Pseudopotential Calculations on Actinium and Thorium by Quantum Monte Carlo

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Abstract: **Pseudopotential calculations of the ground state energies of actinium and thorium neutral atoms and some of their corresponding cations by using variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods have been performed. The fluctuation of the local energy that has been obtained is found to be below 2 a.u. in all cases under study. We also study the dependence of DMC energy on the size of the time step for actinium. The available results are quite encouraging for these heavy atoms.**

Keywords: **Variational Monte Carlo; Diffusion Monte Carlo; Ground state energy; Actinides; Time step**

I. INTRODUCTION

Quantum Monte Carlo (QMC) method has become a powerful tool in quantum chemistry calculations. One of the advantages of the QMC technique is that its computational efforts scales with the number of electrons, N, in the system as approximately N^3 which is favorable over other computational many-body methods. Since we are interested in the ground state energy of the atoms, the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC) will be used. On one hand accurate calculations of extremely light atoms using QMC method are performed by a large number of researchers [1-3, 4]. On the other hand, for the atoms heavier than Ne, pseudopotentials and all-electron calculations are performed by many researchers, e.g., E. Buendia et al. [5] published VMC calculations for atoms up to Ar, L. Wagner and L. Mitas [6] extended their QMC calculations to compounds containing transition elements, X. P. Li et al. [7] studied the Si atom with Green's function Monte Carlo. Finally, noble gases atoms up to Xe have been also studied by A. Ma et al. [8]. Our trial is to use, for the first time, if not at least it will be one of the first trial, QMC calculations to estimate the ground state energy of actinides.

The study of chemical systems that contain f-elements is still a particularly challenging branch of computational chemistry and very limited dealing with them by QMC method. 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, we perform QMC calculations for the ground state energies for Ac and Th neutral atoms and some of their corresponding cations. To allow the QMC calculations of these heavy atoms, valence-only calculations have been performed by using the pseudopotentials since the presence of the inert core electrons introduces a large fluctuation in the energies and this reduces the computational efficiency. The basic form of the wave function that we used 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 method. The results are then presented and discussed. Atomic units are used throughout this work unless otherwise indicated.

II. COMPUTATIONAL METHODS

Quantum Monte Carlo methods have been extensively described in the literatures [9-10, 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 state 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 evaluated with a trial wavefunction ψ_T and is given by

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

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

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

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

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

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

So the VMC is a simple technique in which the statistical efficiency of the results depends on the whole of 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:

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

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

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

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

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:

$$f(R,\tau+\Delta\tau) = \int G(R,R';\Delta\tau).f(R,\tau)dR \tag{6}$$

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 Eq. (6) but the difficulty is that the precise form of $G(R,R';\Delta\tau)$ is not known. Fortunately the comparison of the Schrödinger 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]:

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

$$.\exp\left[-\Delta\tau[E_L(R')+E_L(R)-2E_T]/2\right] \tag{7}$$

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.

An important characteristic of QMC method is its ability to use arbitrary wavefunction forms. Any wavefunction of great functional complexity can be used in QMC, since analytical integration isn't being done (only calculation of the wavefunction, its gradient and Laplacian at several million points distributed in configuration space). In fact, the statistical efficiency of the method depends on the quality of the wavefunction; while in the VMC the accuracy of the energy estimate depends on the whole on the trial wavefunction, in DMC it depends on the form of its nodal surface, as the DMC algorithm gives the lowest energy compatible with the fixed nodal surface. The form of the trial wave function is therefore very important; it must be both accurate and easy to evaluate. The simplest and most common wave function 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

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

where, $R = \{r_1, r_2, \dots r_N\}$ 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 orbital which usually obtained from Hartree-Fock calculations.

III.   RESULTS AND DISSCUSSION

Our purpose in this work is to study the possibility of applying QMC method on actinides. No previous study on the performance of this method on actinides has been found in literature. Here we estimate the VMC and DMC ground state energies of Ac and Th neutral atoms and some of their charged cations. All our QMC calculations were performed by using Qwalk code [15]. The basic form of the wavefunction that we used consists of a product of Slater determinants for spin-up and spin-down electrons multiplied by a Jastrow correlation factor.

Table 1: Ground state total energies computed within Hartree Fock, E_{HF}, variational Monte Carlo, E_{VMC}, and diffusion Monte Carlo, E_{DMC}, for Ac and Th neutral atoms and some of their corresponding cations. σ is the root mean square fluctuation of the local energy in each method.   All energies are in Hartrees.

	E_{HF}	σ_{HF}	E_{VMC}	σ_{VMC}	E_{DMC}	σ_{DMC}
Ac	-28.8731	1.57	-29.0922	1.34	-29.1393	0.76
Ac[1]	-28.9677	1.49	-29.0395	1.13	-29.2563	1.08
Ac[2]	-28.6006	1.42	-28.6684	1.11	-28.8463	0.77
Ac[3]	-27.9826	1.45	-28.1805	1.48	-28.2255	0.96
Th	-35.2761	1.67	-35.5958	0.87	-35.6613	0.77
Th[1]	-35.0862	1.71	-35.3181	1.18	-35.4926	1.25
Th[2]	-34.6128	1.60	-34.8735	0.88	-34.8869	0.86
Th[3]	-33.9926	1.55	-34.2401	0.87	-34.2668	0.76

The initial orbitals of the trial wavefunction are generated in GAMESS package [16] via spin-restricted open Hartree-Fock calculations. In the present work we have used CRENBL ECP [17] basis set which eliminates a large core (78 core electrons) from the atoms so only the 5f-electrons are treated as valence electrons. We used a target population of 2000 walkers. In the DMC calculations a time step of 0.0001 Hartree^{-1} was used.

In table 1 we report our HF, VMC, and DMC calculations for the ground state energy of actinium and thorium neutral atoms and from first to third corresponding cations. The fluctuation of the local energy, σ , for each method are also presented. As it can be seen from the table, that the fluctuation of the local energy in case of DMC, σ_{DMC}, is smaller than 1 a.u. for both of Ac and Th neutral atoms. Although the HF and VMC are less efficient than DMC, the fluctuation of the local energy is found to be below 2 a. u. for all the results that have been obtained.

Table 2: Time step dependence of the diffusion Monte Carlo energy, E_{DMC} , for the Ac 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	-29.1393	-0.0046
0.00025	-29.1332	0.0015
0.00050	-29.1386	-0.0039
0.00100	-29.1520	-0.0173
0.00150	-29.1591	-0.0244
0.00200	-29.1628	-0.0281
0.00400	-29. 1896	-0.0549
0.00600	-29.1828	-0.0481
0.00800	-29.1960	-0.0613
0.01000	-29.1922	-0.0575

Let us know study the dependence of the DMC energies on the size of the time step for Ac atom. In table 2 the results of our calculations are summarized. We estimated the time step errors, finding them to be -0.0046 H for the smallest time step and -0.0575 H in the case of the largest time step. It should be noted that the magnitude of these errors may be not too large according to this heavy atom.
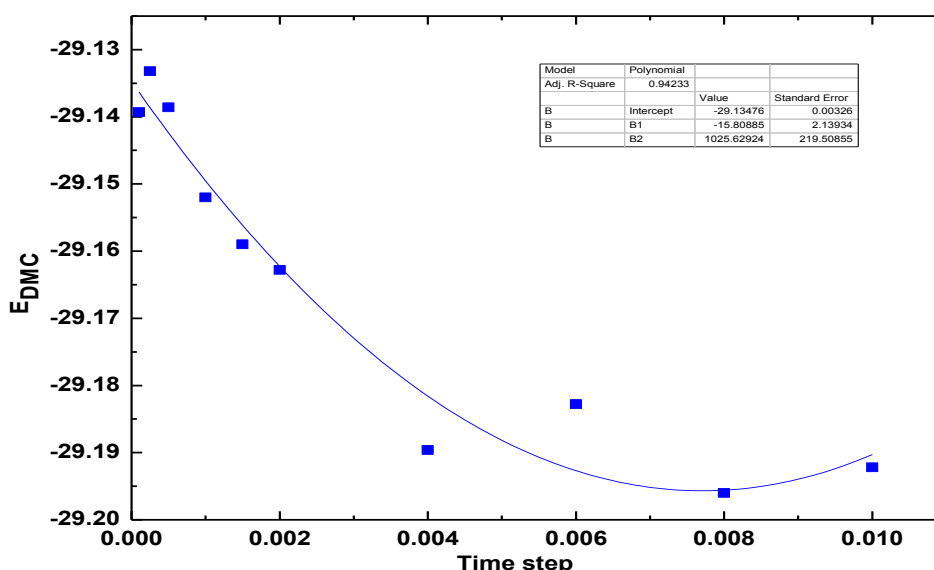

Fig. 1: Time step dependence of the diffusion Monte Carlo (DMC) energies for Ac atom.

Figure 1 shows a plot of the DMC energies as a function of the time step. As it is apparent from the figure that the relation between the DMC energies and the time steps follows a polynomial relation this is related to the presence of the Jastrow factor that introduces a polynomial behavior in the energy as a function of the time step. Furthermore, all the DMC energies have been extrapolated to zero time step and the extrapolated value has been found to be -29.13476 ± 0.00326 H.

IV. CONCLUSION

In conclusion, we have calculated the ground state energies for actinium and thorium neutral atoms and from their first to third corresponding cations. Although the simple Slater Jastrow trial wavefunction has been used in all our calculations, the results are satisfactory. Moreover, we study the dependence of the DMC energies for actinium atom on the size of the time step. We hope that this work will be the starting point for the applications of QMC method on actinides.

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