Equilibrium geometries of low-lying isomers of some Li clusters, within Hartree-Fock theory plus bond order or MP2 correlation corrections

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In a recent study by Kornath et al. [J. Chem. Phys. 118, 6957 (2003)], the Liₙ clusters with n = 2, 4, and 8 have been isolated in argon matrices at 15 K and characterized by Raman spectroscopy. This has prompted us to carry out a theoretical study on such clusters up to n = 10, using Hartree-Fock theory, plus low-order Møller-Plesset perturbation corrections. To check against the above study of Kornath et al., as a by-product we have made the same approximations for n = 6 and 8 as we have for n = 10. This has led us to emphasize trends with n through the Liₙ clusters for (i) ground-state energy, (ii) HOMO-LUMO energy gap, (iii) dissociation energy, and (iv) Hartree-Fock eigenvalue sum. The role of electron correlation in distinguishing between low-lying isomers is plainly crucial, and will need a combination of experiment and theory to obtain decisive results such as that of Kornath et al. for Li₈. In particular, it is shown that Hartree-Fock theory plus bond order correlations does account for the experimentally observed symmetry T₄d symmetry for Li₈.

I. BACKGROUND AND OUTLINE

Lithium clusters by now have been studied by a variety of experimental techniques which include electron spin resonance, laser induced fluorescence, depletion spectroscopy, photoionization, and Raman spectroscopy. This has investigated, in particular, the lithium clusters Liₙ, for n = 2, 4, and 8. This has been done by isolating these clusters in argon matrices at 15 K. Whereas Kornath et al. have pointed out that most of the techniques listed above are difficult to correlate with the cluster geometries, their experimental work was able to determine the geometry of Li₄ as a rhombic structure (D₂h) and for Li₆ a hypertetrahedral structure (T₄d) was shown to be in agreement with their Raman studies.

This experimental work has motivated the present theoretical study of Liₙ clusters. Most attention is focussed here on n = 10, but we have also included n = 6 and n = 8. In the latter case, we must mention the previous theoretical work of Bonacic-Koutecky, Fantucci and Koutecký.

The outline of the paper is then as follows. In Section II some general trends of the electronic structure of Liₙ clusters are depicted with n ranging from 1 to 10. We note that Kornath et al. studied n = 2, 4, and 8 extensively using high quality techniques. For Li₈ our more modest techniques essentially confirmed the findings of Kornath et al. for the equilibrium geometry and the vibrational frequencies. So we focus in Section III dominantly on Li₈. Section IV presents results for Li₁₀. Finally, discussion of some additional trends, plus some suggestions for future work are covered in Section V.

II. QUANTUM CHEMICALLY PREDICTED TRENDS IN Liₙ CLUSTERS FOR n = 1 TO 10

In this Section we present our results of the calculations made on Liₙ clusters (n = 2, 4, 6, 8, 10), by using the Gaussian package (G03 Linux version). All the calculations were performed using the standard self-consistent field Hartree-Fock (HF) theory with the 6-311G* basis set. The correlation energy was obtained using low-order Møller-Plesset (MP2) corrections considering all (valence and core) electrons. For both HF and HF+MP2 level, full geometry optimization and vibrational analysis were performed for all Li clusters.

While Sections III and IV will develop further the systematic studies we have made especially for n = 6 and 10, with the approximate quantum chemical approach set out above, this Section will present the general trends predicted by HF+MP2 theory for n = 1 to 10.

To this end, Fig. I depicts the ground-state energy per atom for increasing n from 1 to 10. No commentary is needed on the results for n = 1 – 4, except to show as an inset the accepted planar structure of Li₄. The HF energy of this cluster is −29.759 and the lowering by second-order Møller-Plesset perturbation theory yields −29.859, both in Hartrees (as all energies below, unless stated otherwise).

As seen in Fig. I two structures were found to be low-lying isomers of Li₆, with symmetries D₄h and D₃h,
FIG. 1: Ground-state energy per atom of $Li_n$ clusters, with $n = 1 - 10$. Inset: accepted $D_{2h}$ planar structure of $Li_4$.

and these will be discussed in detail in Section III below. Likewise, for $Li_8$, $C_s$ and $T_d$ structures emerge and again Section III presents details. $Li_{10}$ has the lowest MP2 energy per atom of the clusters considered and is the subject of Section IV.

Again concerning general trends, Fig. 2 shows the variation of the HOMO-LUMO gap for $Li_n$ clusters with the number of atoms $n$ in the lithium cluster. It is of interest to note that though the variation is irregular for $n = 4 - 8$, the smallest gap is at $n = 10$. It is relevant to add here that solid lithium is metallic, with therefore zero energy gap. Of course the gap at $n = 10$ is still $\sim 5$ eV! It is the trend, not the absolute numbers, which should be the focus here.

With this relatively brief discussion of trends we turn to consider our detailed results for $Li_6$ and, quite briefly, also $Li_8$ in Section III immediately below.

III. GEOMETRY, ENERGY, AND VIBRATIONAL FREQUENCIES OF $Li_6$ AND $Li_8$ USING HF+MP2 THEORY

In Ref. 1, a comment was made in their experimental considerations of a result which 'may indirectly support the absence of a $Li_6$ species.' Motivated by this, we have, by geometry optimization, 'converged' on the geometries of two low-lying isomers which are depicted in Fig. 3. The first of these is the planar structure (Fig. 3 left), with HF energy $-44.658$ and with addition of MP2 is $-44.810$. The present HF+MP2 approach, however, predicts as the isomer we identify as the ground state, the planar square with a 'diatomic' $Li_2$-like species perpendicular to the plane, through the center of gravity. While this has a (very) slightly higher HF energy than the planar structure, it lies below that structure energetically when 'correlation' treated at the MP2 level is added, the results being $E_{HF} = -44.655$ and with the MP2 correction $-44.824$.

Turning quite briefly to $Li_8$, the geometry was settled as $T_d$ from the Raman studies of Ref. 1, whereas as can be seen from Fig. 4 the $C_s$ symmetry is predicted as very slightly lower by our present approximation. This is enough to illustrate the stringent test of many-electron approximate theories that is afforded by attempts to predict decisively the ground-state energies of isomers of $Li_n$ clusters. However, the vibrational frequencies of $Li_8$ ($T_d$) are more in line with the observed values than those of the $C_s$ structure, which is somewhat encouraging in the light of the known geometry ($T_d$) of the lowest lying isomer.

We turn next to discuss, with fuller details, the $Li_{10}$ cluster.

FIG. 3: Low-lying isomers of $Li_6$. Left: Planar structure, with $D_{3h}$ symmetry. Right: Most stable isomer predicted by HF+MP2, with $D_{4h}$ symmetry, and a dimer-like $Li_2$ structure perpendicular to the plane.

FIG. 2: LUMO-HOMO gap for $Li_n$ clusters as a function of $n$. (Note: The actual graph is not included in the text.)
IV. GEOMETRY, ENERGY, AND VIBRATIONAL FREQUENCIES OF TWO LOW-LYING ISOMERS OF Li\(_{10}\)

We have carried out similar calculations which have led us to two geometries of Li\(_{10}\) which appear to be serious candidates for low-lying isomers. The first of these is the very asymmetrical structure shown in Fig. 4 (left). Here, with an atom, roughly speaking, at the ‘center’ of the cluster, there can, of course, be no symmetrical arrangement around it.

We have evaluated the total energies, the distance matrix (in \(\text{Å}\)) and the calculated frequencies (in \(\text{cm}^{-1}\)) of the geometrical structure shown in Fig. 4 (left). The second structure we found as a low-lying isomer is shown in Fig. 4 (right). This second isomer is characterized by \(D_{2d}\) symmetry, and may be thought as obtained from the Li\(_8\) cluster, by ‘adding’ two more Li atoms (with, of course, different bond lengths and angles), shown in Fig. 4 (right) in the top-right-hand and bottom-left-hand positions.

V. DISCUSSION AND SOME FUTURE DIRECTIONS

Let us begin this discussion of the results presented above by dealing first with further trends, to add to those reported in Section IV.

A. Sum of eigenvalues \(E_{sn}\) related to total energy \(E_n\), for \(n\) atom cluster

In Fig. 5 we have plotted for \(n = 2\) to 10 the total energies \(E_n\) versus the eigenvalue sum \(E_{sn}\) from the HF occupied eigenvalues \(\epsilon_{in}\), defined by

\[
E_{sn} = \sum_{\text{occupied } i} \epsilon_{in}.
\]

We find an approximately linear relation, which is compared with a theoretical prediction from initially Thomas-Fermi statistical theory, given by March and Plaskett for neutral atoms:

\[
E = \frac{3}{2} E_s.
\]

The result was found, independently, by Ruedenberg from self-consistent field results for molecules, and its foundation in density functional theory was subsequently discussed by one of us.

B. Trends in dissociation energy \(D_n\) with number of atoms \(n\) in Li\(_n\) clusters defined as \(|E_n - nE_1|\)

As a further trend through the clusters Li\(_n\) with \(n\) going from 2 to 10, we have collected in Table I results from our HF+MP2 calculations for the dissociation energy \(D_n\).

Mucci and March, in early work, stressed the merit of Teller’s theorem, which states that molecules/clusters do not bind in any wholly local density approximation (LDA). To avoid confusion with current terminology, ‘wholly LDA’ in Teller’s theorem refers to also treating the kinetic energy \(T\) by the Thomas-Fermi (TF) result

\[
T_{TF} = c_k \int |\rho(r)|^{5/3} dr, \quad c_k = \frac{3h^2}{10m} \left( \frac{3}{8\pi} \right)^{2/3},
\]

where \(\rho(r)\) denotes the electron density of the molecule/cluster. If \(T\) denotes the correct (single-particle) kinetic energy at the equilibrium geometry, Mucci and March pointed out that the difference between \(T\) and \(T_{TF}\) was entirely due to electron density gradients, e.g. \(\nabla \rho, \nabla^2 \rho\), etc.
characterizing $D_n/N^2$. Therefore, in Fig. 6 we have made a further plot of $D_n/N^2$ already given in Table II versus $|T^{(n)}_{HF} - T^{(n)}_{TF}|$, the latter quantity being expected to reflect $T_{vW}^{(n)}$, albeit approximately. There is a quite clear correlation from Fig. 5 between $D/N^2$ and the ‘gradient difference’ $T_{HF} - T_{TF}$, substantiating the work reported in Refs. 9, 11, 12.

**C. Comments on individual clusters and especially role of electron correlation**

In cases when $n = 6$ and 8, two low-lying isomers have emerged from our studies using the HF+MP2 approximation. A strong pointer to the importance of electron correlation in any quite decisive prediction of the true ground-state geometry is afforded by the two structures, considered for Li$_6$, where Kornath et al. have experimentally verified from their Raman studies that the correct structure is $T_d$. This is indeed predicted to be lower in energy than $C_8$ in our HF studies, but the situation is (wrongly!) changed over by treating electron correlation at MP2 level. However, as noted, HF+MP2 vibrational frequencies are considerably higher for $T_d$ than for $C_8$, the latter clearly being in marked disagreement with experiment! On the other hand, a comparison of HF+MP2 energies and HF energy plus bond-order correlation energy (Sec. V D) shows that indeed inclusion of bond-order correlation allows to confirm the experimentally observed $T_d$ structure for Li$_8$.

Turning more briefly to Li$_6$, we find two low-lying isomers, both with lower energies than either 6 isolated Li atoms or 3 isolated Li$_2$ molecules. Also stability with respect to isolated Li$_4$ and Li$_2$ components is clear. Again, however, while $D_{4h}$ lies higher in energy than $D_{2d}$ at the HF level of approximation, including electron correlation at order MP2 reverses the ordering. Our conclusion here then which seems to us firm is that two low lying isomers of Li$_6$ are found. However, the energy ordering is not decisive, though our prejudice here is in favor of the MP2 addition, namely $D_{4h}$ symmetry, but that must remain conjecture until electron correlation is treated by more refined approaches such as the coupled cluster approximation. Finally, the largest cluster studied here seems fairly ‘strongly’ bound, being stable again with respect to 10 Li atoms, 5 Li$_2$ dimers, and also the isolated ‘fragments’ Li$_6$ + Li$_4$ and Li$_8$ + Li$_2$. None of this must be taken to mean that our structure for Li$_{10}$ is the lowest-lying isomer of this cluster, though that is our prediction at the HF+MP2 level.

In the light of the importance of electron correlation, we shall now present some ‘heuristic’ ideas on this subject, in which appeal will be made to bond-order versus bond-length relations which we have used earlier for polyatomic molecules. We note here that the study of Kornath et al. already includes extensive and careful $ab$ initio MO calculations with high level of treatment of electronic correlations.
D. Some approximate considerations on the magnitude of electron correlation energy in the Liₙ clusters with n from 2 to 10

Using the Löwdin definition\textsuperscript{14,15,16} of electron correlation, say \( E_c^{L} \), as

\[
E_c^{L(n)} = E_c^{(n)} - E_c^{HF}, \tag{5}
\]

we might use, as a first approximation to \( E_c^{L(n)} \) the correlation energy in the K shells, namely

\[
E_c^{L(n)} \approx n E_c^{(1)}. \tag{6}
\]

One can utilize, for example, the recent study of Alonso \textit{et al.}\textsuperscript{17} to estimate \( E_c^{(1)} \) for the Li atom ground state. Their pairing energy \( E_{ss} \) is, for neutral atoms, given in their Table 2 as \(-1.28 \text{ eV} \), and hence for the Li₁₀ cluster we estimate (essentially from 10 separate K shells) the correlation energy in magnitude to be 0.47 Hartree. The upper curve in Fig. 7 shows this K-shell–like magnitude of \( E_c \) for the Liₙ clusters under consideration. Of course, the original 2s electrons will form molecular orbitals where again there is pairing of electrons with antiparallel spins, and we therefore suppose that the uppermost curve in Fig. 7 will be below the ‘true’ magnitude of the correlation energy curve.

For comparison with this K shell estimate, we have plotted the ‘correlation energy’ given by HF + MP2 perturbation theory. The circles in Fig. 7 show our results for Liₙ \((n = 2, 4, 6, 8 \text{ and } 10)\). Two low-lying isomers were considered in the present study of both Li₆ and Li₈. The small-dashed curve is proportional to \( n \) as in Eq. (6), whereas the long-dashed curve is linear in \( n \) but does not pass through the origin, in contrast to Eq. (6).

Evidently, while MP2 corrections obviously improve the HF energies, they yield only \(~50 \text{ to } 60 \% \) the Li correlation energies, the poorest result being for the dimer.

Following the technique reported in Ref. 13, we have calculated the correlation energies for lithium clusters using the HF bond orders. Fig. 7 compares our results with the values obtained from MP2 calculations. In particular, the experimental correlation energy \( E_{c,exp} \) is defined as:

\[
E_{c,exp} = E_S - E_{HF}, \tag{7}
\]

with \( E_S \) the exact Schrödinger energy and \( E_{HF} \) the Hartree-Fock energy. Following Ref. 13, we calculate the theoretical correlation energy \( E_{c,BO} \) as the sum of atomic and bond contributions:

\[
E_{c,BO} = \sum_{i=1}^{N} E_i^A n_{eff} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} a_{ij} B_{ij}, \tag{8}
\]

with \( N \) the number of atoms in the cluster. The \( E_i^A \) term is the atomic Schrödinger correlation energy that can be obtained from experimental data, as explained in Ref. 13, \( n_{eff} \) denotes the effective atomic electron number, which takes into account the electrons not involved in the bonds, \textit{i.e.}

\[
n_{eff} = \frac{Z - n_{bond}}{Z}, \tag{9}
\]

with \( Z \) the atomic number and \( n_{bond} \) the total number of electrons involved in molecular bonds for each atom. \( B_{ij} \) is the bond order (BO) between atoms \( i \) and \( j \), as obtained from HF calculations, and \( a_{ij} \) is a parameter depending on the particular bond \( i - j \). For Li clusters, this parameter was obtained from the experimental correlation energy of Li₂ molecule and its value is 0.06157 a.u. While up to now all binding and correlation energies have

| \( n \) | \( E_{c,BO} \) | \( E_{c,MP2} \) | \( E_{c,BO} - E_{c,MP2} \) | \( c_c = E_{c,BO}/Z \) |
|---|---|---|---|---|
| 4 | -0.27126 | -0.09887 | -0.17239 | -0.06782 |
| 6 | D₄h | -0.41049 | -0.15191 | -0.25858 | -0.06842 |
| 6 | D₄h | -0.42966 | -0.16724 | -0.25972 | -0.07116 |
| 8 | T₄ | -0.57063 | -0.23078 | -0.33985 | -0.07133 |
| 8 | C₄ | -0.57561 | -0.24506 | -0.33055 | -0.07195 |
| 10 | D₄d | -0.72000 | -0.30339 | -0.41661 | -0.07290 |
| 10 | C₁ | -0.72041 | -0.31088 | -0.40953 | -0.07204 |

TABLE II: Correlation energies from both bond order (BO) and MP2 calculations. The second column lists the symmetry of the cluster. All energies are in Hartree.
been calculated within HF+MP2, with full geometry optimization, the bond order correlation energies discussed here refer to the optimized geometries within HF.

Table I reports the calculated correlation energies for Li clusters obtained from MP2 calculations ($E^c_{\text{MP2}}$) and by using Eq. (5) ($E^c_{\text{BO}}$), along with the HF energies. As shown in Table I and in Fig. 4, the calculated correlation energies from Eq. (5) are higher than the MP2 energies, giving for each Li cluster a total molecular energy less than that calculated at HF+MP2 level. Moreover, it is noteworthy that the difference $E^c_{\text{MP2}} - E^c_{\text{BO}}$ increases with increasing number of atoms in the cluster, and that the correlation energy per electron, $\epsilon_c = E^c_{\text{BO}} / Z$, is about constant for all clusters, indicating that the total correlation energy is proportional to the total number of electrons in the molecule. In addition, a comparison of the total HF+MP2 and the HF+BO energies in Table I shows that, while for $n = 6$ both models predict the cluster with $D_{4h}$ symmetry to be stabler than the cluster with $D_{3d}$ symmetry, at variance with the HF result, both for $n = 8$ and $n = 10$ only the HF+BO energies do predict the $T_d$ and $D_{2d}$ to be stabler than the $C_6$ and $C_1$, respectively, in agreement with the purely HF results and, in the case of Li$_{10}$, in agreement with the experimental results.

Fig. 4 shows that the MP2 correlation energy estimated with the 6-311G* basis set is systematically much smaller than the sum of the $(1s)^2$ atomic pair correlation. The referee has pointed out to us that this probably results from the basic set deficiency for the inner shell correlation.

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| n   | $E_{\text{HF}}$ | $E_{\text{BO}}$ | $E_{\text{MP2}}$ | $\Delta E_{\text{HF}}$ | $\Delta E_{\text{BO}}$ | $\Delta E_{\text{MP2}}$ |
|-----|----------------|----------------|----------------|---------------------|---------------------|---------------------|
|     |               |                    |            | $(\times 1000)$     | $(\times 1000)$     | $(\times 1000)$     |
| 4   | $-29.75973$   | $-30.03099$       | $-29.85860$ |                     |                     |                     |
| 6   | $D_{3h}$      | $-44.65841$       | $-45.06890$ | $-44.81032$         |                     |                     |
| 6   | $D_{4h}$      | $-44.65633$       | $-45.08329$ | $-44.82357$         | $D_{4h} - D_{3h}$   | $2.0800$            | $-14.390$           | $-13.252$          |
| 8   | $T_d$         | $-59.56615$       | $-60.13678$ | $-59.79693$         |                     |                     |
| 8   | $C_s$         | $-59.55893$       | $-60.13454$ | $-59.80399$         | $C_s - T_d$         | $7.2191$            | $2.239$             | $-7.058$           |
| 10  | $D_{2d}$      | $-74.46031$       | $-75.18031$ | $-74.76370$         |                     |                     |
| 10  | $C_1$         | $-74.45665$       | $-75.17706$ | $-74.76753$         | $C_1 - D_{2d}$      | $3.6587$            | $3.249$             | $-3.827$           |

**TABLE III:** Hartree-Fock and total energies from both bond order (BO) and MP2 calculations, defined as $E_{\text{BO}} = E_{\text{HF}} + E_{\text{c}}^{\text{BO}}$ and $E_{\text{MP2}} = E_{\text{HF}} + E_{\text{c}}^{\text{MP2}}$. The second column lists the symmetry of the cluster. Last three columns list differences of these energies between clusters with same $n$ but different symmetry ($D_{4h} - D_{3h}$, for $n = 6$; $C_s - T_d$, for $n = 8$; $C_1 - D_{2d}$, for $n = 10$). All energies are in Hartree.