Calculate the Ground State Energy of Hydro Helium Cation (2+) (He++H)

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Abstract

The purpose of this work is to calculate the ground energy of hydro helium cation (2+) by using the Quantum Monte Carlo method. Using the Diffusion Quantum Monte method, we have to calculate the ground energy of hydro helium Cation (2+). our calculation is based on Slater-Jastrow form. We have developed python code and run this on high-performing computers. A very large number of iterations is required to find the best result. We have used the 'Hartree unit' in the calculation of electronic wave functions for atoms and molecules.

Keywords: Hydro helium cation; Quantum Monte Carlo; Slater-Jastrow.

1. Introduction

When we have a single electron, we use Schrodinger Equation. But, for a system containing more than one electron, we have to go through some approximate method to solve the equation. Different approximation method is used to solve approximately many-body problems. Initially, one of the basic concepts and approximation was introduced in 1927 by Max Born and J.Robert Oppenheimer to separate the electronic and nuclear wave function with neglecting of electron-nuclear interaction and obtained the wave function and energy by solving time independent Schròdinger Equation. First quantum Mechanical Understanding of chemically bounded system by Heitler and London in 1927. they calculate the binding energy and inter nuclear separation of hydrogen molecules [1]. In 1928 D.R Hartree introduced a new method at that time this method is called the self -the consistent field method. By using this method he wanted to solve many-body complex problems. But this method is insufficient because of neglecting the antisymmetric behavior of wave function. This deficiency was overcome by Fock. Then this method is called the Hartree-Fock method [2]. Moreover, other approximation methods have been developed in which many-electron theory (DFT) was introduced in 1964.

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The assumption made in this is that a many electron system is reduced in a single electron problem with effective electron potential that relies on electron density. In 1942, Frosted developed high accuracy approximation in the variational Quantum Monte Carlo (QMC) method. Other types of QMC had been developed later. Like Diffusion QMC, Green function QMC, Path Integral QMC, and Auxilary -Field QMC method. QMC method gives the most accurate wavefunction including co-relation terms of electron and finds energies for small and large molecules as well as for liquid, solids, and clusters [3].

1.1 Purpose of Study

We want to calculate ground state energy of hydro helium cation by using simulation of Diffusion of Quantum Montee Carlo (DMC). As the number of electrons increases, systems are going to many problems in which interaction terms are increased. Because, every electron interacts with the nucleus, proton, and electron. For many problem systems, we use different approximation methods and simulation techniques. For QMC, our result is based on the trial wave function.

1.2 Literature Review

● Calculate lattice energy for different molecular crystals using the diffusion Quantum Monte Carlo approach and compared their result with experimental results. They calculated lattice energy for three polymorphs of ice; hexagonal ice, ice II and ice III, carbon Dioxide (CO_2), Ammonia (NH_3) Naphthalene ($C_{10}H_8$) and ANthracene ($C_{14}H_{10}$) [4]

Table 1

Crystal	DMC(large supercell)	DMC (small Supercell)	Experiment
Ice I_h	59.3±0.5	59.2±0.2	58.8
Ice II	59.1±0.6	59±0.3	58.8
Ice VIII	57.3±0.6	57.4±0.1	57.4
CO_2	28.2+1.3	28.5±0.4	28.4
NH_3	37.1±0.4	51.2+0.2	50.6
C_6H_6	52.1±0.4	51.2±0.2	50.6
$C_{10}H_8$	78.8±8	78.0±0.6	79.2
$C_{14}H_{10}$	105.5±1.7	103.9±1	105.8

● Calculated the binding energies of isolated trions and biexcitons using the approach of VMC and DMC. [5]

● Studied and calculated the ground state energy of free and confined hydrogen atoms by using variational Quantum Montee Carlo (VMC). [6]

● Calculated the dielectric permittivity of suspended graphene by using the simulation technique of QMC for a set of temperatures and extrapolated to zero distance. [7]

● Calculate the Helmholtz free energy (sum of electronic energy and harmonic vibrational free energy) of TiO2 Polymorphs using Diffusion Quantum Monte Carlo (DMC) method and Density Function Theory (DFT).[8]

● Calculated the total energy of lithium Dime (Li+2 and Li-2) by using the quantum Monte Carlo(DMC) method.[9]

2. Methodology

We use the DMC method to calculate the ground energy of hydro helium cation. Our trial wave function is based on Slater-Jastrow type and used importance sampling technique to improve accuracy for the DMC method, trial wave function is based on a basic set of slater type orbitals (STOs). we have developed the QMC code for this cation and simulated it as a python programming language.

DMC Algorithm

The DMC algorithm used to calculate the ground energy is almost similar to those in reference [10][11].

I. At the start of the simulation

For time 0 to t

For walker 0 to Nwalker

For particles 0 to N particles

a. Initial walker Ni are distributed in configuration space to prepare some initial wave function

b. The reference energy Er is taken as an average potential of walker

II. At each iteration of the simulation

a. The time t is chosen by a small change.

b. The position of walker is reformed by an arbitrary variate from a gaussian distribution with mean 0 and standard deviation $\sigma = \sqrt{(\hbar\Delta\Tau/ m_n)}$

c. Reference energy is calculated from the new configuration of walkers by the function

$$Er=<V>+\alpha(1-N/Ni) \qquad (1)$$

Where $<V>$ is the average potential of all the walkers and N is the present number of walkers.

d. For every walker, a number m_n is calculated by

$$m_n=[w(x_n)+U] \quad (2)$$

U is a random number that is equally distributed from 0 to 1 and $w(x_n)$ is the weight of the walker with $x_n=1,,2,3,….$ defined as

$$w(x_n)=(\ \ \ (3)$$

If Mn=0 walker is destroyed and diffusion will be stopped this termed as the death of the particle

If Mn=1 continues with the next diffusion and particle will remain unaffected

Mn>0 continues with diffusion with the birth of particle

3. Repeat the configuration moves for several steps.

4. To calculate the ground state energy, the reference energies of alliteration are averaged.

5. Repeat until sufficient data is obtained

2.1   DMC Flow Diagram

The flow diagram of the DMC method for a computer program is shown in Figure 1.

Input

 All initial data to start the simulation which consists of The number of coordinates, particles, and iterations, the number of walkers, reference energy, Value of time step.

Initialize Replicas

 Estimate the diffusion and branching terms in the form of an N dimensional matrix and impose the limitation on the birth of a new particle to control the birth

Walk

 This performs the task of diffusion process which generates a new successive position of x for different values of n by generating the series of random numbers p_n, n=1,2,3,…. $X_0 X_1 = X_0 + \sigma p_1 X_2 = X_1 + \sigma p_2$ Where σ is the standard deviation from the mean position.

Branch

 This performs the task of the birth-death process which depends on the diffusion process and replication number m_n

Count

 This performs the task of obtaining the ground state wave function. This will start when we get a stationary state wave function. This will start when we get a stationary state and convergence in which energy values almost remain the same every time stops.

Test

To check the stationary state and convergence, if not then back to step 3 and repeat the steps.

Output

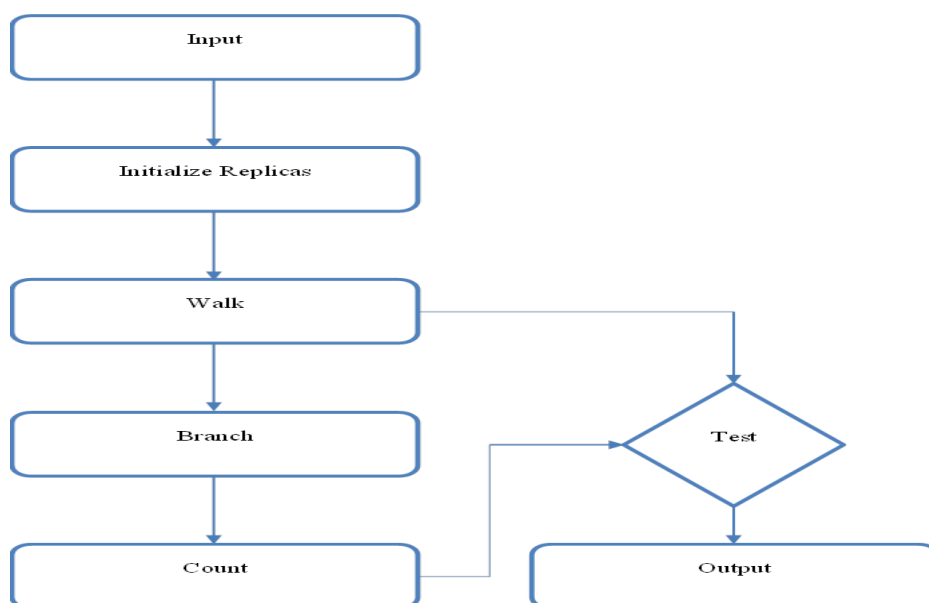Result of the simulation which is the average energy of reference energy of successive iterations.[12]

Figure 1: Flow diagram of DMC algorithm

3. Results and Discussion

Results of Hydro helium cation two (He++H) obtained from DMC simulations using Python programming language and corresponding energies are given in the tabulated form.

Table 1: An example of a table.

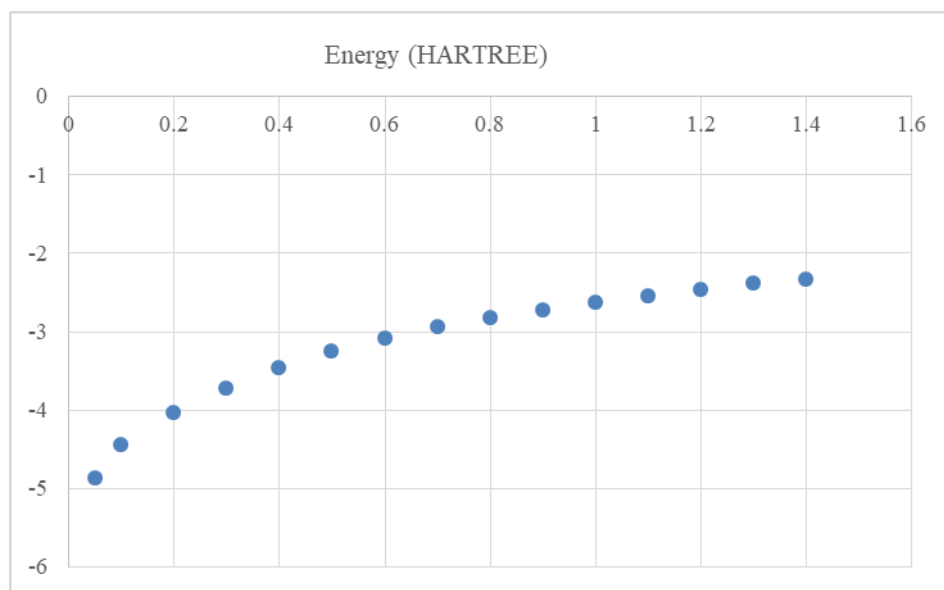| BOND LAENGTH(A)	ENERGY(HARTREE)
0.05	-4.86187
0.1	-4.44004
0.2	-4.04331
0.3	-3.7165
0.4	-3.45833
0.5	-3.24678
0.6	-3.0819
0.7	-2.93652
0.8	-2.82746
0.9	-2.72232
1	-2.63332
1.1	-2.54052
1.2	-2.46285
1.3	-2.37703
1.4	-2.34162

Figure 2: represents the potential energy curve (PEC) of the ground state of He++H using DMC simulation. As an increasing the bond length, Potential energy is increased until the equilibrium bond length is reached where the interatomic forces are zero. Equilibrium bond length for He++H is 0.4 Angston and corresponding energy is -3.45833 Hartree -94.11845 ev. At this equilibrium bond length, the attractive force between the proton of helium and the electron of the hydrogen atom is balanced by repulsive force between the proton of the helium atom and the proton of the hydrogen atom. After the equilibrium bond length, attractive force becomes dominant from repulsive force and these two atoms feel the force of attraction. As we increase the bond length more and more slope of the graph approaches to zero which means at a larger distance, the atom feels the weak force of attraction. Dissociation bond length for He++H is 1.4 Angstron. After this dissociation, both atoms are free and have no force of attraction.

4. Conclusion

We have calculated the ground state energy of ground state of hydro helium cation (2++) He^{++}H using approximation method i.e Diffusion Quantum Monte Carlo (DMC), which is one type of Quantum Monte Carlo (QMC) method. We have developed the code of simulation of QMC in python programming language. We have prepared the trial wave function of slater-jastrow type with introduction of important sampling technique to improve the accuracy of our result for DMC. The ground state energy of He^{++}H is -3.45833 Hartree or -94.11845 ev for DMC method at equilibrium wavelength of 0.4 Angston.

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