

Monte Carlo Variational Method and the Ground-State of Helium

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Abstract

The Variational Monte Carlo method is used to evaluate the energy of the ground state of the helium atom. Trial wave functions depending on the variational parameters are constructed for this purpose. Energies as well as standard deviations are plotted versus the variational parameters. The experimental data are presented for comparison.

1. Introduction

The term Monte Carlo refers to group of methods in which physical or mathematical problems are simulated by using random numbers. Quantum Monte Carlo (QMC) techniques provide a practical method for solving the many-body Schrödinger equation.

It is commonly used in physics to simulate complex systems that are of random nature in statistical physics [1]. There are many versions of the QMC methods which are used to solve the Schrödinger equation for the ground state energy of a quantum particle. Among them are the diffusion Monte Carlo method [2], which is used to solve the time-dependent Schrödinger equation. Another method is the fixed-phase Monte Carlo method [3] which is used for wave equations that consider a magnetic field.

The simplest of QMC methods is the variational Monte Carlo (VMC) technique which has become a powerful tool in Quantum Chemistry calculations [4]. It is based on evaluating a high-dimensional integral by sampling the integrand using a set of randomly generated points. It can be shown that the integral converges faster by using VMC technique than more conventional techniques based

on sampling the integrand on a regular grid for problems involving more than a few dimensions. Moreover, the statistical error in the estimate of the integral decreases and the square root of the number of points is sampled, irrespective of the dimensionality of the problem. The major advantage of this method is the possibility to freely choose the analytical form of the trial wave function which may contain highly sophisticated term, in such a way that electron correlation is explicitly taken into account. This is an important valid feature for QMC methods, which are therefore extremely useful to study physical cases where the electron correlation plays a crucial role.

2. Variational Monte Carlo Calculations

The Variational Monte Carlo method [5] is based on a combination of two ideas namely the variational principle and Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm. It is used to compute quantum expectation values of an operator. In particular, if the operator is the Hamiltonian, its expectation value is the variational energy E_{VMC} .

$$E_{VMC} = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T d\mathbf{R}} \quad (2.1)$$

where, Ψ_T is a trial wave function and $\mathbf{R}$ is the $3N$ dimensional vector of electron coordinates. According to the Variational principal, the expectation value of the Hamiltonian is an upper bound on the exact ground state energy E_0 , that is, $E_v \geq E_0$.

To evaluate the integral in Eq. (2.1) we construct first a trial wave function $\Psi_T^\alpha(\mathbf{R})$ depending on variational parameters $a = (a_1, a_2, \dots, a_N)$ and then varies the parameters to obtain the minimum energy.

Variational Monte Carlo calculations determine E_{VMC} by writing it as

$$E_{VMC} = \int P(\mathbf{R}) E_L(\mathbf{R}) d\mathbf{R}, \quad (2.2)$$

$$\text{where } P(\mathbf{R}) = \frac{|\Psi_T(\mathbf{R})|^2}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}}$$

is positive everywhere and interpreted as a probability distribution and

$$E_L = \frac{\hat{H} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \text{ is the local energy}$$

function. The value of $\langle E_L \rangle$ is evaluated using a series of points, R_{ij} proportional to $P(\mathbf{R})$. At each of these

points the "Local energy", $\frac{\hat{H} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}$,

is evaluated. After a sufficient number of evaluations the VMC estimate of E_{VMC} will be:

$$E_{VMC} = \lim_{N \rightarrow \infty} \lim_{M \rightarrow \infty} \frac{1}{N} \frac{1}{M} \sum_{j=1}^N \sum_{i=1}^M E_L(R_{hj}) \quad (2.3)$$

where M is the ensemble size of random numbers $\{R_1, R_2, \dots, R_M\}$ and N is the number of ensembles. These ensembles so generated must reflect

the distribution function itself. A given ensemble is chosen according to the Metropolis algorithm [6]. This method uses an acceptance and rejection process of random numbers that have a frequency probability distribution like Ψ^2 . The acceptance and rejection method is due to the work of von Neuman [7] and is performed by obtaining a random number from the probability distribution, $P(\mathbf{R})$, then testing its value to determine if it will be acceptable for use in approximation of the local energy. Random numbers may be generated using a variety of methods [8,9]. Finally, it is important to calculate the standard deviation of the energy,

$$s = \sqrt{\frac{\langle E_{VMC}^2 \rangle - \langle E_{VMC} \rangle^2}{M(N-1)}}$$

3. The Statement of the Problem

For nucleus with charge Z and infinite mass the non-relativistic Hamiltonian in atomic units (a. u) reads [10]:

$$H = T + V = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V \quad (3.1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the relative coordinates of the two electrons with respect to the nucleus. The potential V is defined as

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}},$$

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

In Hylleraas coordinates the above Hamiltonian can be written as:

$$\begin{aligned} H = & -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right. \\ & + 2\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12} \frac{\partial^2}{\partial r_1 r_{12}} \left. \right) - \frac{1}{2} \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_{12}^2} \right. \\ & + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - 2\hat{\mathbf{r}}_2 \cdot \hat{\mathbf{r}}_{12} \frac{\partial^2}{\partial r_2 r_{12}} \left. \right) + V(r_1, r_2, r_{12}) \end{aligned}$$

where $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2$ and $\hat{\mathbf{r}}_{12}$ denotes the unit vectors of the corresponding distance. In writing Eq. (3.1) we have taken into account the Coulomb interactions between the particles, but have neglected small corrections arising from spin-orbit and spin-spin interactions.

The electronic eigenvalue is determined from the Schrödinger equation:

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (3.2)$$

where, $y(\mathbf{r}_1, \mathbf{r}_2)$ is the electronic wave function. Our goal, now, is to solve the six-dimensional partial differential eigenvalues Eq. (3.2) for the lowest eigenvalue.

4. The Trial Wave Function

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

$$P(\mathbf{R}) = \frac{|\Psi_T(\mathbf{R})|^2}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}}$$

generated by the trial wave function. The trial wave function must approximate an exact eigen state in order that accurate results are to be obtained. Improved trial wave function also improve the importance sampling, reducing the cost of obtaining a certain statistical accuracy. A good trial wave function should exhibit much of the same features as does the exact wave function. One possible guideline in choosing the trial wave function is the use of the constraints about the behavior of the wave function when the distance between one electron and the nucleus or two electron approaches zero. These constraints are called “cusp conditions” and are related to the derivative of the wave function. Usually the correlated wave function, y , used in VMC is built as the product

of a symmetric correlation factor, f , which includes the dynamic correlation among the electrons, times a model wave function, j , that provides the correct properties of the exact wave function such as spin and the angular momentum of the atom, and is antisymmetric in the electronic coordinates $y = j f$.

With this type of wave function, and by using different correlation factor, the atoms He to Kr have been extensively studied [11-14]. The aim of this work is to extend this methodology to obtain ground state, and similarly excited states, of the helium atom. This will be done within the context of the accurate Born-Oppenheimer approximation, which is based on the notion that the heavy nucleus move slowly compared to the much lighter electrons.

5. The ground state of the helium atom

For the ground state, the trial wave function used in this work is given by

$$y(\mathbf{r}_1, \mathbf{r}_2) = j(\mathbf{r}_1)j(\mathbf{r}_2)f(\mathbf{r}_{12}) \quad (5.1)$$

where $j(\mathbf{r}_i)$ is the single-particle wave function for particle i , and $f(\mathbf{r}_{12})$ account for more complicated two-body correlations. For the helium atom, we have placed both electrons in the lowest hydrogenic orbit 1s to calculate the ground state. A simple choice for $j(\mathbf{r}_i)$ is [15]:

$$j(\mathbf{r}_i) = \exp(\mathbf{r}_i / a), \quad (5.2)$$

with the variational parameter a to be determined. The final factor in the trial wave function, f , expresses the correlation between the two electrons due to their coulomb repulsion. That is, we expect f to be small when r_{12} is small and to approach a large constant value as the electrons become well separated. A convenient and reasonable choice is

Table-1 Energy of the ground state in (a. u.) units obtained in frame of (VMC) method, together with the standard deviation and the experimental data for comparison.

	Calculated	Experimental
E_{VMC}	-2.8689	2.9037
Standard deviation	0.0024	NA

$$f(r) = \exp\left[\frac{r}{a(1+br)}\right] \quad (5.3)$$

where a, b are additional positive variational parameters. The variational parameter b controls the distance over which the trial wave function heals to its uncorrelated value as the two electrons separate. Using the cusp conditions [16] we can easily verify that the variational parameters a, b satisfy the transcendental equations :

$$a = \frac{\hbar^2}{2me^2} \quad \text{and} \quad a = \frac{2\hbar^2}{me^2}. \quad \text{Thus } b \text{ is}$$

the only variational parameter at our disposal. With the trial wave function specified by Eq. (6), explicit expression can be worked out for the local energy $E_L(\mathbf{R})$ in terms of the values and derivatives of j, f . The Monte Carlo process described here has been employed for the ground state of the helium atom.

Figure-1 shows the variation of the ground state energy with respect to the variational parameter b .

In Fig-2 we present the variations of the standard deviation with respect to the variational parameter b .

The variational parameters appear in the trial wave function for the 2^1S state are taken as $t_1 = .865$, $t_2 = .522$ and $C = 1.2$.

A Variational Monte Carlo (VMC) has been used to obtain numerical ground state energy. Figures-1,2 show

that minimum in energy is accompanied with a minimum in the standard deviation. The numerical results are in good agreement with the experimental results [17].

Table-1 indicates that the energy minima are in agreement with the experimental data.

Calculations of the radial wave functions and the excited states of the helium atom by using the same technique of the variational Monte Carlo method gave results in good agreement with the corresponding experimental findings [18].

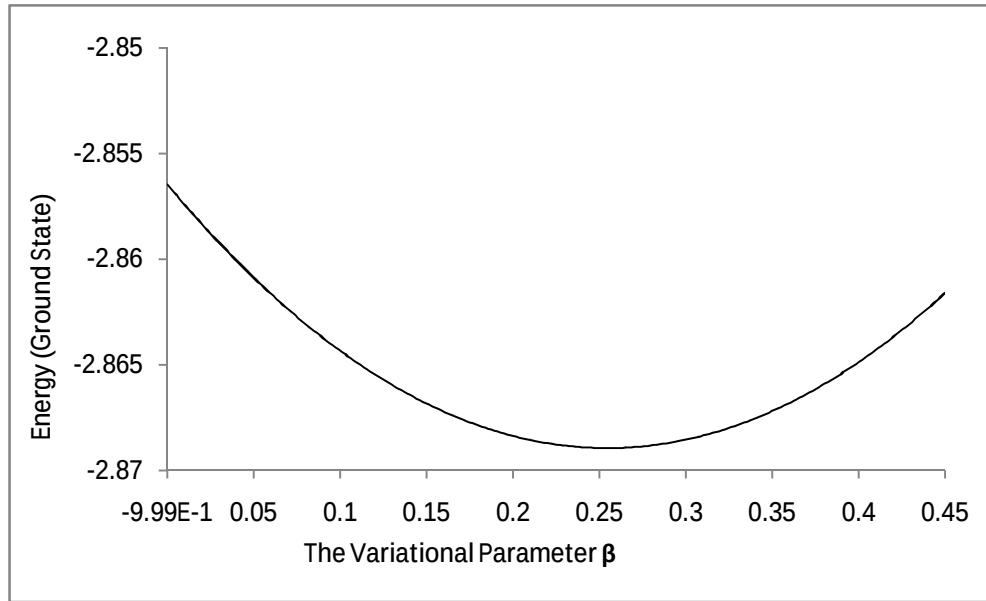


Fig-1 The Ground state energy of helium as function of the variational parameter b .

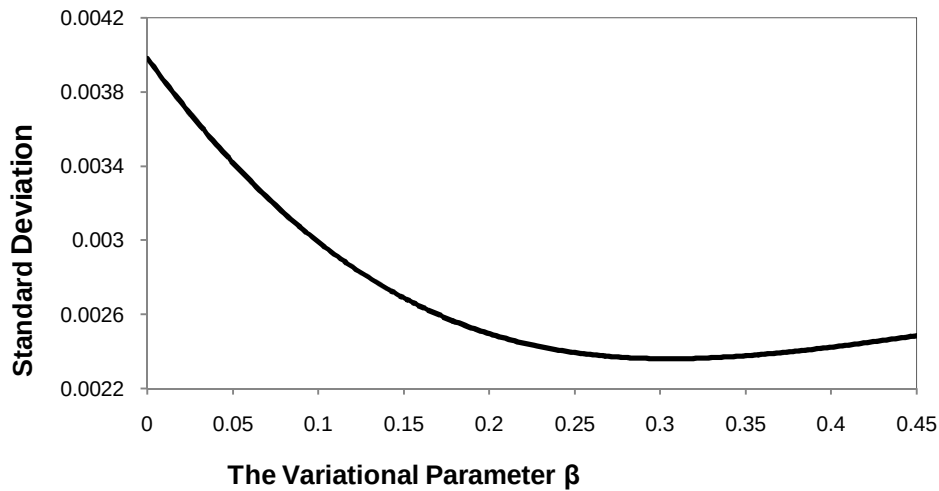


Fig-2 The standard deviation versus the variational parameter b .

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