DFT Implementation Using STO-3G Basis Sets: A Computational Approach to Electronic Structure Calculations

Magane Tamandja

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1 abstract

This report presents an efficient implementation of Density Functional Theory (DFT) using the STO-3G basis set for electronic structure calculations. We develop analytical expressions for the Laplacian operator, electron repulsion terms, and exchange-correlation potentials within the Local Density Approximation (LDA) framework. Our implementation demonstrates [briefly mention a key result or advantage of your approach]. The mathematical framework established here provides a foundation for more advanced implementations that could significantly reduce computational costs while maintaining accuracy for molecular systems.

2 Introduction

1. Introduction

Density Functional Theory (DFT) has emerged as one of the most powerful and widely used methods for electronic structure calculations in computational chemistry and materials science. The popularity of DFT stems from its favorable balance between computational efficiency and accuracy, making it suitable for studying systems ranging from small molecules to extended materials.

Despite its widespread use, implementing DFT algorithms that are both accurate and computationally efficient remains challenging. The treatment of exchange-correlation functionals, basis set selection, and numerical integration schemes all significantly impact the performance and reliability of DFT calculations.

In this report, we present a detailed implementation of a DFT algorithm using the STO-3G basis set. We focus specifically on three critical components: 1) The mathematical treatment of the Laplacian operator 2) The computation of electron repulsion integrals 3) The implementation of exchange-correlation potentials within the Local Density Approximation (LDA)

Our goal is to develop a computational framework that balances accuracy with efficiency for electronic structure calculations, providing a foundation for future extensions to more complex molecular systems.

3 DFT

3.1 Treatment of the Laplacian

Given the Khon-Sham equation,

$$\left(-\frac{1}{2}\nabla^2 + \left[\sum_j^N \int \frac{|\varphi_j(\vec{r_2})|^2}{r_{12}} d\vec{r_2} + V_{XC}(\vec{r_1}) - \sum_A^M \frac{Z_A}{r_{1A}}\right]\right)\varphi_i = \epsilon_i \varphi_i$$

We choose to use the STO-3G basis set, which is given by :

$$\psi_{\text{STO-3G}}(s) = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

where

$$\phi_1 = \left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2}$$
$$\phi_2 = \left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2}$$
$$\phi_3 = \left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2}$$

So we can rewrite the Laplacian as

$$\begin{aligned}\frac{d^2(c_1\phi_1 + c_2\phi_2 + c_3\phi_3)}{d^2r} &= \frac{d^2(c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} + c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} + c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2})}{d^2r} \\ &= (4\alpha_1^2 r^2 - 2\alpha_1)c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} \\ &+ (4\alpha_2^2 r^2 - 2\alpha_2)c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} \\ &+ (4\alpha_3^2 r^2 - 2\alpha_3)c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2}\end{aligned}$$

In the spirit of constructing a matrix hamiltonian, we diagonilize the expression to get the expression
$\frac{d^2(c_1\phi_1+c_2\phi_2+c_3\phi_3)}{d^2r} =$

$$\begin{bmatrix} (4\alpha_1^2 r^2 - 2\alpha_1) & 0 & 0 \\ 0 & (4\alpha_2^2 r^2 - 2\alpha_2) & 0 \\ 0 & 0 & (4\alpha_3^2 r^2 - 2\alpha_3) \end{bmatrix} (c_1 \left(\tfrac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} + c_2 \left(\tfrac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} + c_3 \left(\tfrac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2}).$$

This provides a computable expression for the Laplacian.

3.2 Treatment of the Electron Repulsion Term

We assume the integral is defined by infinity here.
We also need to keep in mind values for alpha and c dependence on orbital type.
Given the term $|\varphi_j(\vec{r_2})|^2$ can be written as $(\varphi_j(\vec{r_2}))^2$ for a real basis function, we write:

$$|\varphi_j(\vec{r_2})|^2 = \left[c_1 \left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} + c_2 \left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} + c_3 \left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2} \right]^2$$

$$
\begin{aligned}
|\varphi_j(\vec{r_2})|^2 &= \left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} + c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} + c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2}\right]^2 \\
&= \left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_1 r^2} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{-\alpha_1 r^2 - \alpha_2 r^2} \\
&+ 2\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{-\alpha_1 r^2 - \alpha_3 r^2} + \left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_2 r^2} \\
&+ \left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_3 r^2} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right] e^{-\alpha_2 r^2 - \alpha_3 r^2} \\
|\varphi_j(\vec{r_2})|^2 &= \left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_1 r^2} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{(-\alpha_1 - \alpha_2) r^2} \\
&+ 2\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{(-\alpha_1 - \alpha_3) r^2} + \left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_2 r^2} \\
&+ \left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_3 r^2} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right] e^{(-\alpha_2 - \alpha_3) r^2} \\
\int |\varphi_j(\vec{r_2})|^2 dr &= \int \left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_1 r^2} dr + \int 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{(-\alpha_1 - \alpha_2) r^2} dr \\
&+ \int 2\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] e^{(-\alpha_1 - \alpha_3) r^2} dr + \int \left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_2 r^2} dr \\
&+ \int \left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]^2 e^{-2\alpha_3 r^2} dr + \int 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right] e^{(-\alpha_2 - \alpha_3) r^2} dr \\
\int |\varphi_j(\vec{r_2})|^2 &= \left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]^2 \int e^{-2\alpha_1 r^2} dr + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] \int e^{(-\alpha_1 - \alpha_2) r^2} dr \\
&+ 2\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right] \int e^{(-\alpha_1 - \alpha_3) r^2} dr + \left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]^2 \int e^{-2\alpha_2 r^2} dr \\
&+ \left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]^2 \int e^{-2\alpha_3 r^2} dr + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right] \int e^{(-\alpha_2 - \alpha_3) r^2} dr
\end{aligned}
$$

Using the Gaussian integral formula:

$$\int_{-\infty}^{\infty} e^{-\alpha r^2} dr = \sqrt{\frac{\pi}{\alpha}};$$

we can rewrite the integral terms as :

$$\begin{aligned}\int |\varphi_j(\vec{r_2})|^2 = &\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]^2\sqrt{\frac{\pi}{2\alpha_1}} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]\sqrt{\frac{\pi}{\alpha_1+\alpha_2}} \\ &+ 2\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\left[c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\right]\sqrt{\frac{\pi}{\alpha_1+\alpha_2}} + \left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]^2\sqrt{\frac{\pi}{2\alpha_2}} \\ &+ \left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]^2\sqrt{\frac{\pi}{2\alpha_3}} + 2\left[c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\right]\left[c_3\left(\frac{2\alpha_3}{\pi}\right)^{3/4}\right]\sqrt{\frac{\pi}{\alpha_2+\alpha_3}}\end{aligned}$$

This provides us with a relatively easy to compute a coulomb contribution.

3.3 Treatment of the exchange potential : LDA

Using the LDA approximation, we get

$$V_X^{LDA} = -(\frac{3}{\pi})^{\frac{1}{3}}\varphi^{\frac{1}{3}}(r)$$