Development of a Computer Program for Electronic Structure Calculation using Lagrange Basis Functions

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Outline

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- Lagrange basis functions
- Implementation
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Introduction

- Electronic structure calculations play important role for investigation of materials properties.
- Much of electronic structure calculations are based on Kohn-Sham density functional theory.
- Several computer packages can already carry out electronic structure calculations for systems containing of few atoms (characteristic length in angstrom) to ten thousands atoms (10-10^3 nm)

Problems

- These computer programs can "simplify" electronic structure calculations, espescially for non-specialists. However, they are not suitable for development of new methodologies. It is quite difficult to extend the program if we want to do some customized calculations.
- Much details are hidden beneath the programs. They usually contain thousands of lines codes or more which can be very intimidating for beginner developers to work with.

This research

- We will to write our own electronic structure calculations program.
- **Downside**: It might takes several years to reach the same level of maturity with state-of-the-art well-established electronic structure programs.
- In this presentation, I will describe some of our preliminary works to implement electronic calculation based on Kohn-Sham equations and Lagrange basis functions and results of the calculations for several simple systems.

Kohn-Sham total energy functional

Total energy of a system of interacting electrons according to Kohn-Sham can be written as:

$$E_{\text{tot}}\left[\{\psi_{i_{st}}(\mathbf{r})\}, \rho(\mathbf{r})\right] = E_{\text{kin}} + E_{\text{ion}} + E_{\text{Ha}} + E_{\text{xc}}$$

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

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

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

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

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

Kohn-Sham equations

Ground state energy can be found by minimizing the Kohn-Sham energy functional or by solving the Kohn-Sham equation:

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

with the following potential terms

$$\begin{aligned} V_{\mathrm{KS}}(\mathbf{r}) &= V_{\mathrm{ion}}(\mathbf{r}) + V_{\mathrm{Ha}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}) \\ V_{\mathrm{Ha}}(\mathbf{r}) &= \int \frac{\rho(\mathbf{r}')}{\mathbf{r}-\mathbf{r}'}\,\mathrm{d}\mathbf{r}' \\ \nabla^2 V_{\mathrm{Ha}}(\mathbf{r}) &= -4\pi\rho(\mathbf{r}) \end{aligned}$$

Kohn-Sham equations

- 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 such as finite-difference or finite-elements.
- 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 work, we will use expansion based on Lagrange basis functions, which is relatively new and currently there are no widely-available programs which implement this.

Lagrange basis functions

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

$$x_\alpha = \frac{L}{2}\frac{2\alpha - 1}{N} \tag{2}$$

with $\alpha = 1, \dots, N$. Number of points N should be an odd number. The periodic cardinal functions $\phi_\alpha(x)$, defined at grid point i are given by:

$$\phi_\alpha(x) = \frac{1}{\sqrt{NL}} \sum_{n=1}^{N} \cos\left(\frac{\pi}{L}(2n - N - 1)(x - x_\alpha)\right). \tag{3}$$

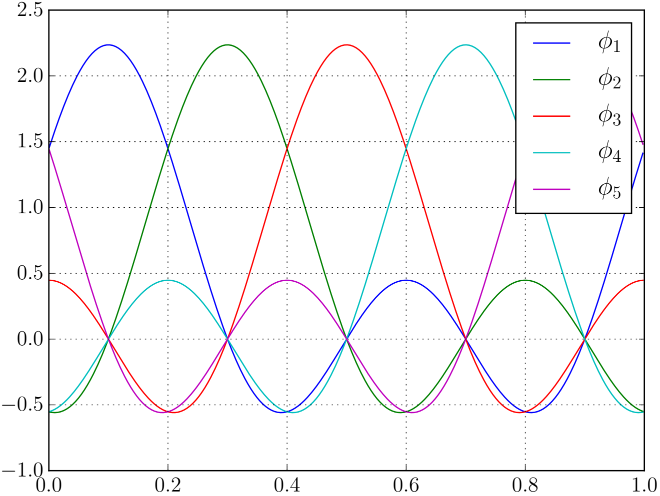
The expansion of periodic function in terms of Lagrange functions:

$$f(x) = \sum_{\alpha=1}^{N} c_\alpha \phi_\alpha(x) \tag{4}$$

with expansion coefficients $c_\alpha = \sqrt{L/N} f(x_\alpha)$.

Lagrange basis functions

Plot of for Lagrange basis functions for $N = 5$, $L = 1.0$



Using Lagrange basis function for Schrodinger equation

Given the 1D Schrodinger equation:

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right]\psi(x) = \epsilon\psi(x)$$

Lagrange basis function to expand the one-electron wavefunction:

$$\psi(x) = \sum_{\alpha}^{N} c_\alpha \phi_\alpha(x)$$

Matrix equation:

$$(\mathbf{T} + \mathbf{V})\,\mathbf{C} = \epsilon\mathbf{C}$$

Analytic expression for matrix $\mathbf{T}$ can be obtained from reference [1]. Matrix $\mathbf{V}$ is diagonal. Eigenvalue ϵ can be found using standard eigenvalue solver.

[1] See for example: *J. Phys. Chem. A* **110**, 5549-5560, (2006)

Extension to 3D

Expansion of function in 3D using Lagrange basis function:

$$\psi(\mathbf{r} = (x, y, z)) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} C_{\alpha\beta\gamma} \phi_{\alpha}(x) \phi_{\beta}(y) \phi_{\gamma}(z)$$

Similar matrix equation can be obtained in 3D case.
Potential matrix is still diagonal and kinetic matrix now is expressed as:

$$\mathbf{T}_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} = \mathbf{T}_{\alpha\alpha'} \delta_{\beta\beta'} \delta_{\gamma\gamma'} + \mathbf{T}_{\beta\beta'} \delta_{\alpha\alpha'} \delta_{\gamma\gamma'} + \mathbf{T}_{\gamma\gamma'} \delta_{\alpha\alpha'} \delta_{\beta\beta'}$$

where $\mathbf{T}_{ii'}$, $i = \alpha, \beta, \gamma$ are kinetic matrix for 1D case.
Similar matrix representation can be found in for finite-difference methods [2].
Once we know how to calculate $\mathbf{T}$ and $\mathbf{V}$, we can find solution to Kohn-Sham equations using standard self consistent cycle (SCF) procedure.

[2] See for example: *Phys. Rev. Lett.* **72**, 1240 (1994).

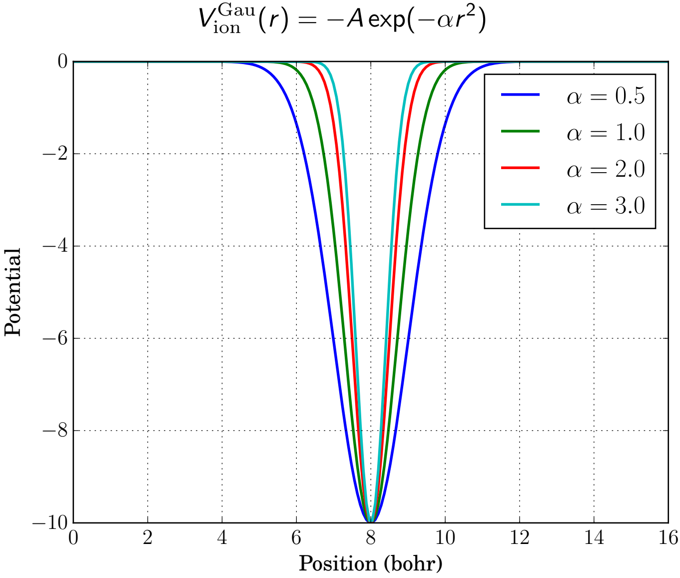
Numerical results

We carry out total energy calculations for systems with the following simple potentials:

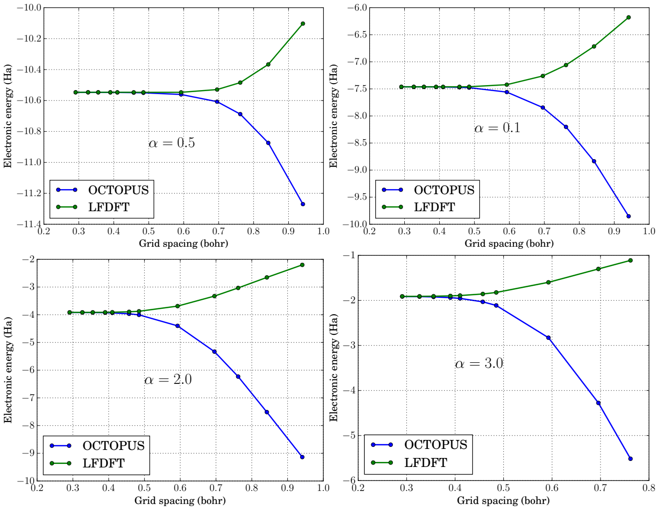
- Gaussian potentials: convergence of total energy with respect to grid spacing
- atomic pseudotentials: hydrogen and lithium pseudopotentials

All calculations are done in $16 \times 16 \times 16$ bohr periodic box. Center of the potential is set to the center of the box.
We will also validate the results of our program against result from well-established program OCTOPUS which uses finite difference method.

Gaussian potentials

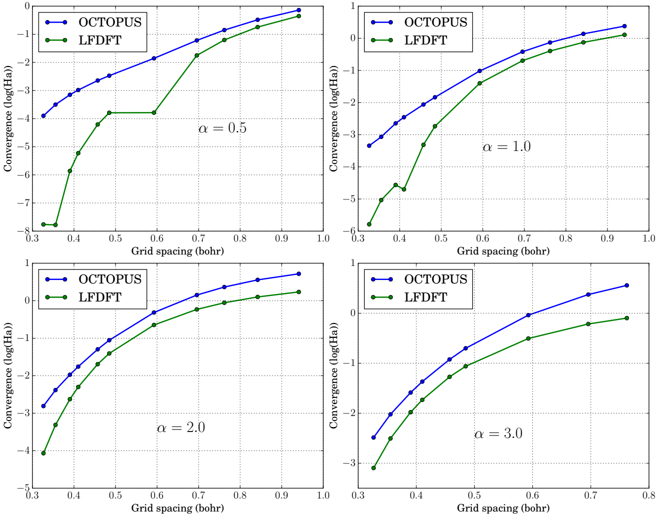


Total energy



Both our program (LFDFT) and OCTOPUS converge to the same total energy value

Total energy convergence



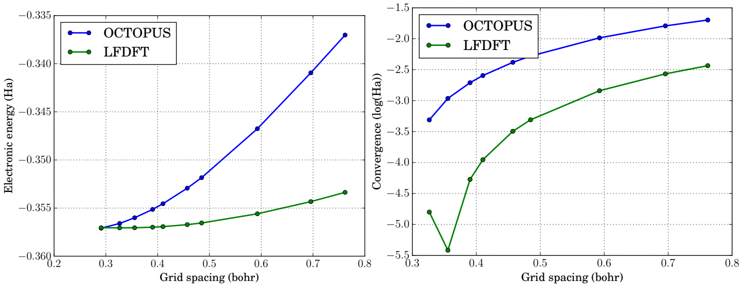
LFDFT converges faster than OCTOPUS (finite difference)
For smoother potential (smaller α) both methods converge faster
(typicall for real-space methods)

Hydrogen atom

$$V_{\rm loc}^{\rm H}(\mathbf{r}) = -\frac{Z_{\rm ion}}{r}\mathrm{erf}\left(\frac{r}{\sqrt{2}r_{\rm loc}}\right) + \exp\left[-\frac{1}{2}\left(\frac{r}{r_{\rm loc}}\right)^2\right] \times \left[C_1 + C_2\left(\frac{r}{r_{\rm loc}}\right)^2 + \right] \quad (5)$$

with the following parameters: $Z_{\rm ion} = 1$, $r_{\rm loc} = 0.2$, $C_1 = -4.1802372$, and $C_2 = 0.725075$. [3]

[3] *Phys. Rev. B* **58**, 3641 (1998).



LFDFT converges faster than OCTOPUS (finite difference)

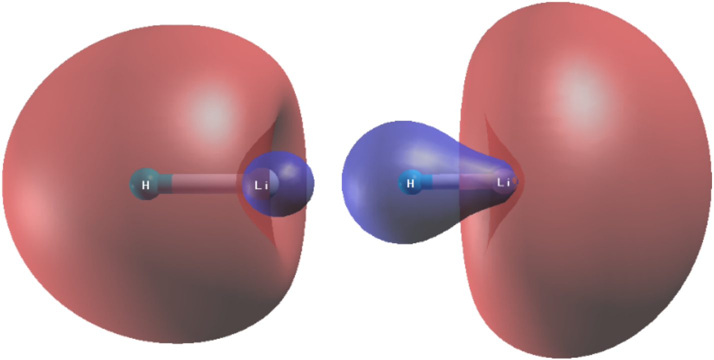
Lithium atom

$$V_{\mathrm{loc}}^{\mathrm{Li}}(\mathbf{r}) = -\frac{Z_{\mathrm{ion}}}{r}\mathrm{erf}\left(\frac{r}{\sqrt{2}r_{\mathrm{loc}}}\right) +$$
$$\exp\left[-\frac{1}{2}\left(\frac{r}{r_{\mathrm{loc}}}\right)^2\right] \times \left[C_1 + C_2\left(\frac{r}{r_{\mathrm{loc}}}\right)^2 + C_3\left(\frac{r}{r_{\mathrm{loc}}}\right)^4 + C_4\left(\frac{r}{r_{\mathrm{loc}}}\right)^6\right]$$

with the following parameters: $Z_{\mathrm{ion}} = 3$, $r_{\mathrm{loc}} = 0.4$, $C_1 = -14.034868$, $C_2 = 9.553476$, $C_3 = -1.7664885$ and $C_4 = 0.084370$. [4]

[4] *Phys. Rev. B* **58**, 3641 (1998).

LiH HOMO and LUMO



HOMO (left image) and LUMO (right image) of LiH

Remarks and future works

Remarks

- Use of Lagrange basis functions to Kohn-Sham equation gives matrix-representation which is very similar to the one obtained by using finite-difference methods
- Compared to finite difference method, use of Lagrange basis functions gives better total energy convergence with respect to grid size (number of basis functions).

Future works will focus on:

- Larger systems
- Paralellization

Thank you for your attention!

Public repository: `https://github.com/f-fathurrahman/ffr-LFDFT`.