

CLOSED-SHELL VARIATIONAL QUANTUM MONTE CARLO SIMULATION FOR THE ELECTRIC DIPOLE MOMENT CALCULATION OF HYDRAZINE MOLECULE USING CASINO-CODE

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Abstract: A quantum Monte Carlo (QMC) study of the electric dipole moment of hydrazine molecule using CASINO-code is presented. The variational quantum Monte Carlo (VQMC) technique used in this work employed the restricted Hartree-Fock (RHF) scheme. The components dependence of the electric dipole moment from the QMC technique is studied with a single determinant Slater-Jastrow trial wave-function obtained from the Hartree-Fock orbitals. The simulation requires that the configurations must evolve on the time scale of the electronic motion, and after equilibration, the estimated effective time-step be obtained. From our result, though the VQMC method showed much fluctuation, the technique calculated the electric dipole moment of hydrazine molecule as 2.0 D, which is in closer agreement with 1.85 D experimental value than others in literature. Thus, the result from this study is found to be precisely approaching the required order of chemical accuracy.

Keywords: CASINO code, Electric dipole moment, Hydrazine (N_2H_4) molecule, QMC, VQMC.

1. INTRODUCTION

The nitrogen atom is present in a large number of functional groups contained in many organic and inorganic compounds. There are, however, comparatively few compounds containing the singly bonded $>N-N<$ fragment, because such systems are destabilized by the repulsion of nitrogens' lone electron pairs. The parent compound, hydrazine (N_2H_4), is kinetically stable, but thermodynamically unstable [1]. Hydrazine is one of the simplest nitrogen compounds and an important rocket fuel; and is extremely toxic, but is at the same time a very reactive and efficient reagent, which in combination with Dinitrogen Tetroxide as fuel oxidant gives a missile a much faster response time than all other propellants used before [2]. The properties of hydrazine are of interest due to their biological activities and their use as metal extracting agencies. It is also known that the carcinogenic and toxicologic consequences associated with inhalation or ingestion of Hydrazine include damage to internal organs, creation of blood abnormalities, irreversible deterioration of the nervous system, and even teratogenic and mutagenic effects [3]. Hydrazine (N_2H_4) as strong reducing agent used both in thermal and nuclear power plants because of its ability to eliminate dissolved oxygen and protect structural materials against corrosion [4–6], has its oxygen scavenging properties that can prevent the formation of iron hydroxide and other rusts in the heat transport system [4]. Along with their use as high-energy propellants in thrusters

for rockets, satellites and space shuttles, and as a monopropellant in gas turbine generators [7–9], the multipurpose chemical reagent – hydrazine – also have a number of commercial applications, including its role as

essential building blocks in the synthesis of various polymers, pesticides, pharmaceuticals and chemotherapeutic agents; and are used as explosives to military fuel cells, in metal finishing (nickel plating), in boiler water-feed deoxygenation, and in photographic development [10]. As it is very toxic and unstable, very little is currently known about its electric dipole moment.

The dipole moment of an isolated molecule occurs where the center of gravity of the negative charge and the center of gravity of the positive charge do not coincide. If placed in an electric field, all molecules have an induced dipole moment, aligned parallel to the field, due to polarization caused by distortion. Polar molecules, however, have a permanent dipole moment, which exists without an electric field. This is caused by partial charges that reside in the molecule [11].

On the other hand, due to the crucial and safety issues associated with the handling of Hydrazine (N_2H_4), molecular modeling and simulation can play a particularly important role for the investigation of the energetic and non-energetic (–electric dipole moment–) properties of this molecule. According to a recent study however, classical molecular simulations, comprising molecular dynamics (MD) and Monte Carlo (MC) calculations are still

uncommon for Hydrazine and its derivatives in scientific literature [2], especially for the accurate description of the electric dipole moment of hydrazine molecule.

One of the first theoretical work to study the electric dipole moment of hydrazine molecule using the data prepared by Maryott and Buckley (1953) was the work of Nelson Jr. et al., in 1967 [12]. Their calculation of the hydrazine's electric dipole moment was based on principal methods of dipole moment measurement and they obtained a value of 1.75 D, which though in good agreement, underestimated the experimental value of 1.85 D reported by Seddon et al., [13].

However, due to the advent of more powerful computational techniques and methods, researchers have shown more interest in calculating the electric dipole moment of hydrazine to the nearest accuracy, all in an attempt to bridge the gap between theory and experiment.

Recently, in the work of Kaczmarek et al., (2009), the electric dipole moment of hydrazine molecule was calculated using molecular dynamics and obtained a static equilibrium value of 2.22 D [14]. This value differs from the experimental value [13] by 0.37 D. More recently, Elts et al., (2014), calculated from their molecular model the electric dipole moment of hydrazine molecule as 2.25 D [2] which agrees well with the work of [14]; but differs from experimental value by 0.4 D, which is much more farther from experiment. However, both dipole moments [14, 2] overestimated the experimental value with a deviation of 20.0% and 21.6% respectively. These are relatively high. The reason for this significant deviation in both results could be attributed to the fact that both authors used basis-set correlated methods, which goes a long way to limiting the accuracy of the electric dipole moment, since the dipole moment can be very sensitive to basis set, and convergence for weakly bonded systems can be very slow [15]. In addition, the dipole moment appears highly sensitive to the level of correlation used, especially for problems which require multi-reference treatment. This fact is well known, but a systematic study can be found in Ref. [15]. It is therefore important to explore other types of methods to understand the impact of many-body effects more thoroughly. That is why we employ the highly accurate alternative approach, which is quantum Monte Carlo (QMC) [16, 17]. QMC is very attractive since it is in principle exact; and in practice due to approximations it has a residual weak sensitivity to the size of basis sets, and it captures the correlations at a level of 90–95% [16,18, 19]. This is something that is quite difficult to achieve by correlated methods based on expansions in basis sets. In fact, there are previous studies of molecular dipole moments calculated by QMC methods for a few molecular systems [20 – 23].

We present in this paper, the quantum Monte Carlo CASINO – code, for the simulation and calculation of the electric dipole moment of hydrazine (N2H4) molecule

using variational quantum Monte Carlo (VQMC) technique. More importantly, the trial wave functions (used as a sampling function) employed in this work are the Slater Jastrow type.

The rest of this paper is structured as follows: Section 2 briefly introduce the VQMC method with an inclusion of the trial wave functions. Section 3 explains the computational details. In Section 4, the results and discussion are presented. Finally, the paper ends with concluding remarks in Section 5.

2. THE METHOD: QUANTUM MONTE CARLO METHOD

The term “quantum Monte Carlo” encompasses different techniques based on random sampling, which involves the combination of quantum approach in physics with Monte Carlo procedures as applied to a system. There are many types of QMC techniques but this work focuses mainly on variational quantum Monte Carlo (VQMC) which depends on the availability of an appropriate trial wave-function to determine the zero-point energy or electric dipole moment; and this is because there are more recent researches [14, 2] that could be compared with the result of this work.

2.1. Variational quantum Monte Carlo method

The variational quantum Monte Carlo (VQMC) method is based on the combination of the variational principle and the Monte Carlo evaluation of integrals. The VQMC method relies on the availability of a trial wave-function ψ_T that is a reasonably good approximation of the true ground-state wave-function. The way to produce good trial wave-function is describe further in this review. The trial wave-function must satisfy some functional conditions. Both ψ_T and $\nabla\psi_T$ must be continuous wherever the potential is finite, and the integrals $\int\psi_T^*\psi_T$ and $\int\psi_T^*\hat{H}\psi_T$ must exist [18]. To keep the variance of the energy finite we also require $\int\psi_T^*\hat{H}^2\psi_T$ existing. The expectation value of \hat{H} computed with the trial wave-function ψ_T provides an upper bound on the exact ground-state energy E_0 :

$$E_V = \frac{\int\psi_T^*(\mathbf{R})\hat{H}\psi_T(\mathbf{R})d\mathbf{R}}{\int\psi_T^*(\mathbf{R})\psi_T(\mathbf{R})d\mathbf{R}} \geq E_0 \quad (2.1)$$

In a VQMC simulation this bound is calculated using the Metropolis Monte Carlo method. Equation (2.1) is rearranged as follows:

$$E_V = \frac{\int|\psi_T(\mathbf{R})|^2\left[\psi_T(\mathbf{R})^{-1}\hat{H}\psi_T(\mathbf{R})\right]d\mathbf{R}}{\int|\psi_T(\mathbf{R})|^2d\mathbf{R}} \quad (2.2)$$

and the Metropolis algorithm is used to sample a set of points $\{\mathbf{R}_m : m = 1, M\}$ from the configuration-space probability density given in Equation (2.3) as

$$\rho(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int|\psi_T(\mathbf{R})|^2d\mathbf{R}} \quad (2.3)$$

Here, the equilibrium walker density $n(\mathbf{R})$ is proportional to $\rho(\mathbf{R})$, and the probability of finding any given walker in $d\mathbf{R}$ is $\rho(\mathbf{R})d\mathbf{R}$. The trial moves are sampled from the current position of the walker, the variance of the Gaussian being chosen such that average acceptance probability is roughly 50% [24].

At each of these points the “local energy” $E_L(\mathbf{R}) = \psi_T(\mathbf{R})^{-1} \hat{H} \psi_T(\mathbf{R})$ is evaluated and the average energy accumulated is given by

$$E_V \approx \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m). \quad (2.4)$$

2.2. Trial wave functions

The trial wave functions used in this work are of the Slater–Jastrow type [25] written as:

$$\psi_T(\mathbf{R}) = \sum_i d_i D_i^\alpha(\mathbf{R}) D_i^\beta(\mathbf{R}) e^{J(\mathbf{R})} \quad (2.5)$$

where $D_i^{\alpha(\beta)}(\mathbf{R})$ is a Slater determinant of spin $\alpha(\beta)$ electrons, d_i is the coefficient and $J(\mathbf{R})$ is the Jastrow function. The nodes of a trial wave-function are determined by the antisymmetric Slater component. The Jastrow function containing one-body and two-body explicit correlation terms is given by

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) + \sum_I \sum_I \chi_I(r_{iI}) \quad (2.6)$$

where $i(j)$ and I are electron and nuclei indices, respectively, and r_{ii} , r_{ij} are the corresponding distances. The u and χ terms describe electron–electron and electron–nucleus correlations respectively. Although the accuracy of the simulation relies on the Slater component, the Jastrow factor is also important for the efficiency of the simulation as it helps to reduce fluctuations and the cost of the computation. Again, though VQMC can be quite powerful when applied to the right problem, the necessity of guessing the functional form of the trial function limits its accuracy and there is no known way to systematically improve it all the way to the exact non-relativistic limit. Thus in practice, the main use of VQMC is in providing the optimized trial wave function required as an important sampling function by the much more powerful DQMC (diffusion quantum Monte Carlo) technique.

3. COMPUTATIONAL DETAILS

In this work, the QMC calculations were carried out by using the QMC software package, CASINO-code [24]. The CASINO-code simulation was run for a single expectation value, and thereby used for calculating the electric dipole moment of hydrazine molecule by VQMC, with the imaginary time-step set at 0.002. The VQMC step is an input parameter corresponding to the total number of particle configurations for which the simulation depends. In order to calculate the dipole moment by means of QMC, the energy calculations need to be carried out separately. The correlated wave-function from VQMC is then

optimized using the variance minimization method to obtain an efficient and more accurate convergence of the energy. Thus, one of the most important steps in our QMC calculations is to obtain suitable trial wave function. Following the generation of the Slater components, the optimization of the Jastrow function containing one-body and two-body explicit correlation terms was carried out. The optimization of the Jastrow function was as important as obtaining the Slater components since inadequacy in the Jastrow can increase the locality approximation bias. In our present paper, up to 27 Jastrow variational parameters were used and their optimization was performed with a variance – minimization scheme [26] in the framework of variational quantum Monte Carlo (VQMC), a variant of QMC.

The CASINO-code used was run on a Linux based operating system (Ubuntu environment) having a working Fortran 90 compiler.

4. RESULTS AND DISCUSSION

Every VQMC step generates a new configuration of electrons and nuclei, and because of the difference in inter-particle separation, each of these will have a different energy leading to different electric dipole moment. The correct expectation value of the electric dipole moment is the average dipole moment of thousands of these configurations. The graph of the dorsal view and lateral view results of the VQMC run for a hydrazine molecule, generated from 40,000 configurations are shown in Figure 1(a) and Figure 1(b) below. The number of equilibration steps underwent is 2000 moves, at an imaginary time-step set to 0.002 having a target weight of 1000. The simulation took 10000 lines of data between accepted configurations, and gave the best estimate effective time-step to be 0.00198821.

The calculated electric dipole moment from the output file is obtained at 10.262209405 a.u. (which is the maximum distance from origin), with an acceptance ratio of 50.3498% which is in good agreement as predicted by [24]. The results presented in Figure 1(a), and Figure 1(b), indicates that the more the VQMC steps simulated, the more likely that the calculated value of the electric dipole moment will be closer to the experimental value. The electric dipole moment value obtained from the VQMC components is 2.0 D with its symmetry directed along the x-component as shown in Figure 1(b).

Thus, the electric dipole moment calculated in this work using CASINO-code is in closer agreement with the experimental value of 1.85 D [13], than the other theoretical values reported in literature. In our study, we observed from the graphs that the deviation from experiment is 0.15 D which is highly reduced compared to the recently calculated values in the literature [14, 2]. Comparing our result with the works of Kaczmarek et al., [14] and Elts et al., [2] which are respectively 20.0% and 21.6% deviations away from the experimental value [13],

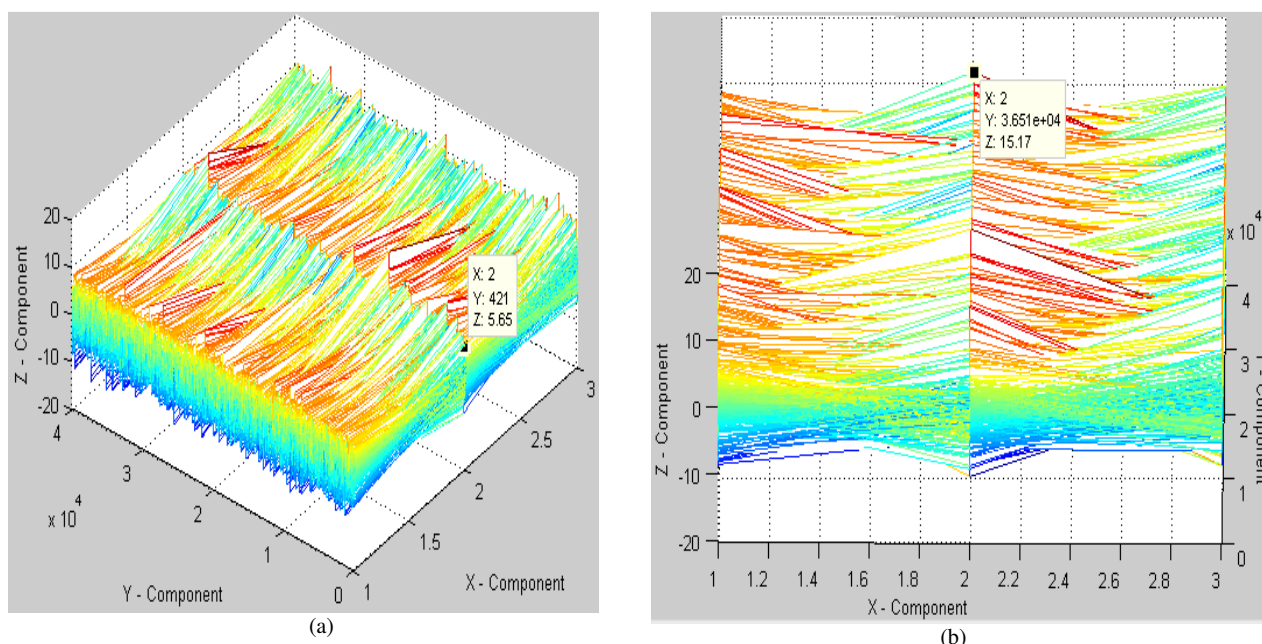


Figure 1: (a) VQMC Dorsal View of Electric Dipole Moment Components and (b) VQMC Lateral View of Electric Dipole Moment Components.

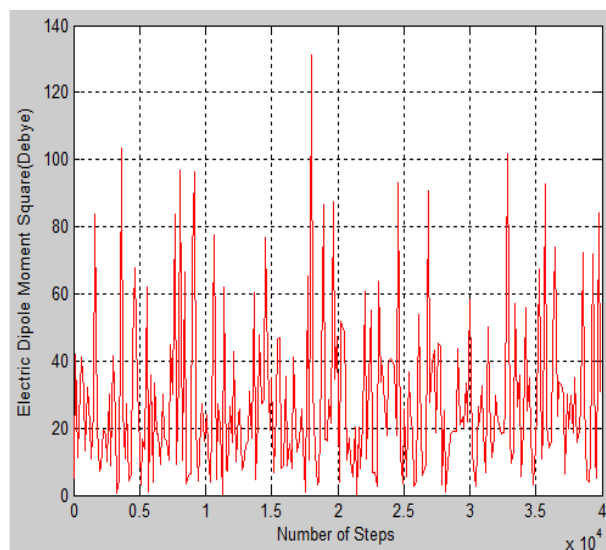


Figure 2: Graph of electric dipole moment square versus number of VQMC steps.

we have obtained a value with a lesser deviation of 8.1%. This result support claims that QMC provides near chemical accuracy however as predicted by [27]. In relation to Figure 1(a) and Figure 1(b), the difference in the calculated electric dipole moment of the hydrazine molecule from experiment is considerably low compared to other techniques [14, 2].

Table 1: Comparative analysis of the electric dipole moment of hydrazine molecule calculated by different researchers

S/N	Authors	Techniques/Methods	E.D.M
1	Seddon et al., (1976)	Experimental Value	1.85
2	Nelson et al., (1967)	Principal Methods	1.75
3	Kaczmarek et al., (2009)	Molecular Dynamics	2.22
4	Eltis et al., (2014)	Molecular Model	2.25
5	This work	VQMC (CASINO – Code)	2.00

E.D.M. = Electric dipole moment

Thus, the deviation of the electric dipole moment in the present work may be due to the single determinant Slater-Jastrow trial wave-function used, since inadequacy in the Jastrow can increase the locality approximation bias. Nevertheless, Figure 2 show that the convergence in VQMC method is reached at a point where a continual increase in the VQMC steps did not result in any further significant increase in the electric dipole moment value of the hydrazine molecule; but indicating an instability in VQMC method as its electric dipole moment square fluctuated above 120 within the numbers of the VQMC steps.

However, the standout points in the graph of Figure 2 may be due to inclusion of unequilibrated data in the final average data which will give a systematic bias to the averages obtained. Again, from the output file, an acceptance ratio of 50.3498% obtained, implies an improved stability in the energy from the use of VQMC method in the CASINO – code which is in conformity with the prediction of Foulkes et al. [18]. This indicates that the chosen time-step does not limit the number of accepted

Monte Carlo moves. Hence, as more configurations are included, the sampling is improved. The results of the electric dipole moment calculated in this study and the work of other researchers is as shown in Table 1.

5. CONCLUSION

In our study, a QMC calculation has been carried out using variational method with focus on the electric dipole moment of the polar molecule, hydrazine (N_2H_4). The results obtained from our graphs indicates that although the electric dipole moment of the hydrazine molecule calculated from VQMC method is 2.0 D, which is in good agreement with experiment, the fluctuations in the VQMC method was enormous. Also, in this work, the difference between the calculated value and the experimental value is 0.15 D which is about 8.1% closer to experiment, compared to the deviations of 20.0% [14] and 21.6% [2] respectively. We also observed from our study that the main source of the fluctuations leading to the deviation (from experiment) in our calculations, may be due to the variational technique which uses a guiding function as a starting function; and which can be improved upon by using a more powerful QMC method: diffusion quantum Monte Carlo, as a future work in this direction.

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