

# Thesis title: Monte Carlo and density functional theory studies of atoms

The aim of this thesis is to study the structure of several light atoms using variational and Green's function Monte Carlo techniques, combining results from Hartree-Fock calculations in order to achieve a as good as possible variational wave function. The thesis will explore various Monte Carlo optimization strategies and use these to define the best possible density functional. The functional will in turn be used to parameterize a semi-classical potential to be used in quantum-molecular dynamical studies of properties of materials.

This thesis entails the development of variational Monte Carlo (VMC) and Green's function Monte Carlo (GFMC) programs to solve Schrödinger's equation and obtain various expectation values of interest, such as the energy of the ground state and excited states. The GFMC approach allows, in principle, for a numerically exact solution of Schrödinger's equation. However, it needs a reasonable starting point. It is there where a variational Monte Carlo calculation of the same system provides a variationally optimal trial wave function of a many-body system and its pertinent energy. The Slater determinant for the variational wave function is set up using single-particle wave functions from a Hartree-Fock calculation. The methods are briefly described in the following section.

A progress plan for this thesis project is given at the end.

## Variational Monte Carlo

The variational quantum Monte Carlo (VMC) has been widely applied to studies of quantal systems. The recipe consists in choosing a trial wave function  $\psi_T(\mathbf{R})$  which we assume to be as realistic as possible. The variable  $\mathbf{R}$  stands for the spatial coordinates, in total  $3N$  if we have  $N$  particles present. The trial wave function serves then as a mean to define the quantal probability distribution

$$P(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int |\psi_T(\mathbf{R})|^2 d\mathbf{R}}. \quad (1)$$

The expectation value of the energy  $E$  is given by

$$\langle E \rangle = \frac{\int d\mathbf{R} \Psi^*(\mathbf{R}) H(\mathbf{R}) \Psi(\mathbf{R})}{\int d\mathbf{R} \Psi^*(\mathbf{R}) \Psi(\mathbf{R})}, \quad (2)$$

where  $\Psi$  is the exact eigenfunction. Using our trial wave function we define a new operator, the so-called local energy,

$$E_L(\mathbf{R}) = \frac{1}{\psi_T(\mathbf{R})} H \psi_T(\mathbf{R}), \quad (3)$$

which, together with our trial PDF allows us to rewrite the expression for the energy as

$$\langle H \rangle = \int P(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R}. \quad (4)$$

This equation expresses the variational Monte Carlo approach.

The first part of this thesis deals thus with a VMC calculation of light atoms from He to Ca, where the main goals are to study various approximations to the trial wave function and testing optimization techniques based on energy and variance optimization.

The trial wave function is a combination of a Slater determinant and a correlation part. The Slater determinant will be constructed using both Hydrogen-like single-particle wave functions and single-particle wave functions based on Hartree-Fock theory.

## Green's function Monte Carlo (GFMC)

The GFMC method is based on rewriting the Schrödinger equation in imaginary time, by defining  $\tau = it$ . The imaginary time Schrödinger equation is then

$$\frac{\partial \psi}{\partial \tau} = -\hat{\mathbf{H}}\psi, \quad (5)$$

where we have omitted the dependence on  $\tau$  and the spatial variables in  $\psi$ .

A Green's function Monte Carlo, although it allows for a formally exact solution of Schrödinger's equations, needs a clever starting point for the energy. This trial energy is initially chosen to be the VMC energy of the trial wave function, and is updated as the simulation progresses. Use of an optimised trial function minimises the difference between the local and trial energies, and hence minimises fluctuations in the calculations. A wave function optimised using VMC is ideal for this purpose, and in practice VMC provides the best method for obtaining wave functions that accurately approximate ground state wave functions locally.

The final aim of this thesis is thus to develop a GFMC program for studying light atoms, based on a VMC calculation first.

These calculations will in turn provide the basis for determining a as good as possible ground state wave function. This wave function will in turn be used to define the quantum mechanical density. The density will be used to construct a density functional for atoms using the adiabatic-connection method as described by Teale *et al* in J. Chem. Phys. **130**, 104111 (2009). The results will be compared with existing density functional for various atoms and used in studies of materials with atoms like silisium.

## Progress plan and milestones

The aims and progress plan of this thesis are as follows

- Fall 2009: Develop first a Hartree-Fock code for electrons in atoms. This part entails developing a code for computing the Coulomb interaction.
- Fall 2009: Write a code which solves the variational Monte-Carlo (VMC) problem for light atoms, typically with up to 20 electrons. Both closed-core and open shell atoms will be studied. Construct a Green's function Monte Carlo code based on the Variational Monte Carlo code. The GFMC code receives as input the optimal variational energy and wave function from the VMC calculation and solves in principle the Schrödinger equation exactly. The Slater determinant used in the VMC calculation includes also single-particle wave functions from Hartree-Fock calculations.
- Fall 2010: The obtained ground states will in turn be used to define a as exact as possible density functional for atoms using the adiabatic-connection method. The density functional can in turn be used to model systems with a large number of atoms. Possible applications are to mechanical studies of materials.

The thesis is expected to be handed in June 1 2010.

## References

- [1] A. M. Teale, S. Coriani, and T. Helgaker, J. Chem. Phys. **130**, 104111 (2009).