Computational Physics: Explaining the Periodic Table

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May 14 2024

Contents

1 Introduction

[1]

2 Physics of Atoms and Mean Field Theory

From a theoretical point of view, an atom is a quantum mechanical system in which electrons are bound by a central nuclear charge which is often approximated as a point charge of magnitude Ze. Despite their abundance and the limited number of particles involved, the fermionic nature of electrons is a major hindrance to the treatment of the electronic structure of atoms. As the wave function of a system with N_e electrons is a function of $3N_e$ variables (neglecting the spin degree of freedom), the memory required to represent it on a grid with m points per dimension scales rather unpleasantly as m^{3N_e}. For a conservative number of $m = 100$ and $N_e = 6$ electrons for, e.g., Carbon, $100^{18} = 10^{36}$ numbers would have to be stored, which by far overwhelms the collective storage capacity of all computers on Earth.

Luckily, the full wave function is not actually needed. According to a theorem due to Hohenberg and Kohn [2], the ground state wave function is a unique functional of the ground state electron density, which is only a function of 3 variables, and vice versa. That is, in principle, all information that can be extracted from the wave function $\psi(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_{N_e}, \sigma_{N_e})$ can also be extracted from the density

$$n(\mathbf{r}) = N_e \sum_{\sigma_i} \int_{\mathbb{R}^3} \mathrm{d}^{3(N_e-1)}x \; |\psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \sigma_2, \ldots, \mathbf{x}_{N_e}, \sigma_{N_e})|^2 \,. \tag{1}$$

This is the motivation behind density functional theory (DFT), which is today arguably the most important computational method in quantum chemistry. In this report, we explore a simple version of this approach that relies on finding a self-consistent single particle potential $v^{ee}(\mathbf{r})$ such that the Slater-determinant associated with the single-particle Hamiltonian (in atomic units)

$$\mathcal{H} = -\frac{1}{2}\partial_{\mathbf{x}}^2 - \frac{Z}{r} + V^{ee}(r) \tag{2}$$

approximates the ground state of the full N_e-particle Hamiltonian. The ansatz for V^{ee} includes two terms. The first is the direct electrostatic potential

3 Implementation and Numerics

4 Results

References

[1] Max Maschke. *compphys*. URL: https://github.com/max-mas/compphys (visited on 04/22/2024).

[2] P. Hohenberg and W. Kohn. "Inhomogeneous Electron Gas". In: *Phys. Rev.* 136 (3B Nov. 1964), B864–B871. DOI: 10.1103/PhysRev.136.B864.