

# Development of a computer program for electronic structure calculation using Lagrange basis functions

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**Abstract.** Electronic structure calculation is one approach that can be used to study material, especially at nanoscale where quantum nature of electrons might play important role to determine material properties. Among various methods for electronic structure calculation, density functional theory (DFT) based on Kohn-Sham equations is considered to be a popular one. In the the implementation to solve Kohn-Sham equations, single-electron wave function must be represented as an expansion of basis functions or discretized using some discretization schemes. Several existing computer programs for DFT calculations, such as QUANTUM ESPRESSO and GAUSSIAN09, expand single-electron wave function using plane wave and Gaussian functions, respectively. Others, such as OCTOPUS and GPAW use discretization based on finite-difference scheme. In this article, we report our initial effort to implement a new computer program to solve Kohn-Sham equations using expansion in Lagrange basis functions (LFs). Use of this basis set in Kohn-Sham equation results in matrix eigenproblem which is similar to matrix eigenproblem in finite difference schemes. Two methods to solve Kohn-Sham equation, namely self-consistent field iterations and direct minimization, are reported. Comparisons done with finite difference scheme implemented in Octopus for several simple systems shows that total energy convergence with respect to the number of grid points is better when using Lagrange basis functions.

## 1. Introduction

Nowadays electronic structure calculations are being used extensively in the field of physics, chemistry, condensed matter, materials design, and drugs discovery. Among various approaches to electronic structure, density functional theory [10] is very popular one due to its good predictive power and relatively cheap computational costs. Using Kohn-Sham density functional theory [11] the difficult many-electrons Schrodinger equation is mapped on to a set of single-electron equations, widely known as Kohn-Sham equations.

To solve Kohn-Sham equations, one needs to use basis set expansions or some discretization schemes. One choice for such basis set is Gaussian basis set which is used in various popular computer programs such as GAUSSIAN09 [6] and GAMESS [21, 9]. In condensed matter community, plane wave basis set is very popular which is used in several computer programs such as QUANTUM ESPRESSO [8, 7]. Instead of using specific basis set, alternatively one can discretize Kohn-Sham equations using standard finite-difference schemes such as implemented in computer programs such as OCTOPUS [19, 3, 1] and GPAW [12].

Lagrange basis functions are a family of functions which have been utilized for solving several differential equations in physics, which is reviewed in a comprehensive review [2]. It uses in the context of solving Kohn-Sham equations are probably first introduced in several publications

from Tuckerman's group [16, 16, 15] and quite recently in several publications of Kim's group. Lagrange-sinc: [4, 5] Lagrange-sinc + CI based on HF and KS: [14] Lagrange-sinc PAW [13]

Objective: create implementation of total energy calculation using Lagrange basis functions comparison to other real space

Scope: We limit our discussion to several simple forms of potential such as gaussian and GTH local pseudopotential.

## 2. Theory

### 2.1. Kohn-Sham density functional theory

Kohn-Sham density functional theory, total energy of a system of interacting electrons can be written as [11]:

$$E_{\text{tot}} [\{\psi_i(\mathbf{r})\}, \rho(\mathbf{r})] = E_{\text{kin}} + E_{\text{ion}} + E_{\text{Ha}} + E_{\text{xc}} \quad (1)$$

where  $\{\psi_i(\mathbf{r})\}$  is a set of single-electron wave functions or Kohn-Sham orbitals and  $\rho(\mathbf{r})$  is electronic density:

$$\rho(\mathbf{r}) = \sum_{i_{st}=1}^{N_{st}} f_{i_{st}} \psi_{i_{st}}^*(\mathbf{r}) \psi_{i_{st}}(\mathbf{r}) \quad (2)$$

$E_{\text{kin}}$  is kinetic energy of independent electrons described by Kohn-Sham orbitals:

$$E_{\text{kin}} = -\frac{1}{2} \sum_{i_{st}} \int f_{i_{st}} \psi_{i_{st}}^*(\mathbf{r}) \nabla^2 \psi_{i_{st}}(\mathbf{r}) d\mathbf{r} \quad (3)$$

$E_{\text{ion}}(\mathbf{r})$  represents ion-electron interaction energy:

$$E_{\text{ion}} = \int V_{\text{ion}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (4)$$

$E_{\text{Ha}}$  represents energy of classical distribution of charges (electrons) density which is also known as Hartree energy:

$$E_{\text{Ha}} = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5)$$

The last energy term,  $E_{\text{xc}}$  is the exchange-correlation energy. It has several forms, however, in this work we will use on the so-called local density approximation of  $E_{\text{xc}}$ :

$$E_{\text{xc}} = \int \epsilon_{\text{xc}} [\rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r} \quad (6)$$

Application of variational principle to energy functional 1 under the constraint

$$\int \psi_{i_{st}}^*(\mathbf{r}) \psi_{i_{st}}(\mathbf{r}) d\mathbf{r} = 1 \quad (7)$$

results in the so-called Kohn-Sham equation:

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right] \psi_{i_{st}}(\mathbf{r}) = \epsilon_{i_{st}} \psi_{i_{st}}(\mathbf{r}) \quad (8)$$

where  $\epsilon_{i_{st}}$  and  $\psi_{i_{st}}(\mathbf{r})$  is known as Kohn-Sham eigenvalues and eigenvectors (orbitals). Quantity  $V_{\text{KS}}$  is called the Kohn-Sham potential, which can be written as sum of several potentials:

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + V_{\text{Ha}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \quad (9)$$

$V_{\text{ion}}$  denotes attractive potential between ion (or atomic nuclei) with electrons. This potential can be written as:

$$V_{\text{ion}}(\mathbf{r}) = \sum_I^{N_{\text{atoms}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \quad (10)$$

This potential is Coulombic and has singularities at the ionic centers. It is generally difficult to describe this potential numerically, so it is common to replace the full Coulombic potential with softer potential which is known as pseudopotential. Note that this potential can also represent any external local potential, for example harmonic confining potential in quantum dot system.

$V_{\text{Ha}}$  is the classical electrostatic potential or commonly known as the Hartree potential. It is defined as

$$V_{\text{Ha}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (11)$$

Alternatively, Hartree potential can also be obtained via solving Poisson equation:

$$\nabla^2 V_{\text{Ha}}(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (12)$$

The last term in Equation (9) is exchange-correlation potential.

## 2.2. Lagrange basis functions

Use of Lagrange basis functions in electronic structure calculation is relatively new. Family:

For a given interval  $[0, L]$ , with  $L > 0$ , the grid points  $\alpha_i$  appropriate for periodic Lagrange function are given by:

$$x_\alpha = \frac{L}{2} \frac{2\alpha - 1}{N} \quad (13)$$

with  $\alpha = 1, \dots, N$ . Number of points  $N$  should be an odd number.

The periodic cardinal functions  $\phi_\alpha^{\text{per}}(x)$ , defined at grid point  $x_\alpha$  are given by:

$$\phi_\alpha^{\text{per}}(x) = \frac{1}{\sqrt{NL}} \sum_{n=1}^N \cos\left(\frac{\pi}{L}(2n - N - 1)(x - x_i)\right). \quad (14)$$

The expansion of periodic function in terms of Lagrange functions:

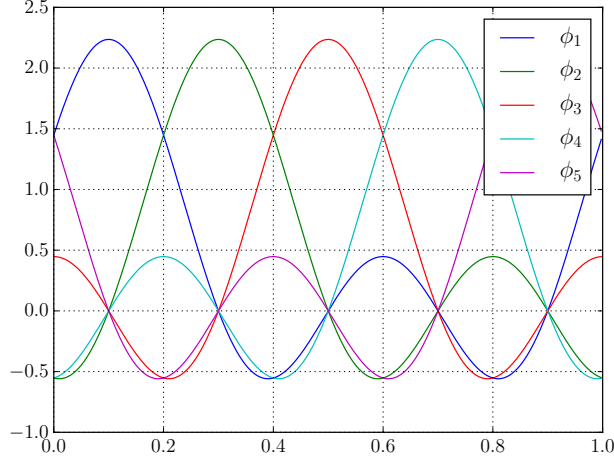
$$f(x) = \sum_{\alpha=1}^N c_\alpha \phi_\alpha^{\text{per}}(x) \quad (15)$$

with expansion coefficients  $c_i = \sqrt{L/N} f(x_\alpha)$ . When doing variational calculation, the coefficients  $c_\alpha$  are the variational parameters. The actual function values  $f(x_\alpha)$  at grid points  $x_\alpha$  is obtained by  $f(x_\alpha) = \sqrt{N/L} c_\alpha$ . The prefactor is sometimes abbreviated by  $h = L/N$  and is also referred to as scaling factor.

In this work, we will be using periodic Lagrange functions.

## 3. Implementation

In this section, we will describe our implementation of various terms in Kohn-Sham equations using Lagrange basis functions. The computer program which contains our implementation can be found in public repository: <https://github.com/f-fathurrahman/ffr-LFDFT>.



**Figure 1.** Plots of periodic LF

### 3.1. Kohn-Sham equations in Lagrange basis functions representation

Using Lagrange basis function 14 and its extension in 3d, Kohn-Sham orbitals at point  $\mathbf{r} = (x, y, z)$  can be written as

$$\psi_{i_{st}}(x, y, z) = \sum_{\alpha}^{N_x} \sum_{\beta}^{N_y} \sum_{\gamma}^{N_z} C_{\alpha\beta\gamma}^{i_{st}} L_{\alpha}(x) L_{\beta}(y) L_{\gamma}(z) \quad (16)$$

Using this expansion, kinetic operator can be written as

$$T_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} = -\frac{1}{2} \sum_{i_{st}} f_{i_{st}} \langle \psi_{i_{st}} | \nabla^2 | \psi_{i_{st}} \rangle \quad (17)$$

$$= -\frac{1}{2} \sum_{i_{st}} f_{i_{st}} \sum_{\alpha\alpha'} \sum_{\beta\beta'} \sum_{\gamma\gamma'} C_{\alpha\beta\gamma}^{i_{st}} \mathbb{L}_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} C_{\alpha'\beta'\gamma'}^{i_{st}} \quad (18)$$

were the Laplacian matrix  $\mathbb{L}_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'}$  has the following form:

$$\mathbb{L}_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} = D_{\alpha\alpha'}^{(2)} \delta_{\beta\beta'} \delta_{\gamma\gamma'} + D_{\beta\beta'}^{(2)} \delta_{\alpha\alpha'} \delta_{\gamma\gamma'} + D_{\gamma\gamma'}^{(2)} \delta_{\alpha\alpha'} \delta_{\beta\beta'} \quad (19)$$

Specifically, for periodic Lagrange basis function  $D_{ij}^{(2)}$ ,  $i, j = \alpha, \beta, \gamma$  can be written as follows.

$$D_{ij}^{(2)} = -\left(\frac{2\pi}{L}\right)^2 \frac{N'}{3} (N' + 1) \delta_{ij} + \frac{\left(\frac{2\pi}{L}\right)^2 (-1)^{i-j} \cos\left[\frac{\pi(i-j)}{N}\right]}{2 \sin^2\left[\frac{\pi(i-j)}{N}\right]} (1 - \delta_{nn'}) \quad (20)$$

where  $N' = (N - 1)/2$ .

While the matrix  $D_{ij}^{(2)}$  is dense, its counterpart in 3D is sparse. So, we can use sparse matrix data structure to do matrix-vector multiplication in when calculating action of kinetic operator to wavefunction. Specifically, we used compressed sparse column (CSC) format as representation of Laplacian operator in (19). SPARSKIT

The remaining potential terms which are local have very simple matrix form, i.e. diagonal:

$$V_{\text{KS}}(r_{\alpha\beta\gamma}) = V_{\text{ion}}(r_{\alpha\beta\gamma}) + V_{\text{Ha}}(r_{\alpha\beta\gamma}) + V_{\text{xc}}(r_{\alpha\beta\gamma}) \quad (21)$$

The action of potential operator to Kohn-Sham orbital at point  $(r_{\alpha\beta\gamma})$  can simply be obtained by pointwise multiplication with the potential on that point:

$$V_{\text{KS}\alpha\beta\gamma}^{\alpha'\beta'\gamma'}\psi(r_{\alpha\beta\gamma}) = V_{\text{KS}}(r_{\alpha\beta\gamma})\psi(r_{\alpha\beta\gamma}) \quad (22)$$

### 3.2. Methods to solve Kohn-Sham equations

We implement two methods to solve the Kohn-Sham equations, namely via the self-consistent field (SCF) iterations and direct energy minimization.

Outline of SCF iterations:

- Guess density  $\rho(\mathbf{r})$
- Iterate until convergence
  - Calculate Kohn-Sham potentials  $V_{\text{KS}}$  and build the Kohn-Sham Hamiltonian  $H_{\text{KS}}$
  - Diagonalize  $H_{\text{KS}}$  to obtain  $\psi_{\text{ist}}(\mathbf{r})$  and  $\epsilon_{\text{ist}}$ .
  - Calculate charge density and total energy. If the calculation converges the stop the calculation, if not iterate.

Outline of direct minimization, using

- Generate guess Kohn-Sham orbitals, orthonormalize if needed.
- Calculate charge density, build Kohn-Sham potential and calculate total energy for this
- Iterate until convergence:
  - Calculate Kohn-Sham electronic gradient  $\mathbf{g}_\psi$  and the preconditioned gradient  $\mathbf{K}\mathbf{g}_\psi$  where  $\mathbf{K}$  is a preconditioner.
  - Calculate search direction:

$$\beta = \frac{\mathbf{g}_\psi^\dagger \mathbf{K} \mathbf{g}_\psi}{\mathbf{g}_{\psi,\text{prev}}^\dagger \mathbf{K} \mathbf{g}_{\psi,\text{prev}}} \quad (23)$$

If  $\mathbf{g}_{\psi,\text{prev}}$  is not available (first iteration) then set  $\beta = 0$ .

- Calculate preconditioned search direction (with  $K$  is a preconditioner)

$$\mathbf{d} = -K\mathbf{g} + \beta d_{n-1} \quad (24)$$

- Update wavefunction as:

$$\mathbf{C}_{n+1} = \mathbf{C}_n + \alpha \mathbf{d}_n \quad (25)$$

where  $\alpha$  is:

$$\alpha = \alpha_t \frac{\mathbf{g} \cdot \mathbf{d}}{(\mathbf{g} - \mathbf{g}_t) \cdot \mathbf{d}_n} \quad (26)$$

and

$$\mathbf{g}_t = \nabla_\psi E(\mathbf{C} + \alpha_t \mathbf{d}_n) \quad (27)$$

## 4. Numerical results

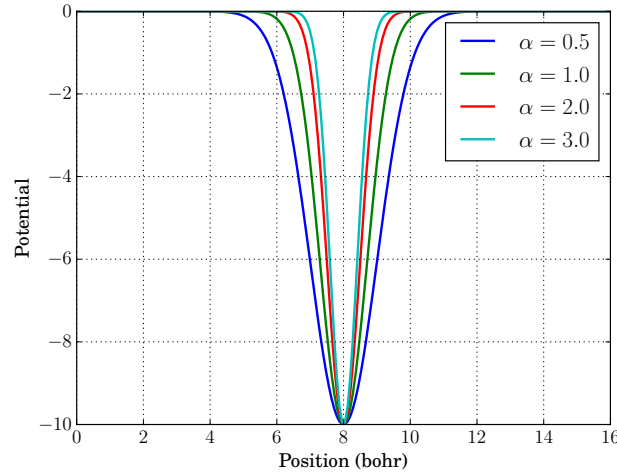
### 4.1. Gaussian potential

To validate our implementation, we will calculate total energy of a system with attractive "ionic" potential which has the following general form:

$$V_{\text{ion}}(r) = -A \exp(-\alpha r^2) \quad (28)$$

where  $A$  and  $\alpha$  are positive constants. We compare the obtained electronic total energy using the one obtained by OCTOPUS program [19, 3, 1] which implements finite difference approaches to solve Kohn-Sham equations.

The calculations are done using  $16 \times 16 \times 16$  bohr periodic unit cell and the center of the potential is set to be the center of the cell, i.e. at coordinate (8,8,8) bohr. The value of  $A$  is set to 10 and we use 4 different values of  $\alpha$ , i.e. 0.5, 1.0, 2.0, and 3.0. The visualization of the potential is shown in Figure 2. Notice that the potential becomes sharper as value of  $\alpha$  becomes larger.



**Figure 2.** Gaussian potential

Result for Gaussian potential

Comparison between SCF and direct minimization:

### 4.2. Hydrogen pseudopotential

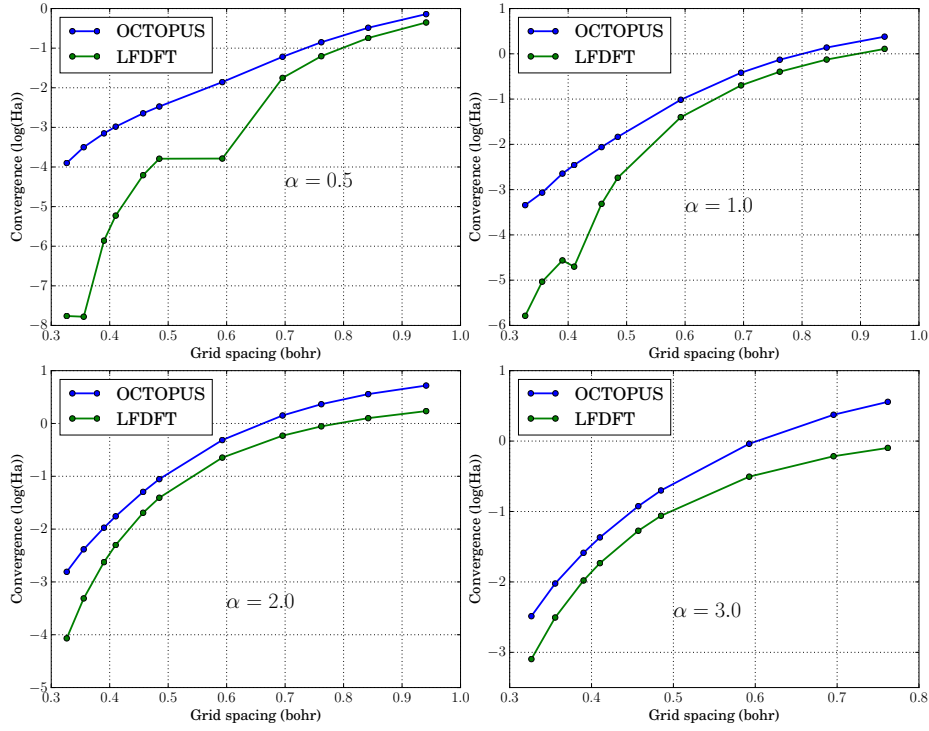
Result for atomic system

### 4.3. Lithium pseudopotential

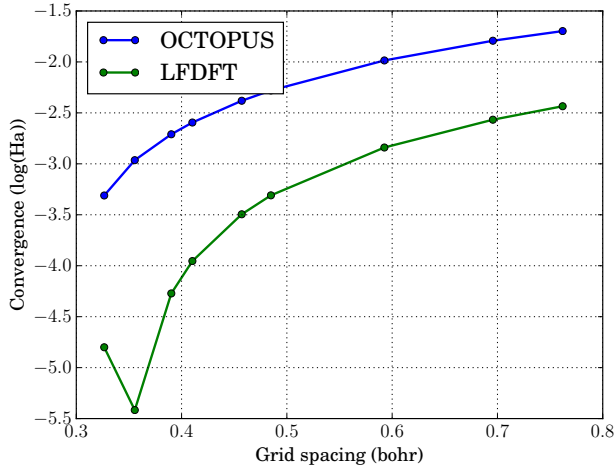
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**Figure 3.** Convergence



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