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. The relativistic effect is taken into account. 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.

Keywords: Variational methods, Monte Carlo methods, Atomic structure. Ground state of the helium atom.

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 [1-4].

It is commonly used in physics to simulate complex systems that are of random nature in statistical physics. 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, there are the diffusion Monte Carlo method [5], Green's function Monte Carlo [6] and fixed-phase Monte Carlo method [7] 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 [8-10]. It is used to 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 as 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 terms, 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 Mont Carlo method [11] is based on a combination of two ideas namely the variational principal 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 varitional energy E_{VMC},

$$E_{VMC} = \frac{\int \Psi_T^*(R)\hat{H}\Psi_T(R)dR}{\int \Psi_T^*(R)\Psi_T(R)dR} \qquad (2.1)$$

where, $\Psi_T(R)$ is a trial wave function and "$\boldsymbol{R}$" is the $3N$ dimensional vector of electron coordinates. According to the Varitional principal, the expectation value of the Hamiltonian is an upper bound to the exact ground state energy E_0, that is, $E_{VMC} \geq E_0$.

To evaluate the integral in Eq. (2.1) we construct first a trial wave function $\Psi_T^{\alpha}(\boldsymbol{R})$ depending on variational parameter $\alpha = (\alpha_1, \alpha_2, \ldots\ldots\ldots\ldots \alpha_N)$ and then varies the parameters to obtain the minimum energy.

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

$$E_{VMC} = \int P(\boldsymbol{R})E_L(\boldsymbol{R})d(\boldsymbol{R}) \qquad (2.2)$$

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

is positive everywhere and interpreted as a probability distribution and $E_L = \frac{\hat{H}\,\Psi_T(\boldsymbol{R})}{\Psi_T(\boldsymbol{R})}$ is the local energy function. The value of E_L is evaluated using a series of points, R_{ij} proportional to $P(\boldsymbol{R})$. At each of these points the "Local energy ",$\frac{\hat{H}\,\Psi_T(\boldsymbol{R})}{\Psi_T(\boldsymbol{R})}$, is evaluated. After a sufficient number of evaluations the VMC estimate of E_{VMC} will be:

$$E_{VMC} = \langle E_L \rangle = \lim_{N\to\infty}\lim_{M\to\infty} \frac{1}{N}\frac{1}{M}\sum_{j=1}^{N}\sum_{i=1}^{M} E_L \qquad (2.3)$$

where M is the ensemble size of random numbers $\{\boldsymbol{R}_1, \boldsymbol{R}_1, \ldots\ldots\ldots, \boldsymbol{R}_M\}$ 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 [12]. 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 performed by obtaining a random number from the probability distribution, $P(\boldsymbol{R})$, 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 [13]. Finally, it is important to calculate the standard deviation of the energy

$$\sigma = \sqrt{\frac{\langle E_L^2 \rangle - \langle E_L \rangle^2}{M(N-1)}}$$

3. The Statement of the Problem

For nucleus with charge Z and infinite mass the Hamiltonian in atomic units (a. u) reads [14]:

$$H = H_0 + H_1 \qquad (3.1)$$

where,

$$H_0 = \frac{-1}{2}\sum_{i=1,2}\left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i}\right) - \sum_{i=1,2}\left(\frac{Ze^2}{r_i}\right) + \frac{e^2}{r_{12}},$$

and

$$H_1 = -\frac{1}{8c^2}(p_1^4 + p_2^4).$$

Here $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$ denote the relative coordinates of the two electrons with respect to the nucleus and $r_{12} = |r_1 - r_2|$.

In the Hamiltonian given by Eq. (3.1) the term H_0 represents the Coulomb interactions between the particles whereas the term H_1 is due to the relativistic correction to the kinetic energy and it represents the dependence of the mass of the electron on the velocity.

The electronic eigenvalue is determined from the Schrödinger equation:

$$H\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}) = E\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}), \quad (3.2)$$

where, $\Psi(\boldsymbol{r_1}, \boldsymbol{r_2})$ is the electronic wave function. Our goal, now, is to solve the six-dimensional partial differential equation (3.2) for the lowest energy 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

$$P(\boldsymbol{R}) = \frac{|\Psi_T(\boldsymbol{R})|^2}{\int |\Psi_T(\boldsymbol{R})|^2 dR}$$

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 function also improves the importance sampling and 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, Ψ, 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, φ, that provides the correct properties of the exact wave function such as spin and the angular momentum of the atom, and is anti symmetric in the electronic coordinates $\Psi = \varphi f$.

With this type of wave function, and by using different correlation factor, the atoms He to Kr have been extensively studied [15-18]. The aim of this work is to extend this methodology to obtain ground state of 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

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r_2}) = \varphi(\boldsymbol{r_1})\varphi(\boldsymbol{r_2})f(\boldsymbol{r_{12}}), \quad (5.1)$$

where $\varphi(\boldsymbol{r_i})$ is the single-particle wave function for particle i, and $f(\boldsymbol{r_{12}})$ 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 $\varphi(\boldsymbol{r_i})$ is [19]:

$$\varphi(\boldsymbol{r_i}) = exp(\boldsymbol{r_i}/a), \quad (5.2)$$

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 $\boldsymbol{r_{12}}$ is small and to approach a large constant value as the electrons become well separated. A convenient and reasonable choice is

$$f(\boldsymbol{r}) = ex\,p\left[\frac{r}{\alpha(1+\beta r)}\right], \quad (5.3)$$

where α and β are additional positive variational parameters. The variational parameter β controls the distance over which the trial wave function heals to its uncorrelated value as the two electrons separate. Using the cusp conditions [20] we can easy verify that the variational parameters a, α satisfy the transcendental equations:

$$a = \frac{\hbar^2}{2m_e e^2} \quad \text{and} \quad \alpha = \frac{2\hbar^2}{m_e e^2}.$$

Thus, b is the only variational parameter at our disposal. With the trial wave function specified by Eq. (5.1), explicit expression can be worked out for the local energy $E_L(\boldsymbol{R})$ in terms of the values and derivatives of φ and f.

6. Results and Conclusion

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 β.

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

Fig. 3 shows the trial wave function for the ground state as a function of r_1, r_2.

The calculated value of the ground state of the helium atom is given in Table-1, together with the standard deviation. The corresponding experimental energy of the helium atom is also given in this table for comparison. The experimental standard deviation is not allowed.

Table-1 Energy of the ground state of helium in (a. u.) units together with the standard deviation and the experimental data

	Calculated	Experiment
E_{VMC}	-2.898324	-2.9037
Standard deviation	0.0032	NA

It is clear that the obtained numerical result is in good agreement with the corresponding experimental value [21].

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 [22].

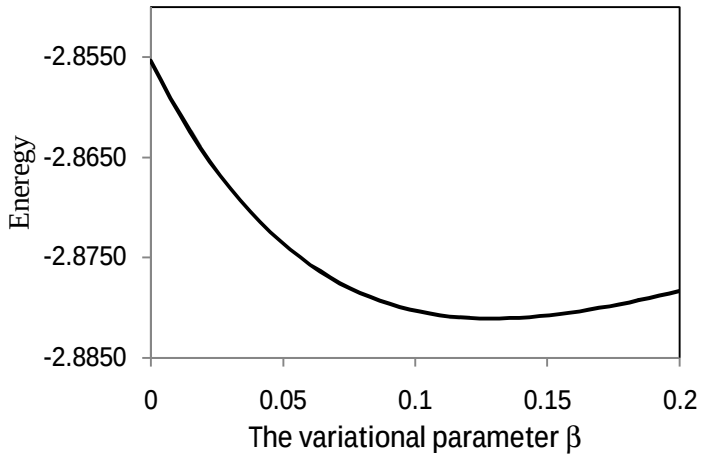

Fig-1 The Ground State Energy versus the variational parameter b .

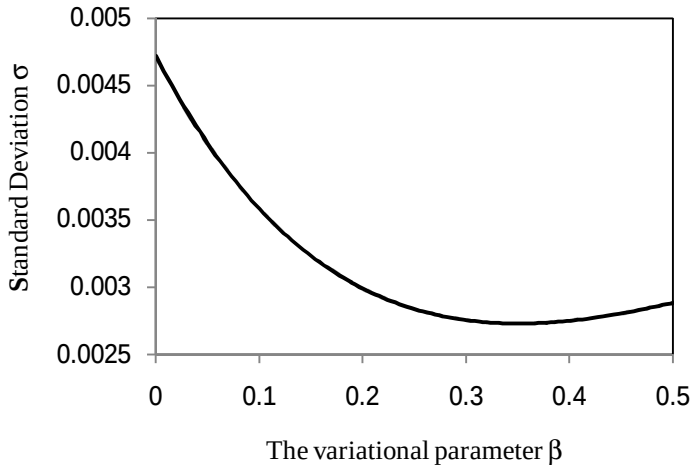

Fig-2 The standard deviation versus the variational parameter b .

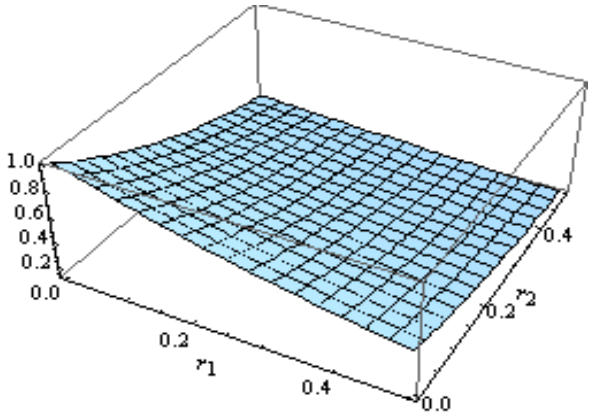

Fig. 3 The wave function for the ground state as a function of r_1, r_2.

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