

Summer Research Project: Proposal

Density Functional Theory

Simon Bignold Supervisor: Christoph Ortner

May 31, 2012

Introduction

We give a brief introduction to Density Functional Theory (DFT), alternatively see [1] for a short exposition and [5] for a much longer introduction with a greater focus on quantum theory. DFT is a commonly used technique in both physics and chemistry, however we believe that work is still required on the mathematical background of this theory. DFT was originally developed to obtain a description, given the electron density, of the properties of a many-electron system in its ground state using the model of an interacting electron gas acting under an external potential; see [2]. This technique can be used for many other particle systems, e.g. classical molecular mechanics which is what we will initially focus on. One can show that by minimising a given density functional the ground state energy of a many-body system can be obtained, see [5]. Density functional theory relies on the fact that the density distribution of the particles (in this case one particle density $n(\mathbf{r})$) is a conjugate variable to the potential function ($v(\mathbf{r})$) see [5].

Classical Models

Density Functional Theory can be applied equally to classical and quantum systems. However we choose to concentrate on classical models as we hope that these will be simpler and more tractable. Thus these models provide a starting platform which may allow us to study more complex quantum problems. By considering classical systems we will be intimately linked to the statistical physics of classical thermodynamics a link emphasised in [1]. For our initial problem we will consider a one dimensional model, which we hope will be the most tractable type of model.

1D Hard Core Gas

In this model we consider N particles of mass m which move freely in the interval $[0, L]$. Any two particles are excluded from coming within a distance d of each other. To do this for any two particles with positions x_1 and x_2 we have the potential.

$$\begin{aligned} u(x_1, x_2) &= 0 & |x_1 - x_2| > d \\ u(x_1, x_2) &= \infty & |x_1 - x_2| \leq d \end{aligned}$$

This can be extended to M dimensions by using the interval $[0, L]^M$ the M -dimensional vectors $\mathbf{r}_i = (x_1^i, x_2^i \dots x_M^i)$ in place of x_1 and x_2 and the Euclidean norm in place of the modulus.

Brief Summary of Methodology

In general our Hamiltonian can be written as:

$$\mathcal{H} = \mathcal{T} + \mathcal{U} + \mathcal{V}$$

where for N particles of mass m , positions \mathbf{r}_i and momenta \mathbf{p}_i

$$\mathcal{T} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \quad \mathcal{U} = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j) \quad \mathcal{V} = \sum_{i=1}^N v(\mathbf{r}_i)$$

which simplifies considerably in one-dimension. Here we take $u(\mathbf{r}_i, \mathbf{r}_j)$ as defined above and $v(\mathbf{r})$ is the external potential. The Hohenberg-Kohn Theorem (see [5] for a statement) proves the existence of a functional $F_{HK}[n]$ such that the free energy Ω can be given as:

$$\Omega = F_{HK}[n] + \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r})$$

Thus the ground state energy is given by:

$$E[v] = \inf_{n \in \mathcal{A}} \left\{ F_{HK}[n] + \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r}) \right\}$$

(eq 34 [5]) where \mathcal{A} is the set of densities from a non-degenerate ground state.

We can then find the external potential through:

$$\frac{\delta F_{HK}}{\delta n(\mathbf{r})} = -v(\mathbf{r})$$

A short exposition on classical DFT with slightly different notation is given in section 2 of [3].

Aims

Here we give a brief summary of the aim of this project. The first aim is the main aim of our project, the other two will be completed subject to time constraints. We aim to:

- calculate the functional F_{HK} explicitly for the 1D hard core model,
- test the analytical results obtained above against numerical results for different internal potentials u ,
- extend our hard core model to higher dimensions which is more realistic. We propose first an extension to two dimensions and then to three.

Numerical Results

We believe that numerics will be very complicated for a hard-core potential. Therefore we will investigate a range of potentials u that we hope will give simpler numerics.

Further Work

The models used above have been chosen as it is hoped they will be relatively simple to work with, however they may not be very realistic. Therefore we suggest selecting a more realistic potential to use for both numerical results and explicit calculations. We suggest that an ideal potential would be the Lennard–Jones potential however this may not be tractable so we propose investigating which types of interaction potentials the analysis and numerics can be carried out on. If we wish to investigate quantum systems we recall that it is not always true that for any density we will have an associated potential [4]. This is the case for degenerate ground states which is only of real concern in quantum systems.

References

- [1] N. Argaman and G. Makov. Density functional theory– an introduction. *American Journal of Physics*, 68:69–79, 1999.
- [2] P. Hohenberg and W. Kohn. Inhomogenous electron gas. *Physical Review*, 136:B864–B871, 1964.
- [3] G .Kahl and H. Löwen. Classical density functional theory an ideal tool to study heterogeneous crystal nucleation. *Journal of Physics: Condensed Matter*, 21(46).
- [4] E. H. Lieb. Density functionals for coulomb systems. *International Journal of Quantum Chemitstry*, XXIV:243–277, 1983.
- [5] R. van Leeuwen. Density functional approach to the many-body problem: Key concepts and exact functionals. *Advances in Quantum Chemistry*, 43:25–94, 2003.