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-boy 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. It 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. (1) with the potential $V(r)$ being replaced by $\hat{V}_{\text{eff}}[\rho_e(r)]$ where ρ_e is the *electronic density*. Hence, eq. (1) can be rewritten as:

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

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. (3) 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. (2) 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

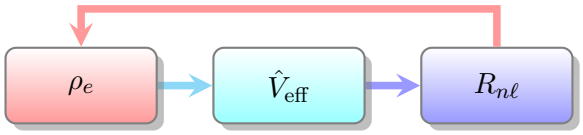
The electronic density ρ_e is calculated by adding all (n, ℓ, m) states together, counting each one twice (for spin up $\uparrow$ and spin down $\downarrow$) such that

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

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:



2 Weak form

The weak form (principle of virtual work) or equivalently the minimization of the potential energy functional is derived next.

2.1 Radial Kohn-Sham Equation

We multiply eq. (2) by an arbitrary *test or weighting function* $v(r)$ and integrate over the spherical volume of radius a to obtain:

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{a}\Big\{\Big(-\frac{1}{2}r^2R'_{n\ell}(r)\Big)' + \Big(r^2\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)\Big\}v(r)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$
$$= \varepsilon_{n\ell}\int_0^{\pi}\int_0^{2\pi}\int_0^{a} R_{n\ell}(r)v(r)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \qquad \forall v(r),$$

where v is at least a piece-wise continuous function ($v \in C^0([0\ a])$ will suffice). Integrating over the angles gives 4π which cancels from both sides, resulting in:

$$\int_0^{a}\Big\{\Big(-\frac{1}{2}r^2R'_{n\ell}(r)\Big)' + \Big(r^2\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)\Big\}v(r)r^2\mathrm{d}r = \varepsilon_{n\ell}\int_0^{a} R_{n\ell}(r)v(r)r^2\mathrm{d}r. \tag{5}$$

Applying integration by parts on the first-term of the left hand side of eq. (5), we obtain,

$$\int_0^{a}\Big\{\frac{1}{2}R'_{n\ell}(r)v'(r) + \Big(\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)v(r)\Big\}r^2\,\mathrm{d}r - \frac{1}{2}\left[r^2R'_{n\ell}(r)v(r)\right]_0^a$$
$$= \varepsilon_{n\ell}\int_0^{a} R_{n\ell}(r)v(r)r^2\,\mathrm{d}r.$$

The boundary term is zero at the origin ($r = 0$), so we get:

$$\int_0^{a}\Big\{\frac{1}{2}R'_{n\ell}(r)v'(r) + \Big(\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)v(r)\Big\}r^2\,\mathrm{d}r - \frac{1}{2}a^2R'_{n\ell}(a)v(a)$$
$$= \varepsilon_{n\ell}\int_0^{a} R_{n\ell}(r)v(r)r^2\,\mathrm{d}r.$$

We usually want to have the boundary term $\frac{1}{2}a^2R'_{n\ell}(a)v(a)$ equal to zero. This is equivalent to either letting $R'_{n\ell}(a) = 0$ (we prescribe the zero derivative of the $R_{n\ell}$ at a) or we set $v(a) = 0$ (which corresponds to zero Dirichlet condition for $R_{n\ell}$, i.e. setting $R_{n\ell}(a) = 0$). In either of these situations, the last equation simplifies to:

$$\int_0^{a}\Big\{\frac{1}{2}R'_{n\ell}(r)v'(r) + \Big(\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)v(r)\Big\}r^2\,\mathrm{d}r = \varepsilon_{n\ell}\int_0^{a} R_{n\ell}(r)v(r)r^2\,\mathrm{d}r.$$

This point onwards we will only consider the case of $R_{n\ell}(0) = R_{n\ell}(a) = 0$, i.e., Dirichlet condition at both ends.
Formally, the weak form is written as: find the *trial function* (eigenfunction) $R_{n\ell}(r) \in \mathcal{S}$ and the eigenvalue $\varepsilon_{n\ell} \in \mathbb{R}$ such that

$$\int_0^a \Big\{\frac{1}{2}R'_{n\ell}(r)v'(r) + \Big(\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1)\Big)R_{n\ell}(r)v(r)\Big\}r^2\,\mathrm{d}r =$$

$$\varepsilon_{n\ell}\int_0^a R_{n\ell}(r)v(r)r^2\,\mathrm{d}r \qquad \forall v(r) \in \mathcal{V} \quad (6)$$

where the trial and test function spaces, respectively, are

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

where $H^k([0\ a])$ is the *Sobolev space* that contains functions that are square-integrable ($L^2([0\ a])$) up to order k.

2.2 Radial Poisson Equation

To derive the weak form of radial Poisson equation, we proceed along the similar route as the last section. To this end, we first multiply eq. (4) by an arbitrary test function $w(r)$ and integrate over the spherical volume of radius a to obtain:

$$\int_0^{\pi}\int_0^{2\pi}\int_0^a \frac{1}{r^2}\Big(r^2V'_H(r)\Big)'w(r)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = -4\pi\int_0^{\pi}\int_0^{2\pi}\int_0^a \rho_e(r)w(r)r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \quad \forall w(r)$$

Next, after cancelling the 4π arising from the integrals over the angles on both sides, and by applying integration by parts on the left hand side, we obtain

$$\big[r^2V'_H(r)w(r)\big]_0^a - \int_0^a r^2V'_H(r)w'(r)\mathrm{d}r = -4\pi\int_0^a \rho_e(r)w(r)r^2\mathrm{d}r$$

which, upon assuming $w(0) = w(a) = 0$ (or $w(0) = 0$ and $V'_H(a) = 0$) simplifies to

$$\int_0^a V'_H(r)w'(r)r^2\,\mathrm{d}r = 4\pi\int_0^a \rho_e(r)w(r)r^2\,\mathrm{d}r.$$

Writing the last equation in more formal setting- the weak form statement of radial Poisson equation is: find the trial function $V_H(r) \in \mathcal{S}$ such that

$$\int_0^a V'_H(r)w'(r)r^2\,\mathrm{d}r = 4\pi\int_0^a \rho_e(r)w(r)r^2\,\mathrm{d}r \qquad \forall w(r) \in \mathcal{V} \quad (7)$$

where the trial and test function spaces are as defined previously.

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)

$$R^h(r) = \sum_{j=1}^{N} \phi_j(r) R_j \in \mathcal{S}^h \subset \mathcal{S}, \tag{8}$$

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 R_j are the finite element degrees of freedom. The derivative of $R^h(r)$ is:

$$\big(R^h(r)\big)' = \sum_{j=1}^{N} \phi_j'(r) R_j. \tag{9}$$

In the interest of conciseness, I'll suppress the dependence on r for the functions that appear in the weak form. On substituting R^h and $(R^h)'$ from (8) and (9), respectively, in eq. (6) and letting v^h be the test functions, we obtain:

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

Upon setting $v^h = \phi_i$ and denoting by $\mathbf{c} = \{R_1, \ldots, R_N\}$ leads to the *generalized eigenproblem*:

$$\mathbf{H}\mathbf{c} = \varepsilon \mathbf{S}\mathbf{c}, \tag{10a}$$

$$\mathbf{H}_{ij} = \int_0^a \Big[\frac{1}{2} \phi_i' \phi_j' + \Big(\hat{V}_{\text{eff}}(r) + \frac{1}{2}\ell(\ell+1) \Big) \phi_i \phi_j \Big] r^2 \mathrm{d}r \tag{10b}$$

$$\mathbf{S}_{ij} = \int_0^a \phi_i \phi_j r^2 \mathrm{d}r. \tag{10c}$$

In the context of Schrödinger equation, $\mathbf{H}$ 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 (trial function) can be written as (dropping the subscript H for brevity)

$$V^h(r) = \sum_{j=1}^{N} \phi_j(r) V_j \in \mathcal{S}^h \subset \mathcal{S}. \tag{11}$$

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:

$$\big(V^h(r)\big)' = \sum_{j=1}^{N} \phi_j'(r) V_j. \tag{12}$$

On substituting V^h and $(V^h)'$ from (11) and (12), respectively, in eq. (7) and letting w^h be the test functions, we obtain:

$$\int_0^a \Big\{ \sum_{j=1}^{N} (w^h)' \phi_j' V_j \Big\} r^2 \mathrm{d}r = 4\pi \int_0^a \rho_e w^h r^2 \mathrm{d}r \qquad \forall w^h \in \mathcal{V}^h.$$

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

$$\mathbf{K}\mathbf{u} = \mathbf{b}, \tag{13a}$$

$$\mathbf{K}_{ij} = \int_0^a \phi_i' \phi_j' r^2 \mathrm{d}r \tag{13b}$$

$$\mathbf{b}_i = 4\pi \int_0^a \rho_e \phi_i r^2 \mathrm{d}r. \tag{13c}$$

4 Self-Consistent Fields (SCF) Iterations

Owing to the nonlinear nature of generalized eigenvalue problem in eq. (10a) as alluded in Section 1.1, the problem is solved using the following self-consistent field technique: