OFDFT Background Theory

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1 Background

This document gives a brief overview of the theoretical background of OFDFT and provides all of the important equations used in my code. A large amount of the information I learned here comes from these OFDFT reviews [1, 2, 3] and this DFT textbook [4]. Most of the text here is taken from my capstone project thesis "Minimization of the Non-Interacting Kinetic Energy Functional".

2 Density Functional Theory (DFT)

Instead of relying on the complex wavefunction $\Psi(r_1, r_2, ..., r_{N_e})$ for N_e electrons, DFT reframes electron structure calculations directly in terms of the three-dimensional electron density $\rho(\mathbf{r})$. DFT was put on strong theoretical foundation by the Hohnberg-Kohn theorems [5], which state that the total energy of a system is uniquely determined by a functional of the electron density, and that this functional is minimized at the ground-state density. In this context, the functional is a mapping that takes the function $\rho(\mathbf{r})$ to a real number (i.e. the energy). In an external potential $v_{ext}(\mathbf{r})$, this energy functional takes the form

$$E[\rho] = F[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{1}$$

were $F[\rho]$ comprises of the universal kinetic energy functional $T[\rho]$, and the electron-electron interaction energy functionals. The non-interacting kinetic energy density functional (KEDF) $T_s[\rho]$ can then be isolated from the total kinetic energy functional $T[\rho]$. Furthermore, the classical Coulomb repulsion between electrons (described by the Hartree energy functional) can be singled out from the electron-electron interaction functional. The remaining terms in $F[\rho]$ can be bundled into the exchange-correlation energy functional $E_{XC}[\rho]$. Although the Hohnberg-Kohn theorems are exact in principle, the specific forms of $T_s[\rho]$ and $E_{XC}[\rho]$ are unknown, requiring the use of approximations for their evaluation. There exists a wide array of functionals available to approximate $E_{XC}[\rho]$, however $T_s[\rho]$ has historically been dealt with not by approximation, but by the the Kohn-Sham (KS) approach [6].

A natural consideration to make is that the KS method is not an integral part of the formalism of DFT. Instead of calculating the non-interacting kinetic energy in terms of KS orbitals, finding an approximate expression for the non-interacting KEDF would remove a

major bottleneck, leading organically to $\mathcal{O}(N_e)$ scaling [1, 2, 3]. The direct minimization of Eq. (1) using an approximate KEDF is known as orbital-free DFT (OFDFT). The main advantage of OFDFT over KSDFT is that, due to its innate linear scaling, OFDFT prioritizes computational speed over KSDFT. The accuracy of OFDFT relative to KSDFT is determined by the quality of the KEDF used to minimize Eq. (2). The formidable challenge of this theory is to find a sufficiently accurate expression for the non-interacting KEDF.

3 DFT Euler-Lagrange Equation

The second Hohnberg-Kohn theorem states that the energy functional given by Eq. (1) is minimized for the ground-state density, under the constraints that the total number of electrons remains constant $\left(\int \rho(\mathbf{r})d\mathbf{r} = N_e\right)$, and that the density is non-negative $\left(\rho(\mathbf{r}) \geq 0\right)$. The constraint that N_e must be constant is incorporated using the method of Lagrange multipliers from mulitvariable calculus, so that the Lagrangian function to minimize is given by

$$L[\rho] = E[\rho] - \mu\left[\int \rho(\mathbf{r})d\mathbf{r} - N_e\right], \tag{2}$$

where μ is the Lagrange multiplier [4] (μ can also be identified as the chemical potential from statistical mechanics).

In order to find the ground-state density which minimizes this equation, we need to take the functional derivative of $L[\rho]$ with respect to $\rho(\mathbf{r})$ and let $\frac{\delta L[\rho]}{\delta \rho(\mathbf{r})} = 0$. When the ground-state density is inputted into this equation, $\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})}$ will take the constant value of the chemical potential for all $\mathbf{r}$. The non-linear, multidimensional minimization problem we solve in OFDFT is given by

$$\frac{\delta L[\rho]}{\delta \rho} = \frac{\delta E[\rho]}{\delta \rho} - \mu = 0. \tag{3}$$

4 Determining the Ground-state by Direct Minimization

To determine the ground-state density, Eq. (3) must be satisfied. This is achieved by directly minimizing this Euler-Lagrange equation with respect to $\rho(\mathbf{r})$. Upon obtaining this ground-state density, it can then be substituted into Eq. (1) to compute the total energy, which serves as a foundation for deriving various other physical properties of the system.

In practice, this minimization problem must be evaluated numerically. As a consequence of the Hohnberg-Kohn theorems, we can calculate the direction of steepest descent towards the ground-state density for a given trial density. After k iterations of the minimization algorithm, one can calculate steepest descent direction p_k using Eq. (3). Namely, p_k is exactly

$$p_k = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu. \tag{4}$$

We can use p_k to get iteratively closer to the ground-state density starting from an arbitrary initial guess density. In principle, the algorithm should proceed at each iteration as

$$\rho_{k+1} = \rho_k + \alpha_k p_k \tag{5}$$

where ρ_{k+1} is an improved density that is closer to the true ground-state density than ρ_k, and α_k is a scalar value (iteration step size). Convergence of this algorithm is achieved when the condition that

$$\left[\int \left(\frac{\delta E[\rho_{k+1}]}{\delta \rho_{k+1}} - \mu \right)^2 d\mathbf{r} \right]^{\frac{1}{2}} < \tau \tag{6}$$

is satisfied for a small tolerance value τ. Once successful minimization has been indicated by the evaluation of Eq. (7), we can conclude that the Euler-Lagrange equation of Eq. (3) is satisfied and ρ_{k+1} has converged on the ground-state density with precision determined by the tolerance value τ.

In practice, one usually implements a much more complex algorithm to prevent divergence due to numerical instabilities. The primary difficulty in this picture is that there is no guarantee the updated density ρ_{k+1} will uphold the requirements that $\int \rho(\mathbf{r}) d\mathbf{r} = N_e$ and that $\rho(\mathbf{r}) \geq 0$. These conditions limit the admissible densities to a constrained space during the minimization.

5   Single Electron System

As a correction term to the Thomas-Fermi functional, Von Weiszäcker [7] introduced a KEDF that accounts for the intrinsic inhomogeneity of the electron density. The von Weiszäcker (vW) functional is given by

$$T_{vW}[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}. \tag{7}$$

It can be shown from first principles that $T_{vW}[\rho]$ is exact for a single orbital (i.e. two singlet-coupled fermions or any number of bosons) system by deriving it directly from the Schrödinger equation. Letting $\hat{H} = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r})$, and multiplying both sides of the Schrödinger equation by $\langle \Psi |$ yields

$$-\frac{1}{2}\langle \Psi | \nabla^2 | \Psi \rangle + \langle \Psi | v_{ext} | \Psi \rangle = \langle \Psi | E | \Psi \rangle.$$

Integrating both sides over $\mathbb{R}^3$ and applying the definition of electron density $\langle \Psi | \Psi \rangle = |\Psi(\mathbf{r})|^2 = \rho(\mathbf{r})$, one obtains

$$-\frac{1}{2} \int \langle \Psi | \nabla^2 | \Psi \rangle d\mathbf{r} + \int v_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = E \int \rho(\mathbf{r}) d\mathbf{r}.$$

Applying the normalization condition that $\int \rho(\mathbf{r}) d\mathbf{r} = N_e$, where N_e is the number of electrons, and using the chain rule for the relation $\nabla^2 |\Psi(\mathbf{r})|^2 = \nabla^2 \rho(\mathbf{r})$, we obtain the expression

$$\frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} - \frac{1}{4} \int \nabla^2 \rho(\mathbf{r}) d\mathbf{r} + \int v_{ext}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} = N_e E.$$

The second Laplacian integral term then becomes zero as a consequence of the Green-Gauss theorem [8]. Hence, for a single electron system ($N_e = 1$), the final expression takes the form

$$E[\rho(\mathbf{r})] = \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} + \int v_{ext}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}, \tag{8}$$

where E evidently becomes a functional of $\rho(\mathbf{r})$. It is clear that this is the special, singular electron case of Eq. (1), where $F[\rho] = T_{vW}[\rho]$ and all other electron-electron interaction energy functionals are zero. This is the only variant of Eq. (1) where no approximate functionals are necessary. In fact, Eq. (1) is simply a reformulation of the Schrödinger equation for a single electron, as derived here. If the electron density of a one-electron system is known, it may be substituted into this equation to determine the energy of the system.

For the case of a single electron, the Lagrangian problem to solve is given by

$$L[\rho] = T_{vW}[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} - \mu \left[\int \rho(\mathbf{r}) d\mathbf{r} - N_e \right]. \tag{9}$$

The final result of functional differentiation on Eq. (9) is the Euler-Lagrange equation given by

$$\frac{\delta L[\rho]}{\delta \rho} = \frac{\delta E[\rho]}{\delta \rho} - \mu = \frac{\delta T_{vW}[\rho]}{\delta \rho} + v_{ext}(\mathbf{r}) - \mu, \tag{10}$$

where the vW functional derivative is expressed as

$$\frac{\delta T_{vW}[\rho]}{\delta \rho} = \frac{1}{4}\frac{\nabla^2 \rho}{\rho} + \frac{1}{8}\frac{|\nabla\rho|^2}{\rho^2}. \tag{11}$$

The expression for $\frac{\delta L[\rho]}{\delta \rho}$ enables us to optimize the electron density for a single electron since it directly gives us the search direction p_k.

6   Conclusion

This project focuses exclusively on a single electron to give a simple, illustrative example of how OFDFT algorithms work. Additionally, since there's only a single electron, we can numerically solve the Schrödinger equation (by matrix diagonalization) for the same external potential, and then compare these results with the optimized density. The computations of this project are implemented entirely on a one-dimensional real-space grid of interval $[0, 1]$ segmented into N_g gridpoints. Dirichlet boundary conditions that the density go to zero were imposed. This meant that in the absence of an external potential, the Schroedinger equation is being solved for an infinite well. The code effectively solves the Schroedinger equation in two very different ways, firstly by diagonalization of the Hamiltonian to obtain the eigenvectors, and secondly by an OFDFT minimization that achieves the same result (sometimes faster then the diagonalization).

7 References

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