Binding energies of small lithium clusters (Lin) and hydrogenated lithium clusters (LinH)

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Binding energies of small lithium clusters (Li_n) and hydrogenated lithium clusters (Li_nH)

Steven E. Wheeler, Kurt W. Sattelmeyer, Paul v. R. Schleyer, and Henry F. Schaefer III[a]
Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Large coupled cluster computations utilizing the Dunning weighted correlation-consistent polarized core-valence (cc-pwCVXZ) hierarchy of basis sets have been conducted, resulting in a panoply of internally consistent geometries and atomization energies for small Li_n and Li_nH ($n = 1-4$) clusters. In contrast to previous *ab initio* results, we predict a monotonic increase in atomization energies per atom with increasing cluster size for lithium clusters, in accordance with the historical Knudsen-effusion measurements of Wu. For hydrogenated lithium clusters, our results support previous theoretical work concerning the relatively low atomization energy per atom for Li_2H compared to LiH and Li_3H. The CCSD(T)/cc-pwCVQZ atomization energies for LiH, Li_2H, Li_3H, and the most stable isomer of Li_4H, including zero-point energy corrections, are 55.7, 79.6, 113.0, and 130.6 kcal/mol, respectively. The latter results are not consistent with the most recent experiments of Wu. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1645242]

I. INTRODUCTION

Small clusters of alkali metal atoms, particularly lithium clusters, have been the subject of numerous experimental and theoretical studies in recent decades;[1–7] however, a relatively large degree of inconsistency in computed energies and geometries for these structures still remains. The primary interest in studying small metal clusters is the characterization of changes that occur in energetics and bonding in going from small clusters to the bulk material—the transformation from the simple covalent bond in Li_2, to multicenter bonding in small to moderately sized clusters, to the limit of delocalized electrons in the bulk metal.[7]

Additionally, the study of hydrogenated lithium clusters has received attention,[5,8–11] due to a desire to understand the interaction of conductor and insulator portions of such clusters as well as the chance to examine the influence of the interplay between metallic and partly polar bonding on structural characteristcs of these species.[9–11] Hydrogenated lithium clusters are expected to exhibit similar behavior to alkali halides, while possessing distinct binding properties due to the difference in electron affinity of hydrogen compared to the halides.[10,11] More lofty potential applications in hydrogenated metal clusters involve the development of novel hydrogen storing materials.[8,12,13]

The most often cited previous theoretical works on lithium clusters and hydrogenated lithium clusters are a series of large multireference configuration interaction (MRD-CI) studies carried out by the research group of Bonačić-Koutecký in the late 1980s and early 1990s.[3,5,9–11] In an attempt to employ a method that can accurately reproduce these CI results while being easily applied to larger clusters, consisting of possibly dozens of lithium atoms, more recent studies are primarily based on density functional theory (DFT).[13–17] The application of robust *ab initio* electronic structure methods to clusters of this size is impracticable, making a turn to less computationally demanding methods such as DFT not only desirable but necessary. Given the lack of a means of systematically improving DFT computations, comparison of results using a series of functionals to more reliable *ab initio* results for a set of test cases will help gauge the accuracy of DFT results for larger clusters. However, as indicated previously by Rousseau and Marx,[18] justification of DFT results upon comparison with the MRD-CI results of Bonačić-Koutecký *et al.* should be done with caution since the MRD-CI structures of Bonačić-Koutecký are optimized primarily at the Hartree–Fock level, with the bond lengths then scaled by a common factor to yield the MRD-CI results. Rousseau and Marx[18] answered the clarion call for a systematic comparison of popular DFT functionals with *ab initio* results for a series of small, closed-shell lithium clusters (Li_2, Li_3^+, Li_4, Li_5^+, and Li_6), though their warnings concerning the justification of DFT geometries and energetics based on Bonačić-Koutecký's CI results, as well as their findings regarding the performance of DFT functionals for these small lithium clusters, seem to have gone largely unnoticed.

The systematic comparison of DFT and *ab initio* methods conducted by Rousseau and Marx is somewhat lacking, however, in that the primary emphasis is on the behavior of geometrical parameters with basis set and method, largely ignoring the resulting energetics. An additional weakness is the limitation to exclusively closed-shell clusters, as evaluation of DFT methods for both closed- and open-shell lithium clusters will be necessary before such methods can be applied with confidence to larger clusters.

A primary goal of the present study is to provide a set of definitive *ab initio* geometries and energies for small lithium and hydrogenated lithium clusters, through large coupled cluster computations, in order to provide a standard against

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[a] Electronic mail: hfsiii@uga.edu

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which DFT computations may be evaluated before being applied to larger clusters. We also wish to provide reliable atomization energies for these clusters, in an attempt to rectify the currently inconsistent body of experimental energetics data—current experimental atomization energies exhibit discrepancies as large as 19 kcal/mol.

Experimental observation of lithium clusters larger than the dimer was initially conducted by Wu in the mid 1970s, with the first identification of gaseous Li_3 and measurement of the atomization energies of Li_2 and Li_3 through Knudsen-effusion mass spectrometry,[19] followed by the first experimental evidence of Li_4 in 1983.[20] More recent Knudsen-effusion measurements of hydrogenated lithium clusters (Li_nH, $n=1-4$) have also been conducted.[21] Bréchignac *et al.*[6] have determined the binding energies of Li_n^+ ($n=2-42$) through evaporative experiments, which were then used to derive atomization energies of the corresponding neutral clusters via experimental ionization potentials. The resulting relative atomization energies for small clusters are in disagreement with the results of Wu.

Partly due to the small number of electrons involved, lithium clusters have received a great deal of attention from theorists over the years, and no attempt will be made here to provide a review of this voluminous body of work. Instead, we will focus on several representative theoretical works that have systematically treated the lithium clusters and hydrogenated clusters. These works include the MP2 and CISD geometry optimizations and energies of Rao and Jena,[2,4] the MRDCI scaled geometries and energies of Bonačić-Koutecký *et al.*,[3,5,9] and the comparative study of Rousseau and Marx.[18] The lithium trimer, due in part to a combination of computational accessibility and exhibition of complex behavior, has been the subject of multitudinous high level *ab initio* studies and dynamics simulations.[22–25] In this work the focus will be entirely on the geometry and energy of the well-characterized Li_3 C_{2v} doublet ground state.

Similarly, there has been a large amount of previous computational work on Li_nH clusters. Studies against which we compare our current results include the MP4 geometries and energies of Rao and Jena[8] and Bonačić-Koutecký's CI work.[9–11]

II. THEORETICAL METHODS

All geometries were optimized via finite differences of energies, using both the singles and doubles coupled cluster (CCSD) method[26,27] and perturbative inclusion of triple excitations [CCSD(T)].[28–31] This was accomplished in conjunction with the Dunning weighted correlation-consistent polarized core-valence basis sets through quadruple-ζ quality,[32–34] cc-pwCVXZ (X=T and Q) for lithium and hydrogen. The lithium cc-pwCVXZ basis sets are formed by augmenting the standard cc-pVXZ basis sets[33] with two s and p functions and one d function for cc-pwCVTZ (α_s =5.008, 1.641; α_p=4.222, 0.930; α_d=0.850) and three s and p functions, two d functions, and one f function for cc-pwCVQZ (α_s=10.393, 3.684, 1.306; α_p=11.244, 3.377,
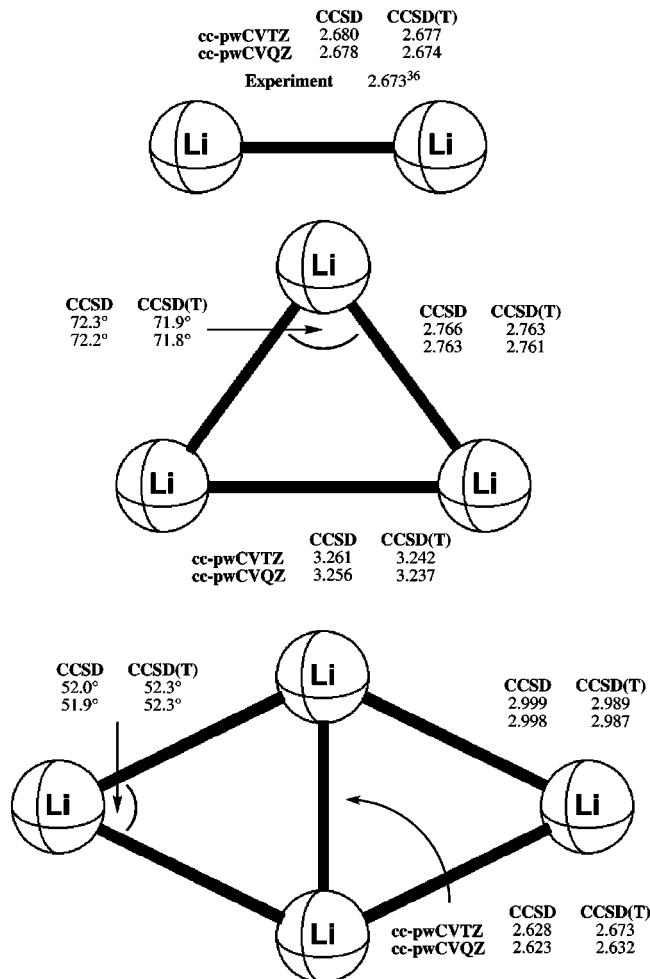

FIG. 1. Optimized Li_n geometries (bond lengths in angstroms and angles in degrees).

1.014; α_d=6.333, 1.168; α_f=0.974).[34] No orbitals were frozen in any of the computations, i.e., all electrons were explicitly correlated.

Zero point energy corrections were found by computing harmonic vibrational frequencies through finite differences of energy points. For the closed shell systems (Li_2, Li_4, LiH, and Li_3H) a restricted Hartree Fock (RHF) wavefunction was used as the CCSD reference, while a restricted open-shell Hartree Fock (ROHF) reference was used for the open-shell clusters (Li, Li_3, Li_2H, and Li_4H). All computations were carried out using a local version of the ACESII program package.[35]

Geometries were optimized and vibrational frequencies computed using both CCSD and CCSD(T) with both basis sets for Li_n ($n=1-4$) and Li_nH ($n=1-3$). For Li_4H, geometries were optimized at the CCSD/cc-pwCVXZ (X=T and Q) and CCSD(T)/cc-pwCVXZ (T and Q) levels, and frequencies were computed using the triple-ζ basis sets with both CCSD and CCSD(T). The ZPVE-corrected CCSD/cc-pwCVQZ energy was computed from the CCSD/cc-pwCVQZ optimized geometry with the ZPVE energy from the CCSD/cc-pwCVTZ frequencies. The ZPVE-corrected CCSD(T)/cc-pwCVQZ energy was computed using the ZPVE from the CCSD(T)/cc-pwCVTZ frequencies with a
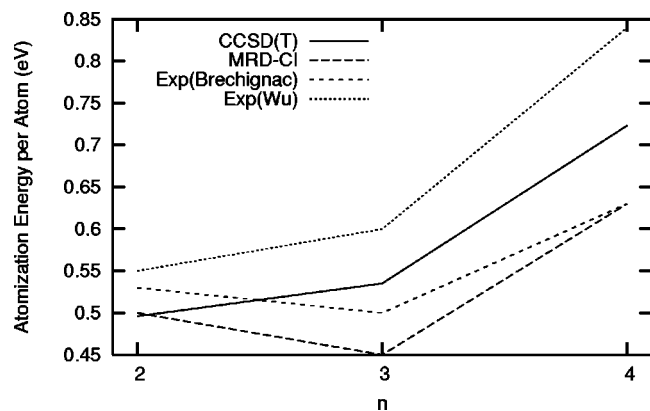
FIG. 2. Computed and experimental atomization energies per atom for Li_n.

single point CCSD(T)/cc-pwCVQZ energy at the CCSD/cc-pwCVQZ geometry.

III. RESULTS

In the following we present optimized geometries, included as Figs. 1–4, as well as the results of frequency computations for Li_n and Li_nH ($n = 1$–4) at both the CCSD and CCSD(T) levels of theory with the cc-pwCVXZ (X = T and Q) correlation consistent basis sets. We begin with results for the lithium clusters, followed by a discussion of the hydrogenated clusters. For the two cluster types, it is clear that

both the optimized bond lengths and energies are well converged with respect to both basis set size and inclusion of electron correlation.

A. Li_n geometries and atomization energies

As an indication of the accuracy of the employed methods, we note that at the CCSD(T)/cc-pwCVQZ level, the experimentally derived equilibrium bond length of 2.673 Å for the lithium dimer[36] is reproduced to within 0.001 Å—a value that is approached systematically with increased basis set size and level of correlation. For comparison, the CCSDT/6-311G* results of Rousseau and Marx (2.680 Å) and the CISD/STO-6G results of Rao et al. (2.646) differ from experiment by 0.007 and 0.027 Å, respectively.

The CCSD(T)/cc-pwCVQZ optimized geometry for Li_3 yields similar accuracy, with bond lengths of 2.761 and 3.237 Å, compared to experimentally determined equilibrium bond lengths of 2.73 and 3.20 Å, respectively.[37] An additional stationary point of C_s symmetry, with an apex angle of approximately 50°, is well established in the experimental and theoretical literature as a first-order saddle point[15,22–25,37] and was therefore not included in the current study. Given the glut of both theoretical and experimental investigations on the lithium trimer in the literature, attention was focused primarily on attempting to validate the ability of CCSD(T)/cc-pwCVQZ to reproduce previous Li_3 results for the ground state (C_{2v}) geometry and energy only. Krämer et al.[25] have computed accurate potential energy surfaces for the lowest
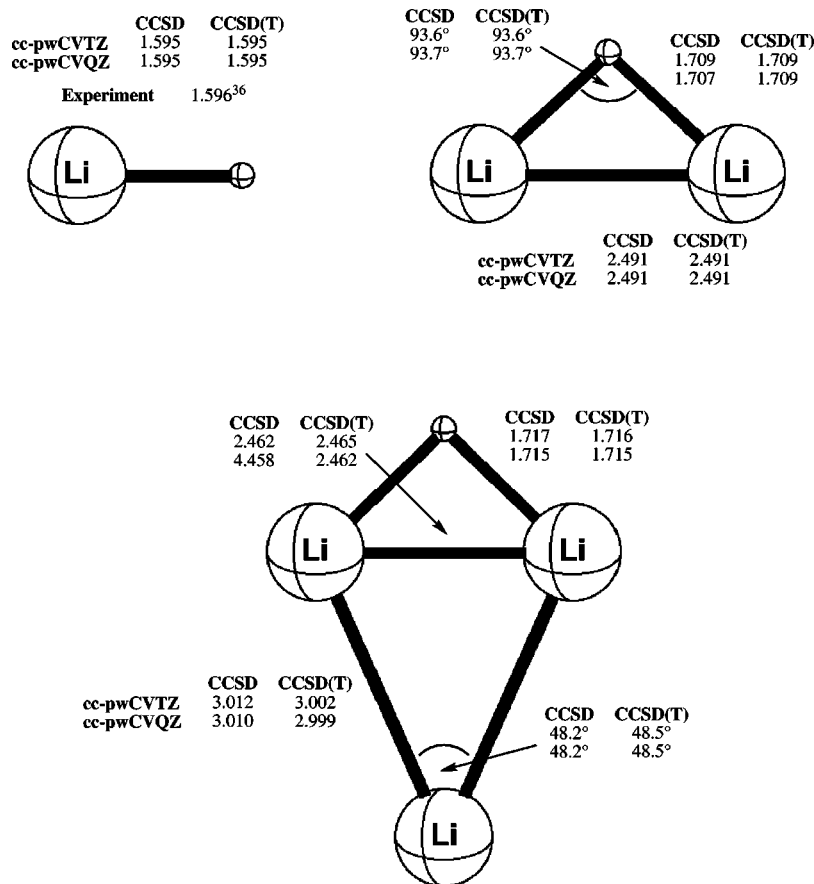
FIG. 3. Optimized Li_nH geometries.
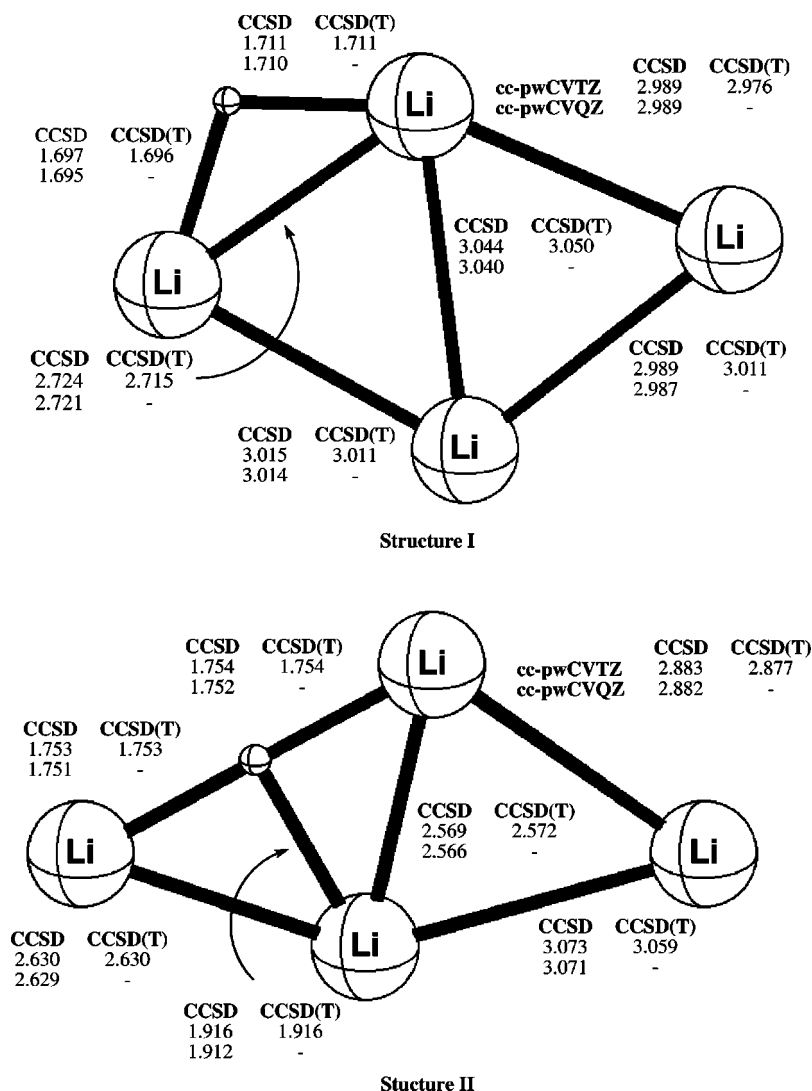
FIG. 4. Optimized Li_4H geometries.

few electronic states of the lithium trimer via large MR-CI computations, arriving at an equilibrium geometry corresponding to bond lengths of 2.765 and 3.235 Å, in excellent agreement with our best CCSD(T) result. Simulated rovibrational spectra using these MR-CI PESs give excellent agreement with high resolution spectra, supporting Krämer's computed potential surfaces and his Li_3 equilibrium geometry.[23–25] The ZPVE corrected atomization energy from these PES computations is 37.5 kcal/mol, in good agreement with our ZPVE corrected value of 37.0 kcal/mol.

For the lithium tetramer, in D_{2h} symmetry, we again see a systematic convergence of geometries with both increasing basis set size and correlation, approaching the CCSD(T)/cc-pwCVQZ geometry corresponding to Li–Li distances of 2.987 and 2.632 Å between lithium atoms along the side of the Li_4 rhombus and across the minor diagonal, respectively. A recent investigation by Alexandrova and Boldyrev[38] included a CCSD(T)/6-311+G* optimized geometry for Li_4, yielding optimized bond lengths of 3.01 and 2.68 Å along an edge and across the minor diagonal, respectively. This geometry is consistent with our results using the similarly sized cc-pwCVDZ basis set[39] and points to the need to utilize a

TABLE I. Absolute energies (hartree) [zero-point vibrational energies in parentheses(kcal/mol)].

	Basis Set	CCSD	CCSD(T)
Li	cc-pwCVTZ	−7.471 52	−7.471 55
	cc-pwCVQZ	−7.475 88	−7.475 92
Li_2 $(D_{\infty h}, {}^1\Sigma_g^+)$	cc-pwCVTZ	−14.980 89 (0.50)	−14.981 47 (0.50)
	cc-pwCVQZ	−14.989 84 (0.50)	−14.990 47 (0.50)
Li_3 $(C_{2v}, {}^2B_2)$	cc-pwCVTZ	−22.472 09 (1.00)	−22.474 67 (0.97)
	cc-pwCVQZ	−22.485 57 (1.00)	−22.488 30 (0.97)
Li_4 $(D_{2h}, {}^1A_g)$	cc-pwCVTZ	−29.991 18 (1.97)	−29.994 89 (1.96)
	cc-pwCVQZ	−30.009 24 (1.97)	−30.013 12 (1.96)
LiH $(C_{\infty v}, {}^1\Sigma^+)$	cc-pwCVTZ	−8.061 90 (2.01)	−8.062 03 (2.01)
	cc-pwCVQZ	−8.067 61 (2.01)	−8.067 77 (2.01)
Li_2H $(C_{2v}, {}^2A_1)$	cc-pwCVTZ	−15.573 41 (3.57)	−15.574 04 (3.56)
	cc-pwCVQZ	−15.583 59 (3.58)	−15.584 30 (3.58)
Li_3H $(C_{2v}, {}^1A_1)$	cc-pwCVTZ	−23.099 01 (4.88)	−23.100 80 (4.87)
	cc-pwCVQZ	−23.113 68 (4.89)	−23.115 61 (4.88)
Li_4H (I) $(C_s, {}^2A')$	cc-pwCVTZ	−30.598 33 (5.48)	−30.601 00 (5.46)
	cc-pwCVQZ	−30.617 41 (-)	−30.620 24 (-)
Li_4H (II) $(C_s, {}^2A')$	cc-pwCVTZ	30.594 14 (5.45)	−30.596 66 (5.43)
	cc-pwCVQZ	−30.613 21 (-)	−30.615 90 (-)

TABLE II. Atomization energies (kcal/mol) (zero-point corrected energies in parentheses).

	Basis Set	CCSD	CCSD(T)
Li$_2$	cc-pwCVTZ	23.75 (23.25)	24.08 (23.57)
	cc-pwCVQZ	23.90 (23.40)	24.24 (23.74)
Li$_3$	cc-pwCVTZ	36.10 (35.10)	37.66 (36.70)
	cc-pwCVQZ	36.36 (35.36)	37.99 (37.03)
Li$_4$	cc-pwCVTZ	65.95 (63.98)	68.20 (66.24)
	cc-pwCVQZ	66.34 (64.37)	68.68 (66.72)
LiH	cc-pwCVTZ	56.83 (54.82)	56.90 (54.89)
	cc-pwCVQZ	57.49 (55.40)	57.67 (55.66)
Li$_2$H	cc-pwCVTZ	81.92 (78.36)	82.28 (78.72)
	cc-pwCVQZ	82.76 (79.18)	83.16 (79.58)
Li$_3$H	cc-pwCVTZ	115.86 (110.98)	116.93 (112.05)
	cc-pwCVQZ	116.78 (111.88)	117.92 (113.03)
Li$_4$H (I)	cc-pwCVTZ	133.31 (127.82)	134.98 (129.52)
	cc-pwCVQZ	134.26 (128.77)	136.03 (130.57)
Li$_4$H (II)	cc-pwCVTZ	130.68 (125.23)	132.18 (126.75)
	cc-pwCVQZ	131.67 (126.17)	133.21 (127.78)

larger basis set to compute equilibrium geometries to within 0.01 Å for these systems.

In Table I we report the absolute energies (in hartrees) for Li$_n$ ($n=1-4$) clusters, along with the zero point vibrational energies in terms of basis set and electron correlation. We see a systematic decrease in absolute energies with both increasing basis set size and with perturbative inclusion of connected triple excitations.

Table II contains the computed atomization (binding) energies and ZPVE corrected atomization energies, in kcal/mol, defined, respectively, by

$$E_{atom} = nE(\text{Li}) - E(\text{Li}_n),$$

$$E_{atom,ZPVE} = nE(\text{Li}) - [E(\text{Li}_n) + ZPVE(\text{Li}_n)].$$

Atomization energies per atom have been computed from the ZPVE corrected CCSD(T)/cc-pwCVQZ results and are listed, along with results from representative previous theoretical and experimental reports, in Table III. These en-

ergies are typically computed to compare relative binding strengths as a function of cluster size and allow for the observation of general trends in the evolution of bonding in Li$_n$ clusters from small clusters toward that of the bulk metal. Included in Table III are the atomization energies per atom (eV) of the "CI scaled" results of Bonačić-Koutecký et al.,[3,9] the CISD optimized results of Rao and Jena,[2,4] and two sets of experimental energies. The experimental energies are those of Bréchignac et al.,[6] obtained indirectly by measuring dissociation energies of cationic lithium clusters and then computing the atomization energies of the corresponding neutral Li$_n$ clusters via experimental ionization potentials,[40] and the Knudsen Cell results of Wu.[19,20]

While both theory and experiment reveal the same qualitative trends in binding energies per atom, there are significant deviations in relative energies and deviations from our CCSD(T)/cc-pwCVQZ results. As expected, since the CI results of Bonačić-Koutecký et al. are primarily optimized at only the SCF level, the agreement with our CCSD(T) results is sub-par. It is worth noting, however, that utilizing a larger basis set, the CI scaled result for the lithium dimer is improved to 0.50 eV,[9] bringing this value into agreement with our CCSD(T)/cc-pwCVQZ energy of 0.496 eV. For the CISD/STO-6G results of Rao et al.,[2,4] which include fully optimized geometries, there is surprisingly good agreement with our results for Li$_2$ and Li$_4$. Comparison of the experimental results with our CCSD(T) computations for Li$_2$ suggests that Bréchignac and Wu have both slightly overestimated the binding in Li$_2$, while for the tetramer our computed value (0.723 eV), along with the CISD results, fall in between the two quoted experimental values of 0.63 and 0.84 eV from Bréchignac and Wu, respectively. There is a coincidental agreement between the CI scaled Li$_4$ atomization energy per atom and the experimental result of Bréchignac et al.

As shown in Fig. 2, the binding energy per atom for the lithium trimer is smaller than for both Li$_2$ and Li$_4$ for the CI scaled, CISD, and one of the experimental reports—a trend

TABLE III. Binding energies (eV) per atom.

	CCSD(T)[a]	MRD-CI[b]	CISD[c]	UMP4[d]	Expt.[e]	Expt.[f]
Li$_2$	0.496	0.45[g]	0.498		0.53	0.55
Li$_3$	0.535	0.45	0.478		0.50	0.60
Li$_4$	0.723	0.63	0.732		0.63	0.84
LiH	1.207	1.10		1.00	1.214[h]	
Li$_2$H	1.150	1.06		0.96		
Li$_3$H	1.225	1.13		1.04		
Li$_4$H (I)	1.132[i]	1.02[j]		0.94		
Li$_4$H (II)	1.108[i]	1.00[j]		⋯		

[a]CCSD(T)/cc-pwCVQZ optimized geometries with ZPVE corrections.
[b]References 5, 9–11.
[c]References 2, 4.
[d]Reference 8.
[e]Reference 6.
[f]References 19 and 20.
[g]0.50 eV using larger basis set including d functions.
[h]Reference 36.
[i]CCSD(T)/cc-pwCVQZ single point at CCSD/cc-pwCVQZ geometry with CCSD(T)/cc-pwCVTZ ZPVE correction.
[j]MP2 optimized structures yielded MRD-CI energies of 1.11 and 1.09 eV for structures I and II, respectively.

that has been previously used to explain the observed relative abundances of certain cluster sizes in ensembles of lithium clusters. In fact, the jellium model,[41] which has at times been prevalent in metal cluster studies, predicts such behavior in binding energies per atom for alkali metal clusters.[1,42,43] Our results, however, predict a monotonic increase in atomization energies per atom with increasing cluster size, in agreement with the experimental results of Wu.[19,20]

Comparing the CI scaled atomization energies per atom as a function of basis set size,[44] we see that the lithium trimer is considerably more sensitive to basis set size compared to Li_2 and Li_4—the CI scaled energies for the dimer and tetramer exhibit no discernible change when computed using a $(6s1p/2s1p)$ basis compared to the 6-31G basis, while the binding energy for Li_3 increases significantly. The anomalous local minimum in the atomization energies per atom predicted by the CI scaled results[45] may be partially attributed to an incomplete description of the Li_3 wave function due to the utilization of exiguous basis sets.

We offer no explanation for the discrepancy in relative atomization energies per atom from the experimental results,[6,19,20] but merely point out that the two experimental determinations approached the problem from two different directions: Wu determined the atomization energies of the neutral clusters by measuring reactions of neutral clusters, while Bréchignac derived the properties of the neutral clusters via cationic cluster energies, a procedure that relies heavily on the reliability of the experimental ionization potentials utilized. Additionally, the experimental IPs employed by Bréchignac were obtained by linear extrapolations of photoionization efficiency curves,[40] which are expected to yield a value that falls in between the vertical and adiabatic ionization potentials, while to derive the energies of the equilibrium neutral structures from the cationic energetics one would need to employ the true adiabatic IP. The resulting errors are expected to be significant for these clusters given the large differences in geometry between the cation and neutral species.

B. Li_nH geometries and atomization energies

Geometries were fully optimized using both CCSD and CCSD(T) with the cc-pwCVXZ (X=T and Q) basis sets for Li_nH $(n=1-4)$.[46] Comparison of the CCSD(T)/cc-pwCVQZ LiH optimized bond length (1.595 Å) with the experimentally determined[36] equilibrium bond length (1.596 Å) again suggests we are accurately describing these systems at this level.

Comparison of the CCSD(T) optimized Li_2H structure (1.707 and 2.491 Å for the Li–H and Li–Li bond lengths, respectively) with the results from multiphoton ionization spectroscopy (1.715 and 2.52 Å)[47] shows reasonable agreement between our predicted results and experimental determinations. The Li_2H and Li_3H clusters, described either in terms of the addition of a bridging hydrogen to the corresponding Li_n cluster or as distorted versions of the analogous Li_{n+1} clusters, both exhibit shortening of the Li–Li bonds across which the hydrogen is bound, and for Li_3H a lengthening of the other two Li–Li bonds.

For the case of Li_4H, we investigated two stable minima, both planar C_s structures, since previous studies have indicated that these two isomers were of comparable energy.[9–11] The first (structure I), which we found to be slightly more stable (see the following), is best described as a distorted Li_4 rhombus with a bridging hydrogen. The dominant deformations of the rhombus subunit are a shortening of the Li–Li bond across which the hydrogen atom is bridged and a lengthening of the minor diagonal. In the second isomer (structure II), also a minimum, the hydrogen is inserted into one of the external Li–Li bonds, creating a system in which hydrogen appears to be bound to three lithium atoms.

In Table I we list the absolute energies (in hartrees) as well as ZPVE corrections (kcal/mol) for the hydrogenated clusters. Table II shows the binding energies (in kcal/mol) for the hydrogenated lithium clusters, as well as the zero point corrected binding energies, defined, respectively, by

$$E_{atom} = nE(Li) + E(H) - E(Li_nH),$$

$$E_{atom,ZPVE} = nE(Li) + E(H) - [E(Li_nH) + ZPVE(Li_nH)].$$

Table III compares the computed CCSD(T)/cc-pwCVQZ atomization energies per atom with the CI scaled results of Bonačić-Koutecký[3,9] and the MP4 results from Rao *et al.*[8]

Both the CI scaled and MP4 computations underestimate the atomization energy per atom of the simplest Li_nH cluster, lithium hydride, which our CCSD(T)/cc-pwCVQZ results place at 1.207 eV, corroborated by previously published experimental values.[36] For Li_2H, both the CI scaled and MP4 optimized results predict a decrease in binding energy per atom compared to LiH and Li_3H, analogous to the anomalous local minimum in atomization energies for Li_3. However, this time our CCSD(T) results support the previous theoretical work—the CCSD(T)/cc-pwCVQZ atomization energy per atom is found to be 1.150 eV for Li_2H, compared to 1.207 and 1.225 eV for LiH and Li_3H, respectively. For the Li_3H and Li_4H clusters, the CI scaled results underestimate the binding energy per atom by roughly 0.10 and 0.05 eV, respectively, while the MP4 optimized computations lead to differences of 0.19 and 0.13 eV.

For Li_4H, we support earlier findings[10] that the cluster described as a slightly distorted rhombus with a bridging hydrogen atom (structure I) is more stable than the structure with an inserted hydrogen atom. The relative energy difference of 2.8 kcal/mol at the CCSD(T)/cc-pwCVQZ level includes ZPVE effects. The 1994 study of Bonačić-Koutecký *et al.*[10] presented MRD-CI energies at MP2 optimized geometries for the two Li_4H geometries considered here, resulting in atomization energies per atom of 1.11 and 1.09 eV for structures I and II, respectively, which are in agreement with our CCSD(T)/cc-pwCVQZ results.

IV. CONCLUSIONS

We have presented atomization energies and optimized geometries for small lithium clusters Li_n and hydrogenated lithium clusters Li_nH $(n=1-4)$. The accuracy of the methods employed is established by excellent agreement with ex-

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perimental bond lengths (within 0.001 Å) for Li_2 and LiH and agreement with previous large scale MR-CI PES computations for Li_3.

We see that the CI scaled results of Bonačić-Koutecký *et al.* and the CISD optimized results of Rao and Jena predict an anomalous decrease in binding energy per atom for Li_3 relative to Li_2 and Li_4. An experimental determination of Li_n binding energies through measurement of binding energies of the corresponding cationic clusters gave a similar incorrect relative atomization energy for Li_3.[6] We attribute this effect to the utilization of inappropriate IP values. Our CCSD(T) results support the monotonic increase in binding energies per atom observed in Wu's experiments,[19,20] though the atomization energies of Wu are consistently higher than our computed values.

For the hydrogenated lithium clusters the situation is reversed—our results support the trend found in the MRD-CI and MP4 atomization energies, which include a local minimum in binding energy per atom for Li_2H, though these earlier theoretical results underestimate the binding energy per atom in all cases.

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