

Radial Density Functional Theory

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Abstract

The formulation and implementation of spectral finite element method is presented for radial density functional theory.

1 Kohn-Sham equations for an atom

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-body quantum mechanics applied to such atomic systems, one is interested in 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. It can further be simplified (via 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:

$$\left(-\frac{1}{2}r^2R'_{n\ell}(r)\right)' + \left(r^2V(r) + \frac{1}{2}\ell(\ell+1)\right)R_{n\ell}(r) = \varepsilon_{n\ell}r^2R_{n\ell}(r), \quad (1)$$

where $(\cdot)' \equiv d(\cdot)/dr$. In radial density functional theory, the radial Kohn-Sham equation is solved in a *self-consistent* manner. The radial Kohn-Sham equation is of the form (1) with the potential $V(r)$ being replaced by $\hat{V}_{\text{eff}}[\rho_e(r)]$, where ρ_e is the electronic density. Hence, (1) can be rewritten as:

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

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where

$$\hat{V}_{\text{eff}}[\rho_e(r)] = V_H[\rho_e(r)] + V_{xc}[\rho_e(r)] + V_n(r). \quad (2b)$$

In (2b), V_{xc} is known as the *exchange-correlation* functional, $V_n(r) = -\frac{Z}{r}$ is the potential arising from the Coulomb attraction of the nucleus and V_H is the *Hartree potential*. The Hartree potential is governed by the radial Poisson equation:

$$\frac{1}{r^2} \left(r^2 V_H'(r) \right)' = V_H''(r) + \frac{2}{r} V_H'(r) = -4\pi \rho_e(r). \quad (3)$$

Note that (2a) 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

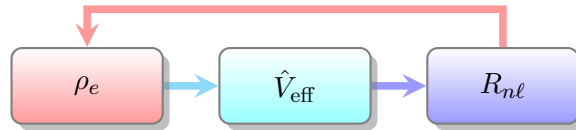
The electronic density ρ_e is calculated by adding all (n, ℓ, m) states together, counting each one twice (for spin up \uparrow and spin down \downarrow) such that

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

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

$$f_{n\ell} = 2 \left(4\pi \sum_m |Y_{\ell m}|^2 \right).$$

Hence, we get the following circular dependency:



1.2 $P_{n\ell}$ and V_P

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

Radial Kohn-Sham Equation

$$-\frac{1}{2} P_{n\ell}''(r) + \left(\hat{V}_{\text{eff}}[\rho_e(r)] + \frac{1}{2} \frac{\ell(\ell+1)}{r^2} \right) P_{n\ell}(r) = \varepsilon_{n\ell} P_{n\ell}(r).$$

Radial Poisson Equation

$$V_P''(r) = -4\pi r \rho_e(r).$$

Electron Density

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

2 Weak form

The weak form for the radial Kohn-Sham problem ($P_{n\ell}$ as the primary variable) and the radial Poisson problem (V_P as the primary variable) are stated. To this end, we first define the following function spaces:

$$\begin{aligned} \mathcal{S} &= \{P : P \in H^1(0, a), P(0) = 0, P(a) = 0\}, \\ \mathcal{V} &= \{v : v \in H^1(0, a), v(0) = 0, v(a) = 0\}, \end{aligned}$$

where a denotes the radius of the spherical domain under consideration, and $H^k(0, a)$ is the Sobolev space that contains functions that are square-integrable 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

$$\begin{aligned} \int_0^a \left\{ \frac{1}{2} P_{n\ell}'(r) v'(r) + \left[\hat{V}_{\text{eff}}[\rho_e(r)] + \frac{1}{2} \frac{\ell(\ell+1)}{r^2} \right] P_{n\ell}(r) v(r) \right\} dr = \\ \varepsilon_{n\ell} \int_0^a P_{n\ell}(r) v(r) dr \quad \forall v(r) \in \mathcal{V}. \quad (4) \end{aligned}$$

Observe that we use $P_{n\ell}(0) = P_{n\ell}(a) = 0$, i.e., Dirichlet conditions are imposed at $r = 0$ and $r = a$.

2.2 Radial Poisson equation

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

$$\int_0^a V_P'(r) w'(r) dr = 4\pi \int_0^a r \rho_e(r) w(r) dr \quad \forall w(r) \in \mathcal{V}, \quad (5)$$

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 conditions 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 (5) 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 Trial and test approximations and discrete generalized eigenproblem

3.1 Radial Kohn-Sham equation

The spectral finite element (FE) approximation (trial function) can be written as (dropping the subscript n, ℓ for brevity)

$$P^h(r) = \sum_{j=1}^N \phi_j(r) P_j \in \mathcal{S}^h \subset \mathcal{S}, \quad (6)$$

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:

$$(P^h(r))' = \sum_{j=1}^N \phi_j'(r) P_j. \quad (7)$$

In the interest of conciseness, I will suppress the dependence on r for the functions that appear in the weak form. On substituting P^h and $(P^h)'$ from (6) and (7), respectively, in (4) and letting v^h be the test functions, we obtain:

$$\int_0^a \left\{ \sum_{j=1}^N \left(\frac{1}{2} (v^h)' \phi_j' + \left[\hat{V}_{\text{eff}} + \frac{1}{2} \frac{\ell(\ell+1)}{r^2} \right] v^h \phi_j \right) P_j \right\} dr = \varepsilon \int_0^a \sum_{j=1}^N v^h \phi_j P_j dr \quad \forall v^h \in \mathcal{V}^h.$$

On setting $v^h = \phi_i$ and letting $\mathbf{c} = \{P_1, \dots, P_N\}$, we obtain the following generalized eigenproblem:

$$\mathbf{H}([\rho_e]) \mathbf{c} = \varepsilon \mathbf{S} \mathbf{c}, \quad (8a)$$

$$\mathbf{H}_{ij} = \int_0^a \left\{ \frac{1}{2} \phi_i' \phi_j' + \left[\hat{V}_{\text{eff}} + \frac{\ell(\ell+1)}{2r^2} \right] \phi_i \phi_j \right\} dr \quad (8b)$$

$$\mathbf{S}_{ij} = \int_0^a \phi_i \phi_j dr. \quad (8c)$$

In the context of the Schrödinger equation, \mathbf{H} is known as the Hamiltonian matrix and \mathbf{S} is the overlap matrix.

3.2 Radial Poisson equation

Proceeding along similar lines 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)

$$V^h(r) = \sum_{j=1}^N \phi_j(r) V_j \in \mathcal{S}^h \subset \mathcal{S}. \quad (9)$$

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:

$$(V^h(r))' = \sum_{j=1}^N \phi_j'(r) V_j. \quad (10)$$

On substituting V^h and $(V^h)'$ from (9) and (10), respectively, in (5) and letting w^h be the test functions, we obtain:

$$\int_0^a \left\{ \sum_{j=1}^N (w^h)' \phi_j' V_j \right\} dr = 4\pi \int_0^a r \rho_e w^h dr \quad \forall w^h \in \mathcal{V}^h.$$

Once again, setting $w^h = \phi_i$ and letting $\mathbf{d} := \{V_1, \dots, V_N\}$ leads to the linear system:

$$\mathbf{K} \mathbf{d} = \mathbf{f}, \quad (11a)$$

$$\mathbf{K}_{ij} = \int_0^a \phi_i' \phi_j' dr \quad (11b)$$

$$\mathbf{f}_i = 4\pi \int_0^a r \rho_e \phi_i dr. \quad (11c)$$

4 Self consistent field (SCF) iterations

Owing to the nonlinear nature of the generalized eigenvalue problem in (8a) and as alluded to in Section 1.1, the problem is solved using the self-consistent field procedure (see Fig. 1).

5 Numerical examples

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

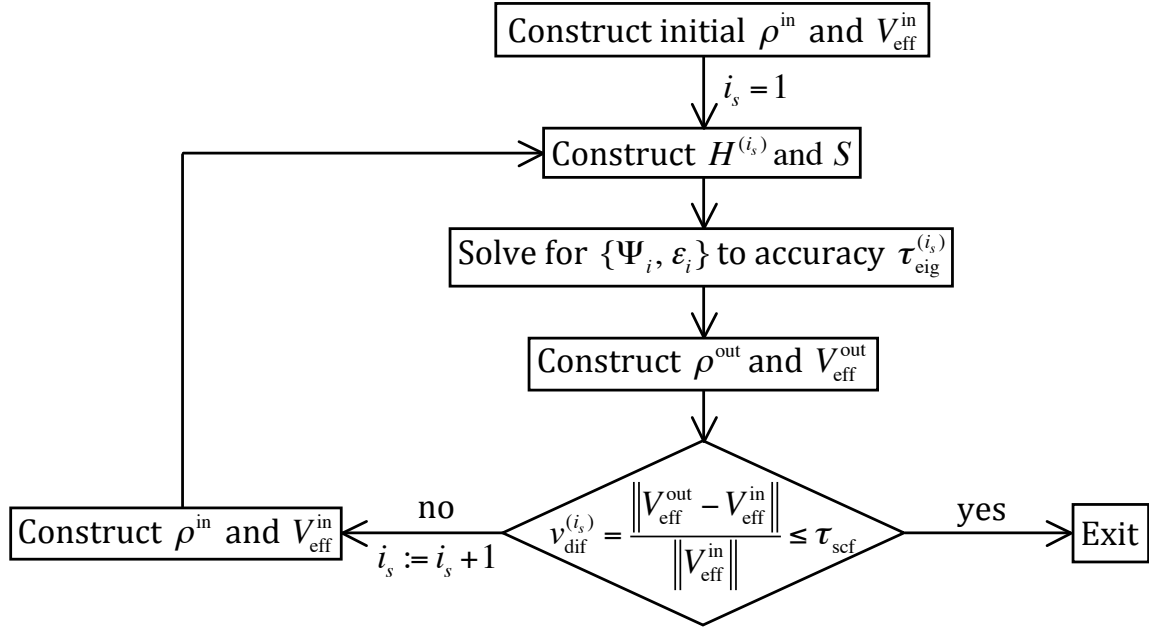


Figure 1: Schematic of the self-consistent field procedure.

5.1 p -convergence

For a fixed `numel`, the element order p is varied as $1, 2, \dots, 10$. For each of these p , the finite element result E_0^h is computed. Increasing p increases the number of DOFs, and we should converge to the exact E_0 . Subsequently, we also consider `numel` = 10, 20, and 40. This set of numerical experiments are performed using the script `testpconvergence.m`.

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^h value is reported. Increasing `numel` once again increases the number of DOFs, and we should converge to the exact E_0 . Cases with $p = 2, 4$, and 8 are considered. This set of numerical experiments are performed using the script `testhconvergence.m`.

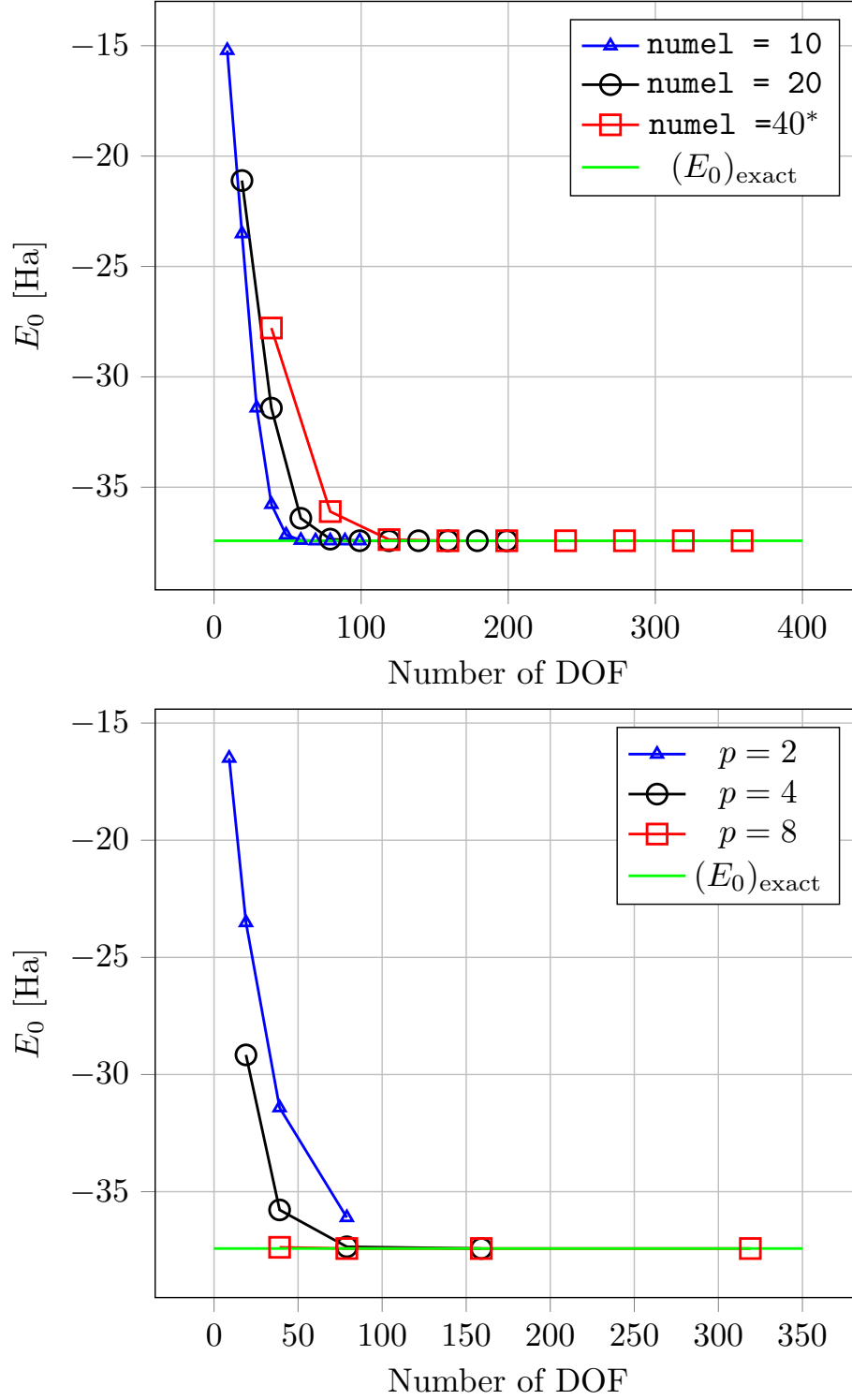


Figure 2: Convergence of ground state energy. (a) p -refinement. MatlabTM eigen-solver `eigs` failed for `numel` = 40 with p = 10; and (b) h -refinement.