Quantum Monte Carlo calculated potential energy curve for the helium dimer

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Abstract

We report results of both Diffusion Quantum Monte Carlo (DMC) method and Reptation Quantum Monte Carlo (RMC) method on the potential energy curve of the helium dimer. We show that it is possible to obtain a highly accurate description of the helium dimer. An improved stochastic reconfiguration technique is employed to optimize the many-body wave function, which is the starting point for highly accurate simulations based on the Diffusion Quantum Monte Carlo (DMC) and Reptation Quantum Monte Carlo (RMC) methods. We find that the results of these methods are in excellent agreement with the best theoretical results at short range, especially recently developed Reptation Quantum Monte Carlo (RMC) method, yield practically accurate results with reduced statistical error, which gives very excellent agreement across the whole potential. For the equilibrium internuclear distance of 5.6 bohr, the calculated electronic energy with Reptation Quantum Monte Carlo (RMC) method is $5.807483599 \pm 0.000000015$ hartrees and the corresponding well depth is $-11.003 \pm 0.005$ K.

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I. INTRODUCTION

The interaction between noble gas has been a subject of intense theoretical and experimental studies in the last two decades\cite{1-5}. Highly accurate calculations are required to describe the van der Waals (vdW) long range attraction due to the very small energy differences. Despite of its simplicity, so far there is no general unanimity about its equilibrium properties from the experimental side. Actually, it is very difficult to determine experimentally the complete energy dispersion. On the other hand, this compound represents a numerical challenge for theoretical methods, because the general density approximation (GGA) and other standard treatments based on the density functional theory (DFT) are not supposed to work well, when dispersive forces are the critical constituent in the chemical bond. Despite some progress has been made very recently\cite{6-11}, a general and practical answer of this problem is still lacking in the DFT formalism.

Another family of methods, the sophisticated wavefunction based post Hartee-Fock methods, such as configuration interaction, coupled cluster and many-body perturbation theory, could be very accurate only when they employed extensive large basis sets. However, they are highly basis-dependent and computational prohibitive, they have rather steep computational scaling with system size [e.g., $O(N^7)$ for CCSD(T), CC with single and double excitations and perturbational triplets, where $M$ is the number of basis functions], higher order coupled cluster (CC) methods are much more expensive.

Quantum Monte Carlo (QMC) methods offer a very promising unified approach with the accuracy required to van der Waals (vdW) bonded systems, they are able to deal with a highly correlated variational wave function, which can explicitly contain all the key ingredients of the physical system. unlike the sophisticated wavefunction methods, Quantum Monte Carlo (QMC) methods are basis-free (complete basis sets) and low scale (often $N^{3-4}$), depending on the method, which makes the QMC framework generally faster than the most accurate wavefunction based post Hartree-Fock (HF) schemes for large enough $N$. Moreover, recent important developments in the QMC field allow now to optimize the variational ansatz with much more parameters and higher accuracy. In turn this can be substantially improved by projection QMC methods such as the diffusion Quantum Monte Carlo (DMC)\cite{12} and Reptation Quantum Monte Carlo (RMC)\cite{13,14}. The famous Diffusion Quantum Monte Carlo method (DMC) have been successfully applied, and highly accurate results have been obtained for $He_2$, $He - LiH$, $HeH$, $He_3$, $H - PsH$.\cite{15}

In the present work we report a systematic study of the helium dimer, using the latest
developments in the QMC framework: an improved optimization algorithm based on the stochastic reconfiguration (SR) technique, the DMC and RMC methods. All our QMC calculations have been performed with the QWalk program.

II. METHOD

A. Quantum Monte Carlo

We use the Variational, Diffusion, and Reptation flavors of Quantum Monte Carlo (VMC, DMC, and RMC) in our calculations as implemented in the QWalk program. QWalk use a Diffusion Quantum Monte Carlo algorithm very similar to that described in Ref. The Reptation Quantum Monte Carlo algorithm is from Ref., except that we use the approximation to the Green’s function as described in Ref. These techniques are able in principle to predict the ground state energy of the system, since they are based on a direct stochastic solution of the Schrodinger equation.

However, both the Reptation Quantum Monte Carlo and Diffusion Quantum Monte Carlo suffer from the sign problem for fermions, which forces us to make the fixed-node approximation, where the nodal surface of the exact wave function is assumed to be the same as the trial wave function, so the calculation is highly depend on the trial wave function. This approximation typically results in recovering 95-99% of the correlation energy for single reference system. This is the only uncontrolled approximation in our calculations. All calculations will be done using this approximation. For more techniques and implement details, please read Ref.

We can control the fixed node approximation somewhat by varying (optimizing) the orbitals in the trial wave function using the stochastic reconfiguration (SR) technique at VMC level then minimize the DMC and RMC energy. The DMC and RMC calculations in the HF case were done after optimizing the two-body and three-body Jastrow factors, without changing the HF determinant.

B. Computational Details

The trial wave functions of the Slater-Jastrow type, which write as:

$$\Psi_T = e^J D_D$$

(1)
where $D_{\uparrow}$ or $D_{\downarrow}$ are Slater determinants of spin-up(down) electrons and $J$ is a Jastrow factor. This form of wave function is very general and has been successfully applied to a wide variety of electronic systems, from single atom to solids containing many hundreds of electrons. The single determinant trial wave functions were constructed using HF orbitals generated using GAMESS(US) code which were then cusp corrected using the scheme of Ma et al. The basis set used a very large and accurate Atomic Nature Orbits(ANO) style Gaussian functions on each of the helium atoms, this basis contains 19s9p8d/8s7p6d contacted functions. The exponents of these basis functions were optimized to provide the lowest HF energy of the dimer at 5.6 a.u. The Jastrow factor used in this work contains electron-electron, electron-ion, and electron-electron-ion correlation terms expanded in natural polynomials with explicit range cutoffs, this means we use up to Three-Body-Jastrow.

The FN-DMC calculations in this study were performed with a target population of 5000 configurations, to minimize any population control error. All calculations contained a minimum of $10^7$ statistical samples with extra calculations being performed until the desired error was arrived upon. This was generally the case for calculations using small values of the time step, to account for the increase in serial correlation. To calculate the binding energy in FN-DMC, we first extrapolated the dimer energies to timestep $\tau = 0$ separately. The extrapolation to timestep $\tau = 0$ was performed by fitting a quadratic polynomial to the DMC data.

While the FN-RMC calculations were also based on the above VMC optimized trial wave functions. Similar to the FN-DMC calculations, these calculations contained a minimum of $10^7$ statistical samples with extra calculations being performed until the desired error was arrived upon. In RMC, the random variable is the path, which, for finite length, can be a probability density. Therefore, there’s no branching and no population control bias. To calculate the binding energy in FN-RMC, we extrapolated dimer energies to timestep $\tau = 0$ and length $N = \infty$ separately. The extrapolation to timestep $\tau = 0$ and length $N = \infty$ was also performed by fitting a quadratic polynomial to the RMC data.

III. RESULTS AND DISCUSSION

Since there is no node for the $1^1S$ ground state of helium atom, QMC simulations can solve this state exactly. Our FN-DMC and FN-RMC gives the same value with the exact value. The energy calculated for the dimer at 5.6 bohr for FN-RMC, is
5.807483599±0.000000015 hartrees, this corresponds to -11.003±0.005 K; while for FN-DMC, is -5.807483624±0.000000029 hartrees, and the computed interaction energy is -0.000034870±0.000000029 hartrees, this corresponds to -11.014±0.015 K. These results are significant better results, and they are also in accurate agreement with the most recent ab initio estimates of the same quantity, namely -10.96 K, -10.98 K, -11.008 K, -10.998 K, -11.009 K, -10.978 K, -10.980 K, -11.003 K, -11.000 K, and 10.9985 K.

Recently, several points of the helium dimer potential were calculated by Anderson using the exact (flexible nodes) quantum Monte Carlo (QMC) method. These results, for the three distances where a comparison is possible, are consistent with ours with the error bars overlap. At R=5.6 bohr, Anderson’s result of -10.998±0.005 K has only slightly narrow the same error bar with our FN-RMC result. The agreement with the 2001 Anderson’s results is very good. The present interaction energy at R=5.6 bohr is in good agreement with the SAPT result from ref, equal to -11.000±0.011 K.

A detailed comparison with other high-level ab initio calculated interaction energies for the helium dimer was presented in ref. Therefore, in the present work we focus on some new results. For the equilibrium distance, R=5.6 bohr, there exists now an very interesting improved upper bound to the interaction energy, -10.9985 K, obtained from four-electron "monomer contracted" ECG calculations. Our present predictions, -11.014±0.015 K and -11.003±0.005 K, are fully consistent with this upper bound. Let us further note that for all the distances considered here, the upper bounds given by Komasa are above our error bars.

In recent, Springall and co-workers reported quantum Monte Carlo calculations on the potential energy curve of the helium dimer. Their FN-DMC result for helium-helium interaction energy at R=5.6 a.u is very accurate, predicted -10.89±0.17 K or -10.96±0.15 K, which are in very good agreement with the current accepted values of around 11.00 K. But their error bars are larger than our FN-DMC and FN-RMC results. For separated distance at R=4.5 a.u, our FN-DMC and FN-RMC result are 58.425±0.034 K and 58.475±0.013 K, respectively. And their FN-DMC result is 49.76±0.29 K, while the "exact" QMC 58.3±0.5 K. The well published results are listed in TABLE I. And for the separated distance at R=4.3 a.u, the corresponding well published and accepted results are all around 118.0 K, our FN-DMC and FN-RMC result are 117.879±0.059
K and 118.019±0.022 K, respectively. And their FN-DMC result is 102.24±0.32 K [1].

As is shown in the TABLE II, our results of FN-DMC and FN-RMC are totally significant different from the very recent FN-DMC results [1] at some separated distances. For the separated distance small than \( R=5.6 \) a.u, their FN-DMC results are unambiguous smaller than our FN-DMC and FN-RMC corresponding results; while for the separated distance large than \( R=5.6 \) a.u, like \( R=5.9 \) a.u, their FN-DMC result is -10.31±0.15 K, and our’s corresponding FN-DMC and FN-RMC results are -10.19±0.014 K and -10.18±0.005 K, respectively. And for \( R=7.4 \) a.u, their FN-DMC and our FN-RMC results are -2.57±0.18 K and -3.33±0.002 K, respectively. As also may be seen in Table II, our FN-DMC and FN-RMC results are accurate consistent with the SAPT calculations in ref. [30] to fit an analytic potential for the helium dimer [30] and Hurly and Mehl’s [44] analytic potential. Our FN-RMC results (interaction energies and error bars) for helium dimer potential energy curve are better.

IV. CONCLUSIONS

In summary, in this work we used the FN-DMC and FN-RMC methods to compute accurate values for the interaction energies of He-He dimer. Our results show that fixed node DMC and RMC combine with conventional Slater-Jastrow wave functions can give very accurate results for a helium dimer, which are of comparable accuracy to many other methods. The computed values are in excellent agreement with those of prior ”state of the art” electronic structure calculations available for this system. Due to the aforementioned features, the relatively new Reptation Quantum Monte Carlo method (FN-RMC) can easily account much more correlation energy and can systematically reduce the statistical biases compared to the sophisticated FN-DMC method [13], which opens a new path of research for Quantum Monte Carlo.

As is also shown in present work, the FN-RMC shows generally better results (more accurate interaction energies and much smaller error bars) than FN-DMC under the same conditions. Furthermore, the FN-RMC method have a very similar scaling compare to FN-DMC method, so it should be a very promising method in the future. Our results also suggest that the fixed-node error could be almost negligible in the FN-DMC and FN-RMC calculations for these systems, which has been suggested previously by Massimo Mella and James B. Anderson. [2]
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TABLE I: Comparison of selected predictions of the helium-helium interaction at R=4.5 bohr.
Energies in Kelvin.

| Method                              | Interaction energy |
|-------------------------------------|--------------------|
| Fixed node DMC[1]                   | 49.76±0.29         |
| EQMC [23]                           | 58.3               |
| ECG [27]                            | 58.517             |
| r12-MR-ACPF [28]                    | 58.49              |
| CCSDT(Q)/CBS[29]                    | 58.397             |
| CCSD(T) [30]                        | 59.470             |
| SAPT [30]                           | 58.371             |
| Green function QMC[32]              | 60.0               |
| Analytical potential[33]            | 60.44              |
| CCSD(T)+FCI correction[34]          | 59.54              |
| SAPT [35]                           | 58.037             |
| CCSD(T)-R12 [36]                    | 59.543             |
| CCSD(T)/CBS+FCI [37]                | 58.407             |
TABLE II: Interaction energy values of the helium dimer at different values of the atom separation.

The interaction energies are given in K.

| R (bohr) | FN-RMC $^a$ | FN-DMC $^b$ | FN-DMC $^c$ | Hurly$^d$ | SAPT FIT$^e$ |
|----------|-------------|-------------|-------------|-----------|--------------|
| 0.9      | 350482.26±1.44 | 350133.52±3.64 | 314409.15±3.79 | 348590.96 | 350152.17    |
| 1.9      | 44852.74±0.91  | 44801.15±2.28  | 45959.52±4.11  | 44863.43 | 44847.24     |
| 2.3      | 18718.39±0.37  | 18700.28±0.93  | 20159.33±0.64  | 18728.15 | 18716.36     |
| 2.8      | 6021.23±0.16   | 6015.01±0.45   | 5575.28±5.37   | 6021.75  | 6020.67      |
| 3.2      | 2334.11±0.11   | 2331.66±0.37   | 2271.94±1.45   | 2333.37  | 2333.58      |
| 3.8      | 508.75±0.08    | 507.53±0.23    | 537.78±1.77    | 508.66   | 508.42       |
| 4.3      | 118.019±0.022  | 117.879±0.059  | 102.24±0.32    | 118.13   | 117.93       |
| 4.5      | 58.475±0.013   | 58.425±0.034   | 49.76±0.29     | 58.547   | 58.406       |
| 4.7      | 24.229±0.012   | 24.205±0.031   | 19.49±0.27     | 24.312   | 24.220       |
| 5.6      | -11.003±0.005  | -11.014±0.015  | -10.89±0.17    | -10.9957 | -11.0048     |
| 5.9      | -10.184±0.005  | -10.195±0.014  | -10.31±0.15    | -10.1793 | -10.1865     |
| 7.4      | -3.332±0.004   | -3.335±0.012   | -2.57±0.18     | -3.3297  | -3.3330      |

$^a$this work
$^b$this work
$^c$Reference [1]
$^d$Reference [44]
$^e$Reference [30]