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 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]

II. THEORY

A. Kohn-Sham density functional theory

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

$$E_{\text{LDA}}\left[\{\psi_i(\mathbf{r})\}\right] = E_{\text{kin}} + E_{\text{ion}} + E_{\text{Ha}} + E_{\text{xc}} \quad (1)$$
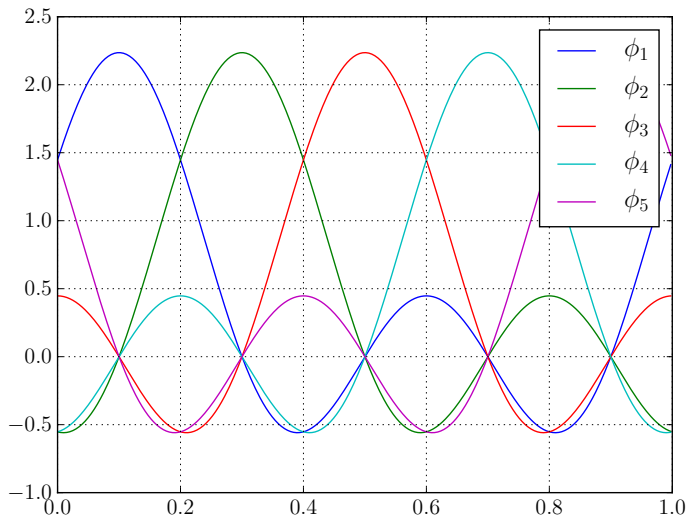
with the following energy terms.

- Kinetic energy:

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

- 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):

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

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 ϵi_{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:

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

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 the availability of analytic forms both in real and reciprocal space.

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

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

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

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

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

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

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. Familiy:

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

III. IMPLEMENTATION

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/ffr-LFDFT`.

IV. NUMERICAL RESULTS

First, we carry out calculations for gaussian potential:

$$V(r) = A\exp(-\alpha r) \tag{13}$$

We compare our calculation using the one obtained by using OCTOPUS program.

Result for Gaussian potential

Result for atomic system

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