The Art of Scientific Computing: Introduction to Quantum Chemistry

Harry Quiney

January 28, 2018

1 Introduction

Paul Dirac, one of the principal architects of quantum theory, stated that

> "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to soluble. It therefore becomes desirable that approximate practical methods of applyin quantum mechanics should be developed which can lead to an explanation of the main features of complex atomic systems without too much computation". P.A.M. Dirac Proc. Roy. Soc. (London) A, **123**, 792 (1930).

The approximation methods to describe the properties of atoms, molecules and solids usin the principles of quantum mechanics include a range of physical models that attempt to capture the important effects that lead to the structure and prioperties of materials and, increasingly, computational techniques that are described as *ab initio*; they are first-principles applications of the theory of quantum mechanics that are applied in layers that systemmatically approach the complete theory.

The two most significant approaches to molecular physics and quantum chemistry describe the electronic properties of molecules using either a representation of the wave-function or of the electron density. The Nobel Prize in Chemistry was awarded in 1999 to the pioneers of these two approaches:

- John Pople, for the development of computational methods based on the Hartree-Fock approximation
- Walther Kohn, for the discovery of the Hohenberg-Kohn theorems and the establishment of density functional theory.

2 Project

In the modern context, these wavefunction- and density-based approaches are implemented within sophisticated, highly optimized computer codes, typically involving millons of lines of code. Our purpose here is not to compete with these codes or to perform production runs on chemically relevant systems by treating the available codes as "black boxes". This project will acquaint the student with the basic computational elements of modern quantum chemistry by writing a simple code with most of the functionality of the production codes. Simplified computational formulations of the wavefunction and density-based methods will be implemented but which contain the essential elements contained within th black box codes. We now provide a quick sketch of these two methods but defer technical details to later sections.

2.1 Scope

Write a computer program that implements the Hartree-Fock and local density Kohn-Sham methods, restricted to a basis of s-type spherical Gaussian functions. The Hartree-Fock method may be extended to include electron correlation effects using second-order many-body (Moller-Plesset) perturbation theory. The local density Kohn-Sham method may be extended to include more sophisticated density functionals that better represent exchange and correlation effects. The computational tools developed in this program may be used to investigate the chemical properties of He, H_2,H_3^+, LiH and Li_2.

2.2 Computational elements

To complete the project the following numerical techniques are required

- Computational linear algebra
- Evaluation of special functions
- Numerical Solution of differential and integro-differential equations
- Minimization procedures

2.3 Assumed knowledge

Basic calculus and linear algebra equivalent to MAST10000 Calculus 2 and MAST10000 Linear Algebra. Introductory quantum mechanics and electrostatics equivalent to PHYC10004 Physics 2.

2.4 Progression Plan

The project consists of five steps that should be completed in order. A detailed description of the tasks involved is provided for each step.