Radial Density Functional Theory

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Abstract

The formulation and implementation of radial Density Functional Theory is presented.

1 Strong form

Consider the case of an isolated atom. Let this atomic system consists of N electrons. In an uncharged atom, the atomic number Z is also equal to N. In the paradigm of many-b0dy quantum mechanics applied to such atomic systems one is interested determining the single-particle (electronic) *wavefunctions* (*orbitals*) $\{\psi_i(x_i)\}$. For spherically symmetric potential, as is the case for an isolated atom, the wavefunctions are often expressed as $\psi_{n\ell m}(\mathbf{x})$ where n is the principal quantum number, ℓ is the orbital angular momentum quantum number, and m is the magnetic quantum number.
$\psi_{n\ell m}(\mathbf{x})$ can further be simplified (separation of variables):

$$\psi_{n\ell m}(\mathbf{x}) \equiv \psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$

where $Y_{\ell m}(\theta,\phi)$ are the *spherical harmonics* and $R_{n\ell}(r)$ satisfies the *radial Schrödinger equation*:

$$\Big(-\frac{1}{2}r^2R'_{n\ell}(r)\Big)' + \Big(r^2V(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r) = \varepsilon_{n\ell}r^2R_{n\ell}(r) \tag{1}$$

where $(\cdot)' \equiv \dfrac{d(\cdot)}{dr}$. In *Radial Density Functional Theory* the *radial Kohn-Sham equation* is solved in a *self consistent* manner. The radial Kohn-Sham equation, in spirit, is of similar form as eq. (**??**) with the potential $V(r)$ being replaced by $\hat{V}_{\text{eff}}[\rho_e(r)]$ where ρ_e is the *electronic density*. Hence, eq. (**??**) can be rewritten as:

$$\Big(-\frac{1}{2}r^2R'_{n\ell}(r)\Big)' + \Big(r^2\hat{V}_{\text{eff}}[\rho_e(r)] + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r) = \varepsilon_{n\ell}r^2R_{n\ell}(r) \tag{2}$$

where

$$\hat{V}_{\text{eff}}[\rho_e(r)] = V_H[\rho_e(r)] + V_{xc}[\rho_e(r)] + V_n(r). \tag{3}$$

In eq. (**??**) V_{xc} is known as the *exchange-correlation* functional, $V_n(r) = -\frac{Z}{r}$ is the potential arising from the coulomb attraction of nucleus and V_H is the *Hartree potential*. The Hartree potential is governed by the *radial Poisson equation*:

$$\frac{1}{r^2}\Big(r^2 V_H'(r)\Big)' = V_H''(r) + \frac{2}{r}V_H'(r) = -4\pi\rho_e(r). \tag{4}$$

Note that eq. (**??**) is a nonlinear ordinary differential equation. This can further be elucidated by expressing $\rho_e(r)$ in terms of $R_{n\ell}$ which is done next.

1.1 Electron Density ρ_e

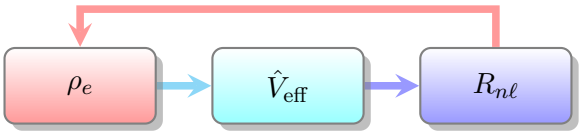
The electronic density ρ_e is calculated by adding all (n, ℓ, m) states together, counting each one twice (for spin up $\uparrow$ and spin down $\downarrow$) such that

$$\begin{aligned}\rho_e(r) &= 2\sum_{n\ell m} |\psi_{n\ell m}|^2 \\ &= 2\sum_{n\ell m} R_{n\ell}^2 |Y_{\ell m}|^2 \\ &= \Big(\sum_{n\ell} R_{n\ell}^2\Big)\Big(2\sum_{m}|Y_{\ell m}|^2\Big) = \frac{1}{4\pi}\sum_{n\ell} f_{n\ell} R_{n\ell}^2\end{aligned}$$

where the *occupation numbers* $f_{n\ell}$ are defined as

$$f_{n\ell} = 2\Big(4\pi\sum_{m}|Y_{\ell m}|^2\Big).$$

Hence, we get the following circular dependency:



1.2 $P_{n\ell}$ and V_P

Please note that in the code `spectatom` we use $u = P_{n\ell} = rR_{n\ell}$ and $V_P = rV_H$ as our primary variables to be solved using spectral FEM. This is solely because of some obvious simplification in the boundary conditions. To this end, the aforementioned strong form statements are modified for these variables as:

Radial Kohn-Sham Equation:

$$-\frac{1}{2}\big(P_{n\ell}[\rho_e(r)]\big)'' + \Big(r^2\hat{V}_{\text{eff}}[\rho_e(r)] + \frac{1}{2}\ell(\ell+1)\Big)P_{n\ell}[\rho_e(r)] = \varepsilon_{n\ell}[\rho_e(r)]P_{n\ell}[\rho_e(r)]; \tag{5}$$

Radial Poisson Equation:

$$\big(V_P(r)\big)'' = -4\pi r \rho_e(r), \tag{6}$$

and lastly
Electron Density:

$$\rho_e(r) = \frac{1}{4\pi} \sum_{n\ell} f_{n\ell} \frac{R_{n\ell}^2}{r^2}. \tag{7}$$

2 Weak form

The weak form statements of the radial Kohn-Sham problem ($P_{n\ell}$ as the primary variable) and radial Poisson problem (V_P as the primary variable) are stated next without any derivation. To this end, we first define the following function spaces:

$$\mathcal{S} = \{P : P \in H^1([0\ a]),\ P(0) = 0,\ P(a) = 0\},$$
$$\mathcal{V} = \{v : v \in H^1([0\ a]),\ v(0) = 0,\ v(a) = 0\},$$

where a denotes the radius of the spherical problem domain under consideration, $H^k([0\ a])$ is the *Sobolev space* that contains functions that are square-integrable ($L^2([0\ a])$) up to order k.

2.1 Radial Kohn-Sham Equation

Formally, the weak form is written as: find the *trial function* (eigenfunction) $P_{n\ell}(r) \in \mathcal{S}$ and the eigenvalue $\varepsilon_{n\ell} \in \mathbb{R}$ such that

$$\int_0^a \left\{ \frac{1}{2} P'_{n\ell}(r) v'(r) + \left[\hat{V}_{\text{eff}}[\rho_e(r)] + \frac{1}{2} \frac{\ell(\ell+1)}{r^2} \right] P_{n\ell}(r) v(r) \right\} \mathrm{d}r =$$

$$\varepsilon_{n\ell} \int_0^a P_{n\ell}(r) v(r)\, \mathrm{d}r \qquad \forall v(r) \in \mathcal{V}. \tag{8}$$

Observe that we use $P_{n\ell}(0) = P_{n\ell}(a) = 0$, i.e., Dirichlet condition at both ends.

2.2 Radial Poisson Equation

The weak form statement of radial Poisson equation is: find the trial function $V_P(r) \in \mathcal{S}$ such that

$$\int_0^a V'_P(r) w'(r)\, \mathrm{d}r = 4\pi \int_0^a r \rho_e(r) w(r)\, \mathrm{d}r \qquad \forall w(r) \in \mathcal{V} \tag{9}$$

where the trial and test function spaces are as defined previously. Note here that we use $V_P(0) = V_P(a) = 0$ as the boundary condition and this defines $V_H = \frac{V_P}{r}$ within some

arbitrary constant. Physically, $V_H(a) = \frac{Z}{a}$ should be satisfied. Hence, we first compute V_P using eq. (**??**) and then scale and shift the solution as

$$V_H = \underbrace{\frac{V_P}{r}}_{\text{Scale}} + \underbrace{\frac{Z}{a}}_{\text{Shift}}$$

to obtain $V_H(r)$.

3 Discrete Formulation of Weak Form

3.1 Radial Kohn-Sham Equation

The spectral finite element (FE) approximation of the trial function $P_{n\ell}$ can be written as (dropping the subscripts n and ℓ for brevity)

$$P^h(r) = \sum_{j=1}^{N} \phi_j(r) P_j \in \mathcal{S}^h \subset \mathcal{S}, \tag{10}$$

where $\mathcal{S}^h$ is a finite-dimensional subspace of $\mathcal{S}$. In addition, $\phi_j(r)$ are higher-order (spectral) finite element basis functions, and P_j are the finite element degrees of freedom. The derivative of $P^h(r)$ is:

$$\big(P^h(r)\big)' = \sum_{j=1}^{N} \phi_j'(r) P_j. \tag{11}$$

On substituting P^h and $(P^h)'$ from (**??**) and (**??**), respectively, in eq. (**??**) and letting v^h be the test functions, we obtain:

$$\int_0^a \Big\{ \sum_{j=1}^{N} \Big(\frac{1}{2} (v^h)' \phi_j' + \Big[\hat{V}_{\text{eff}} + \frac{1}{2} \frac{\ell(\ell+1)}{r^2} \Big] v^h \phi_j \Big) P_j \Big\} \mathrm{d}r =$$

$$\varepsilon \int_0^a \sum_{j=1}^{N} v^h \phi_j P_j \mathrm{d}r \qquad \forall v^h \in \mathcal{V}^h.$$

Upon setting $v^h = \phi_i$ and denoting by $\mathbf{c} = \{P_1, \ldots, P_N\}$ leads to the *generalized eigenproblem*:

$$\mathbf{H}[\rho_e(r)]\mathbf{c} = \varepsilon \mathbf{S}\mathbf{c}, \tag{12a}$$

$$\big(\mathbf{H}[\rho_e(r)]\big)_{ij} = \int_0^a \Big\{ \frac{1}{2} \phi_i' \phi_j' + \Big[\hat{V}_{\text{eff}} + \frac{1}{2} \frac{\ell(\ell+1)}{2r^2} \Big] \phi_i \phi_j \Big\} \mathrm{d}r \tag{12b}$$

$$\mathbf{S}_{ij} = \int_0^a \phi_i \phi_j \mathrm{d}r. \tag{12c}$$

In the context of Schrödinger equation, $\mathbf{H}[\rho_e(r)]$ is known as the *Hamiltonian matrix* and $\mathbf{S}$ is the *overlap matrix*.

3.2 Radial Poisson Equation

Proceeding along the similar line as in the last section, the spectral finite element approximation for the trial function V_P can be written as (dropping the subscript P for brevity)

$$V^h(r) = \sum_{j=1}^{N} \phi_j(r) V_j \in \mathcal{S}^h \subset \mathcal{S}. \tag{13}$$

In addition, $\phi_j(r)$ are higher-order (spectral) finite element basis functions, and V_j are the finite element degrees of freedom. The derivative of $V^h(r)$ is:

$$\big(V^h(r)\big)' = \sum_{j=1}^{N} \phi_j'(r) V_j. \tag{14}$$

On substituting V^h and $(V^h)'$ from (**??**) and (**??**), respectively, in eq. (**??**) and letting w^h be the test functions, we obtain:

$$\int_0^a \Big\{ \sum_{j=1}^{N} (w^h)' \phi_j' V_j \Big\} \mathrm{d}r = 4\pi \int_0^a r \rho_e w^h \mathrm{d}r \qquad \forall w^h \in \mathcal{V}^h.$$

Once again, setting $w^h = \phi_i$ and denoting by $\mathbf{u} = \{V_1, \ldots, V_N\}$ leads to the linear system:

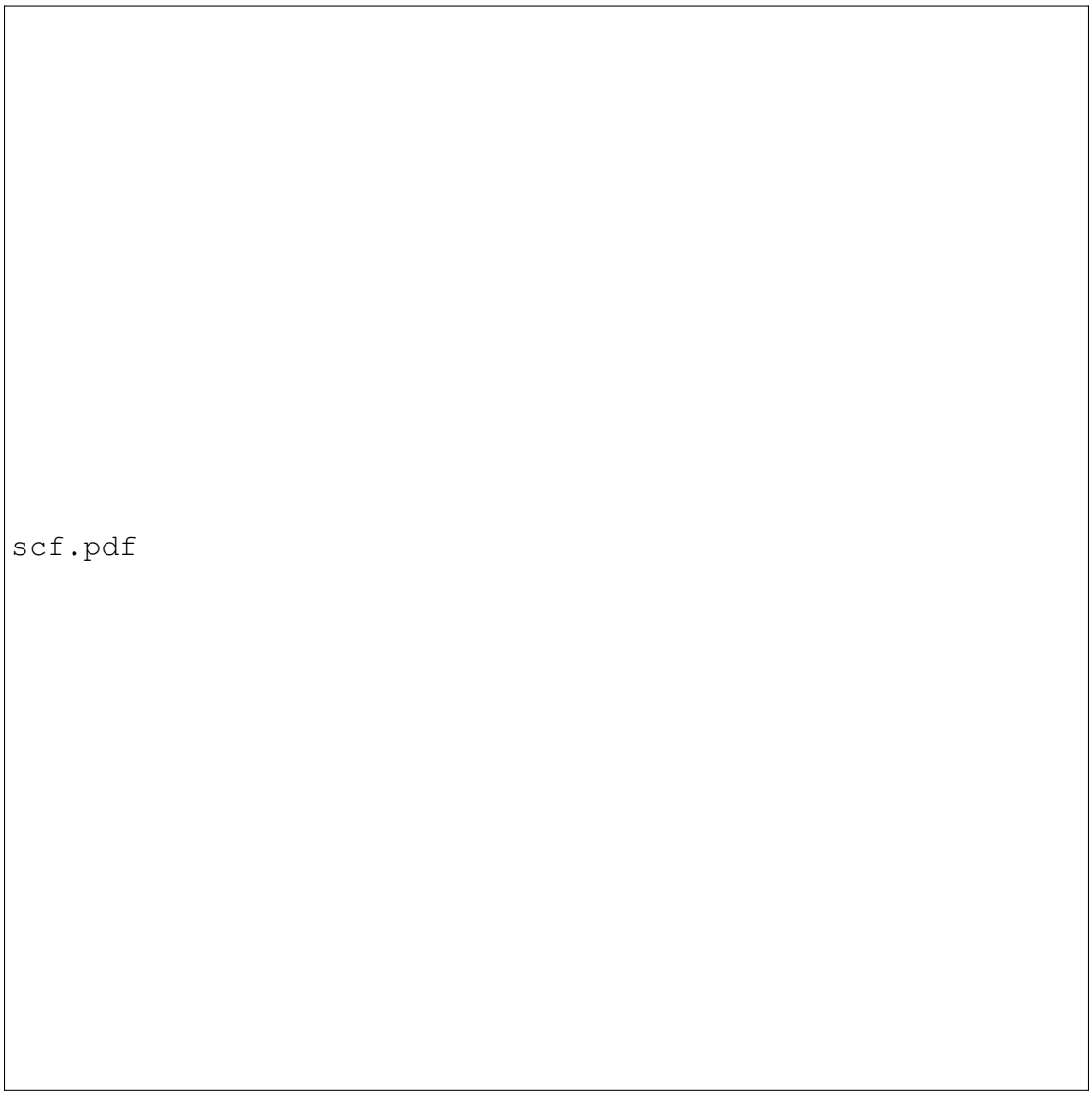
$$\mathbf{K}\mathbf{u} = \mathbf{b}, \tag{15a}$$

$$\mathbf{K}_{ij} = \int_0^a \phi_i' \phi_j' \mathrm{d}r \tag{15b}$$

$$\mathbf{b}_i = 4\pi \int_0^a r \rho_e \phi_i \mathrm{d}r. \tag{15c}$$

4 Self-Consistent Fields (SCF) Iterations

Owing to the nonlinear nature of generalized eigenvalue problem in eq. (**??**) as alluded in Section **??**, the problem is solved using the following self-consistent field technique:



5 Numerical Examples

We perform h- and p- convergence studies on ground state energy (E_0) computation for carbon (C) atom which has 6 electrons. As per the **NIST** standard the E_0 for C is $(E_0)_{\text{exact}} = -37.425749$ Hartree. To this end, we consider the domain $[\texttt{rmin rmax}] = [0\ 10]$ a.u., meshed with `numel` equi-spaced elements.

5.1 p-Convergence

For a fixed `numel` the element order p is varied as $1, 2, \ldots, 10$. For each of these p, E_0 value is reported. Increasing p increases the number of DOF and hence, ideally we should converge to the $(E_0)_{\text{exact}}$. Subsequently, we also consider `numel` $= 10, 20$, and 40. This set of numerical experiments are performed using the script `testpconvergence.m`.

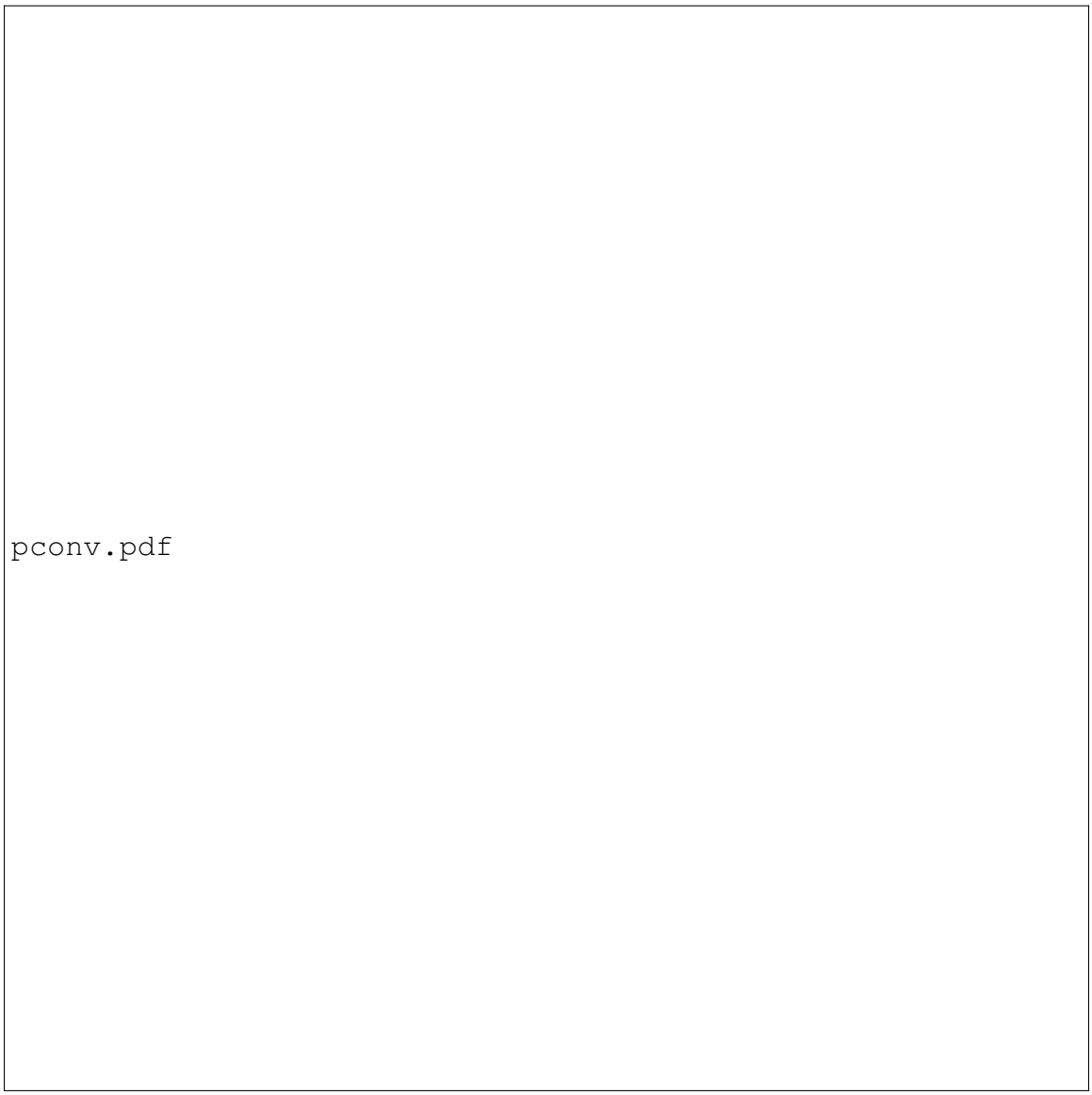


Figure 1: p-Convergence ($*$ `eigs` failed for `numel` $= 40$ with $p = 10$)

5.2 h-Convergence

For a fixed element order p the element order `numel` is varied as $5, 10, 20$, and 40. For each of these `numel`, E_0 value is reported. Increasing `numel` once again increases the number

of DOF and hence, ideally we should converge to the $(E_0)_{\text{exact}}$. Cases with $p = 2, 4$, and 8 are considered. This set of numerical experiments are performed using the script `testhconvergence.m`.

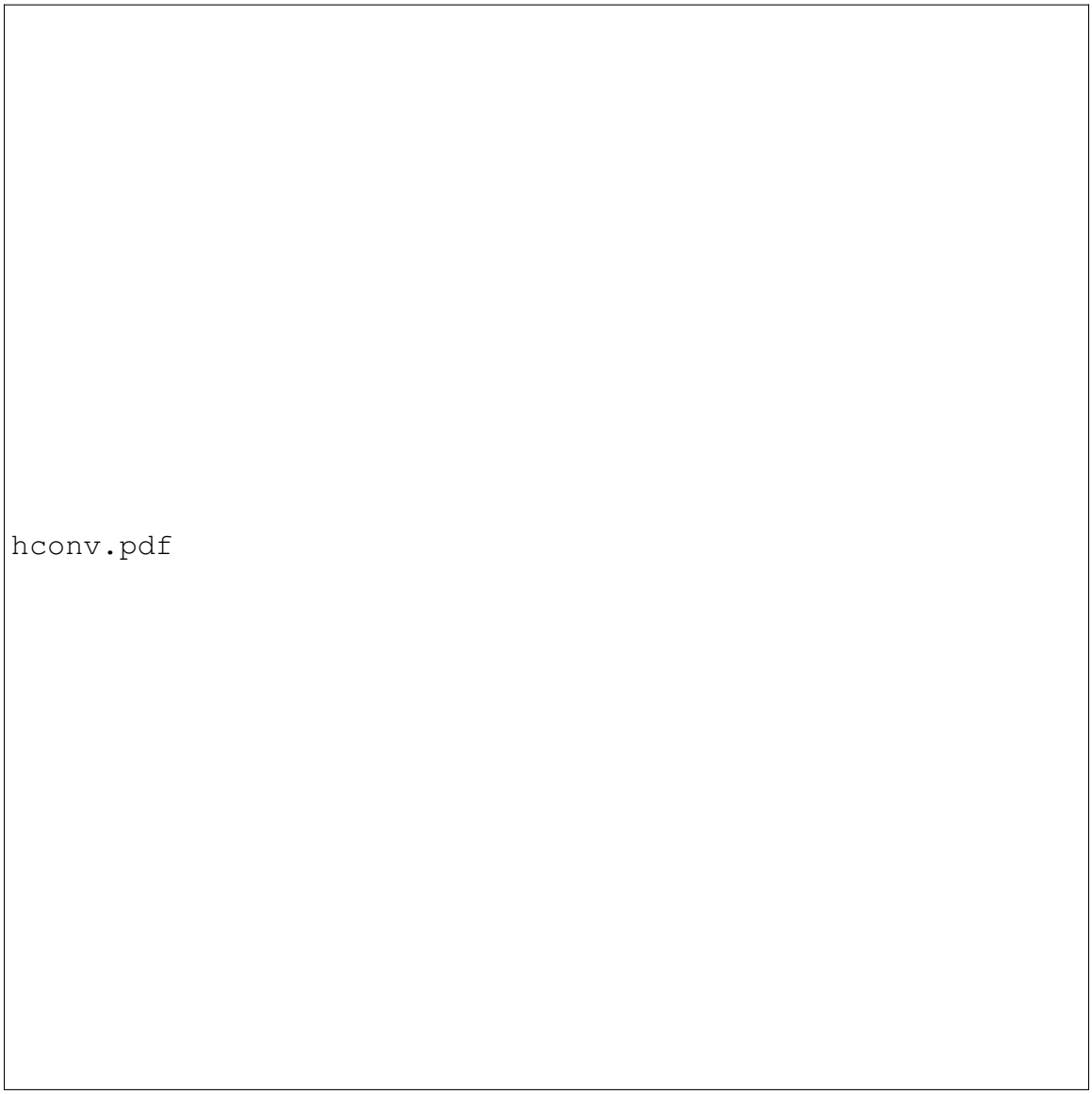


Figure 2: h-Convergence