

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

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# Outline

- ▶ Introduction
- ▶ Kohn-Sham equations
- ▶ Lagrange basis functions
- ▶ Implementation
- ▶ Numerical results

# 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 ( $10\text{-}10^3$  nm)

# Problems

- ▶ These computer programs can "simplify" electronic structure calculations, especially for non-specialists. However, they are not suitable for development of new methodologies. It is quite difficult to extend the program if we want some 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.
- ▶ In this presentation, I will describe some of our current work 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:

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

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

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

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

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

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

# Kohn-Sham equations

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

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

with the following potential terms

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

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

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

# 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.
- ▶ 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.



# Lagrange basis functions

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

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

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

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

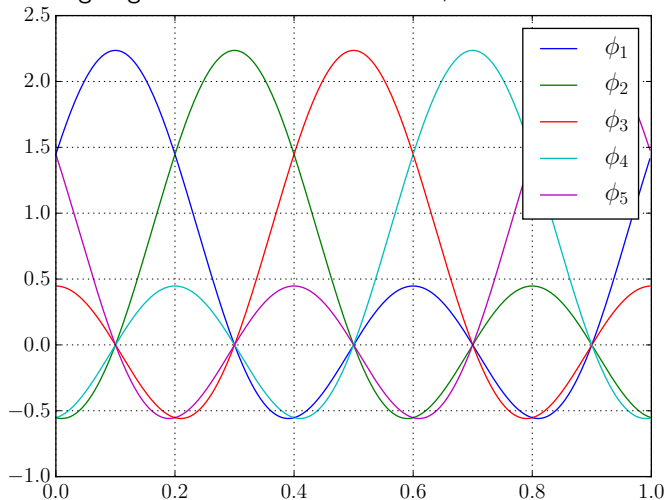
The expansion of periodic function in terms of Lagrange functions:

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

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:

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

Lagrange basis function to expand the one-electron wavefunction:


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

Matrix equation:

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

Analytic expression for matrix  $\mathbf{T}$  can be obtained from reference <sup>1</sup>.  
Matrix  $\mathbf{V}$  is diagonal. Eigenvalue  $\epsilon$  can be found using standard eigenvalue solver.

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<sup>1</sup>See for example: *J. Phys. Chem. A* **110**, 5549-5560, (2006). 

## Extension to 3D

Expansion of function in 3D using Lagrange basis function:

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

Similar matrix equation can be obtained in 3D case.

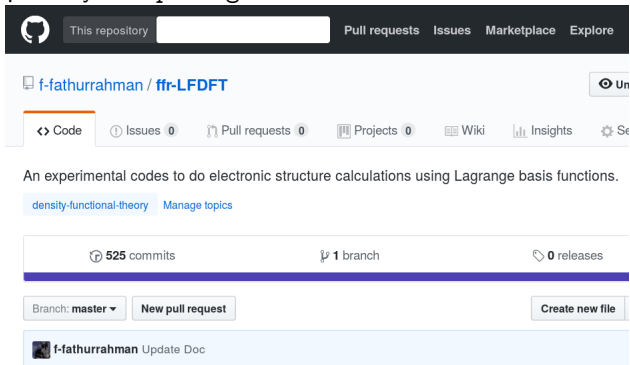
Potential matrix is still diagonal and kinetic matrix now is expressed as:

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

where  $\mathbf{T}_{ii'}$ ,  $i = \alpha, \beta, \gamma$  are kinetic matrix for 1D case. Kinetic matrix is now sparse.

# Our implementation

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



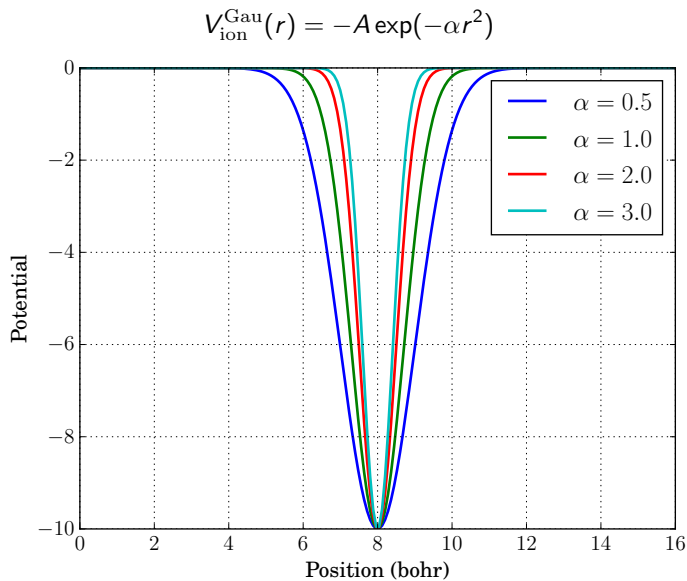
# Numerical results

Total energy calculation on the following simple potentials:

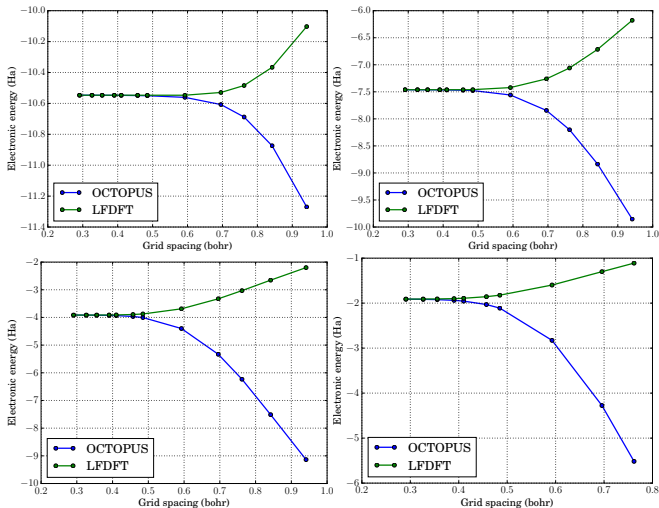
- ▶ Gaussian potentials: convergence of total energy with respect to grid spacing
- ▶ atomic pseudopotentials: hydrogen and lithium pseudopotentials

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.

# Gaussian potentials



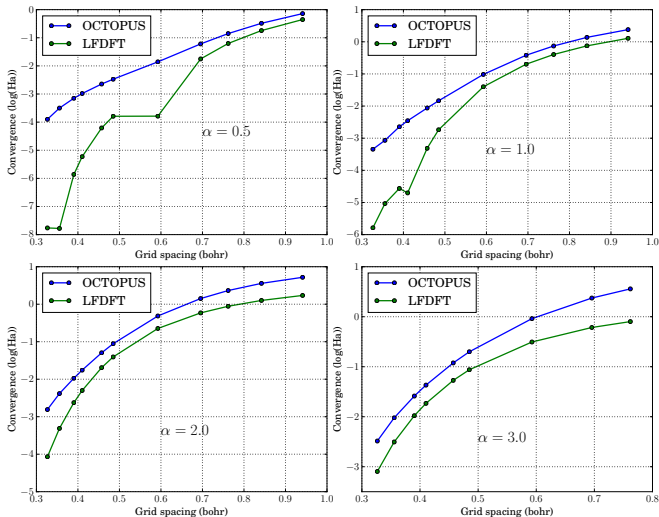
# Total energy



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



# Total energy convergence



LFDFT converges faster than OCTOPUS (finite difference)

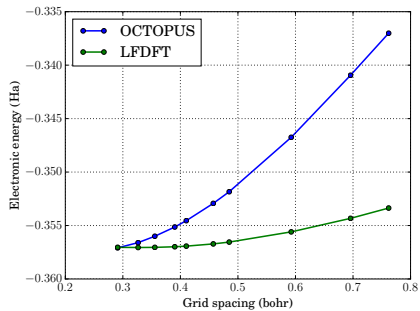
# Hydrogen atom

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

with the following parameters:  $Z_{\text{ion}} = 1$ ,  $r_{\text{loc}} = 0.2$ ,  $C_1 = -4.1802372$ , and  $C_2 = 0.725075$ .<sup>2</sup>

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<sup>2</sup>Hartwigsen, *Phys. Rev. B* **58**, 3641 (1998).



# Lithium atom

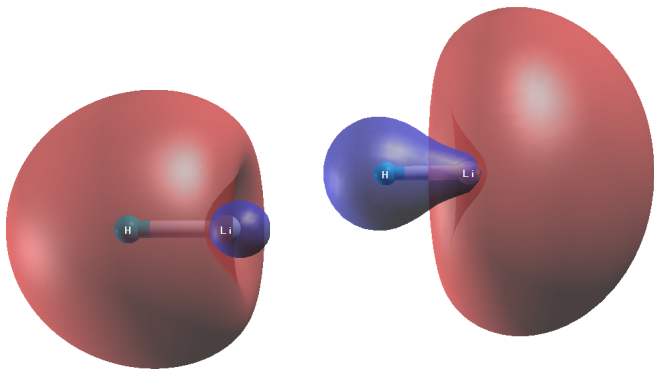
$$V_{\text{loc}}(\mathbf{r}) = -\frac{Z_{\text{ion}}}{r} \text{erf}\left(\frac{r}{\sqrt{2}r_{\text{loc}}}\right) + \exp\left[-\frac{1}{2}\left(\frac{r}{r_{\text{loc}}}\right)^2\right] \times \left[C_1 + C_2\left(\frac{r}{r_{\text{loc}}}\right)^2 + C_3\left(\frac{r}{r_{\text{loc}}}\right)^4 + C_4\left(\frac{r}{r_{\text{loc}}}\right)^6\right]$$

with the following parameters:  $Z_{\text{ion}} = 3$ ,  $r_{\text{loc}} = 0.4$ ,  $C_1 = -14.034868$ ,  $C_2 = 9.553476$ ,  $C_3 = -1.7664885$  and  $C_4 = 0.084370$ .<sup>3</sup>

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<sup>3</sup>Hartwigsen, *Phys. Rev. B* **58**, 3641 (1998).

# LiH HOMO and LUMO



# Conclusions

- ▶ 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).