

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

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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.

I. INTRODUCTION

Electronic structure calculations are one of theoretical tools that can be used to investigate

Density functional theory: [1, 2]

Lagrange mesh [3]

Lagrange-sinc: [4, 5]

Lagrange-sinc + CI based on HF and KS: [6]

Lagrange-sinc PAW [7]

Tuckerman's group: [8–10]

QUANTUM ESPRESSO: [11, 12].

GAUSSIAN09: [13]

OCTOPUS: [14–16]

GPAW: [17]

Objective:

Scope:

- ion-electron interaction energy:

$$E_{\text{ion}} = \int V_{\text{ion}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (3)$$

- Hartree (electrostatic) energy:

$$E_{\text{Ha}} = \int \frac{1}{2} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (4)$$

- Exchange-correlation energy (using LDA):

$$E_{\text{xc}} = \int \epsilon_{\text{xc}}[\rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r} \quad (5)$$

Application of variational principle to energy functional 1 with the constraint

$$\int \psi_{i_{st}}^*(\mathbf{r}) \psi_{i_{st}}(\mathbf{r}) d\mathbf{r} \quad (6)$$

results in the so-called Kohn-Sham equation:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right] \psi_{i_{st}}(\mathbf{r}) = \epsilon_{i_{st}} \psi_{i_{st}}(\mathbf{r}) \quad (7)$$

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

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + V_{\text{Ha}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \quad (8)$$

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

$$V_{\text{ion}}(\mathbf{r}) = \sum_I^{N_{\text{atoms}}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \quad (9)$$

II. THEORY

A. Kohn-Sham density functional theory

Within LDA, Kohn-Sham energy functional can be written as [2]:

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

with the following energy terms.

- Kinetic energy:

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

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. There are various types or flavors of pseudopotentials. In the current implementation, ion-electron potential, V_{ion} is treated by pseudopotential. HGH-type pseudopotential is employed due to the availability of analytic forms both in real and reciprocal space.

V_{Ha} is the classical Hartree potential. It is defined as

$$V_{\text{Ha}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (10)$$

where $\rho(\mathbf{r})$ denotes electronic density:

$$\rho(\mathbf{r}) = \sum_{i_{\text{st}}=1}^{N_{\text{occ}}} f_{i_{\text{st}}} \psi_{i_{\text{st}}}^*(\mathbf{r}) \psi_{i_{\text{st}}}(\mathbf{r}) \quad (11)$$

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 (8) is exchange-correlation potential.

B. 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 x_i appropriate for periodic Lagrange function are given by:

$$x_i = \frac{L}{2} \frac{2i-1}{N} \quad (13)$$

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

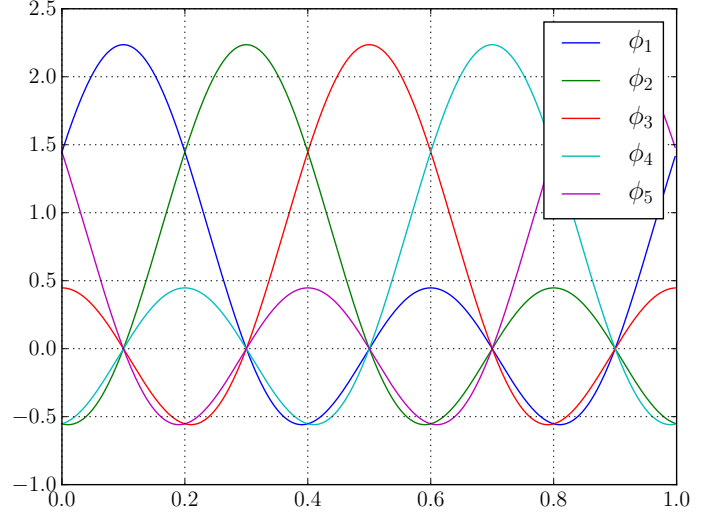
The periodic cardinal functions $L_i^{\text{per}}(x)$, defined at grid point i are given by:

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

The expansion of periodic function in terms of Lagrange functions:

$$f(x) = \sum_{i=1}^N c_i L_i^{\text{per}}(x) \quad (15)$$

with expansion coefficients $c_i = \sqrt{L/N} f(x_i)$. When doing variational calculation, the coefficients c_i are the variational parameters. The actual function values $f(x_i)$ at



grid points x_i is obtained by $f(x_i) = \sqrt{N/L} c_i$. 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.

III. IMPLEMENTATION

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

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

Using this expansion, kinetic operator can be written as

$$\begin{aligned} T_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} &= -\frac{1}{2} \sum_{i_{\text{st}}} f_{i_{\text{st}}} \langle \psi_{i_{\text{st}}} | \nabla^2 | \psi_i \rangle \\ &= -\frac{1}{2} \sum_{i_{\text{st}}} f_{i_{\text{st}}} \sum_{\alpha\alpha'} \sum_{\beta\beta'} \sum_{\gamma\gamma'} C_{\alpha\beta\gamma}^{i_{\text{st}}} \mathbb{L}_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} C_{\alpha'\beta'\gamma'}^{i_{\text{st}}} \end{aligned} \quad (17)$$

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.

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

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:

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

We have implemented a program to solve Kohn-Sham equation using Lagrange basis functions. The program that we have implemented can be found in public repository: <https://github.com/f-fathurrahman/f-fr-LFDFt>.

IV. NUMERICAL RESULTS

A. Gaussian potential

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

$$V_{ion}(r) = -A \exp(-\alpha r^2) \quad (22)$$

where A and α are positive constants. We compare the obtained electronic total energy using the one obtained by OCTOPUS program [14–16] 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 α , i.e. 0.5, 1.0, 2.0, and 3.0. The visualization of the potential is shown in Figure 1. Notice that the potential becomes sharper as value of α becomes larger.

Result for Gaussian potential

Comparison between SCF and direct minimization:

B. Hydrogen pseudopotential

Result for atomic system

C. Lithium pseudopotential

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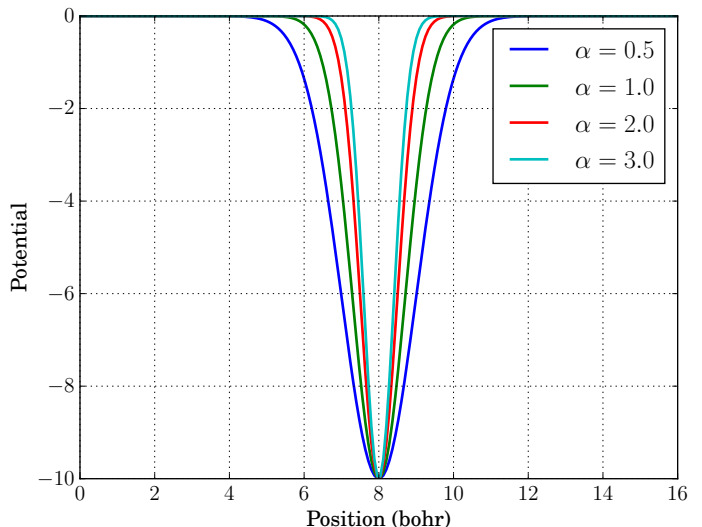


FIG. 1. Gaussian potential

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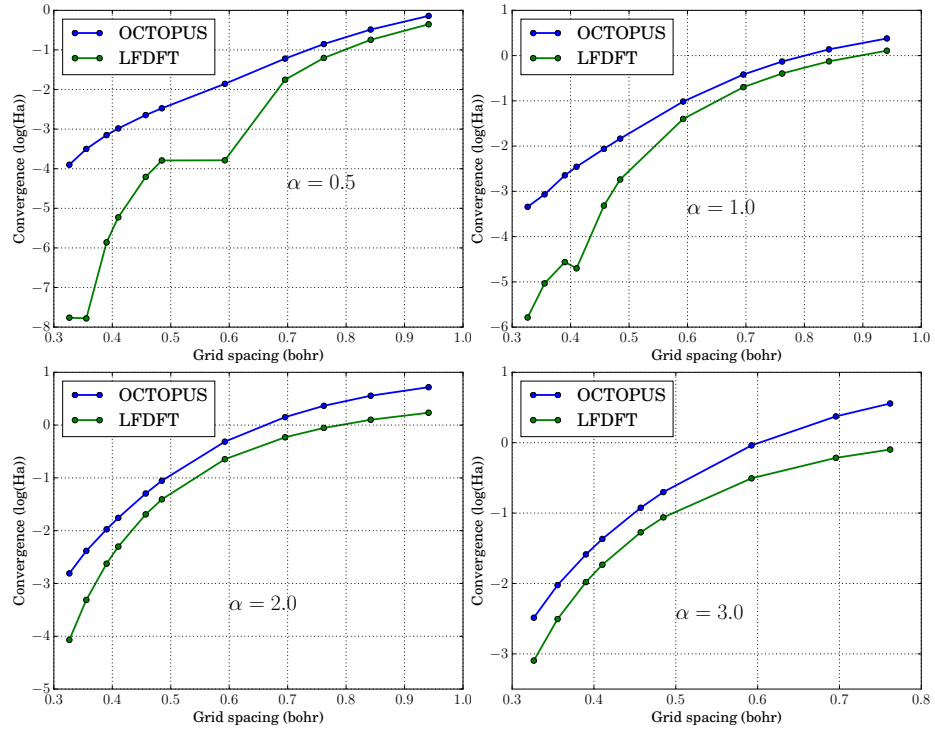
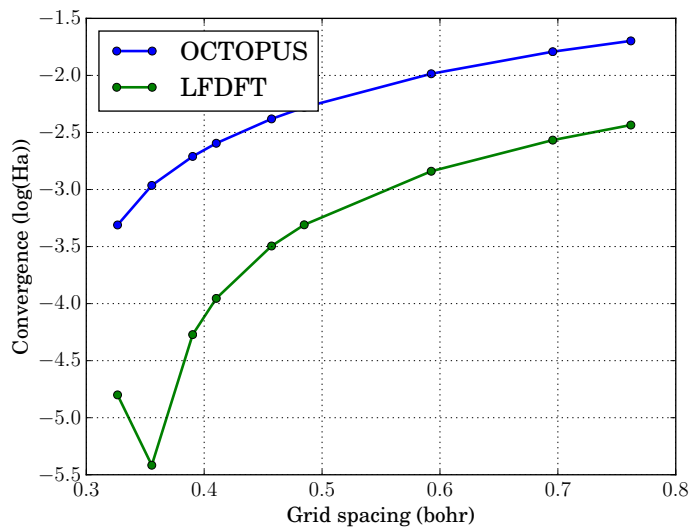


FIG. 2. Convergence



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