# Chapter 11

# Quantum Monte Carlo methods

> If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or atomic fact, or whatever you wish to call it) that all things are made of atoms, little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence you will see an enormous amount of information about the world, if just a little imagination and thinking are applied. *Richard Feynman, The Laws of Thermodynamics.*

## 11.1 Introduction

The aim of this chapter is to present examples of applications of Monte Carlo methods in studies of simple quantum mechanical systems. We study systems such as the harmonic oscillator, the hydrogen atom, the hydrogen molecule, the helium atom and more complicated atoms. Systems with man interacting fermions and bosons such as liquid $^4$He and Bose Einstein condensation of atoms ae discussed in chapter 18. Most quantum mechanical problems of interest in for example atomic, molecular, nuclear and solid state physics consist of a large number of interacting electrons and ions or nucleons. The total number of particles $N$ is usually sufficiently large that an exact solution cannot be found. In quantum mechanics we can express the expectation value for a given $\widehat{\mathbf{O}}$ operator for a system of $N$ particles as

$$\langle \widehat{\mathbf{O}} \rangle = \frac{\int d\mathbf{R}_1 d\mathbf{R}_2 \ldots d\mathbf{R}_N \Psi^*(\mathbf{R_1}, \mathbf{R}_2, \ldots, \mathbf{R}_N) \widehat{\mathbf{o}}(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) \Psi(\mathbf{R_1}, \mathbf{R}_2, \ldots, \mathbf{R}_N)}{\int d\mathbf{R}_1 d\mathbf{R}_2 \ldots d\mathbf{R}_N \Psi^*(\mathbf{R_1}, \mathbf{R}_2, \ldots, \mathbf{R}_N) \Psi(\mathbf{R_1}, \mathbf{R}_2, \ldots, \mathbf{R}_N)}, \quad (11.1)$$

where $\Psi(\mathbf{R_1}, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ is the wave function describing a many-body system. Although we have omitted the time dependence in this equation, it is an in general intractable problem. As an example from the nuclear many-body problem, we can write Schrödinger's equation as a differential equation with the energy operator $\widehat{\mathbf{H}}$ (the so-called energy Hamiltonian) acting on the wave function as

$$\widehat{\mathbf{H}}\Psi(\mathbf{r}_1, .., \mathbf{r}_A, \alpha_1, .., \alpha_A) = E\Psi(\mathbf{r}_1, .., \mathbf{r}_A, \alpha_1, .., \alpha_A)$$

where

$$\mathbf{r}_1, .., \mathbf{r}_A,$$

are the coordinates and

$$\alpha_1, .., \alpha_A,$$

are sets of relevant quantum numbers such as spin and isospin for a system of $A$ nucleons ($A = N + Z$, $N$ being the number of neutrons and $Z$ the number of protons). There are

$$2^A \times \left( \begin{array}{c} A \\ Z \end{array} \right)$$

coupled second-order differential equations in $3A$ dimensions. For a nucleus like $^{10}$Be this number is 215040. This is a truely challenging many-body problem.

Eq. (11.1) is a multidimensional integral. As such, Monte Carlo methods are ideal for obtaining expectation values of quantum mechanical operators. Our problem is that we do not know the exact wavefunction $\Psi(\mathbf{r}_1, .., \mathbf{r}_A, \alpha_1, .., \alpha_N)$. We can circumvent this problem by introducing a function which depends on selected variational parameters. This function should capture essential features of the system under consideration. With such a trial wave function we can then attempt to perform a variational calculation of various observables, using Monte Carlo methods for solving Eq. (11.1).

The present chapter aims therefore at giving you an overview of the variational Monte Carlo approach to quantum mechanics. We limit the attention to the simple Metropolis algorithm, without the inclusion of importance sampling. Importance sampling and diffusion Monte Carlo methods are discussed in chapters 18 and 19.

However, before we proceed we need to recapitulate some of the postulates of quantum mechanics. This is done in the next section. The remaining sections deal with mathematical and computational aspects of the variational Monte Carlo methods, with applications from atomic and molecular physis.

## 11.2 Postulates of Quantum Mechanics

### 11.2.1 Mathematical Properties of the Wave Functions

Schrödinger's equation for a one-dimensional onebody problem reads

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,t) + V(x,t)\Psi(x,t) = \imath\hbar\frac{\partial\Psi(x,t)}{\partial t}, \qquad (11.2)$$

where $V(x,t)$ is a potential acting on the particle. The first term is the kinetic energy. The solution to this partial differential equation is the wave function $\Psi(x,t)$. The wave function itself is not an observable (or physical quantity) but it serves to define the quantum mechanical probability, which in turn can be used to compute expectation values of selected operators, such as the kinetic energy or the total energy itself. The quantum mechanical probability $P(x,t)dx$ is defined as[1]

$$P(x,t)dx = \Psi(x,t)^*\Psi(x,t)dx, \qquad (11.3)$$

representing the probability of finding the system in a region between $x$ and $x + dx$. It is, as opposed to the wave function, always real, which can be seen from the following definition of the wave function, which has real and imaginary parts,

$$\Psi(x,t) = R(x,t) + \imath I(x,t), \qquad (11.4)$$

yielding

$$\Psi(x,t)^*\Psi(x,t) = (R - \imath I)(R + \imath I) = R^2 + I^2. \qquad (11.5)$$

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[1]This is Max Born's postulate on how to interpret the wave function resulting from the solution of Schrödinger's equation. It is also the commonly accepted and operational interpretation.

The variational Monte Carlo approach uses actually this definition of the probability, allowing us thereby to deal with real quantities only. As a small digression, if we perform a rotation of time into the complex plane, using $\tau = it/\hbar$, the time-dependent Schrödinger equation becomes

$$\frac{\partial \Psi(x,\tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,\tau)}{\partial x^2} - V(x,\tau)\Psi(x,\tau). \tag{11.6}$$

With $V = 0$ we have a diffusion equation in complex time with diffusion constant

$$D = \frac{\hbar^2}{2m}.$$

This is the starting point for the Diffusion Monte Carlo method discussed in chapter 18. In that case it is the wave function itself, given by the distribution of random walkers, that defines the probability. The latter leads to conceptual problems when we have anti-symmetric wave functions, as is the case for particles with the spin being a multiplum of $1/2$. Examples of such particles are various leptons such as electrons, muons and various neutrinos, baryons like protons and neutrons and quarks such as the up and down quarks.

The Born interpretation constrains the wave function to belong to the class of functions in $L^2$. Some of the selected conditions which $\Psi$ has to satisfy are

1. Normalization

$$\int_{-\infty}^{\infty} P(x,t)dx = \int_{-\infty}^{\infty} \Psi(x,t)^*\Psi(x,t)dx = 1 \tag{11.7}$$

    meaning that

$$\int_{-\infty}^{\infty} \Psi(x,t)^*\Psi(x,t)dx < \infty \tag{11.8}$$

2. $\Psi(x,t)$ and $\partial\Psi(x,t)/\partial x$ must be finite

3. $\Psi(x,t)$ and $\partial\Psi(x,t)/\partial x$ must be continuous.

4. $\Psi(x,t)$ and $\partial\Psi(x,t)/\partial x$ must be single valued

### *11.2.2 Important Postulates*

We list here some of the postulates that we will use in our discussion.

### Postulate I

Any physical quantity $A(\vec{r}, \vec{p})$ which depends on position $\vec{r}$ and momentum $\vec{p}$ has a corresponding quantum mechanical operator by replacing $\vec{p} - i\hbar\vec{\bigtriangledown}$, yielding the quantum mechanical operator

$$\widehat{\mathbf{A}} = A(\vec{r}, -i\hbar\vec{\bigtriangledown}).$$

| Quantity | Classical definition | QM operator |
|----------|---------------------|-------------|
| Position | $\vec{r}$ | $\widehat{\mathbf{r}} = \vec{r}$ |
| Momentum | $\vec{p}$ | $\widehat{\mathbf{p}} = -i\hbar\vec{\bigtriangledown}$ |
| Orbital momentum | $\vec{L} = \vec{r} \times \vec{p}$ | $\widehat{\mathbf{L}} = \vec{r} \times (-i\hbar\vec{\bigtriangledown})$ |
| Kinetic energy | $T = (\vec{p})^2/2m$ | $\widehat{\mathbf{T}} = -(\hbar^2/2m)(\vec{\bigtriangledown})^2$ |
| Total energy | $H = (p^2/2m) + V(\vec{r})$ | $\widehat{\mathbf{H}} = -(\hbar^2/2m)(\vec{\bigtriangledown})^2 + V(\vec{r})$ |

**Postulate II**

The only possible outcome of an ideal measurement of the physical quantity $A$ are the eigenvalues of the corresponding quantum mechanical operator $\widehat{\mathbf{A}}$.

$$\widehat{\mathbf{A}}\psi_\nu = a_\nu\psi_\nu,$$

resulting in the eigenvalues $a_1, a_2, a_3, \cdots$ as the only outcomes of a measurement. The corresponding eigenstates $\psi_1, \psi_2, \psi_3 \cdots$ contain all relevant information about the system.

**Postulate III**

Assume $\Phi$ is a linear combination of the eigenfunctions $\psi_\nu$ for $\widehat{\mathbf{A}}$,

$$\Phi = c_1\psi_1 + c_2\psi_2 + \cdots = \sum_\nu c_\nu\psi_\nu.$$

The eigenfunctions are orthogonal and we get

$$c_\nu = \int (\Phi)^*\psi_\nu d\tau.$$

From this we can formulate the third postulate:

When the eigenfunction is $\Phi$, the probability of obtaining the value $a_\nu$ as the outcome of a measurement of the physical quantity $A$ is given by $|c_\nu|^2$ and $\psi_\nu$ is an eigenfunction of $\widehat{\mathbf{A}}$ with eigenvalue $a_\nu$.

As a consequence one can show that:
when a quantal system is in the state $\Phi$, the mean value or expectation value of a physical quantity $A(\vec{r}, \vec{p})$ is given by

$$\langle A \rangle = \int (\Phi)^*\widehat{\mathbf{A}}(\vec{r}, -i\hbar\vec{\nabla})\Phi d\tau.$$

We have assumed that $\Phi$ has been normalized, viz., $\int (\Phi)^*\Phi d\tau = 1$. Else

$$\langle A \rangle = \frac{\int (\Phi)^*\widehat{\mathbf{A}}\Phi d\tau}{\int (\Phi)^*\Phi d\tau}.$$

**Postulate IV**

The time development of a quantal system is given by

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{\mathbf{H}}\Psi,$$

with $\widehat{\mathbf{H}}$ the quantal Hamiltonian operator for the system.

### 11.3  First Encounter with the Variational Monte Carlo Method

The required Monte Carlo techniques for variational Monte Carlo are conceptually simple, but the practical application may turn out to be rather tedious and complex, relying on a good starting point for the variational wave functions. These wave functions should include as much as possible of the inherent physics to the problem, since they form the starting point for a variational calculation of the expectation value of the hamiltonian $H$. Given a hamiltonian $H$ and a trial wave function $\Psi_T$, the variational principle states that the expectation value of $\langle H \rangle$, defined through Postulate III

$$\langle H \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})H(\mathbf{R})\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})}, \tag{11.9}$$

is an upper bound to the ground state energy $E_0$ of the hamiltonian $H$, that is

$$E_0 \leq \langle H \rangle. \tag{11.10}$$

To show this, we note first that the trial wave function can be expanded in the eigenstates of the hamiltonian since they form a complete set, see again Postulate III,

$$\Psi_T(\mathbf{R}) = \sum_i a_i \Psi_i(\mathbf{R}), \tag{11.11}$$

and assuming the set of eigenfunctions to be normalized, insertion of the latter equation in Eq. (11.9) results in

$$\langle H \rangle = \frac{\sum_{mn} a_m^* a_n \int d\mathbf{R}\Psi_m^*(\mathbf{R})H(\mathbf{R})\Psi_n(\mathbf{R})}{\sum_{mn} a_m^* a_n \int d\mathbf{R}\Psi_m^*(\mathbf{R})\Psi_n(\mathbf{R})} = \frac{\sum_{mn} a_m^* a_n \int d\mathbf{R}\Psi_m^*(\mathbf{R})E_n(\mathbf{R})\Psi_n(\mathbf{R})}{\sum_n a_n^2}, \tag{11.12}$$

which can be rewritten as

$$\frac{\sum_n a_n^2 E_n}{\sum_n a_n^2} \geq E_0. \tag{11.13}$$

In general, the integrals involved in the calculation of various expectation values are multi-dimensional ones. Traditional integration methods such as the Gauss-Legendre will not be adequate for say the computation of the energy of a many-body system. The fact that we need to sample over a multi-dimensional density and that the probability density is to be normalized by the division of the norm of the wave function, suggests that e.g., the Metropolis algorithm may be appropriate.

We could briefly summarize the above variational procedure in the following three steps.

1. Construct first a trial wave function $\psi_T(\mathbf{R};\alpha)$, for say a many-body system consisting of $N$ particles located at positions $\mathbf{R} = (\mathbf{R_1}, \dots, \mathbf{R_N})$. The trial wave function depends on $\alpha$ variational parameters $\alpha = (\alpha_1, \dots, \alpha_N)$.

2. Then we evaluate the expectation value of the hamiltonian $H$

$$\langle H \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R};\alpha)H(\mathbf{R})\Psi_T(\mathbf{R};\alpha)}{\int d\mathbf{R}\Psi_T^*(\mathbf{R};\alpha)\Psi_T(\mathbf{R};\alpha)}.$$

3. Thereafter we vary $\alpha$ according to some minimization algorithm and return to the first step.

The above loop stops when we reach the minimum of the energy according to some specified criterion. In most cases, a wave function has only small values in large parts of configuration space, and a straight-forward procedure which uses homogenously distributed random points in configuration space will most likely lead to poor results. This may suggest that some kind of importance sampling combined with e.g., the Metropolis algorithm may be a more efficient way of obtaining the ground state energy. The hope is then that those regions of configurations space where the wave function assumes appreciable values are sampled more efficiently.

The tedious part in a variational Monte Carlo calculation is the search for the variational minimum. A good knowledge of the system is required in order to carry out reasonable variational Monte Carlo calculations. This is not always the case, and often variational Monte Carlo calculations serve rather as the starting point for so-called diffusion Monte Carlo calculations. Diffusion Monte Carlo is a way of solving exactly the many-body Schrödinger equation by means of a stochastic procedure. A good guess on the binding energy and its wave function is however necessary. A carefully performed variational Monte Carlo calculation can aid in this context. Diffusion Monte Carlo is discussed in depth in chapter 18.

### 11.4  Variational Monte Carlo for quantum mechanical systems

The variational quantum Monte Carlo has been widely applied to studies of quantal systems. Here we expose its philosophy and present applications and critical discussions.

The recipe, as discussed in chapter 8 as well, 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, following closely the discussion on importance sampling in section 8.4, as a mean to define the quantal probability distribution

$$P(\mathbf{R};\alpha) = \frac{|\psi_T(\mathbf{R};\alpha)|^2}{\int |\psi_T(\mathbf{R};\alpha)|^2 \, d\mathbf{R};\alpha}. \tag{11.14}$$

This is our new probability distribution function (PDF).

The expectation value of the energy Hamiltonian is given by

$$\langle \widehat{\mathbf{H}} \rangle = \frac{\int d\mathbf{R}\, \Psi^*(\mathbf{R}) H(\mathbf{R}) \Psi(\mathbf{R})}{\int d\mathbf{R}\, \Psi^*(\mathbf{R}) \Psi(\mathbf{R})}, \tag{11.15}$$

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

$$\widehat{\mathbf{E}}_L(\mathbf{R};\alpha) = \frac{1}{\psi_T(\mathbf{R};\alpha)} \widehat{\mathbf{H}} \psi_T(\mathbf{R};\alpha), \tag{11.16}$$

which, together with our trial PDF allows us to compute the expectation value of the local energy

$$\langle E_L(\alpha) \rangle = \int P(\mathbf{R};\alpha) \widehat{\mathbf{E}}_L(\mathbf{R};\alpha) d\mathbf{R}. \tag{11.17}$$

This equation expresses the variational Monte Carlo approach. We compute this integral for a set of values of $\alpha$ and possible trial wave functions and search for the minimum of the function $E_L(\alpha)$. If the trial wave function is close to the exact wave function, then $\langle E_L(\alpha) \rangle$ should approach $\langle \widehat{\mathbf{H}} \rangle$. Eq. (11.17) is solved using techniques from Monte Carlo integration, see the discussion below. For most hamiltonians,

$H$ is a sum of kinetic energy, involving a second derivative, and a momentum independent and spatial dependent potential. The contribution from the potential term is hence just the numerical value of the potential. A typical Hamiltonian reads thus

$$\widehat{\mathbf{H}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{onebody}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\text{int}}(\mid \mathbf{r}_i - \mathbf{r}_j \mid). \tag{11.18}$$

where the sum runs over all particles $N$. We have included both a onebody potential $V_{\text{onebody}}(\mathbf{r}_i)$ which acts on one particle at the time and a twobody interaction $V_{\text{int}}(\mid \mathbf{r}_i - \mathbf{r}_j \mid)$ which acts between two particles at the time. We can obviously extend this to more complicated three-body and/or many-body forces as well. The main contributions to the energy of physical systems is largely dominated by one- and two-body forces. We will therefore limit our attention to such interactions only.

Our local energy operator becomes then

$$\widehat{\mathbf{E}}_L(\mathbf{R}; \alpha) = \frac{1}{\psi_T(\mathbf{R}; \alpha)} \left( -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{onebody}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\text{int}}(\mid \mathbf{r}_i - \mathbf{r}_j \mid) \right) \psi_T(\mathbf{R}; \alpha),$$
$$\tag{11.19}$$

resulting in

$$\widehat{\mathbf{E}}_L(\mathbf{R}; \alpha) = \frac{1}{\psi_T(\mathbf{R}; \alpha)} \left( -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \right) \psi_T(\mathbf{R}; \alpha) + \sum_{i=1}^{N} V_{\text{onebody}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\text{int}}(\mid \mathbf{r}_i - \mathbf{r}_j \mid), \tag{11.20}$$

The numerically time-consuming part in the variational Monte Carlo calculation is the evaluation of the kinetic energy term. The potential energy, as long as it has a simple $r$-dependence adds only a simple term to the local energy operator.

In our discussion below, we base our numerical Monte Carlo solution on the Metropolis algorithm. The implementation is rather similar to the one discussed in connection with the Ising model, the main difference residing in the form of the PDF. The main test to be performed is a ratio of probabilities. Suppose we are attempting to move from position $\mathbf{R}$ to $\mathbf{R}'$. Then we perform the following two tests.

1. If

$$\frac{P(\mathbf{R}'; \alpha)}{P(\mathbf{R}; \alpha)} > 1,$$

   where $\mathbf{R}'$ is the new position, the new step is accepted, or

2. 

$$r \leq \frac{P(\mathbf{R}'; \alpha)}{P(\mathbf{R}; \alpha)},$$

   where $r$ is random number generated with uniform PDF such that $r \in [0, 1]$, the step is also accepted.

In the Ising model we were flipping one spin at the time. Here we change the position of say a given particle to a trial position $\mathbf{R}'$, and then evaluate the ratio between two probabilities. We note again that we do not need to evaluate the norm[2] $\int |\psi_T(\mathbf{R}; \alpha)|^2 \, d\mathbf{R}$ (an in general impossible task), since we are only computing ratios.

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[2]This corresponds to the partition function $Z$ in statistical physics.

When writing a variational Monte Carlo program, one should always prepare in advance the required formulae for the local energy $E_L$ in Eq. (11.17) and the wave function needed in order to compute the ratios of probabilities in the Metropolis algorithm. These two functions are almost called as often as a random number generator, and care should therefore be exercised in order to prepare an efficient code.

If we now focus on the Metropolis algorithm and the Monte Carlo evaluation of Eq. (11.17), a more detailed algorithm is as follows

- Initialisation: Fix the number of Monte Carlo steps and thermalization steps. Choose an initial $\mathbf{R}$ and variational parameters $\alpha$ and calculate $|\psi_T(\mathbf{R}; \alpha)|^2$. Define also the value of the stepsize to be used when moving from one value of $\mathbf{R}$ to a new one.

- Initialise the energy and the variance.

- Start the Monte Carlo calculation with a loop over a given number of Monte Carlo cycles

  1. Calculate a trial position $\mathbf{R}_p = \mathbf{R} + r * step$ where $r$ is a random variable $r \in [0, 1]$.
  2. Use then the Metropolis algorithm to accept or reject this move by calculating the ratio

$$w = P(\mathbf{R}_p)/P(\mathbf{R}).$$

  If $w \geq s$, where $s$ is a random number $s \in [0, 1]$, the new position is accepted, else we stay at the same place.
  3. If the step is accepted, then we set $\mathbf{R} = \mathbf{R}_p$.
  4. Update the local energy and the variance.

- When the Monte Carlo sampling is finished, we calculate the mean energy and the standard deviation. Finally, we may print our results to a specified file.

Note well that the way we choose the next step $\mathbf{R}_p = \mathbf{R} + r * step$ is not determined by the wave function. The wave function enters only the determination of the ratio of probabilities, similar to the way we simulated systems in statistical physics. This means in turn that our sampling of points may not be very efficient. We will return to an efficient sampling of integration points in our discussion of diffusion Monte Carlo in chapter 18. This leads to the concept of importance sampling. As such, we limit ourselves in this chapter to the simplest possible form of the Metropolis algorithm, and relegate both importance sampling and advanced optimization techniques to chapter 18.

The best way however to understand the above algorithm and a specific method is to study selected examples.

### 11.4.1   First illustration of variational Monte Carlo methods, the one-dimensional harmonic oscillator

The harmonic oscillator in one dimension lends itself nicely for illustrative purposes. The hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2, \tag{11.21}$$

where $m$ is the mass of the particle and $k$ is the force constant, e.g., the spring tension for a classical oscillator. In this example we will make life simple and choose $m = \hbar = k = 1$. We can rewrite the above equation as

$$H = -\frac{d^2}{dx^2} + x^2, \tag{11.22}$$

The energy of the ground state is then $E_0 = 1$. The exact wave function for the ground state is

$$\Psi_0(x) = \frac{1}{\pi^{1/4}} e^{-x^2/2},\tag{11.23}$$

but since we wish to illustrate the use of Monte Carlo methods, we choose the trial function

$$\Psi_T(x) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-x^2\alpha^2/2}.\tag{11.24}$$

Inserting this function in the expression for the local energy in Eq. (11.16), we obtain the following expression for the local energy

$$E_L(x) = \alpha^2 + x^2(1 - \alpha^4),\tag{11.25}$$

with the expectation value for the hamiltonian of Eq. (11.17) given by

$$\langle E_L \rangle = \int_{-\infty}^{\infty} |\psi_T(x)|^2 E_L(x)dx,\tag{11.26}$$

which reads with the above trial wave function

$$\langle E_L \rangle = \frac{\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2} \alpha^2 + x^2(1-\alpha^4)}{\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2}}.\tag{11.27}$$

Using the fact that

$$\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2} = \sqrt{\frac{\pi}{\alpha^2}},$$

we obtain

$$\langle E_L \rangle = \frac{\alpha^2}{2} + \frac{1}{2\alpha^2}.\tag{11.28}$$

and the variance

$$\sigma^2 = \frac{(\alpha^4 - 1)^2}{2\alpha^4}.\tag{11.29}$$

In solving this problem we can choose whether we wish to use the Metropolis algorithm and sample over relevant configurations, or just use random numbers generated from a normal distribution, since the harmonic oscillator wave functions follow closely such a distribution. The latter approach is easily implemented in few lines, namely

```
...     initialisations, declarations of variables
...     mcs = number of  Monte Carlo samplings
//      loop over Monte Carlo samples
        for ( i=0; i < mcs; i++) {
//      generate random variables from gaussian distribution
            x = normal_random(&idum)/sqrt2/alpha;
            local_energy = alpha*alpha + x*x*(1-pow(alpha,4));
            energy += local_energy;
            energy2 += local_energy*local_energy;
//      end of sampling
        }
//      write out the mean energy and the standard deviation
        cout << energy/mcs <<   sqrt((energy2/mcs-(energy/mcs)**2)/mcs));
```

This variational Monte Carlo calculation is rather simple, we just generate a large number $N$ of random numbers corresponding to the gaussian PDF $\sim |\Psi_T|^2$ and for each random number we compute the local energy according to the approximation

$$\langle \widehat{\mathbf{E}}_L \rangle = \int P(\mathbf{R}) \widehat{\mathbf{E}}_L(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^{N} E_L(x_i), \tag{11.30}$$

and the energy squared through

$$\langle \widehat{\mathbf{E}}_L^2 \rangle = \int P(\mathbf{R}) \widehat{\mathbf{E}}_L^2(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^{N} E_L^2(x_i). \tag{11.31}$$

In a certain sense, this is nothing but the importance Monte Carlo sampling discussed in chapter 8 Before we proceed however, there is an important aside which is worth keeping in mind when computing the local energy. We could think of splitting the computation of the expectation value of the local energy into a kinetic energy part and a potential energy part. If we are dealing with a three-dimensional system, the expectation value of the kinetic energy is

$$-\frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \nabla^2 \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}, \tag{11.32}$$

and we could be tempted to compute, if the wave function obeys spherical symmetry, just the second derivative with respect to one coordinate axis and then multiply by three. This will most likely increase the variance, and should be avoided, even if the final expectation values are similar. Recall that one of the subgoals of a Monte Carlo computation is to decrease the variance.

Another shortcut we could think of is to transform the numerator in the latter equation to

$$\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \nabla^2 \Psi_T(\mathbf{R}) = -\int d\mathbf{R} (\nabla \Psi_T^*(\mathbf{R}))(\nabla \Psi_T(\mathbf{R})), \tag{11.33}$$

using integration by parts and the relation

$$\int d\mathbf{R} \nabla (\Psi_T^*(\mathbf{R}) \nabla \Psi_T(\mathbf{R})) = 0, \tag{11.34}$$

where we have used the fact that the wave function is zero at $\mathbf{R} = \pm\infty$. This relation can in turn be rewritten through integration by parts to

$$\int d\mathbf{R} (\nabla \Psi_T^*(\mathbf{R}))(\nabla \Psi_T(\mathbf{R})) + \int d\mathbf{R} \Psi_T^*(\mathbf{R}) \nabla^2 \Psi_T(\mathbf{R})) = 0. \tag{11.35}$$

The rhs of Eq. (11.33) is easier and quicker to compute. However, in case the wave function is the exact one, or rather close to the exact one, the lhs yields just a constant times the wave function squared, implying zero variance. The rhs does not and may therefore increase the variance.

If we use integration by part for the harmonic oscillator case, the new local energy is

$$E_L(x) = x^2(1 + \alpha^4), \tag{11.36}$$

and the variance

$$\sigma^2 = \frac{(\alpha^4 + 1)^2}{2\alpha^4}, \tag{11.37}$$

which is larger than the variance of Eq. (11.29).

## 11.5   Variational Monte Carlo for atoms

The Hamiltonian for an $N$-electron atomic system consists of two terms

$$\hat{H}(\mathbf{x}) = \hat{T}(\mathbf{x}) + \hat{V}(\mathbf{x}); \tag{11.38}$$

the kinetic and the potential energy operator. Here $\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\}$ is the spatial and spin degrees of freedom associated with the different particles. The classical kinetic energy

$$T = \frac{\mathbf{P^2}}{2m} + \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m}$$

is transformed to the quantum mechanical kinetic energy operator by operator substitution of the momentum ($p_k \rightarrow -i\hbar\partial/\partial x_k$)

$$\hat{T}(\mathbf{x}) = -\frac{\hbar^2}{2M}\nabla_0^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2. \tag{11.39}$$

Here the first term is the kinetic energy operator of the nucleus, the second term is the kinetic energy operator of the electrons, $M$ is the mass of the nucleus and $m$ is the electron mass. The potential energy operator is given by

$$\hat{V}(\mathbf{x}) = -\sum_{i=1}^{N} \frac{Ze^2}{(4\pi\epsilon_0)r_i} + \sum_{i=1,i<j}^{N} \frac{e^2}{(4\pi\epsilon_0)r_{ij}}, \tag{11.40}$$

where the $r_i$'s are the electron-nucleus distances and the $r_{ij}$'s are the inter-electronic distances.

   We seek to find controlled and well understood approximations in order to reduce the complexity of the above equations. The *Born-Oppenheimer approximation* is a commonly used approximation, in which the motion of the nucleus is disregarded.

### 11.5.1   The Born-Oppenheimer Approximation

In a system of interacting electrons and a nucleus there will usually be little momentum transfer between the two types of particles due to their differing masses. The forces between the particles are of similar magnitude due to their similar charge. If one assumes that the momenta of the particles are also similar, the nucleus must have a much smaller velocity than the electrons due to its far greater mass. On the time-scale of nuclear motion, one can therefore consider the electrons to relax to a ground-state given by the Hamiltonian of Eqs. (11.38), (11.39) and (11.40) with the nucleus at a fixed location. This separation of the electronic and nuclear degrees of freedom is known as the Born-Oppenheimer approximation.

In the center of mass system the kinetic energy operator reads

$$\hat{T}(\mathbf{x}) = -\frac{\hbar^2}{2(M+Nm)}\nabla_{CM}^2 - \frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_i^2 - \frac{\hbar^2}{M}\sum_{i>j}^{N}\nabla_i \cdot \nabla_j, \tag{11.41}$$

while the potential energy operator remains unchanged. Note that the Laplace operators $\nabla_i^2$ now are in the center of mass reference system.

   The first term of Eq. (11.41) represents the kinetic energy operator of the center of mass. The second term represents the sum of the kinetic energy operators of the $N$ electrons, each of them having their

mass $m$ replaced by the reduced mass $\mu = mM/(m + M)$ because of the motion of the nucleus. The nuclear motion is also responsible for the third term, or the *mass polarization* term.

The nucleus consists of protons and neutrons. The proton-electron mass ratio is about $1/1836$ and the neutron-electron mass ratio is about $1/1839$, so regarding the nucleus as stationary is a natural approximation. Taking the limit $M \to \infty$ in Eq. (11.41), the kinetic energy operator reduces to

$$\hat{T} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 \tag{11.42}$$

The Born-Oppenheimer approximation thus disregards both the kinetic energy of the center of mass as well as the mass polarization term. The effects of the Born-Oppenheimer approximation are quite small and they are also well accounted for. However, this simplified electronic Hamiltonian remains very difficult to solve, and analytical solutions do not exist for general systems with more than one electron. We use the Born-Oppenheimer approximation in our discussion of atomic and molecular systems.

The first term of Eq. (11.40) is the nucleus-electron potential and the second term is the electron-electron potential. The inter-electronic potentials are the main problem in atomic physics. Because of these terms, the Hamiltonian cannot be separated into one-particle parts, and the problem must be solved as a whole. A common approximation is to regard the effects of the electron-electron interactions either as averaged over the domain or by means of introducing a density functional, such as by Hartree-Fock (HF) or Density Functional Theory (DFT). These approaches are actually very efficient, and about $99\%$ or more of the electronic energies are obtained for most HF calculations. Other observables are usually obtained to an accuracy of about $90 - 95\%$ (ref. [61]).

### 11.5.2   The hydrogen Atom

The spatial Schrödinger equation for the three-dimensional hydrogen atom can be solved analytically, see for example Ref. [62] for details. To achieve this, we rewrite the equation in terms of spherical coordinates using

$$x = rsin\theta cos\phi, \tag{11.43}$$

$$y = rsin\theta sin\phi, \tag{11.44}$$

and

$$z = rcos\theta. \tag{11.45}$$

The reason we introduce spherical coordinates is the spherical symmetry of the Coulomb potential

$$\frac{e^2}{4\pi\epsilon_0 r} = \frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}}, \tag{11.46}$$

where we have used $r = \sqrt{x^2 + y^2 + z^2}$. It is not possible to find a separable solution of the type

$$\psi(x, y, z) = \psi(x)\psi(y)\psi(z). \tag{11.47}$$

as we can with the harmonic oscillator in three dimensions. However, with spherical coordinates we can find a solution of the form

$$\psi(r, \theta, \phi) = R(r)P(\theta)F(\phi) = RPF. \tag{11.48}$$

These three coordinates yield in turn three quantum numbers which determine the enegy of the systems. We obtain three sets of ordinary second-order differential equations which can be solved analytically, resulting in

$$\frac{1}{F}\frac{\partial^2 F}{\partial \phi^2} = -C_\phi^2,$$ (11.49)

$$C_r sin^2(\theta)P + sin(\theta)\frac{\partial}{\partial \theta}(sin(\theta)\frac{\partial P}{\partial \theta}) = C_\phi^2 P,$$ (11.50)

and

$$\frac{1}{R}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + \frac{2mrke^2}{\hbar^2} + \frac{2mr^2}{\hbar^2}E = C_r,$$ (11.51)

where $C_r$ and $C_\phi$ are constants. The angle-dependent differential equations result in the spherical harmonic functions as solutions, with quantum numbers $l$ and $m_l$. These functions are given by

$$Y_{lm_l}(\theta, \phi) = P(\theta)F(\phi) = \sqrt{\frac{(2l+1)(l-m_l)!}{4\pi(l+m_l)!}}P_l^{m_l}(cos(\theta))\exp(im_l\phi),$$ (11.52)

with $P_l^{m_l}$ being the associated Legendre polynomials They can be rewritten as

$$Y_{lm_l}(\theta, \phi) = sin^{|m_l|}(\theta) \times (\text{polynom}(cos\theta))\exp(im_l\phi),$$ (11.53)

with the following selected examples

$$Y_{00} = \sqrt{\frac{1}{4\pi}},$$ (11.54)

for $l = m_l = 0$,

$$Y_{10} = \sqrt{\frac{3}{4\pi}}cos(\theta),$$ (11.55)

for $l = 1$ og $m_l = 0$,

$$Y_{1\pm 1} = \sqrt{\frac{3}{8\pi}}sin(\theta)exp(\pm i\phi),$$ (11.56)

for $l = 1$ og $m_l = \pm 1$, and

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3cos^2(\theta) - 1)$$ (11.57)

for $l = 2$ og $m_l = 0$. The quantum numbers $l$ and $m_l$ represent the orbital momentum and projection of the orbital momentum, respectively and take the values

1.

$$l \geq 0$$

2.

$$l = 0, 1, 2, \ldots$$

3.

$$m_l = -l, -l+1, \ldots, l-1, l$$

## Spherical Harmonics

| $m_l \backslash l$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| +3 | | | | $-\frac{1}{8}(\frac{35}{\pi})^{1/2}sin^3\theta e^{+3i\phi}$ |
| +2 | | | $\frac{1}{4}(\frac{15}{2\pi})^{1/2}sin^2\theta e^{+2i\phi}$ | $\frac{1}{4}(\frac{105}{2\pi})^{1/2}cos\theta sin^2\theta e^{+2i\phi}$ |
| +1 | | $-\frac{1}{2}(\frac{3}{2\pi})^{1/2}sin\theta e^{+i\phi}$ | $-\frac{1}{2}(\frac{15}{2\pi})^{1/2}cos\theta sin\theta e^{+i\phi}$ | $-\frac{1}{8}(\frac{21}{2\pi})^{1/2}(5cos^2\theta-1)sin\theta e^{+i\phi}$ |
| 0 | $\frac{1}{2\pi^{1/2}}$ | $\frac{1}{2}(\frac{3}{\pi})^{1/2}cos\theta$ | $\frac{1}{4}(\frac{5}{\pi})^{1/2}(3cos^2\theta-1)$ | $\frac{1}{4}(\frac{7}{\pi})^{1/2}(2-5sin^2\theta)cos\theta$ |
| -1 | | $+\frac{1}{2}(\frac{3}{2\pi})^{1/2}sin\theta e^{-i\phi}$ | $+\frac{1}{2}(\frac{15}{2\pi})^{1/2}cos\theta sin\theta e^{-i\phi}$ | $+\frac{1}{8}(\frac{21}{2\pi})^{1/2}(5cos^2\theta-1)sin\theta e^{-i\phi}$ |
| -2 | | | $\frac{1}{4}(\frac{15}{2\pi})^{1/2}sin^2\theta e^{-2i\phi}$ | $\frac{1}{4}(\frac{105}{2\pi})^{1/2}cos\theta sin^2\theta e^{-2i\phi}$ |
| -3 | | | | $+\frac{1}{8}(\frac{35}{\pi})^{1/2}sin^3\theta e^{-3i\phi}$ |

Table 11.1: Spherical harmonics $Y_{lm_l}$ for the lowest $l$ and $m_l$ values.

The spherical harmonics for $l \leq 3$ are listed in Table 11.1.

We concentrate on the radial equation, which can be rewritten as

$$-\frac{\hbar^2 r^2}{2m}\left(\frac{\partial}{\partial r}(r^2\frac{\partial R(r)}{\partial r})\right) - \frac{ke^2}{r}R(r) + \frac{\hbar^2 l(l+1)}{2mr^2}R(r) = ER(r). \tag{11.58}$$

Introducing the function $u(r) = rR(r)$, we can rewrite the last equation as

The radial Schrödinger equation for the hydrogen atom can be written as

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u(r)}{\partial r^2} - \left(\frac{ke^2}{r} - \frac{\hbar^2 l(l+1)}{2mr^2}\right)u(r) = Eu(r), \tag{11.59}$$

where $m$ is the mass of the electron, $l$ its orbital momentum taking values $l = 0, 1, 2, \ldots$, and the term $ke^2/r$ is the Coulomb potential. The first terms is the kinetic energy. The full wave function will also depend on the other variables $\theta$ and $\phi$ as well. The energy, with no external magnetic field is however determined by the above equation . We can then think of the radial Schrödinger equation to be equivalent to a one-dimensional movement conditioned by an effective potential

$$V_{\text{eff}}(r) = -\frac{ke^2}{r} + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{11.60}$$

The radial equation can also be solved analytically resulting in the quantum numbers $n$ in addition to $lm_l$. The solution $R_{nl}$ to the radial equation is given by the Laguerre polynomials. The analytic solutions are given by

$$\psi_{nlm_l}(r,\theta,\phi) = \psi_{nlm_l} = R_{nl}(r)Y_{lm_l}(\theta,\phi) = R_{nl}Y_{lm_l} \tag{11.61}$$

The ground state is defined by $n = 1$ og $l = m_l = 0$ and reads

$$\psi_{100} = \frac{1}{a_0^{3/2}\sqrt{\pi}}e^{-r/a_0}, \tag{11.62}$$

where we have defined the Bohr radius $a_0 = 0.05$ nm

$$a_0 = \frac{\hbar^2}{mke^2}. \tag{11.63}$$

The first excited state with $l = 0$ is

$$\psi_{200} = \frac{1}{4a_0^{3/2}\sqrt{2\pi}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}. \tag{11.64}$$

For states with with $l = 1$ and $n = 2$, we can have the following combinations with $m_l = 0$

$$\psi_{210} = \frac{1}{4a_0^{3/2}\sqrt{2\pi}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos(\theta), \tag{11.65}$$

and $m_l = \pm 1$

$$\psi_{21\pm1} = \frac{1}{8a_0^{3/2}\sqrt{\pi}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin(\theta) e^{\pm i\phi}. \tag{11.66}$$

The exact energy is independent of $l$ and $m_l$, since the potential is spherically symmetric.

The first few non-normalized radial solutions of equation are listed in Table 11.2. A problem with the

**Hydrogen-Like Atomic Radial Functions**

| $l\backslash n$ | 1 | 2 | 3 |
|---|---|---|---|
| 0 | $e^{-Zr}$ | $(2 - r)e^{-Zr/2}$ | $(27 - 18r + 2r^2)e^{-Zr/3}$ |
| 1 | | $re^{-Zr/2}$ | $r(6 - r)e^{-Zr/3}$ |
| 2 | | | $r^2 e^{-Zr/3}$ |

Table 11.2: The first few radial functions of the hydrogen-like atoms.

spherical harmonics of table 11.1 is that they are complex. The introduction of *solid harmonics* allows the use of real orbital wave-functions for a wide range of applications. The complex solid harmonics $\mathcal{Y}_{lm_l}(\mathbf{r})$ are related to the spherical harmonics $Y_{lm_L}(\mathbf{r})$ through

$$\mathcal{Y}_{lm_l}(\mathbf{r}) = r^l Y_{lm_l}(\mathbf{r}).$$

By factoring out the leading $r$-dependency of the radial-function

$$\mathcal{R}_{nl}(\mathbf{r}) = r^{-l} R_{nl}(\mathbf{r}),$$

we obtain

$$\Psi_{nlm_l}(r, \theta, \phi) = \mathcal{R}_{nl}(\mathbf{r}) \cdot \mathcal{Y}_{lm_l}(\mathbf{r}).$$

For the theoretical development of the *real solid harmonics* see Ref. [63]. Here Helgaker *et al* first express the complex solid harmonics, $C_{lm_l}$, by (complex) Cartesian coordinates, and arrive at the real solid harmonics, $S_{lm_l}$, through the unitary transformation

$$\begin{pmatrix} S_{lm_l} \\ S_{l,-m_l} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} (-1)^m & 1 \\ -(-1)^m_l i & i \end{pmatrix} \begin{pmatrix} C_{lm_l} \\ C_{l,-m_l} \end{pmatrix}.$$

This transformation will not alter any physical quantities that are degenerate in the subspace consisting of opposite magnetic quantum numbers (the angular momentum $l$ is equal for both these cases). This means for example that the above transformation does not alter the energies, unless an external magnetic field is applied to the system. Henceforth, we will use the solid harmonics, and note that changing the spherical potential beyond the Coulomb potential will not alter the solid harmonics. The lowest-order real solid harmonics are listed in table 11.3.

### Real Solid Harmonics

| $m_l \backslash l$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| +3 | | | | $\frac{1}{2}\sqrt{\frac{5}{2}}(x^2 - 3y^2)x$ |
| +2 | | | $\frac{1}{2}\sqrt{3}(x^2 - y^2)$ | $\frac{1}{2}\sqrt{15}(x^2 - y^2)z$ |
| +1 | | x | $\sqrt{3}xz$ | $\frac{1}{2}\sqrt{\frac{3}{2}}(5z^2 - r^2)x$ |
| 0 | 1 | y | $\frac{1}{2}(3z^2 - r^2)$ | $\frac{1}{2}(5z^2 - 3r^2)x$ |
| -1 | | z | $\sqrt{3}yz$ | $\frac{1}{2}\sqrt{\frac{3}{2}}(5z^2 - r^2)y$ |
| -2 | | | $\sqrt{3}xy$ | $\sqrt{15}xyz$ |
| -3 | | | | $\frac{1}{2}\sqrt{\frac{5}{2}}(3x^2 - y^2)y$ |

Table 11.3: The first-order real solid harmonics $\mathcal{Y}_{lm_l}$.

When solving equations numerically, it is often convenient to rewrite the equation in terms of dimensionless variables. One reason is the fact that several of the constants may differ largely in value, and hence result in potential losses of numerical precision. The other main reason for doing this is that the equation in dimensionless form is easier to code, sparing one for eventual typographic errors. In order to do so, we introduce first the dimensionless variable $\rho = r/\beta$, where $\beta$ is a constant we can choose. Schrödinger's equation is then rewritten as

$$-\frac{1}{2}\frac{\partial^2 u(\rho)}{\partial \rho^2} - \frac{mke^2\beta}{\hbar^2\rho}u(\rho) + \frac{l(l+1)}{2\rho^2}u(\rho) = \frac{m\beta^2}{\hbar^2}Eu(\rho). \tag{11.67}$$

We can determine $\beta$ by simply requiring[3]

$$\frac{mke^2\beta}{\hbar^2} = 1 \tag{11.68}$$

With this choice, the constant $\beta$ becomes the famous Bohr radius $a_0 = 0.05$ nm $a_0 = \beta = \hbar^2/mke^2$.

As a petit digression, we list here the standard units used in atomic physics and molecular physics calculations. It is common to scale atomic units by setting $m = e = \hbar = 4\pi\epsilon_0 = 1$, see table 11.4.

We introduce thereafter the variable $\lambda$

$$\lambda = \frac{m\beta^2}{\hbar^2}E, \tag{11.69}$$

---

[3]Remember that we are free to choose $\beta$.

**Atomic Units**

| Quantity | SI | Atomic unit |
|---|---|---|
| Electron mass, $m$ | $9.109 \cdot 10^{-31}$ kg | 1 |
| Charge, $e$ | $1.602 \cdot 10^{-19}$ C | 1 |
| Planck's reduced constant, $\hbar$ | $1.055 \cdot 10^{-34}$ Js | 1 |
| Permittivity, $4\pi\epsilon_0$ | $1.113 \cdot 10^{-10}$ C$^2$ J$^{-1}$ m$^{-1}$ | 1 |
| Energy, $\frac{e^2}{4\pi\epsilon_0 a_0}$ | 27.211 eV | 1 |
| Length, $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ | $0.529 \cdot 10^{-10}$ m | 1 |

Table 11.4: Scaling from SI to atomic units

and inserting $\beta$ and the exact energy $E = E_0/n^2$, with $E_0 = 13.6$ eV, we have that

$$\lambda = -\frac{1}{2n^2}, \tag{11.70}$$

$n$ being the principal quantum number. The equation we are then going to solve numerically is now

$$-\frac{1}{2}\frac{\partial^2 u(\rho)}{\partial \rho^2} - \frac{u(\rho)}{\rho} + \frac{l(l+1)}{2\rho^2}u(\rho) - \lambda u(\rho) = 0, \tag{11.71}$$

with the hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} + \frac{l(l+1)}{2\rho^2}. \tag{11.72}$$

The ground state of the hydrogen atom has the energy $\lambda = -1/2$, or $E = -13.6$ eV. The exact wave function obtained from Eq. (11.71) is

$$u(\rho) = \rho e^{-\rho}, \tag{11.73}$$

which yields the energy $\lambda = -1/2$. Sticking to our variational philosophy, we could now introduce a variational parameter $\alpha$ resulting in a trial wave function

$$u_T^\alpha(\rho) = \alpha\rho e^{-\alpha\rho}. \tag{11.74}$$

Inserting this wave function into the expression for the local energy $E_L$ of Eq. (11.16) yields (check it!)

$$E_L(\rho) = -\frac{1}{\rho} - \frac{\alpha}{2}\left(\alpha - \frac{2}{\rho}\right). \tag{11.75}$$

For the hydrogen atom, we could perform the variational calculation along the same lines as we did for the harmonic oscillator. The only difference is that Eq. (11.17) now reads

$$\langle H \rangle = \int P(\mathbf{R})E_L(\mathbf{R})d\mathbf{R} = \int_0^\infty \alpha^2\rho^2 e^{-2\alpha\rho}E_L(\rho)\rho^2 d\rho, \tag{11.76}$$

since $\rho \in [0, \infty]$. In this case we would use the exponential distribution instead of the normal distrubution, and our code would contain the following elements

```
...    initialisations , declarations of variables
...    mcs = number of  Monte Carlo samplings

//     loop over Monte Carlo samples
       for ( i=0; i < mcs; i++) {

//     generate random variables from the exponential
//     distribution using ran1 and transforming to
//     to an exponential mapping y = −ln(1−x)
           x=ran1(&idum);
           y=−log (1.−x);
//     in our case y = rho∗alpha∗2
           rho = y/alpha/2;
           local_energy = −1/rho −0.5∗alpha∗(alpha−2/rho);
           energy += (local_energy);
           energy2 += local_energy∗local_energy;
//     end of sampling
       }
//     write out the mean energy and the standard deviation
       cout << energy/mcs << sqrt ((energy2/mcs−(energy/mcs)∗∗2)/mcs));
```

As for the harmonic oscillator case we just need to generate a large number $N$ of random numbers corresponding to the exponential PDF $\alpha^2\rho^2 e^{-2\alpha\rho}$ and for each random number we compute the local energy and variance.

### 11.5.3  Metropolis sampling for the hydrogen atom and the harmonic oscillator

We present in this subsection results for the ground states of the hydrogen atom and harmonic oscillator using a variational Monte Carlo procedure. For the hydrogen atom, the trial wave function

$$u_T^\alpha(\rho) = \alpha\rho e^{-\alpha\rho},$$

depends only on the dimensionless radius $\rho$. It is the solution of a one-dimensional differential equation, as is the case for the harmonic oscillator as well. The latter has the trial wave function

$$\Psi_T(x) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-x^2\alpha^2/2}.$$

However, for the hydrogen atom we have $\rho \in [0, \infty]$, while for the harmonic oscillator we have $x \in [-\infty, \infty]$.

This has important consequences for the way we generate random positions. For the hydrogen atom we have a random position given by e.g.,

```
  r_old = step_length*(ran1(&idum))/alpha;
```

which ensures that $\rho \geq 0$, while for the harmonic oscillator we have

```
  r_old = step_length*(ran1(&idum)-0.5)/alpha;
```

in order to have $x \in [-\infty, \infty]$. This is however not implemented in the program below. There, importance sampling is not included. We simulate points in the $x$, $y$ and $z$ directions using random numbers generated by the uniform distribution and multiplied by the step length. Note that we have to define a
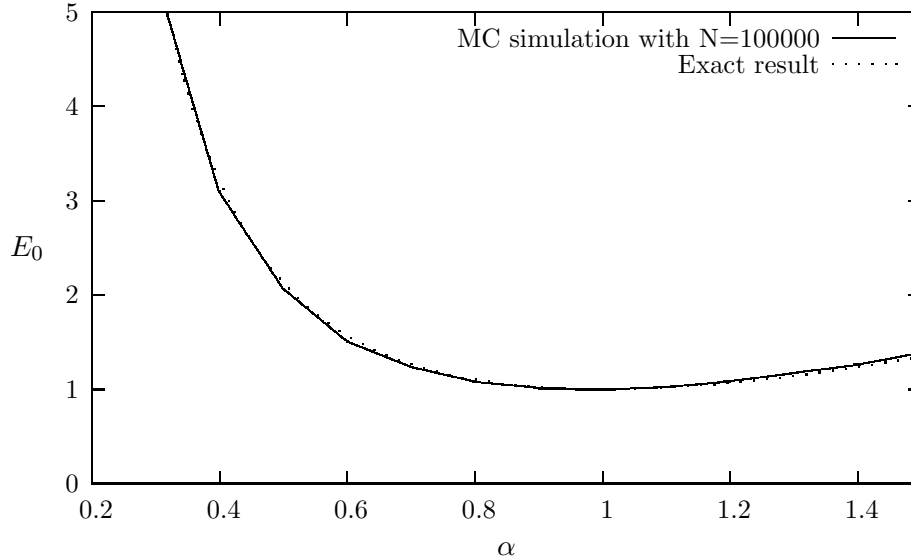
Figure 11.1: Result for ground state energy of the harmonic oscillator as function of the variational parameter $\alpha$. The exact result is for $\alpha = 1$ with an energy $E = 1$. See text for further details

step length in our calculations. Here one has to play around with different values for the step and as a rule of thumb (one of the golden Monte Carlo rules), the step length should be chosen so that roughly 50% of all new moves are accepted. In the program at the end of this section we have also scaled the random position with the variational parameter $\alpha$. The reason for this particular choice is that we have an external loop over the variational parameter. Different variational parameters will obviously yield different acceptance rates if we use the same step length. An alternative to the code below is to perform the Monte Carlo sampling with just one variational parameter, and play around with different step lengths in order to achieve a reasonable acceptance ratio. Another possibility is to include a more advanced test which restarts the Monte Carlo sampling with a new step length if the specific variational parameter and chosen step length lead to a too low acceptance ratio.

In Figs. 11.1 and 11.2 we plot the ground state energies for the one-dimensional harmonic oscillator and the hydrogen atom, respectively, as functions of the variational parameter $\alpha$. These results are also displayed in Tables 11.5 and 11.6. In these tables we list the variance and the standard deviation as well. We note that at $\alpha$ we obtain the exact result, and the variance is zero, as it should. The reason is that we then have the exact wave function, and the action of the hamiltionan on the wave function

$$H\psi = \text{constant} \times \psi,$$

yields just a constant. The integral which defines various expectation values involving moments of the hamiltonian becomes then

$$\langle H^n \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})H^n(\mathbf{R})\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})} = \text{constant} \times \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})} = \text{constant}. \quad (11.77)$$

This explains why the variance is zero for $\alpha = 1$. However, the hydrogen atom and the harmonic oscillator are some of the few cases where we can use a trial wave function proportional to the exact one. These two systems are also some of the few examples of cases where we can find an exact solution to

Table 11.5: Result for ground state energy of the harmonic oscillator as function of the variational parameter $\alpha$. The exact result is for $\alpha = 1$ with an energy $E = 1$. The energy variance $\sigma^2$ and the standard deviation $\sigma/\sqrt{N}$ are also listed. The variable $N$ is the number of Monte Carlo samples. In this calculation we set $N = 100000$ and a step length of 2 was used in order to obtain an acceptance of $\approx 50\%$.

| $\alpha$ | $\langle H \rangle$ | $\sigma^2$ | $\sigma/\sqrt{N}$ |
|---|---|---|---|
| 5.00000E-01 | 2.06479E+00 | 5.78739E+00 | 7.60749E-03 |
| 6.00000E-01 | 1.50495E+00 | 2.32782E+00 | 4.82475E-03 |
| 7.00000E-01 | 1.23264E+00 | 9.82479E-01 | 3.13445E-03 |
| 8.00000E-01 | 1.08007E+00 | 3.44857E-01 | 1.85703E-03 |
| 9.00000E-01 | 1.01111E+00 | 7.24827E-02 | 8.51368E-04 |
| 1.00000E-00 | 1.00000E+00 | 0.00000E+00 | 0.00000E+00 |
| 1.10000E+00 | 1.02621E+00 | 5.95716E-02 | 7.71826E-04 |
| 1.20000E+00 | 1.08667E+00 | 2.23389E-01 | 1.49462E-03 |
| 1.30000E+00 | 1.17168E+00 | 4.78446E-01 | 2.18734E-03 |
| 1.40000E+00 | 1.26374E+00 | 8.55524E-01 | 2.92493E-03 |
| 1.50000E+00 | 1.38897E+00 | 1.30720E+00 | 3.61553E-03 |
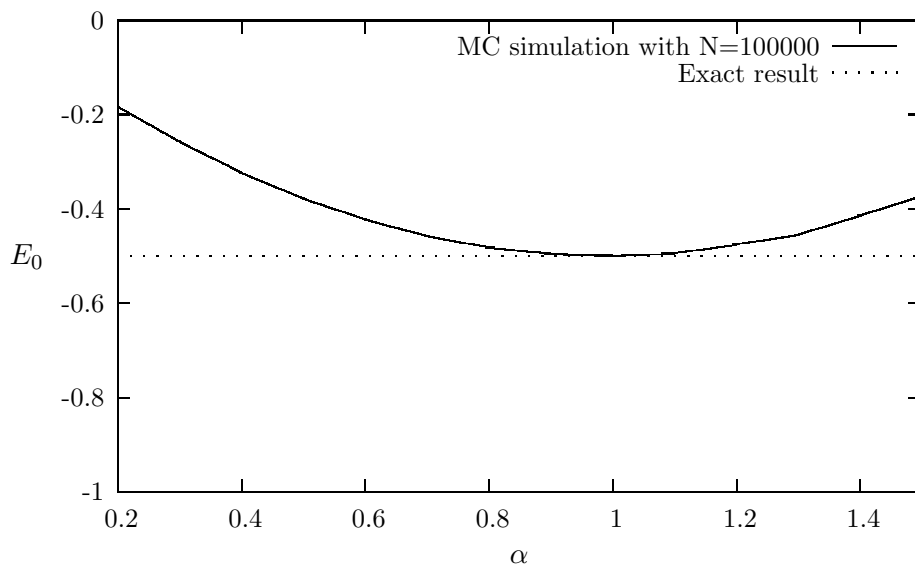


Figure 11.2: Result for ground state energy of the hydrogen atom as function of the variational parameter $\alpha$. The exact result is for $\alpha = 1$ with an energy $E = -1/2$. See text for further details

Table 11.6: Result for ground state energy of the hydrogen atom as function of the variational parameter $\alpha$. The exact result is for $\alpha = 1$ with an energy $E = -1/2$. The energy variance $\sigma^2$ and the standard deviation $\sigma/\sqrt{N}$ are also listed. The variable $N$ is the number of Monte Carlo samples. In this calculation we fixed $N = 100000$ and a step length of 4 Bohr radii was used in order to obtain an acceptance of $\approx 50\%$.

| $\alpha$ | $\langle H \rangle$ | $\sigma^2$ | $\sigma/\sqrt{N}$ |
|---|---|---|---|
| 5.00000E-01 | -3.76740E-01 | 6.10503E-02 | 7.81347E-04 |
| 6.00000E-01 | -4.21744E-01 | 5.22322E-02 | 7.22718E-04 |
| 7.00000E-01 | -4.57759E-01 | 4.51201E-02 | 6.71715E-04 |
| 8.00000E-01 | -4.81461E-01 | 3.05736E-02 | 5.52934E-04 |
| 9.00000E-01 | -4.95899E-01 | 8.20497E-03 | 2.86443E-04 |
| 1.00000E-00 | -5.00000E-01 | 0.00000E+00 | 0.00000E+00 |
| 1.10000E+00 | -4.93738E-01 | 1.16989E-02 | 3.42036E-04 |
| 1.20000E+00 | -4.75563E-01 | 8.85899E-02 | 9.41222E-04 |
| 1.30000E+00 | -4.54341E-01 | 1.45171E-01 | 1.20487E-03 |
| 1.40000E+00 | -4.13220E-01 | 3.14113E-01 | 1.77232E-03 |
| 1.50000E+00 | -3.72241E-01 | 5.45568E-01 | 2.33574E-03 |

the problem. In most cases of interest, we do not know a priori the exact wave function, or how to make a good trial wave function. In essentially all real problems a large amount of CPU time and numerical experimenting is needed in order to ascertain the validity of a Monte Carlo estimate. The next examples deal with such problems.

### 11.5.4   The helium atom

Most physical problems of interest in atomic, molecular and solid state physics consist of a number of interacting electrons and ions. The total number of particles $N$ is usually sufficiently large that an exact solution cannot be found. Typically, the expectation value for a chosen hamiltonian for a system of $N$ particles is

$$\langle H \rangle = \frac{\int d\mathbf{R}_1 d\mathbf{R}_2 \dots d\mathbf{R}_N \Psi^*(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) H(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)}{\int d\mathbf{R}_1 d\mathbf{R}_2 \dots d\mathbf{R}_N \Psi^*(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)}, \quad (11.78)$$

an in general intractable problem. Controlled and well understood approximations are sought to reduce the complexity to a tractable level. Once the equations are solved, a large number of properties may be calculated from the wave function. Errors or approximations made in obtaining the wave function will be manifest in any property derived from the wave function. Where high accuracy is required, considerable attention must be paid to the derivation of the wave function and any approximations made.

The helium atom consists of two electrons and a nucleus with charge $Z = 2$. In setting up the hamiltonian of this system, we need to account for the repulsion between the two electrons as well.

A common and very reasonable approximation used in the solution of equation of the Schrödinger equation for systems of interacting electrons and ions is the Born-Oppenheimer approximation discussed above. In a system of interacting electrons and nuclei there will usually be little momentum transfer between the two types of particles due to their greatly differing masses. The forces between the particles are of similar magnitude due to their similar charge. If one then assumes that the momenta of the particles are also similar, then the nuclei must have much smaller velocities than the electrons due to their far

greater mass. On the time-scale of nuclear motion, one can therefore consider the electrons to relax to a ground-state with the nuclei at fixed locations. This separation of the electronic and nuclear degrees of freedom is the the Born-Oppenheimer approximation we discussed previously in this chapter. But even this simplified electronic Hamiltonian remains very difficult to solve. No analytic solutions exist for general systems with more than one electron.

If we label the distance between electron 1 and the nucleus as $r_1$. Similarly we have $r_2$ for electron 2. The contribution to the potential energy due to the attraction from the nucleus is

$$-\frac{2ke^2}{r_1} - \frac{2ke^2}{r_2}, \tag{11.79}$$

and if we add the repulsion arising from the two interacting electrons, we obtain the potential energy

$$V(r_1, r_2) = -\frac{2ke^2}{r_1} - \frac{2ke^2}{r_2} + \frac{ke^2}{r_{12}}, \tag{11.80}$$

with the electrons separated at a distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The hamiltonian becomes then

$$\widehat{\mathbf{H}} = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} - \frac{2ke^2}{r_1} - \frac{2ke^2}{r_2} + \frac{ke^2}{r_{12}}, \tag{11.81}$$

and Schrödingers equation reads

$$\widehat{\mathbf{H}}\psi = E\psi. \tag{11.82}$$

Note that this equation has been written in atomic units $a.u.$ which are more convenient for quantum mechanical problems. This means that the final energy has to be multiplied by a $2 \times E_0$, where $E_0 = 13.6$ eV, the binding energy of the hydrogen atom.

A very simple first approximation to this system is to omit the repulsion between the two electrons. The potential energy becomes then

$$V(r_1, r_2) \approx -\frac{Zke^2}{r_1} - \frac{Zke^2}{r_2}. \tag{11.83}$$

The advantage of this approximation is that each electron can be treated as being independent of each other, implying that each electron sees just a centrally symmetric potential, or central field.

To see whether this gives a meaningful result, we set $Z = 2$ and neglect totally the repulsion between the two electrons. Electron 1 has the following hamiltonian

$$\widehat{\mathbf{h}}_1 = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{2ke^2}{r_1}, \tag{11.84}$$

with pertinent wave function and eigenvalue

$$\widehat{\mathbf{h}}_1 \psi_a = E_a \psi_a, \tag{11.85}$$

where $a = \{n_a l_a m_{l_a}\}$, are its quantum numbers. The energy $E_a$ is

$$E_a = -\frac{Z^2 E_0}{n_a^2}, \tag{11.86}$$

med $E_0 = 13.6$ eV, being the ground state energy of the hydrogen atom. In a similar way, we obatin for electron 2

$$\widehat{\mathbf{h}}_2 = -\frac{\hbar^2 \nabla_2^2}{2m} - \frac{2ke^2}{r_2}, \tag{11.87}$$

with wave function

$$\widehat{\mathbf{h}}_2 \psi_b = E_b \psi_b, \tag{11.88}$$

and $b = \{n_b l_b m_{l_b}\}$, and energy

$$E_b = \frac{Z^2 E_0}{n_b^2}. \tag{11.89}$$

Since the electrons do not interact, we can assume that the ground state wave function of the helium atom is given by

$$\psi = \psi_a \psi_b, \tag{11.90}$$

resulting in the following approximation to Schrödinger's equation

$$\left(\widehat{\mathbf{h}}_1 + \widehat{\mathbf{h}}_2\right) \psi = \left(\widehat{\mathbf{h}}_1 + \widehat{\mathbf{h}}_2\right) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) = E_{ab} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2). \tag{11.91}$$

The energy becomes then

$$\left(\widehat{\mathbf{h}}_1 \psi_a(\mathbf{r}_1)\right) \psi_b(\mathbf{r}_2) + \left(\widehat{\mathbf{h}}_2 \psi_b(\mathbf{r}_2)\right) \psi_a(\mathbf{r}_1) = \left(E_a + E_b\right) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2), \tag{11.92}$$

yielding

$$E_{ab} = Z^2 E_0 \left(\frac{1}{n_a^2} + \frac{1}{n_b^2}\right). \tag{11.93}$$

If we insert $Z = 2$ and assume that the ground state is determined by two electrons in the lowest-lying hydrogen orbit with $n_a = n_b = 1$, the energy becomes

$$E_{ab} = 8E_0 = -108.8 \text{ eV}, \tag{11.94}$$

while the experimental value is $-78.8$ eV. Clearly, this discrepancy is essentially due to our omission of the repulsion arising from the interaction of two electrons.

**Choice of trial wave function**

The choice of trial wave function is critical in variational Monte Carlo calculations. How to choose it is however a highly non-trivial task. All observables are evaluated with respect to the probability distribution

$$P(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int |\psi_T(\mathbf{R})|^2 \, d\mathbf{R}}. \tag{11.95}$$

generated by the trial wave function. The trial wave function must approximate an exact eigenstate in order that accurate results are to be obtained. Improved trial wave functions also improve the importance sampling, reducing the cost of obtaining a certain statistical accuracy.

Quantum Monte Carlo methods are able to exploit trial wave functions of arbitrary forms. Any wave function that is physical and for which the value, gradient and laplacian of the wave function may be efficiently computed can be used. The power of Quantum Monte Carlo methods lies in the flexibility of the form of the trial wave function.

It is important that the trial wave function satisfies as many known properties of the exact wave function as possible. A good trial wave function should exhibit much of the same features as does the exact wave function. Especially, it should be well-defined at the origin, that is $\Psi(|\mathbf{R}| = 0) \neq 0$, and its derivative at the origin should also be well-defined . One possible guideline in choosing the trial wave function is the use of constraints about the behavior of the wave function when the distance between

one electron and the nucleus or two electrons approaches zero. These constraints are the so-called "cusp conditions" and are related to the derivatives of the wave function.

To see this, let us single out one of the electrons in the helium atom and assume that this electron is close to the nucleus, i.e., $r_1 \to 0$. We assume also that the two electrons are far from each other and that $r_2 \neq 0$. The local energy can then be written as

$$E_L(\mathbf{R}) = \frac{1}{\psi_T(\mathbf{R})} H \psi_T(\mathbf{R}) = \frac{1}{\psi_T(\mathbf{R})} \left( -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} \right) \psi_T(\mathbf{R}) + \text{finite terms.} \tag{11.96}$$

Writing out the kinetic energy term in the spherical coordinates of electron 1, we arrive at the following expression for the local energy

$$E_L(R) = \frac{1}{\mathcal{R}_T(r_1)} \left( -\frac{1}{2} \frac{d^2}{dr_1^2} - \frac{1}{r_1} \frac{d}{dr_1} - \frac{Z}{r_1} \right) \mathcal{R}_T(r_1) + \text{finite terms,} \tag{11.97}$$

where $\mathcal{R}_T(r_1)$ is the radial part of the wave function for electron 1. We have also used that the orbital momentum of electron 1 is $l = 0$. For small values of $r_1$, the terms which dominate are

$$\lim_{r_1 \to 0} E_L(R) = \frac{1}{\mathcal{R}_T(r_1)} \left( -\frac{1}{r_1} \frac{d}{dr_1} - \frac{Z}{r_1} \right) \mathcal{R}_T(r_1), \tag{11.98}$$

since the second derivative does not diverge due to the finiteness of $\Psi$ at the origin. The latter implies that in order for the kinetic energy term to balance the divergence in the potential term, we must have

$$\frac{1}{\mathcal{R}_T(r_1)} \frac{d\mathcal{R}_T(r_1)}{dr_1} = -Z, \tag{11.99}$$

implying that

$$\mathcal{R}_T(r_1) \propto e^{-Zr_1}. \tag{11.100}$$

A similar condition applies to electron 2 as well. For orbital momenta $l > 0$ we have (show this!)

$$\frac{1}{\mathcal{R}_T(r)} \frac{d\mathcal{R}_T(r)}{dr} = -\frac{Z}{l+1}. \tag{11.101}$$

Another constraint on the wave function is found for two electrons approaching each other. In this case it is the dependence on the separation $r_{12}$ between the two electrons which has to reflect the correct behavior in the limit $r_{12} \to 0$. The resulting radial equation for the $r_{12}$ dependence is the same for the electron-nucleus case, except that the attractive Coulomb interaction between the nucleus and the electron is replaced by a repulsive interaction and the kinetic energy term is twice as large. We obtain then

$$\lim_{r_{12} \to 0} E_L(R) = \frac{1}{\mathcal{R}_T(r_{12})} \left( -\frac{4}{r_{12}} \frac{d}{dr_{12}} + \frac{2}{r_{12}} \right) \mathcal{R}_T(r_{12}), \tag{11.102}$$

with still $l = 0$. This yields the so-called 'cusp'-condition

$$\frac{1}{\mathcal{R}_T(r_{12})} \frac{d\mathcal{R}_T(r_{12})}{dr_{12}} = \frac{1}{2}, \tag{11.103}$$

while for $l > 0$ we have

$$\frac{1}{\mathcal{R}_T(r_{12})} \frac{d\mathcal{R}_T(r_{12})}{dr_{12}} = \frac{1}{2(l+1)}. \tag{11.104}$$

For general systems containing more than two electrons, we have this condition for each electron pair $ij$.

Based on these consideration, a possible trial wave function which ignores the 'cusp'-condition between the two electrons is

$$\psi_T(\mathbf{R}) = e^{-\alpha(r_1+r_2)}, \tag{11.105}$$

where $r_{1,2}$ are dimensionless radii and $\alpha$ is a variational parameter which is to be interpreted as an effective charge.

A possible trial wave function which also reflects the 'cusp'-condition between the two electrons is

$$\psi_T(\mathbf{R}) = e^{-\alpha(r_1+r_2)}e^{r_{12}/2}. \tag{11.106}$$

The last equation can be generalized to

$$\psi_T(\mathbf{R}) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\dots\phi(\mathbf{r}_N)\prod_{i<j} f(r_{ij}), \tag{11.107}$$

for a system with $N$ electrons or particles. The wave function $\phi(\mathbf{r}_i)$ is the single-particle wave function for particle $i$, while $f(r_{ij})$ account for more complicated two-body correlations. For the helium atom, we placed both electrons in the hydrogenic orbit $1s$. We know that the ground state for the helium atom has a symmetric spatial part, while the spin wave function is anti-symmetric in order to obey the Pauli principle. In the present case we need not to deal with spin degrees of freedom, since we are mainly trying to reproduce the ground state of the system. However, adopting such a single-particle representation for the individual electrons means that for atoms beyond helium, we cannot continue to place electrons in the lowest hydrogenic orbit. This is a consenquence of the Pauli principle, which states that the total wave function for a system of identical particles such as fermions, has to be anti-symmetric. The program we include below can use either Eq. (11.105) or Eq. (11.106) for the trial wave function. One or two electrons can be placed in the lowest hydrogen orbit, implying that the program can only be used for studies of the ground state of hydrogen or helium.

### 11.5.5 *Program example for atomic systems*

The variational Monte Carlo algorithm consists of two distinct phases. In the first a walker, a single electron in our case, consisting of an initially random set of electron positions is propagated according to the Metropolis algorithm, in order to equilibrate it and begin sampling . In the second phase, the walker continues to be moved, but energies and other observables are also accumulated for later averaging and statistical analysis. In the program below, the electrons are moved individually and not as a whole configuration. This improves the efficiency of the algorithm in larger systems, where configuration moves require increasingly small steps to maintain the acceptance ratio.

The main part of the code contains calls to various functions, setup and declarations of arrays etc. The corresponding Fortran 90/95 program is program1.f90. Note that we have defined a fixed step length $h$ for the numerical computation of the second derivative of the kinetic energy. Furthermore, we perform the Metropolis test when we have moved all electrons. This should be compared to the case where we move one electron at the time and perform the Metropolis test. The latter is similar to the algorithm for the Ising model discussed in the previous chapter. A more detailed discussion and better statistical treatments and analyses are discussed in chapters 18 and 19.

http://folk.uio.no/mhjensen/fys3150/2005/programs/chapter11/program1.cpp

```
// Variational Monte Carlo for atoms with up to two electrons
#include <iostream>
```

```cpp
#include <fstream>
#include <iomanip>
#include "lib.h"
using namespace std;
// output file as global variable
ofstream ofile;
// the step length and its squared inverse for the second derivative
#define h 0.001
#define h2 1000000


// declaraton of functions

// Function to read in data from screen, note call by reference
void initialise(int&, int&, int&, int&, int&, int&, double&) ;

// The Mc sampling for the variational Monte Carlo
void mc_sampling(int, int, int, int, int, int, double, double *, double *);

// The variational wave function
double wave_function(double **, double, int, int);

// The local energy
double local_energy(double **, double, double, int, int, int);

// prints to screen the results of the calculations
void output(int, int, int, double *, double *);



// Begin of main program

//int main()
int main(int argc, char* argv[])
{
  char *outfilename;
  int number_cycles, max_variations, thermalization, charge;
  int dimension, number_particles;
  double step_length;
  double *cumulative_e, *cumulative_e2;

  // Read in output file, abort if there are too few command-line arguments
  if( argc <= 1 ){
    cout << "Bad Usage: " << argv[0] <<
      " read also output file on same line" << endl;
    exit(1);
  }
  else{
    outfilename=argv[1];
  }
  ofile.open(outfilename);
  //    Read in data
  initialise(dimension, number_particles, charge,
             max_variations, number_cycles,
             thermalization, step_length) ;
```

```
  cumulative_e = new double[max_variations+1];
  cumulative_e2 = new double[max_variations+1];

  //   Do the mc sampling
  mc_sampling(dimension, number_particles, charge,
              max_variations, thermalization,
              number_cycles, step_length, cumulative_e, cumulative_e2);
  // Print out results
  output(max_variations, number_cycles, charge, cumulative_e, cumulative_e2)
      ;
  delete [] cumulative_e; delete [] cumulative_e;
  ofile.close();   // close output file
  return 0;
}
```

The implementation of the brute force Metropolis algorithm is shown in the next function. Here we have a loop over the variational variables $\alpha$. It calls two functions, one to compute the wave function and one to update the local energy.

```
// Monte Carlo sampling with the Metropolis algorithm

void mc_sampling(int dimension, int number_particles, int charge,
                 int max_variations,
                 int thermalization, int number_cycles, double step_length,
                 double *cumulative_e, double *cumulative_e2)
{
  int cycles, variate, accept, dim, i, j;
  long idum;
  double wfnew, wfold, alpha, energy, energy2, delta_e;
  double **r_old, **r_new;
  alpha = 0.5*charge;
  idum=-1;
  // allocate matrices which contain the position of the particles
  r_old = (double **) matrix( number_particles, dimension, sizeof(double));
  r_new = (double **) matrix( number_particles, dimension, sizeof(double));
  for (i = 0; i < number_particles; i++) {
    for ( j=0; j < dimension; j++) {
      r_old[i][j] = r_new[i][j] = 0;
    }
  }
  // loop over variational parameters
  for (variate=1; variate <= max_variations; variate++){
    // initialisations of variational parameters and energies
    alpha += 0.1;
    energy = energy2 = 0; accept =0; delta_e=0;
    //  initial trial position, note calling with alpha
    //   and in three dimensions
    for (i = 0; i < number_particles; i++) {
      for ( j=0; j < dimension; j++) {
        r_old[i][j] = step_length*(ran1(&idum)-0.5);
      }
    }
    wfold = wave_function(r_old, alpha, dimension, number_particles);
```

```
  // loop over monte carlo cycles
  for (cycles = 1; cycles <= number_cycles+thermalization; cycles++){
    // new position
    for (i = 0; i < number_particles; i++) {
      for ( j=0; j < dimension; j++) {
        r_new[i][j] = r_old[i][j]+step_length*(ran1(&idum)-0.5);
      }
    }
    wfnew = wave_function(r_new, alpha, dimension, number_particles);
    // Metropolis test
    if(ran1(&idum) <= wfnew*wfnew/wfold/wfold ) {
      for (i = 0; i < number_particles; i++) {
        for ( j=0; j < dimension; j++) {
          r_old[i][j]=r_new[i][j];
        }
      }
      wfold = wfnew;
      accept = accept+1;
    }
    // compute local energy
    if ( cycles > thermalization ) {
      delta_e = local_energy(r_old, alpha, wfold, dimension,
                             number_particles, charge);
      // update energies
      energy += delta_e;
      energy2 += delta_e*delta_e;
    }
  }   // end of loop over MC trials
  cout << "variational parameter= " << alpha
       << " accepted steps= " << accept << endl;
  // update the energy average and its squared
  cumulative_e[variate] = energy/number_cycles;
  cumulative_e2[variate] = energy2/number_cycles;

  }   // end of loop over variational  steps
  free_matrix((void **) r_old); // free memory
  free_matrix((void **) r_new); // free memory
}   // end mc_sampling function
```

The wave function is in turn defined in the next function. Here we limit ourselves to a function which consists only of the product of single-particle wave functions.

```
// Function to compute the squared wave function, simplest form

double  wave_function(double **r, double alpha, int dimension, int
   number_particles)
{
  int i, j, k;
  double wf, argument, r_single_particle, r_12;

  argument = wf = 0;
  for (i = 0; i < number_particles; i++) {
    r_single_particle = 0;
```

```
    for ( j = 0; j < dimension; j++) {
      r_single_particle  += r[i][j]*r[i][j];
    }
    argument += sqrt(r_single_particle);
  }
  wf = exp(-argument*alpha) ;
  return wf;
}
```

Finally, the local energy is computed using a numerical derivation for the kinetic energy. We use the familiar expression derived in Eq. (3.2), that is

$$f_0'' = \frac{f_h - 2f_0 + f_{-h}}{h^2},$$

in order to compute

$$-\frac{1}{2\psi_T(\mathbf{R})}\nabla^2\psi_T(\mathbf{R}). \tag{11.108}$$

The variable $h$ is a chosen step length. For helium, since it is rather easy to evaluate the local energy, the above is an unnecessary complication. However, for many-electron or other many-particle systems, the derivation of an analytic expression for the kinetic energy can be quite involved, and the numerical evaluation of the kinetic energy using Eq. (3.2) may result in a simpler code and/or even a faster one.

```
// Function to calculate the local energy with num derivative

double  local_energy(double **r, double alpha, double wfold, int dimension,
                     int number_particles, int charge)
{
  int i, j , k;
  double e_local, wfminus, wfplus, e_kinetic, e_potential, r_12,
    r_single_particle;
  double **r_plus, **r_minus;

  // allocate matrices which contain the position of the particles
  // the function matrix is defined in the progam library
  r_plus = (double **) matrix( number_particles, dimension, sizeof(double));
  r_minus = (double **) matrix( number_particles, dimension, sizeof(double))
     ;
  for (i = 0; i < number_particles; i++) {
    for ( j=0; j < dimension; j++) {
      r_plus[i][j] = r_minus[i][j] = r[i][j];
    }
  }
  // compute the kinetic energy
  e_kinetic = 0;
  for (i = 0; i < number_particles; i++) {
    for (j = 0; j < dimension; j++) {
      r_plus[i][j] = r[i][j]+h;
      r_minus[i][j] = r[i][j]-h;
      wfminus = wave_function(r_minus, alpha, dimension, number_particles);
      wfplus  = wave_function(r_plus, alpha, dimension, number_particles);
      e_kinetic -= (wfminus+wfplus -2*wfold);
      r_plus[i][j] = r[i][j];
```

```
      r_minus[i][j] = r[i][j];
    }
  }
  // include electron mass and hbar squared and divide by wave function
  e_kinetic = 0.5*h2*e_kinetic/wfold;
  // compute the potential energy
  e_potential = 0;
  // contribution from electron−proton potential
  for (i = 0; i < number_particles; i++) {
    r_single_particle = 0;
    for (j = 0; j < dimension; j++) {
      r_single_particle += r[i][j]*r[i][j];
    }
    e_potential −= charge/sqrt(r_single_particle);
  }
  // contribution from electron−electron potential
  for (i = 0; i < number_particles −1; i++) {
    for (j = i+1; j < number_particles; j++) {
      r_12 = 0;
      for (k = 0; k < dimension; k++) {
        r_12 += (r[i][k]−r[j][k])*(r[i][k]−r[j][k]);
      }
      e_potential += 1/sqrt(r_12);
    }
  }
  free_matrix((void **) r_plus); // free memory
  free_matrix((void **) r_minus);
  e_local = e_potential+e_kinetic;
  return e_local;
}
```

The remaining part of the program consists of the output and initialize functions and is not listed here.

The way we have rewritten Schrödinger's equation results in energies given in atomic units. If we wish to convert these energies into more familiar units like electronvolt (eV), we have to multiply our reults with $2E_0$ where $E_0 = 13.6$ eV, the binding energy of the hydrogen atom. Using Eq. (11.105) for the trial wave function, we obtain an energy minimum at $\alpha \approx 1.75$. The ground state is $E = -2.85$ in atomic units or $E = -77.5$ eV. The experimental value is $-78.8$ eV. Obviously, improvements to the wave function such as including the 'cusp'-condition for the two electrons as well, see Eq. (11.106), could improve our agreement with experiment. Such an implementation is the topic for the next project.

We note that the effective charge is less than the charge of the nucleus. We can interpret this reduction as an effective way of incorporating the repulsive electron-electron interaction. Finally, since we do not have the exact wave function, we see from Fig. 11.3 that the variance is not zero at the energy minimum. Techniques such as importance sampling, to be contrasted to the brute force Metropolis sampling used here, and various optimization techniques of the variance and the energy, will be discussed under advanced topics, see chapter 18.

### 11.5.6  Physics Projects: Studies of light Atoms

The aim of this project is to test the variational Monte Carlo apppled to light atoms. We will test different trial wave function $\Psi_T$. The systems we study are atoms consisting of two electrons only, such as the helium atom, $\text{Li}_{II}$ and $\text{Be}_{III}$. The atom $\text{Li}_{II}$ has two electrons and $Z = 3$ while $\text{Be}_{III}$ has $Z = 4$ but
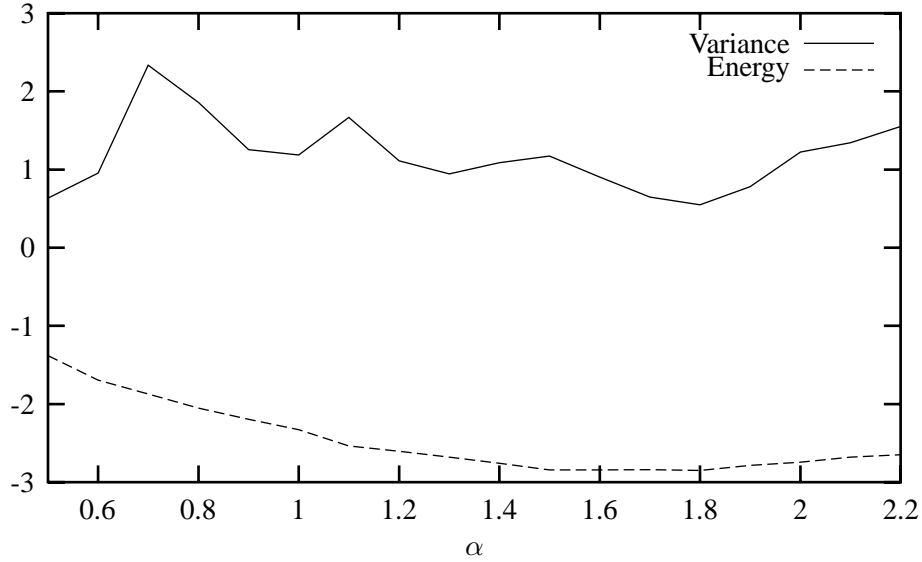
Figure 11.3: Result for ground state energy of the helium atom using Eq. (11.105) for the trial wave function. The variance is also plotted. A total of 100000 Monte Carlo moves were used with a step length of 2 Bohr radii.

still two electrons only. A general ansatz for the trial wave function is

$$\psi_T(\mathbf{R}) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)f(r_{12}). \tag{11.109}$$

For all systems we assume that the one-electron wave functions $\phi(\mathbf{r}_i)$ are described by the an elecron in the lowest hydrogen orbital $1s$.

The specific trial functions we study are

$$\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right), \tag{11.110}$$

where $\alpha$ is the variational parameter,

$$\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right)(1 + \beta r_{12}), \tag{11.111}$$

with $\beta$ as a new variational parameter and

$$\psi_{T3}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right)\exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right). \tag{11.112}$$

a) Find the analytic expressions for the local energy for the above trial wave function for the helium atom. Study the behavior of the local energy with these functions in the limits $r_1 \to 0$, $r_2 \to 0$ and $r_{12} \to 0$.

b) Compute

$$\langle \widehat{\mathbf{H}} \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\widehat{\mathbf{H}}(\mathbf{R})\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})}, \tag{11.113}$$

for the helium atom using the variational Monte Carlo method employing the Metropolis algorithm to sample the different states using the trial wave function $\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$. Compare your results with the analytic expression

$$\langle \widehat{\mathbf{H}} \rangle = \frac{\hbar^2}{m_e} \alpha^2 - \frac{27}{32} \frac{e^2}{\pi \epsilon_0} \alpha. \tag{11.114}$$

c) Use the optimal value of $\alpha$ from the previous point to compute the ground state of the helium atom using the other two trial wave functions $\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ and $\psi_{T3}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$. In this case you have to vary both $\alpha$ and $\beta$. Explain briefly which function $\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$, $\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ and $\psi_{T3}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ is the best.

d) Use the optimal value for all parameters and all wave functions to compute the expectation value of the mean distance $\langle r_{12} \rangle$ between the two electrons. Comment your results.

e) We will now repeat point 1c), but we replace the helium atom with the ions $\text{Li}_{II}$ and $\text{Be}_{III}$. Perform first a variational calculation using the first ansatz for the trial wave function $\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ in order to find an optimal value for $\alpha$. Use then this value to start the variational calculation of the energy for the wave functions $\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ and $\psi_{T3}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$. Comment your results.

### 11.5.7 Helium and beyond

We need to establish some rules regarding the construction of physically reliable wave-functions for systems with more than one electron. The *Pauli principle* was recognized by Wolfgang Pauli **The Pauli Principle** *The total wave function must be antisymmetric under the interchange of any pair of identical fermions and symmetric under the interchange of any pair of identical bosons.*

A result of the Pauli principle is the so-called *Pauli exclusion principle*: **The Pauli Exclusion Principle** *No two electrons can occupy the same state.*

Overall wave functions that satisfy the Pauli principle are often written as *Slater Determinants*.

**The Slater Determinant**

We turn again our attention to the helium atom. It was assumed that the two electrons were both in the $1s$ state. This fulfills the Pauli exclusion principle as the two electrons in the ground state have different intrinsic spin. However, the wave-functions we used above were not antisymmetric with respect to interchange of the different electrons. This is not totally true as we only included the spatial part of the wave function. For the helium ground state the spatial part of the wave function is symmetric and the spin part is antisymmetric. The product is therefore antisymmetric as well. The Slater-determinant consists of single-particle *spin-orbital*s; joint spin-space states of the electrons

$$\Psi_{1s}^{\uparrow}(1) = \Psi_{1s}(1) \uparrow (1),$$

and similarly

$$\Psi_{1s}^{\downarrow}(2) = \Psi_{1s}(2) \downarrow (2).$$

Here the two spin functions are given by

$$\uparrow (I) = \begin{cases} 1 & \text{if } m_s(I) = \frac{1}{2} \\ 0 & \text{if } m_s(I) = -\frac{1}{2} \end{cases},$$

and

$$\downarrow (I) = \begin{cases} 0 & \text{if } m_s(I) = \frac{1}{2} \\ 1 & \text{,if } m_s(I) = -\frac{1}{2} \end{cases}, \tag{11.115}$$

with $I = 1, 2$. The ground state can then be expressed by the following determinant

$$\Psi(1, 2) = \frac{1}{\sqrt{(2)}} \begin{vmatrix} \Psi_{1s}(1) \uparrow (1) & \Psi_{1s}(2) \uparrow (2) \\ \Psi_{1s}(1) \downarrow (1) & \Psi_{1s}(2) \downarrow (2) \end{vmatrix}.$$

This is an example of a *Slater determinant*. This determinant is antisymmetric since particle interchange is identical to an interchange of the two columns. For the ground state the spatial wave-function is symmetric. Therefore we simply get

$$\Psi(1, 2) = \Psi_{1s}(1)\Psi_{1s}(2) \left[\uparrow (1) \downarrow (2) - \uparrow (2) \downarrow (1)\right].$$

The spin part of the wave-function is here anti-symmetric. This has no effect when calculating physical observables because the sign of the wave-function is squared in all expectation values.

The general form of a Slater determinant composed of $n$ orthonormal orbitals $\{\phi_i\}$ is

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix}. \tag{11.116}$$

The introduction of the Slater determinant is very important for treatment of many-body systems, and is the principal building block for various variational wave functions. As long as we express the wave-function in terms of either one Slater determinant or a linear combination of several Slater determinants, the Pauli principle is satisfied. When constructing many-electron wave functions this picture provides an easy way to include many of the physical features. One problem with the Slater matrix is that it is computationally demanding. Limiting the number of calculations will be one of the most important issues concerning the implementation of the Slater determinant. This will be discussed in detail in chapter 18. Chapters 18 and 20 are dedicated to the discussion of advanced many-body methods for solving Schrödinger's equation.

### 11.5.8   Physics Projects: Ground state of He, Be and Ne

The task here is to perform a variational Monte Carlo calculation of the ground state energy of the atoms He, Be and Ne.

a) Here we limit the attention to He and employ the following trial wave function

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right), \tag{11.117}$$

with $\alpha$ and $\beta$ as variational parameters. The interaction is

$$V(r_1, r_2) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \tag{11.118}$$

yielding the following hamiltonian for the helium atom

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}. \tag{11.119}$$

Your task is to perform a Variational Monte Carlo calculation using the Metropolis algorithm to compute the integral

$$\langle H \rangle = \frac{\int d\mathbf{R} \psi_T^*(\mathbf{R}) H(\mathbf{R}) \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^*(\mathbf{R}) \psi_T(\mathbf{R})}. \tag{11.120}$$

b) We turn the attention to the ground state energy for the Be atom. In this case the trial wave function is given by

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \phi_3(\mathbf{r_3}), \phi_4(\mathbf{r_4})\right) \prod_{i<j}^{4} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \tag{11.121}$$

where the $Det$ is a Slater determinant and the single-particle wave functions are the hydrogen wave functions for the $1s$ and $2s$ orbitals. Their form within the variational ansatz is given by

$$\phi_{1s}(\mathbf{r_i}) = e^{-\alpha r_i}, \tag{11.122}$$

and

$$\phi_{2s}(\mathbf{r_i}) = (2 - \alpha r_i) e^{-\alpha r_i/2}. \tag{11.123}$$

Set up the expression for the Slater determinant and perform a variational calculation with $\alpha$ and $\beta$ as variational parameters.

c) Now we compute the ground state energy for the Neon atom following the same steps as in a) and b) but with the trial wave function

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_{10}}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \ldots, \phi_{10}(\mathbf{r_{10}})\right) \prod_{i<j}^{10} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \tag{11.124}$$

Set up the expression for the Slater determinant and repeat steps a) and b) including the Slater determinant. The variational parameters are still $\alpha$ and $\beta$ only. In this case you need to include the $2p$ wave function as well. It is given as

$$\phi_{2p}(\mathbf{r_i}) = \alpha \mathbf{r_i} e^{-\alpha r_i/2}. \tag{11.125}$$

Observe that $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2 + r_{i_z}^2}$.

## 11.6 Simulation of molecular systems

### 11.6.1 The $H_2^+$ molecule

The $H_2^+$ molecule consists of two protons and one electron, with binding energy $E_B = -2.8$ eV and an equilibrium position $r_0 = 0.106$ nm between the two protons.

We define our system through the following variables. The electron is at a distance $\mathbf{r}$ from a chosen origo, one of the protons is at the distance $-\mathbf{R}/2$ while the other one is placed at $\mathbf{R}/2$ from origo, resulting in a distance to the electron of $\mathbf{r} - \mathbf{R}/2$ and $\mathbf{r} + \mathbf{R}/2$, respectively.

In our solution of Schrödinger's equation for this system we are going to neglect the kinetic energies of the protons, since they are 2000 times heavier than the electron. We assume thus that their velocities are negligible compared to the velocity of the electron. In addition we omit contributions from nuclear forces, since they act at distances of several orders of magnitude smaller than the equilibrium position.

We can then write Schrödinger's equation as follows

$$\left\{ -\frac{\hbar^2 \nabla_r^2}{2m_e} - \frac{ke^2}{|\mathbf{r} - \mathbf{R}/2|} - \frac{ke^2}{|\mathbf{r} + \mathbf{R}/2|} + \frac{ke^2}{R} \right\} \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}), \qquad (11.126)$$

where the first term is the kinetic energy of the electron, the second term is the potential energy the electron feels from the proton at $-\mathbf{R}/2$ while the third term arises from the potential energy contribution from the proton at $\mathbf{R}/2$. The last term arises due to the repulsion between the two protons. In Fig. 11.4 we show a plot of the potential energy

$$V(\mathbf{r}, \mathbf{R}) = -\frac{ke^2}{|\mathbf{r} - \mathbf{R}/2|} - \frac{ke^2}{|\mathbf{r} + \mathbf{R}/2|} + \frac{ke^2}{R}. \qquad (11.127)$$

Here we have fixed $|\mathbf{R}| = 2a_0$ og $|\mathbf{R}| = 8a_0$, being 2 and 8 Bohr radii, respectively. Note that in the region between $|\mathbf{r}| = -|\mathbf{R}|/2$ (units are $r/a_0$ in this figure, with $a_0 = 0.0529$) and $|\mathbf{r}| = |\mathbf{R}|/2$ the electron can tunnel through the potential barrier. Recall that $-\mathbf{R}/2$ og $\mathbf{R}/2$ correspond to the positions of the two protons. We note also that if $R$ is increased, the potential becomes less attractive. This has consequences for the binding energy of the molecule. The binding energy decreases as the distance $\mathbf{R}$ increases. Since the potential is symmetric with respect to the interchange of $\mathbf{R} \to -\mathbf{R}$ and $\mathbf{r} \to -\mathbf{r}$ it
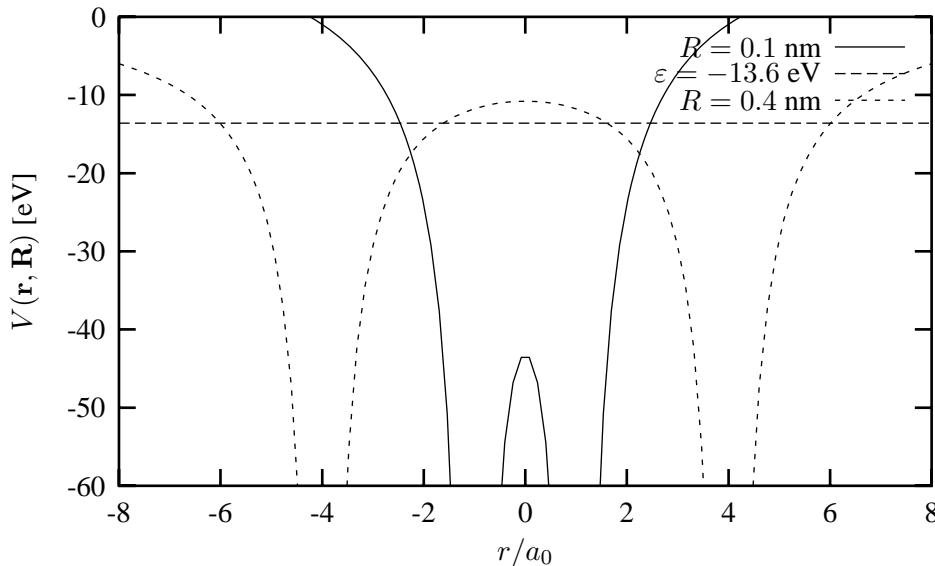


Figure 11.4: Plot of $V(r, R)$ for $|\mathbf{R}|$=0.1 and 0.4 nm. Units along the $x$-axis are $r/a_0$ . The straight line is the binding energy of the hydrogen atom, $\varepsilon = -13.6$ eV.

means that the probability for the electron to move from one proton to the other must be equal in both directions. We can say that the electron shares it's time between both protons.

With this caveat, we can now construct a model for simulating this molecule. Since we have only one elctron, we could assume that in the limit $R \to \infty$, i.e., when the distance between the two protons is

large, the electron is essentially bound to only one of the protons. This should correspond to a hydrogen atom. As a trial wave function, we could therefore use the electronic wave function for the ground state of hydrogen, namely

$$\psi_{100}(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}. \tag{11.128}$$

Since we do not know exactly where the electron is, we have to allow for the possibility that the electron can be coupled to one of the two protons. This form includes the 'cusp'-condition discussed in the previous section. We define thence two hydrogen wave functions

$$\psi_1(\mathbf{r}, \mathbf{R}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-|\mathbf{r} - \mathbf{R}/2|/a_0}, \tag{11.129}$$

and

$$\psi_2(\mathbf{r}, \mathbf{R}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-|\mathbf{r} + \mathbf{R}/2|/a_0}. \tag{11.130}$$

Based on these two wave functions, which represent where the electron can be, we attempt at the following linear combination

$$\psi_{\pm}(\mathbf{r}, \mathbf{R}) = C_{\pm}\left(\psi_1(\mathbf{r}, \mathbf{R}) \pm \psi_2(\mathbf{r}, \mathbf{R})\right), \tag{11.131}$$

with $C_{\pm}$ a constant. Based on this discussion, we add a second electron in order to simulate the $H_2$ molecule. That is the topic for the next project.

### 11.6.2  Physics Project: the $H_2$ molecule

The $H_2$ molecule consists of two protons and two electrons with a ground state energy $E = -1.17460$ a.u. and equilibrium distance between the two hydrogen atoms of $r_0 = 1.40$ Bohr radii. We define our systems using the following variables. Origo is chosen to be halfway between the two protons. The distance from proton 1 is defined as $-\mathbf{R}/2$ whereas proton 2 has a distance $\mathbf{R}/2$. Calculations are performed for fixed distances $\mathbf{R}$ between the two protons.

Electron 1 has a distance $r_1$ from the chose origo, while electron 2 has a distance $r_2$. The kinetic energy operator becomes then

$$-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2}. \tag{11.132}$$

The distance between the two electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The repulsion between the two electrons results in a potential energy term given by

$$+\frac{1}{r_{12}}. \tag{11.133}$$

In a similar way we obtain a repulsive contribution from the interaction between the two protons given by

$$+\frac{1}{|\mathbf{R}|}, \tag{11.134}$$

where $\mathbf{R}$ is the distance between the two protons. To obtain the final potential energy we need to include the attraction the electrons feel from the protons. To model this, we need to define the distance between the electrons and the two protons. If we model this along a chosen $z$-akse with electron 1 placed at a distance $\mathbf{r}_1$ from a chose origo, one proton at $-\mathbf{R}/2$ and the other at $\mathbf{R}/2$, the distance from proton 1 to electron 1 becomes

$$\mathbf{r}_{1p1} = \mathbf{r}_1 + \mathbf{R}/2, \tag{11.135}$$

and

$$\mathbf{r}_{1p2} = \mathbf{r}_1 - \mathbf{R}/2, \tag{11.136}$$

from proton 2. Similarly, for electron 2 we obtain

$$\mathbf{r}_{2p1} = \mathbf{r}_2 + \mathbf{R}/2, \tag{11.137}$$

and

$$\mathbf{r}_{2p2} = \mathbf{r}_2 - \mathbf{R}/2. \tag{11.138}$$

These four distances define the attractive contributions to the potential energy

$$-\frac{1}{r_{1p1}} - \frac{1}{r_{1p2}} - \frac{1}{r_{2p1}} - \frac{1}{r_{2p2}}. \tag{11.139}$$

We can then write the total Hamiltonian as

$$\widehat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_{1p1}} - \frac{1}{r_{1p2}} - \frac{1}{r_{2p1}} - \frac{1}{r_{2p2}} + \frac{1}{r_{12}} + \frac{1}{|\mathbf{R}|}, \tag{11.140}$$

and if we choose $\mathbf{R} = 0$ we obtain the helium atom.

In this project we will use a trial wave function of the form

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{R}) = \psi(\mathbf{r}_1, \mathbf{R})\psi(\mathbf{r}_2, \mathbf{R}) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right), \tag{11.141}$$

with the following trial wave function

$$\psi(\mathbf{r}_1, \mathbf{R}) = \left(\exp\left(-\alpha r_{1p1}\right) + \exp\left(-\alpha r_{1p2}\right)\right), \tag{11.142}$$

for electron 1 and

$$\psi(\mathbf{r}_2, \mathbf{R}) = \left(\exp\left(-\alpha r_{2p1}\right) + \exp\left(-\alpha r_{2p2}\right)\right). \tag{11.143}$$

The variational parameters are $\alpha$ and $\beta$.

One can show that in the limit where all distances approach zero that

$$\alpha = 1 + \exp\left(-R/\alpha\right), \tag{11.144}$$

resulting in $\beta$ kas the only variational parameter. The last equation is a non-linear equation which we can solve with for example Newton's method discussed in chapter 5.

a) Find the local energy as function of $R$.

b) Set up and algorithm and write a program which computes the expectation value of $\langle\widehat{\mathbf{H}}\rangle$ using the variational Monte Carlo method with a brute force Metropolis sampling. For each inter-proton distance $R$ you must find the parameter $\beta$ which minimizes the energy. Plot the corresponding energy as function of the distance $R$ between the protons.

c) Use thereafter the optimal parameter sets to compute the average distance $\langle r_{12} \rangle$ between the electrons where the energy as function of $R$ exhibits its minimum. Comment your results.

d) We modify now the approximation for the wave functions of electrons 1 and 2 by subtracting the two terms instead of adding up, viz

$$\psi(\mathbf{r}_1, \mathbf{R}) = \left(\exp\left(-\alpha r_{1p1}\right) - \exp\left(-\alpha r_{1p2}\right)\right), \qquad (11.145)$$

for electron 1

$$\psi(\mathbf{r}_2, \mathbf{R}) = \left(\exp\left(-\alpha r_{2p1}\right) - \exp\left(-\alpha r_{2p2}\right)\right), \qquad (11.146)$$

for electron 2. Mathematically, this approach is equally viable as the previous one. Repeat your calculations from point b) and see if you can obtain an energy minimum as function of $R$. Comment your results.