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Binding energies of small lithium clusters: A comparison of different theoretical calculations

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ABSTRACT

In order to compare different calculations used in theoretical studies on lithium clusters, we have calculated the binding energies of small lithium clusters using all electron diffusion quantum Monte Carlo (DMC) simulation, coupled-cluster (CCSD(T)) approach, as well as density functional theory (DFT) with different exchange-correlation (xc) functionals. The obtained DMC results are in very good agreement with available experimental data and with CCSD(T) calculations. However, the DFT results depend strongly on the approximations for the xc functional. Furthermore, considering the DMC result as a benchmark, we obtain the electron correlation energy of the clusters and quantify its contribution to the binding energies.

1. Introduction

Over the last few decades, there has been growing interest in the study of metallic clusters [1]. In particular, small lithium clusters Li$_n$ ($n \leq 8$) have called special attention because they are seemingly simple. A lithium atom has only three electrons with simple electronic configuration of just one valence electron [2]. Lithium atom is also the lightest of all the metallic elements. Nevertheless, theorists and experimentalists have faced challenges to characterize small lithium clusters since a considerable number of inconsistencies have been found among the reported results on their properties [3–5]. Experimentally, small masses of Li$_n$ clusters have led to difficulties in obtaining their photon–electron spectroscopy because they can easily reach high speed during the time of flight and are difficult to be decelerated [6]. Theoretically, there is a large amount of computational results. Most of them are from *ab initio* calculations such as multireference configuration interaction (MRCI) [7], density functional theory (DFT) [8–11], and coupled-cluster (CCSD(T)) approaches [12,13] to determine binding energies and geometries of these clusters. It has been shown that electron correlation energy is essential to determine the cluster geometry configuration and stability. Although intensive calculations have focused on structural and electronic properties of Li$_n$ clusters, in some cases it is not sufficient to identify the structural ground state of a cluster by calculating the differences in total energies of different isomers.

In order to clarify the differences among the most commonly used theoretical methods in the study of Li$_n$ clusters, we have performed calculations using different methods such as HF (Hartree–Fock), DMC (diffusion Monte Carlo), CCSD(T), and DFT for a quantitative study of small neutral clusters Li$_n$ ($n = 1$–8). The binding energies are obtained as a quantity for a systematic comparison of different theoretical methods and also with experimental results. Quantum Monte Carlo (QMC) [14] can handle the exchange-correlation (xc) effects more accurately than the DFT and can reach accuracy comparable to the best quantum chemistry methods such as CCSD(T) but with less computational cost. It provides an accurate evaluation of the ground-state energy which enables us to estimate the correlation effects on the binding energies of the clusters. We compare the results obtained from DMC calculation to those from other methods such as DFT and CCSD(T). This will help us to better understand how accurate the functionals are in the DFT calculations for the lithium clusters. Furthermore, from the DMC and HF calculations we can quantify contributions of the electron correlation in these clusters.

2. Computational methods and details

We use different all-electron theoretical approaches to calculate the total energy of lithium clusters Li$_n$ ($n = 1, 2, \ldots, 8$) and determine their binding energies. In addition to the QMC calculation,

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we also perform HF, DFT, and CCSD(T) calculations using GAUSSIAN package [15]. For DFT, different approximations for the xc functionals are used. Within the local density approximation (LDA), we employ the local Slater–Vosko–Wilk–Nusair (SVWN) functional. Within the generalized gradient aproximation (GGA), the standard GGA Perdew–Burke–Ernzerhof (PBE), the hybrid Becke3–Lee–Yang–Parr (B3LYP) and ωB97xD functionals are used.

The QMC calculations are performed using the CASINO code [16] in two steps. First, we use variational Monte Carlo (VMC) method to find an optimized correlated fermionic trial wavefunction of the Slater–Jastrow type written as

$$\Psi_T = D_{\uparrow}(\phi_i)D_{\downarrow}(\phi_i)e^{U}, \qquad (1)$$

where $D_{\uparrow}$ and $D_{\downarrow}$ are the determinants of up- and down-spin orbitals, respectively, ϕ's are the single-particle orbitals which are extracted from a DFT/LDA calculation rather than HF orbitals in order to improve the quality of VMC wavefunctions. The Jastrow factor U in Eq. (1) is a function of the relative positions of electrons and nuclei and contains a sum of homogeneous isotropic electron–electron terms, isotropic electron-core terms centered on the core, and isotropic electron–electron-core terms [17]. These terms are represented by power expansions with variational parameters that are optimized to minimize statistical error and to recover a significant amount of the correlation energy [18–20]. Next, we use the DMC method to simulate stochastically the importance sampling imaginary-time Schrödinger equation [21] with the optimized fermionic trial VMC wavefunction used as a guide wavefunction. The time dependent solution of the Schrödinger equation is obtained through the use of the operator $e^{-\tau H}$, where $\tau = it$ and H are time-step and the Hamiltonian, respectively. It propagates the wavefunction to project out, in principle, the exact ground state after a long enough imaginary-time interval. Usually DMC assumes the fixed-node (FN) approximation [21,22] in which the nodes of the DMC wavefunction are assumed to be the same as those of the trial VMC wavefunction Ψ_T. We have used a time step of 0.001 a.u., which yields calculations with a high acceptance ratio, i.e., more than 99% and an ensemble of 10 000 walkers are considered; checks with up to 50 000 walkers did not change the results within the statistical errors. We have checked for a few clusters the time-step dependence of the total energy which was small enough within the error bars. For the averages, we consider about 80 000 QMC moves in the DMC calculations.

3. Results and discussion

In order to determine the atomic configurations of the Li_n clusters, we take first the initial atomic configuration from previous theoretical calculations [9,12,13,10,23,24] and then we fully relax these structures within the DFT calculations. Both the SVWN and B3LYP approximations are used for the cluster structure relaxation. However, further QMC calculations based on the obtained structures from DFT with different functionals show very small differences in binding energies. We choose the DFT/SVWN results because they agree better with available experimental data of geometrical parameters [25] than the other methods such as DFT/B3LYP, DFT/PBE, and HF. Figure 1 shows the selected optimized structures for small neutral Li_n obtained from the DFT/SVWN calculations as implemented in the GAUSSIAN03 code [15].

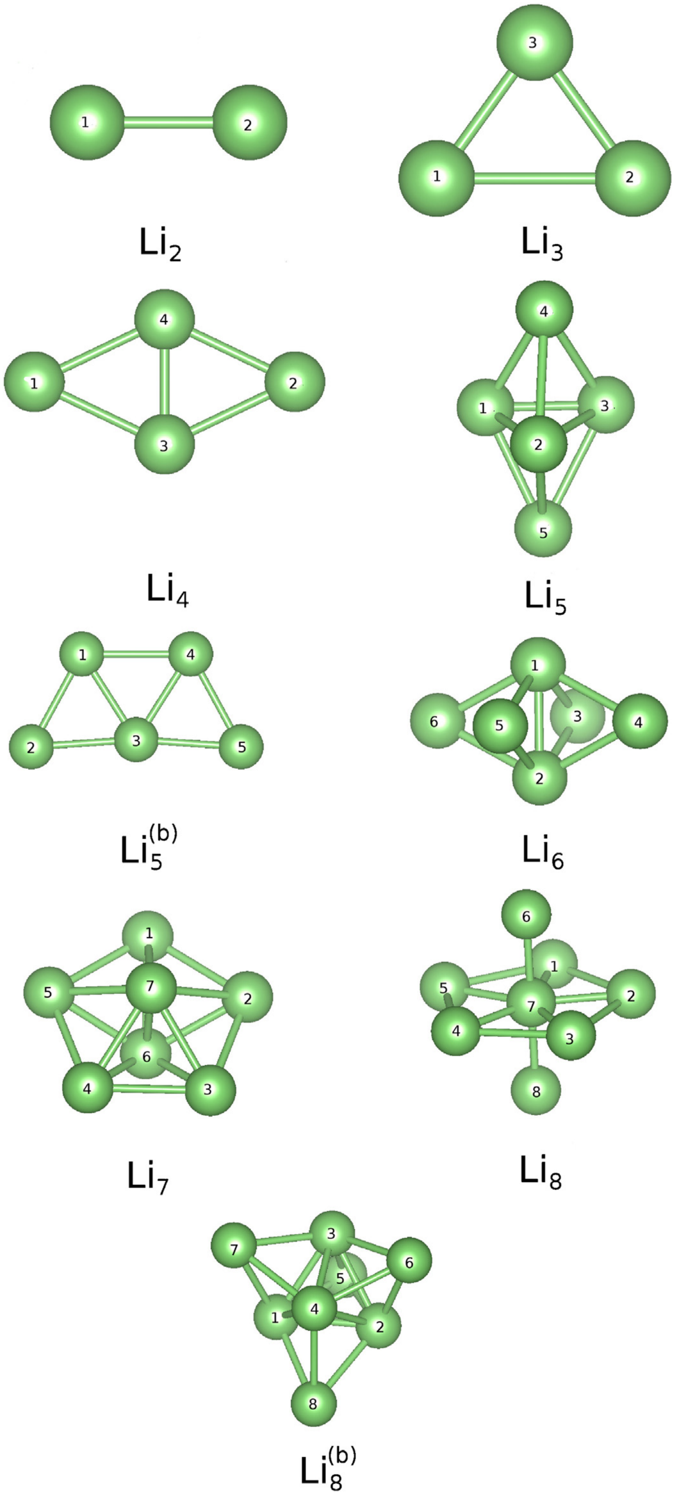

Fig. 1. The optimized structures of neutral lithium clusters Li_n obtained within the DFT/SVWN. The most stable isomers are labelled by Li_n (for $n = 2$–8) whereas the isomers labelled by $Li_n^{(b)}$ (for $n = 5$ and 8) are the second most stable.

Table 1 lists the bond lengths for the structures as indicated in Figure 1. Available experimental values for the two smallest clusters Li_2 and Li_3 are also given in the table. A comparison between the obtained bond length values and the experimental ones shows that the difference for Li_2 is 0.018 Å. For Li_3 such differences for smaller and larger bond lengths are 0.011 and 0.009 Å, respectively. For other clusters, there are no available experimental data for bond lengths. We compare our results with available theoretical values obtained from CCSD(T) calculations [12,13] and find that, for cluster Li_4 (Li_6) the differences for the smaller and larger bond lengths are 0.058 and 0.008 (0.081 and 0.053) Å, respectively. For Li_5 we find that a 3D trigonal bipyramidal structure (as shown in Figure 1) is the most stable configuration with energy very close to the experimental value and slightly smaller than that of its planar isomer $Li_5^{(b)}$