JCTC Journal of Chemical Theory and Computation

Full Configuration-Interaction Study on the Tetrahedral Li$_4$ Cluster

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Abstract: The Li$_4$ cluster low lying electronic states were studied. In particular we investigated the tetrahedral geometry at full CI and coupled cluster level, with basis sets of increasing quality. The $^5A_2$ electronic state, characterized by having all the valence electrons unpaired, forming a quite stable no-pair bonding state, was studied in greater detail. In order to compare the energies we also studied the Li$_4$ rhombus singlet ground state. The ability of coupled cluster with perturbative triples to correctly reproduce energy levels in a quasi-degenerate system was validated with respect to the full CI.

1. Introduction

Alkali metal clusters are very interesting molecular systems which exhibit particular and rather exotic electronic properties. In particular lithium clusters have been extensively studied by Bonačić-Koutecký and co-workers[1−5] as well as by other research groups like for instance Marx's[6] or Goddard's[7] ones. Such systems are known to have bound states in which all the valence electrons have the same spin, giving rise to the so-called "no-paired" chemical bonds, a situation which seems to be in contrast with the common chemical bonding model. For these reasons, these systems have been intensively studied by S. Shaik and co-workers using density functional techniques.[8−11] Moreover, these high-spin alkali metal clusters deserve special interest because of the role they play in the field of ultracold molecules. Although the clusters have never been observed as isolated species, at low temperature, highest-spin cluster states are stabilized by helium droplets, with a very high total spin selectivity. This gives rise to aggregates so stable that it was possible to determine experimentally many

spectroscopic parameters.[12−19] For an exhaustive recent review see for instance ref 20. In this review the authors state that alkali clusters are likely to reside on the surface of the droplets, and since the probability of desorption directly correlates with the binding energy of the cluster, weakly bound high-spin states are preferentially transported by helium droplets. As an example the authors report how the mass spectroscopy signal for dimers in triplet states is enhanced by a factor of 50.[12,20] In this first paper we restrict the study to the Li$_4$ cluster, which, due to its small size, can be analyzed at the Full Configuration-Interaction (FCI) as well as the Coupled Cluster (CC) level of theory. The equilibrium geometry of this system is characterized by a rhomboidal structure, with a singlet spin multiplicity. Just at a slightly higher energy we find a manifold of electronic states with tetrahedral geometries, which are characterized by different spin multiplicity culminating in the no-pair bonding quintet. We decided to perform a systematic study of the low lying quasi-degenerate states of Li$_4$ cluster, at a high level of theory, with particular interest to the somewhat exotic high-spin bound state. Given that FCI is the most reliable method for the description of excited states, we are interested in performing a systematic comparison between FCI and CC to assess the ability of CC to correctly reproduce the energy levels. This is specially important in a situation

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where the spatial symmetry requires more than one determinant to correctly reproduce the wave function.

We performed FCI and CC calculations at the equilibrium geometries of the singlet (rhombus) and quintet (tetrahedron) lowest states.[8−11] The rhomboidal geometrical parameters were obtained by an optimization carried on at the CCSD-(T) level with several basis sets of increasing quality. On these optimized geometries, we performed a fixed-geometry FCI computation with all the basis sets.

As far as the tetrahedral geometries are concerned, we computed both at the FCI and CCSD(T) levels the potential energy curve corresponding to the symmetrical expansion of the tetrahedron ("tetrahedron breathing mode" in spectroscopical terms). From these symmetry-constrained curves we obtained equilibrium bond distances and adjusted harmonic vibrational frequencies. Moreover, we investigated the Basis Set Superposition Error (BSSE) on the computed potential energy curves. The singlet rhomboidal ground state and all the states lying below the $^5A_2$ quintet for the T_d tetrahedral geometry were computed at the FCI and CC levels. Since our CC computations are of single-reference type, we were not able to describe all the multireference levels of this system. In some cases where a single reference CC wave function can be computed, we have a symmetry-breaking problem. In this situation the results are to be taken with caution, as it will be discussed later. This paper is organized as follows: in the second section we present some brief symmetry considerations, in the third section we expose the computational details, while in section four we present our results, drawing final conclusions in section five.

2. Symmetry Considerations

Due to the rather complex nature of the manifold of electronic states in the tetrahedron, some brief symmetry considerations (using the minimal 1s2s basis) can help for the correct analysis of the problem. The symmetry group of tetrahedral Li$_4$ is T_d. The lowest states are obtained by distributing the four valence electrons into the four valence 2s orbitals, while the four doubly occupied 1s orbitals form a totally symmetric core (A_1 symmetry) and do not contribute to the total symmetry. The four singly occupied 2s atomic orbitals give one a_1 molecular orbital and a 3-fold degenerate t_2 set with a slightly higher energy.

Two electronic configurations can be considered. First, if the a_1 orbital is kept doubly occupied, so that one has the $(a_1)^2(t_2)^2$ case, the following states (including the lowest ones) are possible[21]

$$^3T_1 \oplus {}^1A_1 \oplus {}^1E \oplus {}^1T_2$$

In the second case, we have a $(a_1)^1(t_2)^3$ electronic distribution, so the following states result

$$^{5,3}A_2 \oplus {}^{3,1}E \oplus {}^{3,1}T_1 \oplus {}^{3,1}T_2$$

We can call all the states in the first case as "closed-a$_1$-shell" to distinguish them from those of the second case: "open-a$_1$-shell".

A maximum of six singlets, five triplets, and one quintet states can be obtained from the four valence electrons in the a_1t_2 valence orbitals set.

The following five states are found in the lower energy range: (1) one quintet of A_2 symmetry; (2) a "closed-a$_1$-shell" triplet of T_1 symmetry; (3) two "closed-a$_1$-shell" singlets: one of A_1 symmetry and a 2-fold degenerate singlet of E symmetry, and (4) a "closed-a$_1$-shell" singlet of T_2 symmetry. Notice, however, that the difference between the open-a$_1$ and closed-a$_1$ shell singlets is not a rigorous one, and it is here introduced only to make easier the description of the states.

Among all these different states, the triplet is the lowest one. Since there are three degenerate components of the triplets, the system will be Jahn−Teller distorted, giving a triplet minimum that has (as far as the first evidence seems to indicate) D_{2d} symmetry. The study of this distorted Li$_4$ system will be the object of a future work.

By performing a CAS-CI calculation with the four valence ROHF orbitals of the quintet (the only possible nondegenerate ROHF calculation) and using the cc-pVTZ basis set at the ROHF optimized geometry, one obtains the following energies (in hartrees): (1) $^1A_1$: −29.704539; (2) $^1T_2$: −29.725828; (3) ^1E: −29.735939; (4) $^5A_2$: −29.753167; and (5) $^3T_1$: −29.756536.

These CAS-CI states are the starting point for the FCI and CC computations.

Since our ab initio codes are restricted to use Abelian point groups, our computations were performed in the D_{2h} and C_{2v} symmetries for the rhombus and the tetrahedron, respectively.

3. Computational Details

In this section the basis sets and the computational strategy used in the present study are described in full detail.

3.1. Basis Sets. We performed a systematic study using polarized-valence correlation-consistent basis sets (proposed by Dunning and co-workers[22−24]) of increasing quality, in particular the cc-pVDZ, cc-pVTZ, and cc-pVQZ. The bases were retrieved from the EMSL public database.[25] The use of correlation-consistent basis sets allowed us to perform extrapolation to the infinite basis,[26] leading to a better estimation of the cluster properties. Using the smaller bases, i.e., cc-pVDZ and cc-pVTZ, we computed the FCI potential energy curves for the expansion of the tetrahedron, while with the cc-pVQZ basis, only the regions close to the energy minima were calculated. In this case therefore, the curves were drawn using a limited subset of distance points.

3.2. Computational Methods. The core has been kept frozen in all the FCI computations, performed with the Bologna FCI code.[27] The core 1s orbital of each Li atom was doubly occupied and frozen at the SCF level of the $^5A_2$ in tetrahedral geometry cases, while in the rhombus case the 1s orbitals were frozen at the SCF level of the singlet ground state. The FCI space amounts to about 134 ·10^6 symmetry-adapted determinants with the cc-pVQZ basis set in C_{2v} symmetry. Integrals were computed by using the DALTON 2.0 code[28] and subsequently transformed by the Ferrara four-index transformation.[29] These codes were interfaced by using the newly developed Q5Cost format and libraries[30−33]

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designed for code interoperability. CC to the singles and doubles with noniterative correction to the triples,[34] CCSD-(T), were performed by using the MOLPRO 2000 code.[35] In this case both frozen-core (FC) and all-electrons (AE) CCSD(T) computations were carried on. In order to perform CCSD(T) calculations, preliminary ROHF wave functions were computed. The electronic configurations were $1a_1^2 2a_1^2 1 b_1^2 1 b_2^2 3a_1 4a_1 2b_1 2b_2$, $1a_1^2 2a_1^2 1b_1^2 1b_2^2 3a_1^2 4a_1 2b_1$, and $1a_1^2 2a_1^2 1b_1^2 1 b_2^2 3a_1^2 4a_1^2$ in C_{2v} symmetry, for the $^5A_2$, $^3T_1$, and ^1E states, respectively. The corresponding electron configurations in the T_d point group are $1a_1^2 1t_2^6 2a_1 2t_2^3$, $1a_1^2 1t_2^6 2a_1^2 2t_2^2$, and $1a_1^2 1 t_2^6 2a_1^2 2t_2^2$, where the last configuration (singlet) includes a doubly occupied t_2 orbital. The implications of this feature on the CCSD(T) calculations will be discussed later. In all cases the orbitals corresponding to the 1s of the Li atoms were frozen in the FC CCSD(T) computation. In case of triplet and singlet states the single-determinant ROHF wave functions are of broken-symmetry type.

3.3. Constrained Geometry Optimization. A symmetry-constrained optimization of the tetrahedral geometry was performed at the FC FCI level for all the states and at the FC and AE CCSD(T) levels for those states dominated by a single determinant. We kept the tetrahedral conformation during the computation, and our results are expressed as a function of the Li–Li distance R. The equilibrium geometry and the energy well depth were obtained by means of an exponential spline interpolation[36] of the potential. The adjusted harmonic frequency ω of the "breathing mode" of tetrahedral Li_4 was obtained from a fourth-degree polynomial least-square fitting to the energy potential of each state, expressed as a function of the normal coordinate $Q_1 = 2\sqrt{m}$ δ. In this expression δ stands for the displacement from the equilibrium position of each Li vertex along the C_3 tetrahedron axis, while m stands for the mass of Li atom. The ^7Li isotope with $m = 7.0160040$ has been assumed. The procedure was as follows: a number of points around the guessed minimum were selected so that both branches of the potential had a similar depth. A fourth-degree polynomial was then fitted to determine the minimum position. Once such position was known, the δ displacement of each point could be calculated. The resulting set of points (E, Q_1) for each state of interest was then fitted to the following polynomial

$$E = V_0 + \frac{1}{2} V_0'' Q_1^{2} + \frac{1}{3!} V_0''' Q_1^{3} + \frac{1}{4!} V_0^{IV} Q_1^{4}$$

and the corresponding adjusted harmonic frequency was obtained from the square root of the coefficient V_0'' and then converted to wavenumber units. The rhombus singlet state was optimized at the FC and AE CCSD(T) levels. A single-point FC FCI computation was subsequently performed at the FC CCSD(T) optimized geometry. The equilibrium distances were expressed as the two rhombus diagonals, R_1 and R_2 (with $R_1 > R_2$).

4. Results and Discussion

The main results for the tetrahedron geometry are collected in Tables 1–3. At the FC FCI level the states are the same as those obtained at the CAS-CI level, as reported in section

Table 1. Li_4 cc-pVDZ Tetrahedron Spectroscopic Properties[a]

		R	E	$\omega(err)$
$^3T_1$				
	CCSD(T) FC	5.649	−2.178	316.7 (1.2)
	CCSD(T) AE	5.618	−2.218	316.6 (0.8)
	FCI FC	5.649	−2.238	322.4 (1.1)
$^1T_2$				
	FCI FC	5.722	−1.993	320.7 (1.2)
^1E				
	CCSD(T) FC	5.633	−1.760	312.2 (0.9)
	CCSD(T) AE	5.598	−1.800	306.8 (0.5)
	FCI FC	5.639	−1.838	311.7 (1.2)
$^1A_1$				
	FCI FC	5.761	−1.456	317.6 (1.3)
$^5A_2$				
	CCSD(T) FC	5.777	−1.248	271.7 (1.8)
	CCSD(T) AE	5.742	−1.282	269.2 (0.6)
	FCI FC	5.784	−1.267	271.3 (1.0)

[a] R is the equilibrium Li–Li distance in bohr, E is the dissociation energy with respect to four Li atoms in their ground states in eV, and $\omega(err)$ is the adjusted harmonic frequencies and fitting error (in brackets) in cm^{-1}.

Table 2. Li_4 cc-pVTZ Tetrahedron Spectroscopic Properties[a]

		R	E	$\omega(err)$
$^3T_1$				
	CCSD(T) FC	5.535	−2.350	329.5 (1.2)
	CCSD(T) AE	5.453	−2.472	323.8 (0.9)
	FCI FC	5.539	−2.404	318.9 ((1.2)
$^1T_2$				
	FCI FC	5.613	−2.170	316.8 (1.4)
^1E				
	CCSD(T) FC	5.506	−1.956	317.3 (1.1)
	CCSD(T) AE	5.423	−2.081	320.6 (0.9)
	FCI FC	5.517	−2.035	315.5 (1.4)
$^1A_1$				
	FCI FC	5.652	−1.632	312.2 (1.1)
$^5A_2$				
	CCSD(T) FC	5.696	−1.347	271.6 (1.1)
	CCSD(T) AE	5.588	−1.464	274.5 (1.1)
	FCI FC	5.702	−1.367	271.1 (1.1)

[a] R is the equilibrium Li–Li distance in bohr, E is the dissociation energy with respect to four Li atoms in their ground states in eV, and $\omega(err)$ is the adjusted harmonic frequencies and fitting error (in brackets) in cm^{-1}.

2, but the energy order is different. At the CC level only the $^3T_1$, ^1E, and $^5A_2$ states could be computed. The $^3T_1$ is the ground state both at the CAS-CI and FCI levels. On the other hand, the $^5A_2$ state, which is the first excited CAS-CI state, becomes the highest, i.e., the fourth excited one in FCI. This fact is certainly due to the small dynamic correlation associated with the quintet states as compared to the singlets and triplets. Among the singlet states the E and the T_2 are interchanged from the CAS to the FCI description. This is due to the presence of an important nondynamic correlation in the case of the open-shell $^1T_2$ state. The $^3T_1$, ^1E, and $^5A_2$ states dissociate to four Li atoms in their ground ^2S states, while the $^1T_2$ and $^1A_1$ multireference states dissociate to a symmetry adapted combination of three Li atoms in their

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Table 3. Li$_4$ cc-pVQZ Tetrahedron Spectroscopic Properties[a]

		R	E	$\omega(err)$
$^3T_1$				
	CCSD(T) FC	5.527	−2.382	320.7 (1.2)
	CCSD(T) AE	5.305	−2.745	355.3 (1.2)
	FCI FC	5.532	−2.437	310.8 (1.0)
$^1T_2$				
	FCI FC	5.601	−2.206	309.3 (0.8)
^1E				
	CCSD(T) FC	5.500	−1.996	316.9 (1.2)
	CCSD(T) AE	5.275	−2.361	352.8 (1.5)
	FCI FC	5.511	−2.071	306.0 (1.2)
$^1A_1$				
	FCI FC	5.646	−1.669	305.3 (1.1)
$^5A_2$				
	CCSD(T) FC	5.692	−1.364	271.9 (1.0)
	CCSD(T) AE	5.387	−1.700	305.7 (1.3)
	FCI FC	5.646	−1.383	264.1 (1.2)

[a] R is the equilibrium Li−Li distance in bohr, E is the dissociation energy with respect to four Li atoms in their ground states in eV, and $\omega(err)$ is the adjusted harmonic frequencies and fitting error (in brackets) in cm^{-1}.

ground state and one Li atom in a ^2P ($1s^2 2p^1$) state, as it has been verified by an analysis of the FCI wave function in the dissociation region. This fact has also been confirmed by checking that the tetramer energy at the limit of infinite Li−Li distance is equal to the energy of three lithium atoms, in their ground state, plus the energy of one lithium atom in a ^2P state. The equilibrium properties of the tetrahedral states for all the levels of theory are reported in Tables 1−3 for the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis, respectively. The FC FCI potential energy curves for the tetrahedral states are also reported in Figure 1. In Table 4 we report the equilibrium properties for the rhombus geometry. The Complete Basis Set (CBS) extrapolated values for the two geometries are reported in Table 4 for the rhombus and in Table 5 for tetrahedron geometry, respectively. The CBS-(QT) values were computed by extrapolating to the complete basis set limit the obtained equilibrium properties for the various electronic states, by using the formula proposed in ref 26.

As discussed above, the triplet $^3T_1$ tetrahedron ground state is obtained by putting two electrons in two of the triply degenerate t$_2$ orbitals. The energy difference between the tetrahedral states and the rhombus ground state is rather small. The energy difference between the tetrahedral triplet and the rhombus singlet is about 0.5 eV, while the corresponding difference for the quintet is about 1.6 eV. The adjusted harmonic frequencies reported in Tables 1−3 reflect the change of curvature of the potential (in the region around the minima) as one goes from the $^3T_1$ ground state to the $^5A_2$ quintet state. The similarity between the FC FCI and FC CCSD(T) values is confirmed, but some interesting features, related to the AE CCSD(T) results, indicate a quite important core effect that we will discuss in greater detail in the next subsection. Finally, we report in Table 6 the dissociation energy for the reaction 2Li$_2$ → 4Li computed at FC CCSD (which for this system is equivalent to FC FCI) and AE CCSD(T) with the three different basis sets. From

these data one can see that the Li$_2$ dimer is less stable than the rhombus Li$_4$ tetramer and also less stable than the tetrahedral $^3T_1$ state. Our results can be compared with the DFT computation recently reported by Shaik et al. in different papers (see ref 8 and references therein). For the $^5A_2$ state the estimated bond dissociation energy is 1.197 eV, and the equilibrium Li−Li distance is 5.5857 bohr.[8] These results were obtained by using the B3PW91 functional and a 6-311G(2d) basis, although some slight variability is found by using different functionals.

4.1. Core Correlation. If we consider the vibrational frequencies reported in Tables 1−3, we may see that the contribution of the core electrons described with the cc-pVDZ basis set has an opposite sign compared to that of the larger basis sets, and this can be certainly related to the poor description of the core. This is a well-known defect of the cc-pVXZ basis sets, and it is quite large for the triple-ζ (about 3−4 cm^{-1}) and very high for the quadruple-ζ basis (about 35 cm^{-1}). This reflects that the bases are far from being saturated for this property, if one wants to account for the core effects. Of course, better adapted basis sets such as the polarized core-valence XZ can be used but, due to the larger basis dimension, the computational cost would be higher. As can be seen from Figure 2, and from the values of equilibrium properties reported in the tables, the FC FCI results are extremely close to those corresponding to the FC CCSD(T). For instance, for the quintet state the energy difference along the potential is usually less than 0.02 eV (cc-pVQZ basis) and never exceeds 0.08 eV. Finally, the effect of core correlation on the value of the energy well depth appears to be important, although not essential. The difference between the FC and the AE CCSD(T) energy well depth is about 0.4 eV, while the equilibrium distance is much less sensitive. For a comparison, at infinite distance the effect of core correlation amounts to 0.365 eV (cc-pVTZ) and 0.466 eV (cc-pVQZ) per Li atom. For these reasons we decided to perform AE and FC CCSD(T) calculations using the polarized core-valence cc-pCVQZ basis set. The corresponding results are collected in Table 7. As can be seen by using such a basis set, the difference among FC and AE CCSD-(T) computed properties diminishes significantly if compared with the cc-pVQZ FC and AE values, thus confirming the rigidity of the core description in the pVXZ basis set series. Unfortunately, due to the larger basis dimension, the price one has to pay in order to use the cc-pCVXZ basis is a higher computational cost, as already stated. Hence, the FCI computations with these basis sets would have been too expensive, and they have not been performed.

4.2. The Quintet State. From a theoretical point of view, the bound quintet $^5A_2$ state is the most interesting one, and a large amount of literature has been produced (for example see refs 8 and 11 and references therein). In Figure 2, we compare the potential energy curve for this state computed at the SCF, FC CCSD(T), AE CCSD(T), and FC FCI levels. The SCF curve shows a pronounced minimum giving a well depth of almost one-half to that obtained in the FC FCI calculation. This situation is in sharp contrast with the behavior of the triplet Li$_2$ state (see Figure 3), for which the SCF gives a repulsive curve, and only the correlated methods
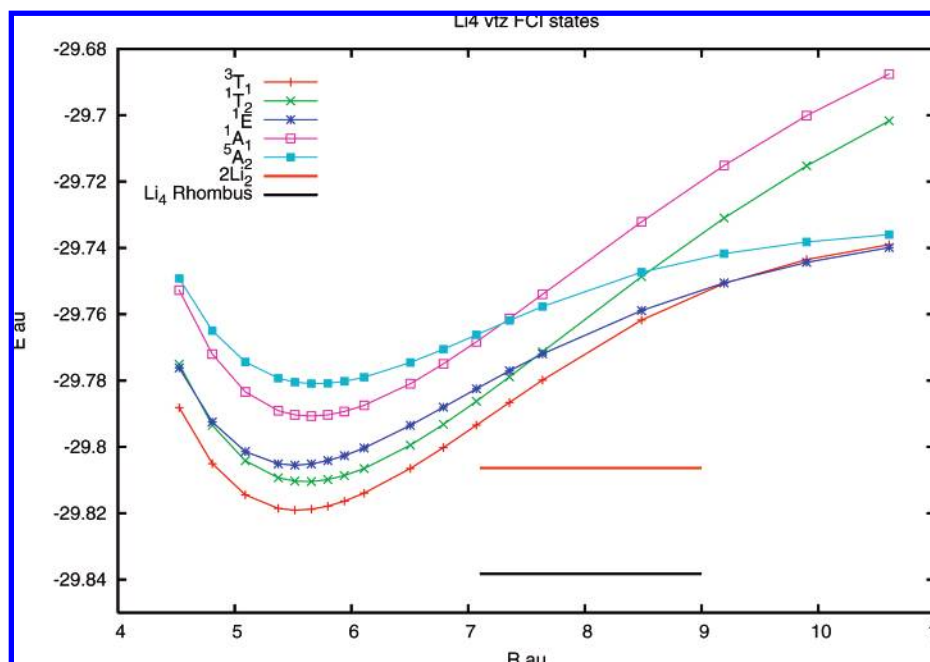
Figure 1. Li_4 FCI cc-pVTZ basis potential energy curves. Li_4 rhombus indicates the energy level of the tetramer in the equilibrium rhombus geometry, while $2Li_2$ is the energy of two isolated Li_2 dimers in the equilibrium $^1\Sigma_g^+$ state. Distances are given in bohrs and energies in hartrees.

Table 4. Li_4 Rhombus Equilibrium Properties[a]

		R_1	R_2	E
cc-pVDZ				
	CCSD(T) FC	10.366	5.160	−2.762
	CCSD(T) AE	10.325	5.113	−2.796
	FCI FC	//	//	−2.783
cc-pVTZ				
	CCSD(T) FC	10.244	5.040	−2.906
	CCSD(T) AE	10.142	4.945	−3.012
	FCI FC	//	//	−2.927
cc-pVQZ				
	CCSD(T) FC	10.238	5.031	−2.940
	CCSD(T) AE	9.902	4.837	−3.237
	FCI FC	//	//	−2.959
infinite basis	set extrapolation			
	CCSD(T) FC	10.235	5.027	//
	CCSD(T) AE	9.782	4.783	//
	FCI FC	//	//	−2.975

[a] R_1 and R_2 are the diagonals of the rhombus (in bohr), and E is the dissociation energy with respect to four Li atoms in their ground states (in eV).

Table 5. Li_4 Tetrahedron Equilibrium Geometry Extrapolated to the Infinite Basis Set[a]

		R	E
$^3T_1$			
	CCSD(T) FC	5.523	−2.248
	CCSD(T) AE	5.231	−2.881
	FCI FC	5.529	−2.454
$^1T_2$			
	FCI FC	5.95	−2.224
^1E			
	CCSD(T) FC	5.497	−2.202
	CCSD(T) AE	5.201	−2.501
	FCI FC	5.508	−2.114
$^1A_1$			
	FCI FC	5.643	−1.688
$^5A_2$			
	CCSD(T) FC	5.690	−1.373
	CCSD(T) AE	5.287	−1.818
	FCI FC	5.618	−1.391

[a] R is the equilibrium Li−Li distance in bohr, and E is the dissociation energy with respect to four Li atoms in their ground states in eV.

Table 6. Li_2 Dimer Dissociation Energy (in eV)[a]

	FC CCSD=FC FCI	AE CCSD(T)
cc-pVDZ	−1.948	−1.968
cc-pVTZ	−2.059	−2.117
cc-pVQZ	−2.085	−2.262

[a] The energy values are given with respect to the dissociation of two dimers (singlet multiplicity) to four Li atoms.

predict a small energy well. By using the cc-pVTZ basis we obtained at the CCSD level, for the Li_2 triplet (note that the FC case is equivalent to the FCI), an equilibrium distance of 3.984 bohr and a well depth of 0.0396 eV only. Instead, in the AE CCSD(T) case, the equilibrium distance amounts to 3.915 bohr and the dissociation energy to −0.0455 eV. The SCF curve of the Li_4 quintet state (see Figure 2) shows a tiny barrier at about 9.5 bohr (9.511 bohr for the cc-pVTZ basis) of about 0.02 hartree (0.024 hartree for the cc-pVTZ basis). This is in agreement with the expected long-range repulsive behavior of the high-spin SCF. These facts, combined with the difference in binding energies for the dimer and the tetramer, indicate that the actual nature of the no-pair bound in these systems is not yet perfectly understood.

As reported by Shaik et al.,[8−11] a key feature of the quintet bound state nature is the strong participation of p type orbitals to the molecular orbitals involved in the bond. The key role of the p orbitals in explaining the nature of the lithium systems was pointed out also by Marx and Rousseau[6] in their
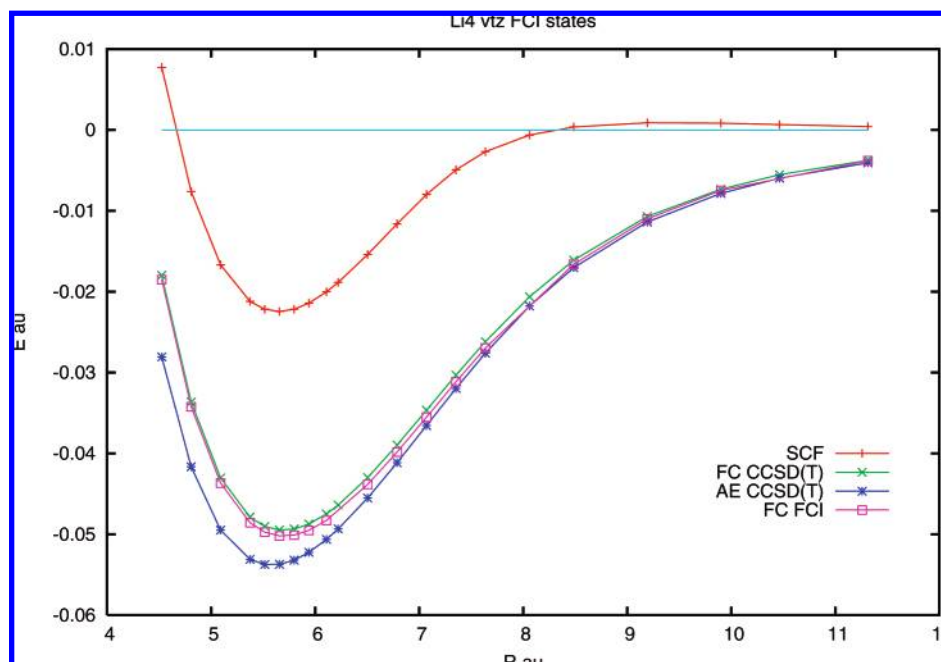
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Figure 2. Li$_4$ $^5A_2$ quintet state potential energy curves at various levels of theory. Distances are given in bohrs and energies in hartrees. Energies are given with respect to the corresponding dissociation limit values.

Table 7. Li$_4$ cc-pCVQZ CCSD(T) Tetrahedron Spectroscopic Properties^a

		R	E	ω(err)
$^3T_1$				
	CCSD(T) FC	5.526	−2.386	321.5 (0.8)
	CCSD(T) AE	5.467	−2.418	325.5 (0.7)
^1E				
	CCSD(T) FC	5.498	−1.999	317.0 (0.7)
	CCSD(T) AE	5.442	−2.025	322.4 (0.7)
$^5A_2$				
	CCSD(T) FC	5.688	−1.366	272.2 (1.0)
	CCSD(T) AE	5.620	−1.368	276.4 (0.8)

^{a} R is the equilibrium Li−Li distance in bohr, E is the dissociation energy with respect to four Li atoms in their ground states in eV, and ω(err) is the adjusted harmonic frequencies and fitting error (in brackets) in cm^{-1}.

analysis of the rhombus Li$_4$ The importance of the *p* orbitals is confirmed, for example, if one performs a SCF computation only using the *s* cc-pVTZ basis without *p* orbitals. In this case a repulsive curve is found. Moreover, the inclusion of *p* orbitals seems to lower the energy gap between the a_1 and the t_2 orbitals, therefore favoring the population of the t_2 shell. With the cc-pVTZ basis at the quintet FC FCI equilibrium geometry (5.702 bohr) one obtains a a_1-t_2 energy gap of 0.09949 hartrees for the complete basis set and a gap of 0.122424 hartrees for the subset comprising only *s* orbitals. Therefore, the elimination of *p* orbitals increases the gap by about 20%. The mixing of *p* orbitals induces a strong distortion in the valence orbitals in the region of the energy minimum. This can be seen if local hybrid orbitals[37] are computed from a ROHF wave function. At long distance the local valence orbitals are spherical, as shown in Figure 4a, where an orbital from an ANO 4s2p basis set,[38] at a Li−Li distance of 12.0 bohr, is represented. In Figure 4b, the corresponding orbital at a distance of 5.5 bohr is plotted. At this last distance one can see how the distorted orbitals allow

a migration of the charge toward the inner region of tetrahedron and in particular around the Li−Li bonds. This can explain the stability of the no-pair bond state and confirms the explanation proposed by Shaik et al.[8]

Moreover, these facts, are in agreement with the analysis performed by Gatti et al.[39] using the Atoms in Molecules formalism. In the case of lithium aggregates, they found an unusual maximum of the electronic density at the midpoint of the Li−Li equilibrium distance. At the FC FCI level the quintet wave function has a very strong single-determinant nature, as it was confirmed by the analysis of the wave function in terms of determinant contributions. This can also be seen from the occupation numbers of the natural orbitals reported in Table 8 for the cc-pVTZ basis. The occupation is mainly restricted to the four quasi-degenerated a_1 and t_2 orbitals, with some small contributions from higher orbitals.

4.3. The Symmetry-Breaking Problem. As stated before in the computational details section, the use of Abelian subgroups leads to symmetry breaking for the triplet and the singlet tetrahedral states for our single-reference CCSD(T) computations. FCI is not affected by this problem. This effect is already present at the ROHF level (see the section on Computational Details). One way to investigate the symmetry breaking is the use of the quintet ROHF state (which is symmetry breaking-free) as a reference state for all the subsequent CC calculations. We performed such a test with the cc-pVTZ basis at the Li−Li equilibrium distance of 5.656 bohr. We computed the FC CCSD(T) energy values for the singlet and triplet states starting respectively from the quintet reference state and from the usual symmetry broken ROHF triplet and singlet determinants, subsequently comparing the obtained values among them and with the FC FCI.

For the singlet ^1E state we obtained a FC CCSD(T) energy value of −29.80123 hartrees starting from the quintet reference state. This value can be compared to the FC CCSD-
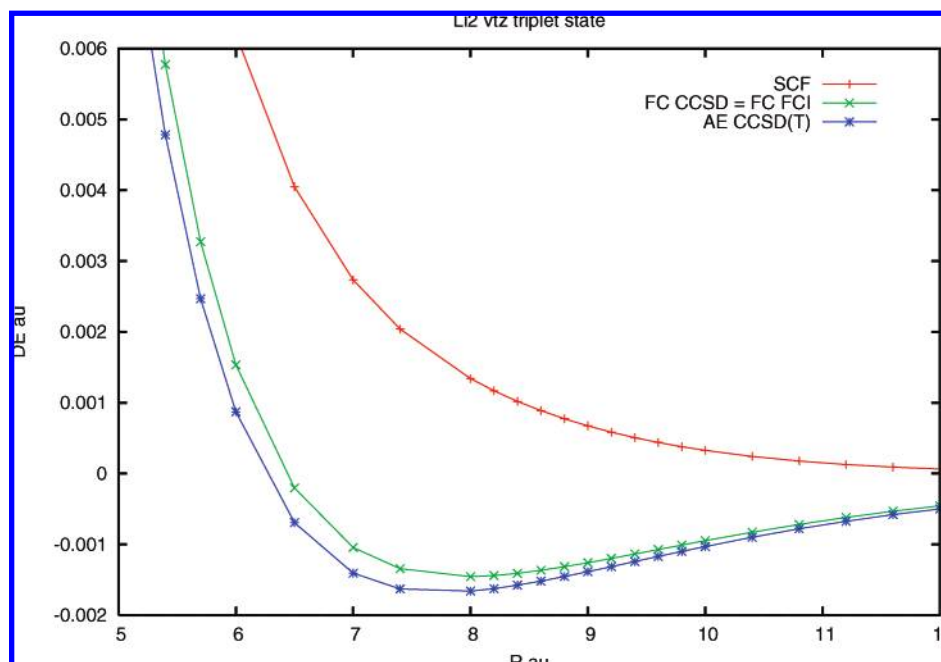
Figure 3. Potential energy curves for the Li_2 triplet $^3\Sigma_u^+$ state at various levels of theory. Distances are given in bohrs and energies in hartrees. Energies are given with respect to the corresponding dissociation limit values.
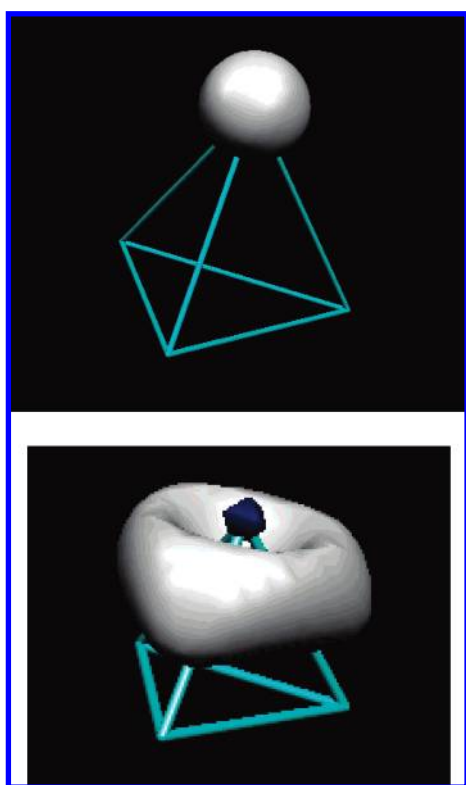

Figure 4. Local valence orbital for the Li_4 $^5A_2$ state at two different distances R: (a) $R = 12.0$ bohr and (b) $R = 5.5$ bohr.

Table 8. FC FCI Natural Orbital Symmetries and Occupation Numbers for the $^5A_2$ Li_4 State

orbital multiplet	symmetry	orbital occupation no.
1	a_1	0.9836
2	t_2	0.9493
3	e	0.0294
4	t_2	0.0224
5	a_1	0.0085
6	t_2	0.0067
7	t_1	0.0020
8	t_2	0.0013
9	a_1	0.0009
10	e	0.0004
11	t_2	0.0003

to the symmetry breaking that are very small, compared with the corresponding differences with FCI. The excitation energies are almost unaffected. The differences in CC excitation energy are $9.0 \cdot 10^{-4}$ for the ^1E state and $1.0 \cdot 10^{-5}$ for the $^3T_1$ state.

4.4. Basis-Set Superposition Error. The Basis-Set Superposition Error[40] effect was evaluated by using the standard Boys−Bernardi Counterpoise Correction.[41] As we are using size-extensive methods, such a procedure is valid on the whole potential energy curve.[33] The behavior of the counterpoise correction is illustrated in Figures 5 and 6 for the FC and the AE cases, respectively. The effect of the BSSE appears to be small with the bases used in this study. In the FC case the effect decreases by using larger basis sets, and it is practically negligible, even with the smallest cc-pVDZ basis. In the AE case, the behavior is less regular although the effect is still small. For these reasons we do not report the BSSE-corrected potential energy curves and spectroscopic properties. A rather surprising nonmonotone behavior of the counterpoise curves is observed in almost all cases. The
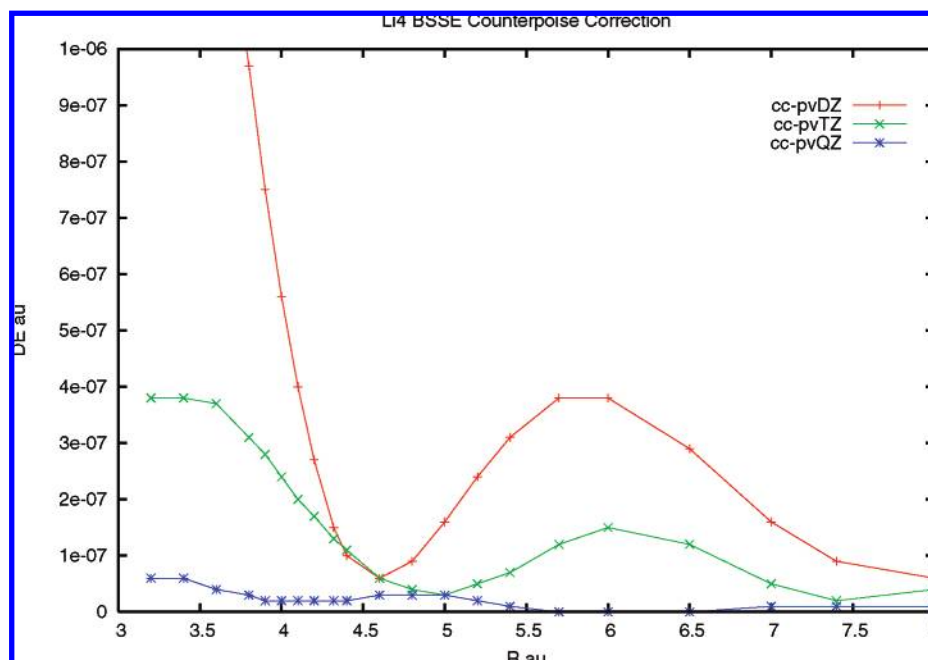
(T) value of -29.80218 hartrees obtained using the singlet reference state and to the FC FCI of -29.80514 hartrees.

Correspondingly, for the triplet $^1T_1$ state we obtained a FC CCSD(T) energy value of -29.81668 hartrees using the quintet as the ROHF reference state. This value can be compared with the FC CCSD(T) value of -29.81669 hartrees using the triplet as the reference state and to the FC FCI value of -29.81879 hartrees. These results show effects due

Figure 5. Frozen core BSSE for all states of Li$_4$ estimated by the counterpoise method. Distances are given in bohrs and energies in hartrees.
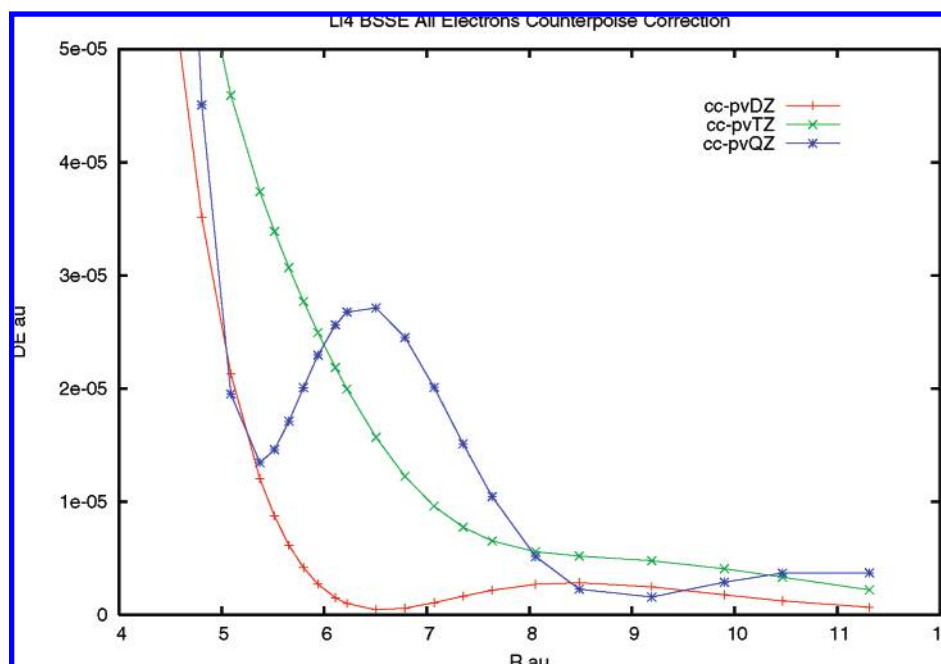

Figure 6. All electrons BSSE for all states of Li$_4$ estimated by the counterpoise method. Distances are given in bohrs and energies in hartrees.

reason for this behavior is probably due to the rather poor description of the core basis functions of the basis sets (as discussed in subsection 4.1).

5. Conclusions

We present a FCI and coupled cluster benchmark study of some low-lying electronic states of the Li$_4$ cluster, in particular the rhombus singlet ground and several tetrahedral states with different spin multiplicity. The CCSD(T) method appears to be an extremely reliable tool for the investigation of these systems, as long as no quasi-degenerate states are involved. The cc-pVTZ and a fortiori the cc-pVQZ basis set can be considered quite close to the basis set limit for the frozen-core approach. CCSD(T) computations with these bases can therefore be used to investigate larger high-spin lithium clusters, where FCI would be unfeasible. In particular coupled cluster is able to reproduce the no-pair bonding state with remarkable accuracy, giving values extremely close to the ones in FCI for the equilibrium properties. As far as the nature of the "no-pair bond" of the quintet state is concerned,

the explanation proposed by Shaik, on the ground of a VB calculation, has been confirmed by an independent method.

We plan to extend this investigation in two directions: on one hand, we will use CC to study other alkali metal clusters (Na_4, K_4, etc.), looking for further insight into the nature of the bonds in high spin states. On the other hand, it will be interesting to perform a FCI and CC study on the Jahn−Teller distortion of the triplet state in Li_4.

Moreover it will be interesting to perform computation of alkali clusters interacting with helium in order to assess theoretically the experimentally observed stabilization mechanism of the high-spin states.

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CT7003319