# *Ab initio* calculations on small lithium clusters

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We present a systematic study of the optimized geometries of several small closed-shell lithium clusters, as well as energy differences between isomers, using a variety of density functional and post-Hartree-Fock quantum chemical methods. Using different Gaussian basis sets we compare and contrast the results of the calculations for $Li_2$, $Li_3^+$, $Li_4$, $Li_5^+$, and $Li_6$ including two and three isomers of the latter two clusters, respectively. On the basis of these results a few guidelines for economically but nevertheless reliably studying lithium clusters are proposed. [S1050-2947(97)00307-7]

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## I. MOTIVATION OF THE STUDY

Small clusters composed of alkali-metal atoms have become an intense field of theoretical study in recent years due to their structural and spectroscopic properties [1]. Lithium is the lightest of the elements, which adopts a metallic structure in the solid state, at ambient conditions. This fact makes the study of both the geometry and electronic structure of clusters composed of lithium atoms, as a function of the number of constituents, an attractive pursuit. This interest is further spurred by the increasing availability of high-quality electron structure calculations based on density functional theory (DFT) [2]. In the literature there is an immense array of electronic structure and dynamics studies on these clusters involving both DFT and more traditional quantum-chemistry-type approaches. These latter methods may be thought of as Hartree-Fock (HF) theory plus contributions from the electron correlation, or as we shall refer to them post-HF methods [3]. In the set of DFT studies there have been several investigations using the local density approximation (LDA) [4] as well as gradient corrected semilocal functionals [5]. There have also been a number of studies using HF theory without correlation corrections [6] including a recent report involving a HF-based *ab initio* molecular-dynamics method [7]. Electron correlation using configuration interaction (CI) methods have been employed [8], as well as a valence bond model proposed to explain the structure and bonding in these compounds [9]. We note also that both HF and post-HF [10], as well as DFT [11] and variational quantum Monte Carlo methods [12] have also been applied to the study of elemental lithium solid.

One needs only to take a quick survey of the literature on these clusters to realize that there is a fair amount of disagreement concerning relative energetic stabilities of isomers and even actual isomer geometries. Clearly, this is in part due to the occurrence of very long bonds in these clusters, the extremely flat nature of the potential energy surfaces, and the small energy differences between isomers. So although these systems are ideal candidates for dynamical simulation and electronic structure studies it appears that calculations on lithium clusters may be somewhat more complicated than intuitively expected. However, these conflicts may also be in part due to a lack of understanding of how various aspects of the first-principles calculations affect the final result. Need-

less to say, that full CI calculations in the basis-set limit are just impossible to conduct with presently available algorithms and computer resources for reasonably large clusters. However, some approaches may be more advantageous than others for a particular case of interest. Besides providing a uniform database for geometries and energetics, our goal is to assess the minimal ingredients that are necessary to provide reliable information about these clusters on a computational level, which can be easily extended to much larger clusters at a later stage.

To address these issues we have undertaken a study of the role of the computational method and basis set on the structure and energy differences of several small closed-shell clusters of lithium atoms. Since the functionals used currently in the most commonly available DFT implementations are essentially parametrizations, it is necessary to compare their performance to post-HF methods to properly gauge their performance. This is so because the quantum chemical methods are well understood and one may, in principle, systematically build up the calculations to any desired degree of accuracy. On first impression, it might be tempting to think that a proper study of this type must involve the use of exceptionally large basis sets, with the most sophisticated CI methods, on an immense array of clusters. However, such a study would be neither practical nor necessary. A much more tractable approach is to perform good quality calculations, with a respectable sized basis set, on a small group of clusters that exhibit a representative sample of bonding types exhibited in the family of the lithium clusters. This assertion is valid based on the fact that the behavior of both basis sets and high-quality correlation methods are understood to an appreciable extent [3]. Thus, one may extract the necessary information by simply evaluating the trends in the behavior of the results as a function of the way they were obtained. We note that there has been one previous study [13] comparing DFT-type methods to the CI results present in the literature [8]. However, the correlation energy is estimated non-self-consistently based on HF densities. In addition, this study does not address the specific concern of the dependence of fully optimized isomer structures upon the nature of the calculations. This aspect of the problem may be at the root of many of the controversies in the literature and is assuredly of importance to those who wish to perform studies on isomerization reactions of these clusters, impurities

and vacancy diffusion in the solid phase, solid-to-solid phase transitions, and many other types of problems.

Towards this end, we present herein the results of a study of the molecules $Li_2$, $Li_3^+$, $Li_4$, $Li_5^+$, and $Li_6$ including two and three isomers of the two latter clusters, respectively. We have chosen these species because of their small size, which allows for fairly sophisticated calculations. Within this series a wide range of coordination numbers up to five-fold topologies with short and long bonds as well as two-dimensional and three-dimensional structures are exhibited. We consider here only closed-shell systems in order to avoid any unnecessary computational complications that may arise for open shells. Finally, let us mention that we present only a representative and necessary selection of all calculations that we have undertaken to understand lithium clusters from a computational point of view.

## II. TECHNICAL ASPECTS

The computational methods used in this investigation are of both the density functional approach and the more traditional quantum chemistry type based on Hartree-Fock theory; see, e.g., Refs. [2] and [3] for respective reviews. The density functional methods are categorized with respect to the functional used to model the exchange and correlation contributions. We denote each exchange-correlation functional combination by a symbol for the exchange functional and the correlation functional. The symbols are presented below in brackets after they are defined. Exchange has been accounted for by using the standard local density approximation of Slater (S) [2], and the semilocal gradient correction of Becke (B) [14]. For correlation, we employ the functional form of the LDA obtained from the random phase approximation to the uniform electron gas of Vosko, Wilk, and Nusair (VWN) [15], the 1986 semilocal gradient correction of Perdew in conjunction with the Perdew-Zunger local correlation functional (P86) [16], and the gradient corrected functional of Lee-Yang-Parr (LYP) [17]. In addition to using either fully local or semilocal exchange-correlation combinations, we also explore the combination of treating only the exchange part with a gradient corrected functional while keeping the correlation contribution at the strictly local level. Finally, we also employ the hybrid HF-DFT nonlocal method proposed by Becke [18], which is obtained by mixing his exchange gradient correction [14] with HF exchange together with the LYP correlation functional in the implementation of the GAUSSIAN 94 program (B3LYP) [19].

The particular quantum chemical methods used are as follows: Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2) [20], quadratic configuration interaction with single and double excitations (QCISD) [21], coupled cluster with single, double, and full triple excitations (CCSDT) [22], and the complete active space self-consistent field (CASSCF) [23] method. Coupled cluster calculations were also performed without triple excitations (CCSD) but yielded essentially indistinguishable results from QCISD, which is not unexpected in view of the close relationship of both methods [21]. Also triple excitations may be included within the framework of QCISD in a static perturbative fashion [QCISD(T)] [21], but are only used here to evaluate single point energies, i.e., without reoptimizing the structure.

The methods CCSD, QCISD, QCISD(T), and CCSDT are known to very accurately describe dynamic correlation. CASSCF calculations are used to estimate the contribution of multiple reference determinants and, thus, nondynamic correlation [23]. We determine this contribution by comparing the total occupation number of electrons of the occupied HF canonical orbitals, as given by the single-particle density matrix from the CASSCF calculation, to the number of electrons in the active space. This fraction we convert into a percentage to evaluate the total contribution of the HF determinant. The parameters used to define the active space are presented for each specific case.

Calculations were performed with the standard basis sets 3-21G$^*$ [24], 6-31G$^*$ [25], and 6-311G$^*$ [26] which are commonly used in both HF-based and DFT calculations, although correlation consistent basis sets would clearly be far superior and more efficient in post-HF calculations. However, the latter two basis sets used are known to give reasonable estimates of the electronic energy for all the methods employed in this investigation. We have deliberately confined ourselves to go up to only a modestly large basis because this allows us to carry out all presented calculations, in particular the full geometry optimizations, uniformly with our largest basis set for a great variety of cluster types and electronic structure methods. Note that the crucial energy differences between reasonably stable isomers can only be obtained if the cluster is composed of at least five or six atoms. In addition, the employed family of basis sets is chosen because of its similar structure; each set is a split valence basis with polarization functions.

All density-functional-based results were obtained by using the GAUSSIAN 94 program [19], as were the results of the HF, MP2, and CASSCF methods. QCISD and coupled cluster calculations were performed using the ACES II program [27], except for the $Li_5^+$ and $Li_6$ QCISD calculations, which were also obtained from GAUSSIAN 94 [19]. All optimization procedures and convergence criteria used were those that are the standard settings of these packages unless otherwise stated. All optimizations were conducted using the full symmetry point group of the molecule for greater computational efficiency with the exception of isomer III of $Li_6$; see Sec. III B for further description. This isomer was optimized within the $C_{2v}$ point group instead of the full $D_{4h}$ point group due to the fact that a similar structure in the former point group has been reported in the literature [8]. However, it was found that this isomer exists in the latter and not the former point group and is reported as such. The nature of the identified minima was characterized by vibrational analysis using the B3LYP force constants and optimized geometry. All the isomers presented in this work are (at least local) minima on the potential energy surface with respect to this method.

## III. PRESENTATION AND DISCUSSION OF THE RESULTS

### A. Structures: The small clusters $Li_2$, $Li_3^+$, and $Li_4$

We first examine the two smallest of the lithium clusters considered in this study, $Li_2$ and $Li_3^+$. These species are depicted in Figs. 1(a) and 1(b), respectively. The choice of these two molecules to start this discussion is based on sev-
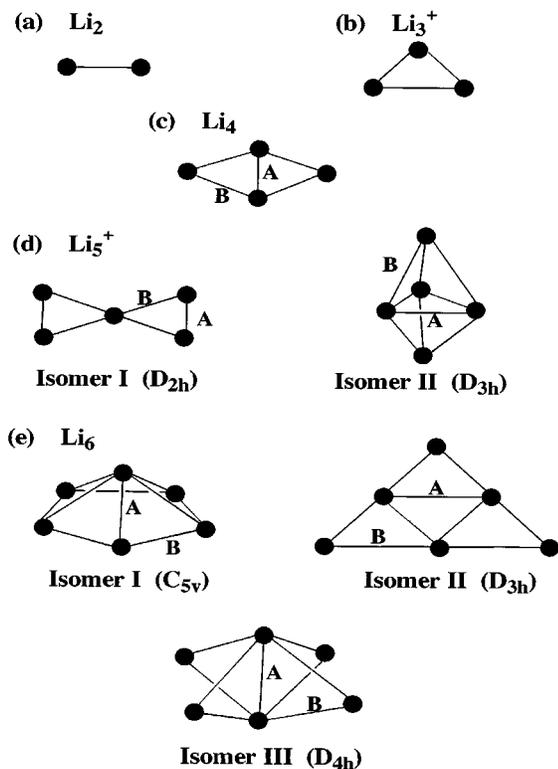
FIG. 1. Molecular geometries of the lithium clusters treated in this study. (a) $Li_2$, (b) $Li_3^+$, (c) $Li_4$, (d) $Li_5^+$: isomer I ($D_{2h}$) and isomer II ($D_{3h}$), (e) $Li_6$: isomer I ($C_{5v}$), isomer II ($D_{3h}$), and isomer III ($D_{4h}$).

eral observations. First, both are extremely small in number of atoms and electrons and, thus, the highest-quality calculations may be performed on these systems. These high-level calculations may then be used to determine which method to choose as a standard reference for larger systems taking into account computational efficiency. Second, both molecules contain only one geometrical parameter. Therefore, geometry optimization may be conducted with a high degree of accuracy for all methods regardless of the availability of ana-

lytical derivatives. Third, each species represents a specific type of bonding that predominates in all lithium clusters. The $Li_2$ molecule has a relatively short bond (experimentally known to be 2.673 Å [28]), which is described as a standard two-center two-electron bond. This is opposed to the $Li_3^+$ molecule, which has a larger bond distance and is described conceptually as an electron-deficient three-center two-electron bond. The bonding pattern in the larger lithium clusters is known to be characterized by an interplay of such two-center and three-center bonds. Thus, the initial phase of this study will revolve around the computational aspects associated with modeling each of these types of bonds separately.

The optimized bond lengths of the two molecules are presented in Table I for our largest selection of methods all obtained with the 6-311G* basis set. The data from various methods are compared relative to those obtained by the CCSDT method [29]. This method is chosen as the reference because it is known to give extremely accurate results for systems that are dominated by a single reference determinant [22]. We note that for $Li_2$ the CCSDT method provides an answer that is only 0.007 Å off from experiment. The CASSCF calculations, spanning the active space with 8 orbitals and using the valence electrons only, provide a slightly larger bond length of 2.690 Å, as expected. An inspection of the CASSCF single-particle density matrix indicates that the wave function can be constructed almost entirely from the HF determinant, or more precisely 92%. It is further pointed out that similar results are obtained for $Li_3^+$. For this species the CASSCF bond length is 3.002 Å, as opposed to 2.985 Å obtained using CCSDT. Again we find that the wave function may be constructed almost entirely from one reference determinant, here 93%. This result is unchanged upon inclusion of core electrons in the active space. We find for $Li_2$ that a CASSCF bond length of 2.690 Å is obtained with the use of 12 valence orbitals and all 6 electrons, and a bond length of 3.010 Å for $Li_3^+$ with 9 valence orbitals and all 8 electrons. In both cases all core electron states were completely occupied. These results are in fact well understood. It is generally known that CASSCF calculations provide larger bond lengths than CI or CC methods when the wave func-

TABLE I. Optimized Li-Li bond lengths of $Li_2$ and $Li_3^+$ for various methods and 6-311G* basis. The molecules are depicted in Figs. 1(a) and 1(b), respectively.

| Method | $Li_2$ (Å) | Error vs CCSDT (%) | $Li_3^+$ (Å) | Error vs CCSDT (%) |
|---|---|---|---|---|
| HF | 2.784 | 5.8 | 3.044 | 2.0 |
| SVWN | 2.700 | 0.7 | 2.943 | −1.4 |
| BVWN | 2.698 | 0.6 | 2.954 | −1.0 |
| BP86 | 2.738 | 2.1 | 2.991 | 0.2 |
| BLYP | 2.715 | 1.3 | 2.958 | −0.9 |
| B3LYP | 2.707 | 0.9 | 2.953 | −1.1 |
| MP2 | 2.749 | 2.5 | 3.014 | 0.9 |
| QCISD | 2.683 | 0.1 | 2.987 | 0.1 |
| CCSD | 2.683 | 0.1 | 2.987 | 0.1 |
| CASSCF [a] | 2.690 | 0.4 | 3.002 | 0.6 |
| CCSDT | 2.680 | | 2.985 | |

[a]CASSCF calculations were performed using valence electrons only with 8 and 12 valence orbitals for $Li_2$ and $Li_3^+$, respectively.

TABLE II. Effect of the basis set on the Li-Li bond lengths (Å) of $Li_3^+$.

| Method | 3-21G* [Error vs 6-311G* (%)] | 6-31G* [Error vs 6-311G* (%)] | 6-311G* |
|---|---|---|---|
| HF | 3.055 (0.4) | 3.075 (1.0) | 3.044 |
| SVWN | 2.961 (0.6) | 2.976 (1.1) | 2.943 |
| BVWN | 2.952 (−0.1) | 2.963 (0.3) | 2.954 |
| BP86 | 3.006 (0.5) | 3.011(0.6) | 2.991 |
| BLYP | 2.958 (0.0) | 2.971 (0.5) | 2.958 |
| B3LYP | 2.955 (0.1) | 2.971 (0.6) | 2.953 |
| MP2 | 3.048 (1.1) | 3.053 (1.3) | 3.014 |
| CASSCF [a] | 3.043 (1.3) | 3.046 (1.5) | 3.002 |
| QCISD | 3.044 (1.9) | 3.050 (2.1) | 2.987 |

[a]CASSCF calculations were performed using valence electrons only and 12 valence orbitals.

tions can be accurately constructed from only one reference determinant. Thus, we conclude that our choice of CCSDT as the reference by which to gauge the results of the other methods is an appropriate one, and that one does not need to include multiple reference determinant wave functions, therefore nondynamic correlation, to accurately describe the geometry of these closed-shell molecules.

From Table I, it can be seen that all these methods provide accurate descriptions of both two-center and three-center bond lengths (relative to CCSDT) with a few notable exceptions. The first is that HF gives in both cases bond lengths that are clearly too long. The second point of interest is that both MP2 and BP86 provide bond lengths for $Li_2$ that deviate by more than 2% from the reference whereas the other methods agree in general with the CCSDT value within less than about 1%. It is interesting to note that the results obtained from the CCSD and QCISD methods are essentially identical to the CCSDT method for both the diatomic and triatomic cases. As expected, triple excitations do not play an important role in determining the geometries of these molecules.

We now examine the effect of basis set on the geometry of these molecules. This is illustrated with the results obtained for the $Li_3^+$; see Table II. From this data set several conclusions may be drawn. First, the DFT-based methods have a much smaller fluctuation in the value of the optimized bond lengths than do the post-HF methods. The second and more important point of note is that, as a general trend, the bond lengths decrease ultimately as a function of increasing size of the basis. This fact is true for both DFT and post-HF methods. Finally, we note that qualitatively similar behavior was found for the bond length of the $Li_2$ molecule, which is therefore not discussed in detail here. Moreover, calculations without polarization functions in the basis set had a similar effect. For example, using the 6-311G* basis set removal of polarization functions—i.e., the 6-311G basis-increased bond lengths on average of 0.1% for DFT methods. However, an average increase of 0.3%, 1.0%, and 1.8% was found for the HF, MP2, and QCISD methods, respectively. Since the maximum fluctuation observed is around 2% for the QCISD results within the quite limited selection and size of our basis sets, and about 1% for the other methods (excluding CASSCF), it may be considered that any method that reproduces the QCISD bond lengths (which were shown in Table I to be essentially indistinguishable from the superior CCSDT results) up to at the most 3% is properly describing

the molecular geometry of these clusters. Furthermore, the quality of the CCSDT and QCISD results on the structure of $Li_2$ relative to experiment indicate that with the 6-311G* basis a respectable representation of the correlation energy is obtained. Thus, we consider the 6-311G* basis as the standard basis for this study, although we are sure that this is still far from the saturated basis set limit especially for the highly correlated post-HF methods. However, this modestly large basis will allow us to carry out full geometry optimizations for several isomers of the larger clusters up to the QCISD level.

As the next phase of this study we present the results of the geometry optimization for the molecule $Li_4$. The molecule is shown in Fig. 1(c). Its structure is that of two edge-sharing triangles, both of which lie in the same plane. The point group of this species is $D_{2h}$. From our QCISD optimization results, we find that this molecule may be described as containing one short bond, of 2.647 Å as in $Li_2$, and four long bonds of 3.007 Å as in $Li_3^+$. Thus, these particular calculations will give us a check on how the various methods behave with both types of bonds present in the same molecule.

The results of our geometry optimizations are given in Table III. The bonds in this table are labeled as in Fig. 1(c). The bond lengths are gauged in percentages relative to the QCISD calculation. We have chosen QCISD as our reference based on the above results and the impracticality of conducting numerical optimizations with CCSDT on this system. CASSCF calculations involving the 4 valence electrons and up to 10 orbitals in the active space were also conducted. These calculations are not included in this set of data due to the fact that again it was found that the resulting optimized wave function was largely associated (91%) with a single determinant wave function. From the data of Table III, it is seen that HF, MP2, and BP86 are the methods that most properly describe the short bonds, whereas all other DFT methods overshoot here by as much as 2–3%. Concerning the long bonds, the trend seems to be reversed: HF yields an exceedingly long bond followed by MP2 and BP86, whereas all other DFT methods give results that are essentially on top of QCISD. In addition, HF provides an error for these long bonds that is outside the 3% margin we have attributed to be due to basis set artifacts. This latter point seems to be a general trend. We find that all the methods compiled in Tables I and III have accurately provided the geometry for

TABLE III. Optimized Li-Li bond lengths of $Li_4$ for various methods and 6-311G* basis. Bonds are labeled as in Fig. 1(c).

| Method | $A$ (Å) | Error vs QCISD (%) | $B$ (Å) | Error vs QCISD (%) |
|---|---|---|---|---|
| HF | 2.654 | 0.3 | 3.144 | 4.5 |
| SVWN | 2.580 | −2.9 | 2.980 | −0.9 |
| BVWN | 2.580 | −2.9 | 3.003 | −0.1 |
| BP86 | 2.625 | −0.3 | 3.042 | 1.2 |
| BLYP | 2.590 | −2.2 | 3.011 | 0.1 |
| B3LYP | 2.578 | −2.6 | 3.010 | 0.1 |
| MP2 | 2.654 | 0.2 | 3.064 | 1.8 |
| CCSD | 2.647 | 0.0 | 3.007 | 0.0 |
| QCISD | 2.647 | | 3.007 | |

the clusters we have studied so far, except HF, which has a tendency to give bond lengths that are too long.

### B. Energy differences: The larger clusters $Li_5^+$ and $Li_6$

In the previous section we focused our discussion on the relative ability of various DFT and quantum chemical methods to reproduce the molecular geometries of lithium clusters. In this section we shall continue this discussion but more importantly introduce the topic of energy differences between isomers. This latter issue is crucial in that it provides insight into how well a particular method is actually representing the potential energy surfaces of these clusters. A proper account of the variation of electronic energy as a function of geometry is a necessary condition for reliable studies of cluster rearrangements and dynamics as they occur in *ab initio* finite-temperature molecular-dynamics simulations. For this reason we concentrate in this section on clusters that possess at least two isomers but that are at the same time still manageable with the techniques that we have identified to be reliable. In particular, we have chosen two isomers of $Li_5^+$ as depicted in Fig. 1(d), and three isomers of $Li_6$ shown in Fig. 1(e).

To begin this section we describe the two isomers of $Li_5^+$ that we have studied. The first, isomer I, consists of two triangles, which lie in the same plane (similar to $Li_4$) and are joined at a corner. Our QCISD optimized structure suggests that this configuration may be described as containing two short bonds of 2.837 Å, which are on the outside edges of the molecule and four longer bonds, 3.130 Å, which join the central lithium to the remaining four. The symmetry point group of this molecule is $D_{2h}$. The second isomer II is the classical trigonal bipyramidal structure. Here again, we find with the QCISD method that there are two distinct types of bonds, short and long. The three bonds along the equator

TABLE IV. Optimized Li-Li bond lengths of $Li_5^+$ isomers I and II with various methods and 6-311G* basis. Bonds are labeled as in Fig. 1(d).

| Method | $A$ (Å) | Error vs QCISD (%) | $B$ (Å) | Error vs QCISD (%) |
|---|---|---|---|---|
| | | Iosmer I | | |
| HF | 2.776 | −2.2 | 3.285 | 5.0 |
| SVWN | 2.818 | −0.6 | 3.023 | −3.4 |
| BVWN | 2.806 | −1.1 | 3.077 | −1.7 |
| BP86 | 2.853 | 0.6 | 3.105 | −0.7 |
| BLYP | 2.808 | −1.0 | 3.087 | −1.4 |
| B3LYP | 2.817 | −0.7 | 3.079 | −1.6 |
| MP2 | 2.874 | 0.2 | 3.144 | 1.8 |
| QCISD | 2.837 | | 3.130 | |
| | | Isomer II | | |
| HF | 2.899 | 5.7 | 3.212 | 1.3 |
| SVWN | 2.679 | −2.3 | 3.123 | −1.5 |
| BVWN | 2.695 | −1.7 | 3.146 | −0.7 |
| BP86 | 2.734 | −0.3 | 3.196 | 0.8 |
| BLYP | 2.695 | −1.7 | 3.146 | −0.7 |
| B3LYP | 2.695 | −1.7 | 3.146 | −0.7 |
| MP2 | 2.765 | 0.8 | 3.212 | 1.3 |
| QCISD | 2.742 | | 3.170 | |

TABLE V. Energy difference between the $Li_5^+$ isomers relative to isomer II for various methods and 6-311G* basis.

| Method | Energy difference (kcal/mol) | Error vs QCISD(T) (kcal/mol) |
|---|---|---|
| HF | 2.29 | −2.06 |
| SVWN | 7.77 | 3.42 |
| BVWN | 2.95 | −1.40 |
| BP86 | 4.44 | 0.09 |
| BLYP | 2.84 | −1.51 |
| B3LYP | 3.27 | −1.08 |
| MP2 | 3.26 | −1.09 |
| QCISD | 3.65 | −0.70 |
| QCISD(T) [a] | 4.35 | |

[a]QCISD(T) calculations were performed on the geometry obtained from the QCISD optimization.

of the trigonal bipyramid are found to be short, 2.742 Å, and the six bonds to the atoms capping the triangle are long, 3.170 Å. So we find that these two systems are ideal to further test the methods for their ability to reproduce bond alternation patterns and also to obtain an estimation of their performance on energy differences between isomers.

The results of our geometry optimizations are presented in Table IV for the same methods and the 6-311G* basis as used for $Li_4$ and percent errors in bond lengths relative to the QCISD result. These data show that, with the exception of HF, all these methods provide acceptable geometries within the errors imposed by the basis set used. This is entirely expected based on the above results. To see if these methods do in fact reproduce the energy differences obtained from the QCISD calculations we present this quantity in Table V. Since the QCISD(T) method does provide a more accurate description of the correlation energy than QCISD we choose this as our reference by which to compare relative isomer stabilities obtained from all the methods. We give this error in the second column of Table V. We note that all methods produce the QCISD(T) energy difference within about 1.5 kcal/mol except HF and SVWN. The former of the two methods provides a rather small value and the latter one is too large. All methods uniformly do place isomer II as the lower in energy. Note that, contrary to the result of the geometry optimizations, the (perturbative) triple excitations do play a role here in that they affect this particular relative energy difference by nearly 1 kcal/mol using our largest basis.

To test the influence of basis set upon the relative energetics we have calculated the energy differences of all these methods via obtaining optimized geometries with the smaller 3-21G* and 6-31G* basis sets. Again we note the trend that the bond distances obtained from these calculations were on average slightly longer, by nearly 2%, than at the 6-311G* level, for the QCISD method and by about 1% for the other methods. This is entirely in agreement with the results obtained with $Li_2$ and $Li_3^+$ from the previous section. The energy difference was found to be 3.05 kcal/mol with the 3-21G* basis and 3.55 kcal/mol for the 6-31G* basis and the QCISD(T) method compared to 4.35 kcal/mol with the 6-311G* basis. For the DFT-based methods the value of the energy difference was found to fluctuate with the basis set

used by about 1.0–1.5 kcal/mol. For example, the BLYP method provided the energy differences of 3.31, 1.51, and 2.84 kcal/mol for the 3-21G*, 6-31G*, and 6-311* basis sets, respectively. It is clear from these results that the energy differences reported in Table V are by no means a converged answer due to too small of a basis. However, it is important to note that with all these basis sets the general conclusions stated above are unchanged. On this reasoning we find that an acceptable variation in this value may be expected to be around 2–3 kcal/mol for the given maximum size of the basis set. With this figure in mind we find that only the SVWN method provides an energy difference that is clearly unacceptable.

The findings for the energy differences raise a more fundamental point. The results of the SVWN and BVWN show that with essentially similar geometries and identical correlation treatments energy differences can only be obtained with a more accurate account of the exchange energy. This is the well-known overbinding effect of the local density approximation [30], and it has been shown by Becke that gradient correction to the local density exchange of Slater compensates for this effect [31]. Thus, it appears that regardless of the functional used to model the correlation energy the necessary condition to obtain proper energy differences is an accurate exchange energy. It is clear, however, from the HF results with exceedingly long bonds that correlation (and more specifically dynamic correlation) is required to obtain a good optimized configuration. We note also that similar conclusions may be drawn from the HF and post-HF [10], DFT [11], and quantum Monte Carlo [12] calculations on elemental lithium solid.

As the final phase of our study we shall test our above observations on three isomers of $Li_6$. The first, isomer I has $C_{5v}$ symmetry and is a capped pentagon. With the QCISD method we have found that the structure has again short and long bonds. There are five bonds to the capping atom, 2.867 Å, and the five bonds between atoms in the pentagon, 3.151 Å. Isomer II is a planar, $D_{3h}$, structure having only long bonds with respect to the QCISD method. These bonds are of two types, those of the inner triangle, 2.986 Å, and those of the outside triangle, 3.038 Å. Isomer III is essentially a distorted octahedron, $D_{4h}$ symmetry, with an axial compression to form a short Li-Li bond across the center of the structure. This structure may be classified as containing only short bonds. With the QCISD method we find that the central bond is quite short, 2.666 Å, and that the remaining eight bonds, to the four atoms in the central plane, of the distorted octahedron, are only slightly larger, 2.839 Å. We note at this point that we were unable to obtain a distorted version of this isomer in the $C_{2v}$ point group within several different optimization attempts.

The results of our geometry optimizations and the energy differences are reported in Tables VI and VII, respectively. From Table VI we find that the same trend is again seen in the results with only HF yielding bond lengths that deviate unacceptably from the QCISD reference. However, we do note that the unusual central bond of isomer III is much more poorly described than the bonds in previous examples by all the methods except MP2. The energy differences presented in Table VII are interesting in that all methods find that isomer III is the lowest in energy. The results of the relative

TABLE VI. Optimized Li-Li bond lengths of $Li_6$ isomers I, II, and III for various methods and 6-311G* basis. Bonds are labeled as in Fig. 1(e).

| Method | $A$ (Å) | Error vs QCISD (%) | $B$ (Å) | Error vs QCISD (%) |
|---|---|---|---|---|
| | | Isomer I | | |
| HF | 2.907 | 1.4 | 3.331 | 5.7 |
| SVWN | 2.794 | −2.5 | 3.054 | −3.1 |
| BVWN | 2.790 | −2.7 | 3.147 | −0.1 |
| BP86 | 2.845 | −0.7 | 3.144 | −0.2 |
| BLYP | 2.804 | −2.2 | 3.133 | −0.6 |
| B3LYP | 2.798 | −2.4 | 3.141 | −0.3 |
| MP2 | 2.881 | 0.5 | 3.184 | 1.0 |
| QCISD | 2.867 | | 3.151 | |
| | | Isomer II | | |
| HF | 3.131 | 4.9 | 3.100 | 2.0 |
| SVWN | 2.926 | −2.0 | 2.938 | −3.3 |
| BVWN | 2.978 | −0.3 | 2.967 | −2.3 |
| BP86 | 3.002 | 0.5 | 3.002 | −1.2 |
| BLYP | 2.979 | −0.2 | 2.969 | −2.3 |
| B3LYP | 2.979 | −0.2 | 2.969 | −2.3 |
| MP2 | 3.057 | 2.0 | 3.022 | −0.5 |
| QCISD | 2.986 | | 3.038 | |
| | | Isomer III | | |
| HF | 2.590 | −2.8 | 2.942 | 3.6 |
| SVWN | 2.584 | −3.1 | 2.762 | −2.7 |
| BVWN | 2.549 | −4.4 | 2.798 | −1.5 |
| BP86 | 2.600 | −2.5 | 2.831 | −0.3 |
| BLYP | 2.654 | −2.8 | 2.800 | −1.4 |
| B3LYP | 2.537 | −4.8 | 2.800 | −1.4 |
| MP2 | 2.628 | −1.4 | 2.868 | 1.0 |
| QCISD | 2.666 | | 2.839 | |

stability of isomer I and isomer II are also consistent with the exception of QCISD and HF. These methods place the planar structure as the lower in energy, whereas the other methods place the capped pentagon as lower. Inclusion of the perturbative triple excitations into QCISD reverses this order. On

first sight, one may be tempted to think that this result shows that triple excitations are necessary to correct for the discrepancy between DFT methods and post-HF calculations. However, keeping in mind that the fluctuation in energy differences as a function of basis set is about 2–3 kcal/mol it

TABLE VII. Energy difference between the $Li_6$ isomers relative to isomer III for various methods and 6-311G* basis.

| Method | Isomer I (kcal/mol) | Error vs QCISD(T) (kcal/mol) | Isomer II (kcal/mol) | Error vs QCISD(T) (kcal/mol) |
|---|---|---|---|---|
| HF | 2.62 | −1.39 | 1.31 | −4.10 |
| SVWN | 7.33 | 3.32 | 13.34 | 7.93 |
| BVWN | 2.39 | −1.62 | 4.26 | −1.15 |
| BP86 | 4.14 | 0.13 | 8.03 | 2.62 |
| BLYP | 2.50 | −1.51 | 4.79 | −0.62 |
| B3LYP | 3.72 | −0.29 | 5.32 | −0.09 |
| MP2 | 5.03 | 1.02 | 7.66 | 2.25 |
| QCISD | 3.82 | −0.19 | 2.81 | −2.60 |
| QCISD(T) [a] | 4.01 | | 5.41 | |

[a]QCISD(T) calculations were performed on the geometry obtained from the QCISD optimization.

TABLE VIII. Average performance of various methods with the 6-311G* basis set. Bond lengths are relative to optimized QCISD structure and energy differences are given relative to QCISD(T).

| Method | Mean absolute % error in bond length (%) | Mean absolute error in energy (kcal/mol) |
|---|---|---|
| HF | 3.3 | 2.52 |
| SVWN | 2.3 | 4.89 |
| BVWN | 1.4 | 1.40 |
| BP86 | 0.6 | 0.94 |
| BLYP | 1.3 | 1.18 |
| B3LYP | 1.3 | 0.52 |
| MP2 | 1.1 | 1.44 |
| QCISD | | 1.16 |

would be perhaps more prudent to view these two species as essentially degenerate within the chosen computational approaches, especially in view of the limited basis set used for such a level of correlation. With this in mind, the results in Table VIII give a similar conclusion as already inferred for $Li_5^+$, i.e., all the methods except SVWN reproduce energy differences reasonably well. However, we do note that HF does provide slightly too small of an energy separation between isomer II and isomer III.

In total we find that with respect to geometry the calculations presented for $Li_5^+$ and $Li_6$ further corroborate the trends noted in the previous section. To evaluate the overall performance of the methods on geometry optimization we compare the mean absolute percent error in bond lengths, relative to QCISD, in Table VIII. This average has been taken over the 52 bond lengths considered in this study. This result clearly shows that HF provides the least accurate estimation of bond lengths with an average error of 3.3%. The propensity of this error is for lengths that are too long relative to the reference QCISD results. The second least accurate method is SVWN with an average error of 2.3%. This method gives lengths that are essentially too short. All other methods, i.e., MP2 and the gradient corrected density functionals, agree with QCISD within about 1% on average, the best method being BP86 for this particular application. Note that we roughly attributed an error bound of about 2–3% due to the incomplete basis set.

Concerning the performance on energy differences, we present the mean absolute deviation in energy relative to the QCISD(T) results in the second column of Table VIII. Here B3LYP is particularly good, as are all methods that use the Becke gradient correction for exchange. We note that the largest error is observed for the SVWN method followed second by HF. The former method clearly has a tendency for too great of an energy difference, as has been stressed above, and the latter has a propensity for too small values. However, we do note that the error for HF is within the limits we have ascribed to be acceptable due to incompleteness within the basis set. Furthermore, both comparisons show that the Becke exchange gradient correction does the major job in improving the accuracy of the DFT calculations concerning both structure and energetics, regardless of the correlation treatment.

## IV. SUMMARY AND MAIN CONCLUSIONS

Based on the study of eight different lithium clusters with a fairly extensive combination of methods and basis sets we have found a remarkable overall agreement between DFT-based and post-HF calculations concerning the optimized geometries and the relative stability of isomers. Exceptions to this observation are the HF approximation in that is overshoots bond lengths, and the local density approximation to DFT, which does not accurately reproduce energy differences between isomers. Despite the danger of an oversimplification, we propose that the most reliable results can be obtained with three simple guidelines. First, to properly describe geometries electron correlation must be included even if it is at the most rudimentary level such as in the local density approximation. Second, that proper energy differences between isomers require a good approximation to the exchange energy. This may be done either exactly as in HF-based methods, or in the form of a exchange gradient corrected density functional such as that of Becke. Third, multiple determinant effects play a minor role in the case of the investigated closed-shell clusters. Thus, methods that favor nondynamic over dynamic correlation are expected to produce artificially long bonds. We further conclude that these ''rules of thumb'' combined with care in other aspects of the calculations, such as reasonably large basis sets including necessarily polarization functions and geometry optimization with a correlated method in case of single point energy calculations, may lead to a much more uniform view of the structure and bonding exhibited in lithium clusters.

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