



# High-Order, Adaptive Methods for Atomic Structure Calculations

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## 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  $\rightarrow$  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:

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

Weak formulation:

$$\int \frac{1}{2}\rho^2 R'v' + (\rho^2 V + \frac{1}{2}l(l+1))Rvd\rho - \frac{1}{2}[\rho^2 R'v]_0^a = \epsilon \int \rho^2 Rvd\rho$$

Discretization in an FE basis produces a generalized eigenvalue problem of the form  $Ax = \lambda Bx$ . Setting boundary term  $\frac{1}{2}[\rho^2 R'(\rho)v(\rho)]_0^a = 0$  imposes  $R'(a) = 0$  but no restriction on  $R$  at  $\rho = 0$ , due to vanishing of  $\rho^2$ . 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:

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

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

Correspondence between the radial Schrödinger and Dirac equation is:

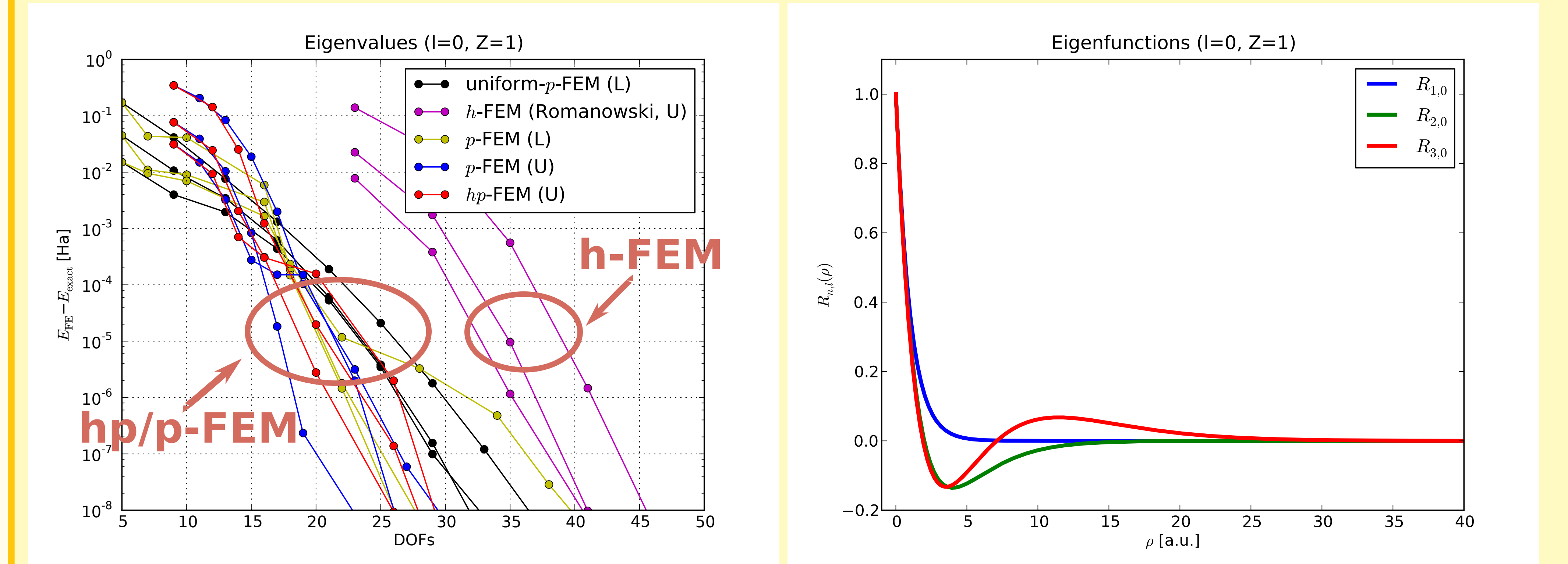
$$\rho^2 R^2(\rho) = P^2(\rho) + Q^2(\rho)$$

## 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 $Z = 1$ )

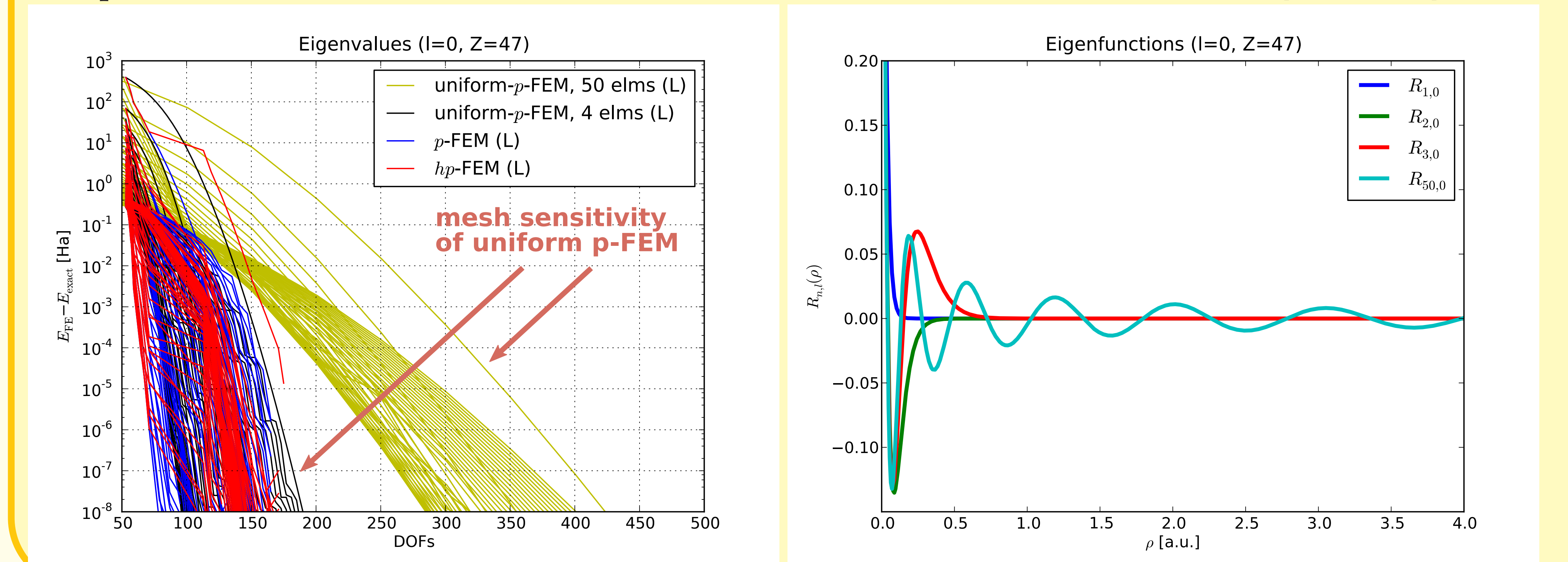
Comparison of uniform- $p$ -FEM,  $h$ -FEM (Romanowski [1]),  $p$ -FEM (two different meshes) and  $hp$ -FEM:



(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  $\rightarrow$  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 $< 10^{-6}$ 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  $4.2 \cdot 10^{-6}$  Ha accuracy

## Acknowledgment

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