,\text{Ha}$

Method (Hydrogen)	h [a.u.]	p	Method (Silver)	h [a.u.]	p
h-FEM (U)	1.56 - 25	6	un-p-FEM 50 (L)	0.08 - 15.44	8
un-p-FEM (L)	3.22 - 64.34	8	un-p-FEM 4 (L)	3.00 - 105.06	44
p-FEM (L)	3.22 - 64.34	5-11	p-FEM (L) *	3.00 - 105.06	33-49
p-FEM (U)	25	2-16	hp-FEM (L) *	3.00 - 52.53	19-49
hp-FEM (U)	12.5 - 25	2-13			

* corresponds to $4.2 \cdot 10^{-6}\,\text{Ha}$ accuracy

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