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A Quantum Monte Carlo Study of Lanthanum

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ABSTRACT

Pseudopotential calculations of the ground state energies of the Lanthanum neutral atom, first and second corresponding cations by means of the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC) methods are performed. The first and the second ionization potentials have been calculated for Lanthanum. The obtained results are satisfactory and comparable with the available experimental data. Studying the DMC energy of the La atom at different time steps, gave us a time step error of the order 0.0019 Hartree for the smallest time step, $\tau = 0.0001$ Hartree^{-1}, and -0.0104 Hartree for the largest time step, $\tau = 0.01$ Hartree^{-1}. This paper demonstrates the ability of extending the QMC method for lanthanides and obtaining highly accurate results.

Keywords: Variational Monte Carlo; Diffusion Monte Carlo; Lanthanum; Hartree; Time Step

1. Introduction

Quantum Monte Carlo (QMC) is a powerful technique by which one can perform computational electronic structure calculations with high accuracy. One of the advantages of the QMC technique is that its computational efforts scales with N^3 where N is the number of electrons in the system. This technique is favorable over other computational many-body methods. The most common QMC techniques, for atoms and molecules, are the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC). Accurate calculations for extremely light atoms using QMC methods are performed by a large number of researchers [1-4]. For the atoms heavier than Ne, the situation is more difficult. However, there have been some studies which gave satisfactory results [5-8]. For our knowledge, it is the first time Qwalk code is to be used in dealing with lanthanides.

The study of chemical systems that contain f-elements is still a particularly challenging branch of computational chemistry. The difficulties presented by f-elements in quantum mechanical calculations arise from the large magnitude of the relativistic effect and the limitation in the electron correlation treatment.

In the present work, by means of VMC and DMC methods, we have done calculations for the ground state energies of La atom and its charged cations with the hope "achieving high accuracy". In addition, we study the DMC energies at different time steps and the accurate extrapolated value of the ground state energy of La atom is derived. To allow the QMC calculations of this heavy atom, pseudopotential valence-only calculations have been performed, since the presence of the inert core electrons introduces a large fluctuation in the energies and this reduces the computational efficiency. In our study, the basic form of the wave function is the Slater-Jastrow wave function which is considered the most common and simplest one.

In the next section, we outline a brief description of the QMC methods. The results are then presented and discussed. Atomic units are used throughout this work unless otherwise indicated.

2. Computational Methods

Quantum Monte Carlo methods have been extensively described in the literatures [9-11], so we give here a brief description of the two methods, the variational and diffusion Monte Carlo methods.

The variational Monte Carlo (VMC) technique depends on the familiar variational principle for finding the ground energies of quantum mechanical systems. By the variational principle, the expectation value of the ground state energy of a many body system of N particles evalu-

ated with a trial wavefunction ψ_T is given by

$$E_T = \frac{\int \psi_T^*(R)\hat{H}\psi_T(R)}{\int \psi_T^*(R)\psi_T(R)dR} \geq E_0 \qquad (1)$$

which provide an upper bound to the exact ground state energy E_0.

The VMC method rewrites the last integral in the following form:

$$E_T = \frac{\int |\psi_T(R)|^2 \dfrac{\hat{H}\psi_T(R)}{\psi_T(R)}dR}{\int |\psi_T(R)|^2 dR} \qquad (2)$$

where $\dfrac{\hat{H}\psi_T(R)}{\psi_T(R)}$ is the local energy E_L of an electronic configuration, and $|\psi_T(R)|^2$ is the probability density for the configuration R.

The Metropolis algorithm is used to sample a series of points, R_i, from the probability density in the configuration space. At each of these points the local energy E_L is evaluated [12]. After a sufficient number of evaluations of the local energy have been made, the average is taken

$$E_{\text{VMC}} = \frac{1}{N} \times \sum_{i=1}^{N} \frac{\hat{H}\psi_T(R_i)}{\psi_T(R_i)} \qquad (3)$$

So the VMC is a simple technique in which the statistical efficiency of the results depends on the whole on the trial wavefunction. The better the wavefunction guess, the more efficient the VMC result.

The more accurate diffusion Monte Carlo (DMC) method is a stochastic projector method for solving the imaginary time many-body Schrödinger equation:

$$-\frac{\partial}{\partial \tau}\psi(R,\tau) = \left(-\frac{1}{2}\nabla^2 + V - E_T\right)\psi(R,\tau) \qquad (4)$$

where τ is the imaginary time, $\tau = it$ and E_T is the energy offset.

Importance sampling with a trial wavefunction $\psi_T(R)$ is used to improve the statistical accuracy of the simulation and this is can be achieved by multiplying Equation (4) by $\psi_T(R)$ and rearranging

$$-\frac{\partial f(R,\tau)}{\partial \tau} = -\frac{1}{2}\nabla^2 f(R,\tau)$$
$$+ \nabla \cdot \left[f(R,\tau) \cdot v_D(R)\right] + \left[E_L - E_T\right]f(R,\tau) \qquad (5)$$

where $f(R,\tau) = \psi(R,\tau)\psi_T(R)$ interpreted as a probability density and $E_L(R) = \dfrac{\hat{H}\psi_T(R)}{\psi_T(R)}$ is the local energy.

This equation can be simulated with a random walk

having diffusion, a draft, and a branching step and may be written in the integral form:

$$f(R,\tau+\Delta\tau) = \int G(R,R';\Delta\tau) \cdot f(R,\tau)dR \qquad (6)$$

where the Green's function $G(R,R';\Delta\tau)$ is a solution of the same initial Equation (5) and can be interpreted as a probability of transition from a state R to R'. It is possible to use QMC method to solve the integral in Equation (6) but the difficulty is that the precise form of $G(R,R';\Delta\tau)$ is not known. Fortunately the comparison of the Schrodinger equation with the diffusion equation gives us a clue about how one might approximate the unknown Green's function.

The evolution during the long time interval τ can be generated repeating a large number of short time steps τ. In the limit $\tau \to 0$, one can make use of the short time approximation for Green's function [13]:

$$G(R,R';\Delta\tau) \approx (2\pi\Delta\tau)^{-3N/2}$$
$$\times \exp\left[-\frac{\left(R-R'-\Delta\tau\nabla\ln|\psi_T|^2\right)^2}{2\Delta\tau}\right] \qquad (7)$$
$$\times \exp\left[-\Delta\tau\left[E_L(R')+E_L(R)-2E_T\right]/2\right]$$

But due to the fermionic nature of electrons, the wavefunction must have positive and negative parts and this is opposite to the assumed nature of ψ which is a probability distribution. So the fixed-node approximation [14] had been used to treat the fermionic antisymmetry which constrains the nodal surface of ψ to equal that of the antisymmetric trial wavefunction ψ_T.

So far, the main difference between VMC and DMC is: In VMC, a Monte Carlo method evaluates the many-dimensional integral to calculate quantum mechanical expectation values. Accuracy of the results depends crucially on the quality of the trial wavefunction, which is controlled by the functional form of the wavefunction and the optimization of the wavefunctions parameters. DMC removes most of the error in the trial wavefunction by stochastically projecting out the ground state using an integral form of the imaginary-time Schrödinger equation [15].

The form of the trial wavefunction is therefore very important; it must be both accurate and easy to evaluate. The simplest and most common wavefunction used in QMC is the Slater Jastrow wavefunction which consists of a Slater determinant multiplied by the exponential Jastrow correlation factor which includes the dynamic correlation among the electrons so it plays a crucial role in treating many-body systems. The basic functional form of the Slater-Jastrow wavefunction is

$$\psi_{sj}(R) = e^{J(R)}\sum_n c_n D_n(R) \qquad (8)$$

where $R = \{r_1, r_2, \cdots r_N\}$ denote the space coordinate of N electrons, $J(R)$ is the Jastrow factor, c_n are coefficient, and $D_n(R)$ is a Slater determinant of single particle orbitals which usually obtained from self-consistent DFT or Hartree-Fock calculations.

3. Results and Discussion

All our QMC calculations were performed by means of Qwalk code [16]. The basic form of the wavefunction is a product of Slater determinants for spin-up and spin-down electrons multiplied by a Jastrow correlation factor. The initial orbitals of the trial wavefunction are generated in GAMESS package [17] via spin-restricted open Hartree-Fock calculations. In the present work we have performed pseudopotential calculations by using the CRENBS ECP basis set [18] which eliminates 54 electrons (Xe-core) so three electrons only are treated as valence electrons in the Lanthanum atom. The usage of large pseudopotential introduces additional errors but the Monte Carlo errors are much decreased. We used a mean population of 2000 configurations. At first, all our calculations in **Table 1** were performed with a time step of $\tau = 0.0001 \; H^{-1}$.

In **Table 1**, we present pseudopotential calculations of the Hartree Fock, E_{HF}, the variational Monte Carlo, E_{VMC}, and the diffusion Monte Carlo, E_{DMC}, ground state energies for the Lanthanum atom, first and second charged cations, alongside with the fluctuations of the local energy; σ, for each method. In the last column, we measure the accuracy of the Jastrow factor by estimating η which is the percentage of the DMC correlation energy retrieved within VMC

$$\eta = \frac{E_{HF} - E_{VMC}}{E_{HF} - E_{DMC}} \times 100\% \qquad (9)$$

It is worth mentioning here that because of the lack of experimental data we didn't able to make a comparison for the estimated values of the pseudopotential ground state energies for La. To our knowledge, these are the first values for La published to date by the QMC method.

The tabulated results in **Table 1** tell us that we have performed high accuracy QMC calculations. As expected the best values for fluctuations is the diffusion Monte Carlo one, σ_{DMC}. Indeed, we obtained the results with high efficiency, η, which is greater than 90% for the La atom and its doubly charged cation, La^{+2}, and greater than 80% for its singly charged cation La^{+1}.

From the estimated DMC energies for the La atom and its cations, we calculated the first and second ionization potentials for La and compared it with the experimental values [19]. These values are shown in **Table 2**. The first ionization potential is in a good agreement with the experimental value while the error is larger for the second

ionization potential, we attributed this to the large difference in the fluctuations of the estimated diffusion Monte Carlo energies, σ_{DMC}, between the La atom and its double charged cation, La^{+2}.

Practical calculations of the DMC energy suffer from the time step error that originates from the use of finite time step in the short time approximation. To investigate the time step error in our diffusion Monte Carlo calculations for La atom, we made calculations for several values of τ to get an accurate extrapolation to zero time step. **Table 3** presents a number of calculations of the DMC energies at different steps. The values of the DMC energy of La atom as a function of the time step are plotted in **Figure 1**.

From **Figure 1**, it can be seen that the relation between

Table 1. Ground state total energies computed within Hartree Fock, E_{HF}, variational Monte Carlo, E_{VMC}, and diffusion Monte Carlo, E_{DMC}, for La, first and second charged cations. All energies are in Hartrees.

	E_{HF}	σ_{HF}	E_{VMC}	σ_{VMC}	E_{DMC}	σ_{DMC}	$\eta\%$
La	-1.2138	0.31	-1.2511	0.20	-1.2535	0.14	93.95
La^{+1}	-1.0106	0.35	-1.0374	0.19	-1.0431	0.17	82.46
La^{+2}	-0.6643	0.23	-0.6724	0.04	-0.6727	0.03	96.42

Table 2. First and second ionization potentials for the La atom computed within diffusion Monte Carlo, IP_{DMC}, compared to the available experimental values, IP_{EXP}. The ionization potentials are in (eV).

	IP_{DMC} (eV)	IP_{EXP} (eV)
First	5.72	5.58
Second	15.80	11.06

Table 3. Time step dependence of the diffusion Monte Carlo Energy, E_{DMC}, for the La atom. The last column indicates the values of the time step errors.

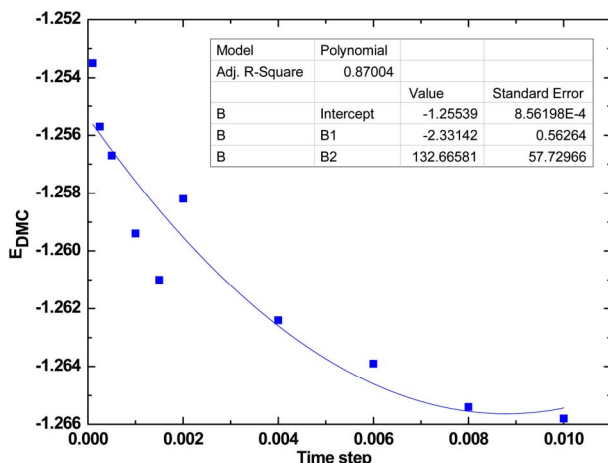| Time step $(Hartree)^{-1}$	E_{DMC} (Hartree)	Time step error (Hartree)
0.00010	-1.2535	0.0019
0.00025	-1.2557	-0.0003
0.00050	-1.2567	-0.0013
0.00100	-1.2594	-0.0040
0.00150	-1.2610	-0.0056
0.00200	-1.2582	-0.0028
0.00400	-1.2624	-0.0070
0.00600	-1.2639	-0.0085
0.00800	-1.2654	-0.0100
0.01000	-1.2658	-0.0104

Figure 1. Time step dependence of the diffusion Monte Carlo (DMC) energies for La atom.

the DMC energies and the time steps follows a polynomial relationship, this is because the presence of Jastrow factor that introduces polynomial behavior in the energy as a function of time step. We performed a polynomial extrapolation of the energies to zero time step. The extrapolated value at $\tau = 0$ for La is -1.25659 ± 0.000839 H. For the smallest time step, $\tau = 0.0001$ H^{-1}, we found a time step error of 0.0019 H and for the largest time step, $\tau = 0.01$ H^{-1}, a value of -0.0104 H has been found.

In conclusion, the small statistical errors which have been reported for La and its charged cations in this paper open the way to the possibility for performing high accuracy QMC calculations for the lanthanides.

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