

# 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 [9] is very popular one due to its good predictive power and relatively cheap computational costs. Using Kohn-Sham density functional theory [10] 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 must use basis set expansions or some discretization schemes.

Lagrange mesh [2]

Lagrange-sinc: [4, 5]

Lagrange-sinc + CI based on HF and KS: [13]

Lagrange-sinc PAW [12]

Tuckerman's group: [15, 15, 14]

QUANTUM ESPRESSO: [8, 7].

GAUSSIAN09: [6]

OCTOPUS: [18, 3, 1]

GPAW: [11]

Objective:

Scope:

## 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 [10]:

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

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.

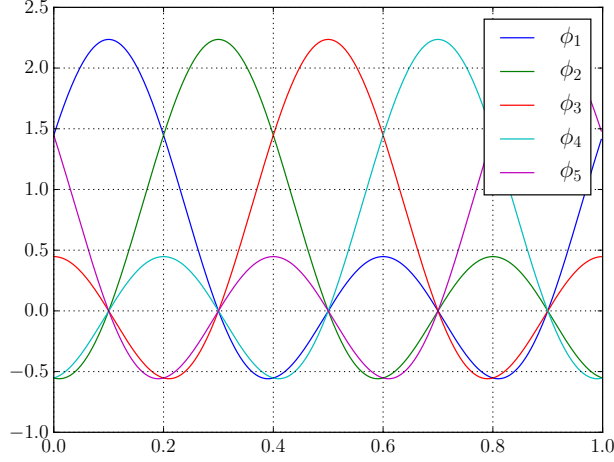
## 3. Implementation

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>.

### 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

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



**Figure 1.** Plots of periodic LF

Using this expansion, kinetic operator can be written as

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

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

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

The matrix representation of kinetic operator is sparse.

The remaining potential terms which are local have very simple matrix form, i.e. diagonal. The action of potential operator to Kohn-Sham orbital at point  $(r_{\alpha\beta\gamma})$  thus can be obtained by pointwise multiplication with the potential on that point:

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

### 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  $\epsilon_{i_{\text{st}}}$ .
  - 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:

$$\beta = \frac{\mathbf{g}_\psi^\dagger \mathbf{K} \mathbf{g}_\psi}{\mathbf{g}_{\psi,\text{prev}}^\dagger \mathbf{K} \mathbf{g}_{\psi,\text{prev}}} \quad (22)$$

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

- Calculate new direction:

$$\mathbf{d} = \quad (23)$$

## 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:

$$V_{\text{ion}}(r) = -A \exp(-\alpha r^2) \quad (24)$$

where  $A$  and  $\alpha$  are positive constants. We compare the obtained electronic total energy using the one obtained by OCTOPUS program [18, 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.

Result for Gaussian potential

Comparison between SCF and direct minimization:

### 4.2. Hydrogen pseudopotential

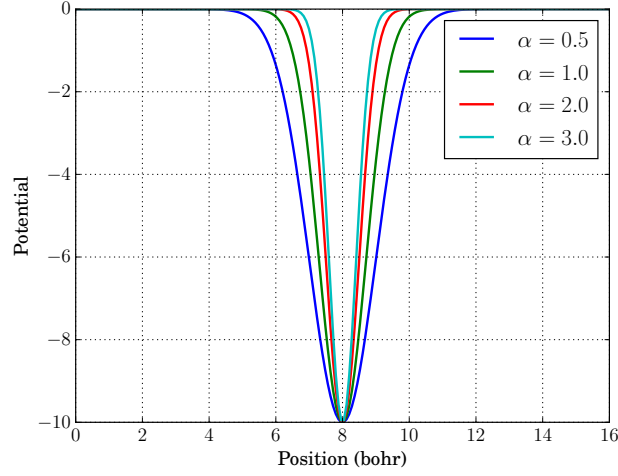
Result for atomic system

### 4.3. Lithium pseudopotential

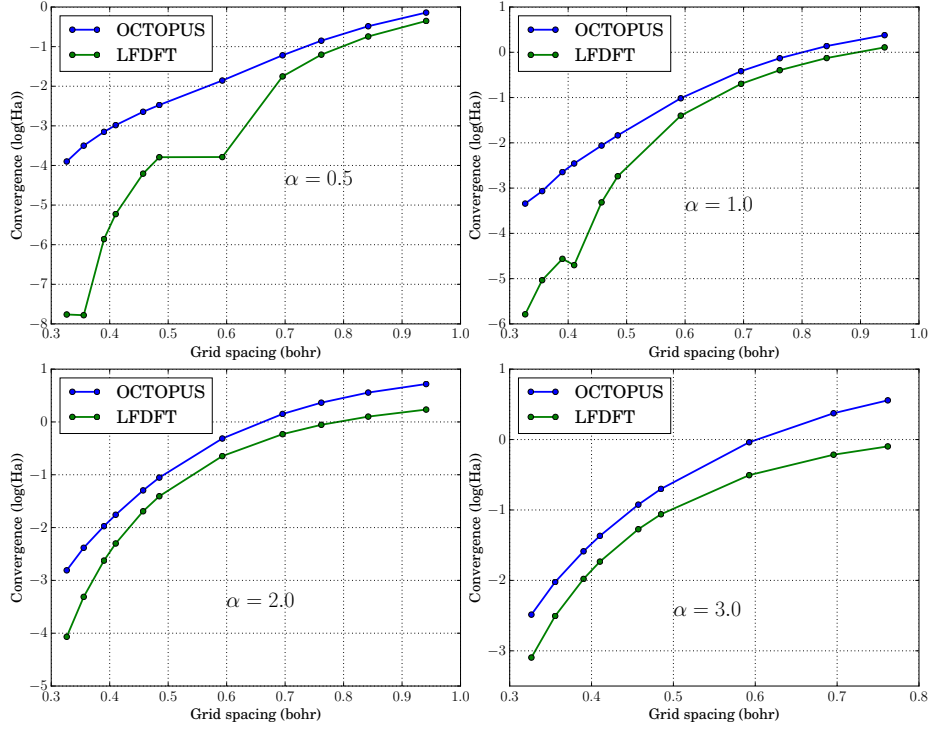
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## References

- [1] Andrade X *et al* 2015 Real-space grids and the Octopus code as tools for the development of new simulation approaches for electronic systems *Phys. Chem. Chem. Phys.* **17** 31371-31396
- [2] Baye D 2015 The Lagrange mesh method *Physics Reports* **565** 1-107
- [3] Castro A *et al* 2006 OCTOPUS: a tool for the application of time-dependent density functional theory *physica status solidi (b)* **243** 2465-2488

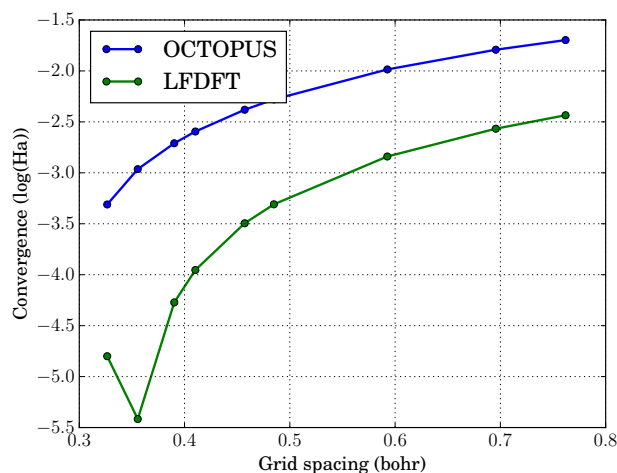


**Figure 2.** Gaussian potential



**Figure 3.** Convergence

- [4] Choi S, Hong K, Kim J, and Kim W Y 2015 Accuracy of Lagrange-sinc functions as a basis set for electronic structure calculations of atoms and molecules *J. Chem. Phys.* **142** 094116
- [5] Choi S, Kwon O.-K., Kim J, and Kim W Y 2016 Performance of heterogeneous computing with graphics processing unit and many integrated core for Hartree potential calculations on a numerical grid *J. Comp. Chem* **37** 2193-2201
- [6] Frisch M J 2009 Gaussian 09 Revision D; Gaussian, Inc.: Wallingford, CT
- [7] Giannozzi P Advanced capabilities for materials modelling with Quantum ESPRESSO *J. Phys.: Cond. Matt.*, 2017, 29, 465901
- [8] Giannozzi P QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials *J. Phys.: Cond. Matt.*, 2009, 21, 395502 (19pp)



- [9] Hohenberg P and Kohn W Inhomogenous Electron Gas *Phys. Rev.*, 1964, 136, B864-871
- [10] Kohn W and Sham 1965 Self-Consistent Equations Including Exchange and Correlation Effects *Phys. Rev.* **140** A1333-1138
- [11] Enkovaara J *et. al.* 2010 Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method *J. Phys. Cond. Matt* **22** 253202
- [12] Kang S, Ryu S, Choi, S, Kim J, Hong K, and Kim W Y 2016 Update to ACE-Molecule: Projector augmented wave method on Lagrange-sinc basis set *Int. J. Quant. Chem* **116** 644-650
- [13] Kim J, Hong K, Choi S, Hwang S-Y, and Kim W Y 2015 Configuration interaction singles based on the real-space numerical grid method: Kohn-Sham versus Hartree-Fock orbitals *Phys. Chem. Chem. Phys.* **17** 31434-31443
- [14] Lee, H -S and Tuckerman M E 2008 Efficient solution of Poisson's equation using discrete variable representation basis sets for Car-Parrinello ab initio molecular dynamics simulations with cluster boundary condition *J. Chem. Phys.* **129** 224108
- [15] Lee H -S and Tuckerman M E 2006 Ab initio molecular dynamics with discrete variable representation basis sets: techniques and application to liquid water *J. Phys. Chem. A* **110** 5549-5560
- [16] Liu Y, Yarne D A and Tuckerman M E 2003 Ab initio molecular dynamics calculations with simple, localized, orthonormal real-space basis sets *Phys. Rev. B* **68** 125110
- [17] Ma Z and Tuckerman M E 2010 Constant pressure ab initio molecular dynamics with discrete variable representation basis sets *J. Chem. Phys.* **133** 184110
- [18] Marques M A, Castro A, Bertsch G F and Rubio A 2003 OCTOPUS: a first-principles tool for excited electron-ion dynamics *Comp. Physics Comm.* **151** 60-78
- [19] Ryu S, Choi S, Hong K and Kim W Y 2016 Supersampling method for Efficient grid-based electronic structure calculations *J. Chem. Phys.* **144** 094101