Li$_5$ as a pseudorotating planar cluster

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Despite a decade of theoretical investigation, the geometric structures of small metallic clusters are poorly understood. This is partly due to the lack of a reliable experimental technique and partly to the inadequate accuracy of ab initio calculations. Only a few geometries have been experimentally determined. Spectroscopic data or other observables using an accurate ab initio method for candidate geometries and to eliminate structures that are inconsistent with the experimental data. Currently available ab initio methods are accurate enough to distinguish quantitative differences in spectra due to different structures. Recently, geometries of a few small lithium clusters have been partially determined in this way.

For Li$_3$, both matrix-isolated and cluster-beam electron paramagnetic resonance (EPR) spectra showed that all three nuclei are magnetically equivalent, indicating that Li$_3$ is an equilateral triangle ($D_{3h}$). On the other hand, theoretical calculations predicted two nearly degenerate energy minima, $^2A_1$ and $^2B_2$ states, corresponding to $C_{2v}$ isosceles triangles. This disagreement was explained by pseudorotation around the $D_{3h}$ symmetry point. Recently, extremum structures of the $^2A_1$ and $^2B_2$ states were determined by high-resolution optical absorption spectroscopy. Furthermore, a fractional quantum number of pseudorotational angular momentum due to Berry’s phase has been observed in the rotational energy spectrum of Na$_3$, supporting the pseudorotation ground state.

A number of theoretical calculations predicted that lithium clusters are planar up to Li$_6$. However, the optical absorption spectrum for Li$_5$ appears to be consistent with the theoretical spectra for a three-dimensional structure, eliminating the possibility of planar geometries. Detailed geometrical parameters are still unknown. For Li$_7$, EPR spectra were interpreted as a pentagonal bipyramid ($D_{5h}$) in agreement with theoretical prediction. As far as we know, no attempt to identify the structure of Li$_5$ has been made.

Recently, Howard et al. investigated Li$_5$ in an adamantane matrix using EPR. The data indicate that all five nuclei are magnetically identical and this is interpreted as a pseudorotating cluster. Furthermore, the authors suggested that the ground state of Li$_5$ is not a planar but a three-dimensional structure, contrary to theoretical predictions. A trigonal bipyramid, which is nearly as stable as the planar structure, is a prime candidate for the most stable three-dimensional structure. Since the pseudorotation mechanism for a trigonal bipyramid molecule such as PF$_5$ is known, their speculation seems reasonable. However, no conclusion can be made from the observed isotropic spin population (ISP). In order to extract the structural information out of the experimental data, quantitative theoretical calculations are desired.

In this paper, we report a pseudopotential local density functional calculation of Li$_5$. Two low-energy isomers, a trigonal bipyramid ($^2B_1$) and a planar structure ($^2A_1$), are studied as candidates for the ground state. The isotropic spin population is computed in order to identify the structure observed by EPR. Furthermore, the possibility of two pseudorotation mechanisms is investigated by searching the lowest potential barriers for permutation of the nuclei.

The computational method used in this work is the same as the one previously used for other systems. The details are given in Ref. 22. The electron density is calculated using the local density approximation (LDA) with a generalized norm-conserving pseudopotential. In order to increase transferability, a fractionally occupied electronic configuration, $1s^2 2s^{0.8} 2p^{0.2}$, is used to construct a pseudopotential. A core radius $R_c = 2.1$ a.u. is sufficiently accurate for all orbitals. Wave functions are expanded in a plane wave basis set using a simple cubic supercell. Since Li$_3$ has a relatively large dipole moment, a large lattice constant, $a = 60$ a.u., was used to avoid a long-range dipole interaction between repeated cells. For other sizes, $a = 30$ a.u. was sufficiently large. The same cutoff energy $E_{cut} = 11.2$ Ry was used for all sizes. This requires more than 130000 plane waves for the...
largest cell. Both electronic and geometric structures are optimized by the steepest descent method. The ISP at the \( i \)th nuclear position, \( \bar{R}_i \), is evaluated as

\[
\rho_i = \sum_\sigma \sum_n \frac{|\psi_{n,\sigma}(\bar{R}_i)|^2}{|\psi_{2s}(0)|^2} \quad (1)
\]

where \( \psi_{n,\sigma} \) is the \( n \)-th molecular orbital with a spin \( \sigma = \pm 1 \) and \( \psi_{2s} \) is the \( 2s \) orbital of an isolated Li atom. All calculations have been carried out using the CM-200 and CM-5 computers.

We have calculated Li\(_3\), Li\(_5\) and Li\(_7\) clusters at the same level of accuracy. The ISP’s for Li\(_3\) and Li\(_5\) is compared with the experimental data in order to provide the degree of accuracy of our calculation for Li\(_5\).

For Li\(_3\), two equilibrium triangle structures, \( ^2B_2 \) (an obtuse isosceles triangle) and \( ^2A_1 \) (an acute isosceles triangle) are nearly degenerate as predicted in other calculations \[14\]. The \( ^2B_2 \) state appeared to be more stable than the \( ^2A_1 \) state. However, the difference in total energy is only 8.3 meV. The experimental value, 3.2 meV \[10\], is within the accuracy of the present calculation. The conical intersection of two Born-Oppenheimer (BO) surfaces at the \( D_{3h} \) symmetry point is only 66 meV (the experimental value = 33 meV) above the \( ^2B_2 \) minimum, indicating that the system is quantum mechanically delocalized and forms a \( D_{3h} \) instead of a \( C_{2v} \) structure. These results are consistent with the pseudorotating state identified by the EPR spectroscopy \[1\]. The ISP’s for both extremum geometries are listed in Table I. The total ISP, \( \rho_{total} \), is 0.48 and 0.78 for the \( ^2A_1 \) and \( ^2B_2 \) states, respectively. Since the pseudorotating state occupies both extremum states, the actual \( \rho_{total} \) should be between these values. Assuming equal weights on the two states, \( \rho_{total} = 0.63 \) is obtained, in good agreement with the experimental value, \( \rho_{total} = 0.69 \).

The EPR experiment determines the number of magnetically equivalent nuclei and the isotropic spin population at each nucleus but it is not capable of determining the detailed geometry such as equilibrium bond distances. Recently, the extremum geometries were precisely determined using high-resolution photoabsorption spectroscopy through the analysis of vibronic spectra \[14\]. The present calculation gives excellent agreement with the experiment, as shown in Table I.

Beyond the trimers, both optical and EPR spectra are so complicated that the assignment or interpretation of spectra is almost impossible without theoretical assistance. For Li\(_7\), however, two distinct groups of nuclei, two nuclei with large ISP (\( \rho_1 = 0.25 \)) and five nuclei with very small ISP (\( \rho_2 = -0.015 \)) were found from EPR \[22\], consistent with the theoretically predicted pentagonal bipyramid \[10\]. The present calculation predicts that two apical nuclei have \( \rho_1 = 0.23 \) and five nuclei forming a pentagonal ring carry \( \rho_2 = -0.01 \), in good agreement with the experiment.

The results for Li\(_3\) and Li\(_7\) suggest that these calculations are sufficiently accurate to predict the ISP of small lithium clusters. Therefore, the geometry of small clusters can be determined by comparing theoretical ISP’s with experimental data.

For Li\(_5\), most theoretical calculations \[14\] predicted that the \( ^2A_1 \) state of a \( C_{2v} \) planar structure \[See Fig. 1(a)\] is the ground state. However, in contradiction to the previous calculations, we found that a distorted trigonal bipyramid with the \( C_{2v} \) symmetry \[See Fig. 1(a)\] is lower in total energy than the \( ^2A_1 \) state within the LDA. This result seems consistent with the speculation by Howard et al. \[22\]. However, the energy difference is only 46 meV/atom. Since the accuracy in LDA total energy is not always satisfactory \[22\], determining the ground state by the total energy alone is not reliable if there are nearly degenerate states.

In Table I, the theoretical ISP values of two structures are compared with the experimental value. The total ISP, \( \rho_{total} = 0.53 \), for the trigonal bipyramid is much smaller than the experimental value, 0.71. On the other hand, \( \rho_{total} = 0.72 \) for the planar structure nearly coincides with the experimental value. This implies that the observed Li\(_5\) cluster is the planar cluster. The small ISP for the trigonal bipyramid is due to the large population of the \( p \)-character electron which stabilizes this geometry significantly. Large \( sp \) mixing is particular to Li clusters and does not appear in other alkali-metal atom clusters.

The experiment also showed that the five nuclei are magnetically equivalent. Only a pentagonal ring (\( D_{5h} \)) has five equivalent nuclei without dynamical transformation. However, it is an unstable state with total energy of 1.06 eV above the the lowest \(^2B_1 \) state and, therefore, energetically not accessible. The observed spectra must be due to the rapid transformation of one of the low energy structures. In this paper, we assume the system is pseudorotating by quantum-mechanical tunneling.

By analogy from the Berry pseudorotation of PF\(_5\), the trigonal bipyramid permutes its nuclei through the \( C_{4v} \) transition state, as illustrated in Fig. 2. For Li\(_5\), however, since the unpaired electron has a node on the atoms 3-1-3 in Fig. 2(a) and on atoms 2-1-2 in Fig. 2(c), the electronic wave functions before and after the transition are orthogonal. Therefore, tunneling through the \( C_{4v} \) point is essentially prohibited. Furthermore, the potential barrier height, 0.33 eV is too high to allow a rapid tunneling at low temperature. The pseudorotation of the trigonal bipyramid is not likely to occur within the experimental time scale.

Similarly to the pseudorotation of Li\(_3\), we expect that the planar Li\(_5\) pseudorotates around the \( D_{5h} \) symmetric point if the potential barrier to the cyclic permutation of nuclei is sufficiently low. The \( D_{5h} \) point is 0.82 eV above the \(^2A_1 \) state, which is too high to pass through even if the zero-point energy is taken into account. However, we found a relatively low transition state to reach a nearest equivalent extremum in the planar structure. The path from one extremum to another is illustrated in Fig. 2. The barrier height, 0.18 eV, is higher than that of Li\(_3\) but significantly lower than that of the trigonal
bipyramid pseudorotation path. In contrast to the trigonal bipyramid, the nodal planes before and after tunneling are nearly parallel and thus the tunneling is allowed. Although a nearly free pseudorotation like the Li$_3$ case is not possible for Li$_5$, the tunneling probability of the planar structure is expected to be much larger than that of the trigonal bipyramid, supporting the idea that the planar structure is expected to be much larger than that of the trigonal bipyramid, and the node planes before and after tunneling are not surprising.

In order to make all nuclei equivalent, tunneling has to be faster than the observation time of the experiment. Unfortunately, a quantum Monte Carlo simulation is necessary to determine the quantum-mechanical behavior of Li nuclei. A recent quantum Monte Carlo simulation\cite{24} indicates that zero-point energy and tunneling play a crucial role even for large clusters. Furthermore, the estimated zero-point energy for the bulk Li crystal is as big as 33 meV/atom.\cite{24} Since lithium is the third lightest element, the quantum-mechanical behavior of the nuclei is not surprising.

The dimension of the pseudorotation is 6 for Li$_5$ in contrast to 2 for Li$_3$. Because of this high dimensionality, the Li$_5$ pseudorotation is not straightforward. The permutation path described in Fig. 3 is actually not a simple rotation. In terms of rotational motion, the transition is not between the nearest neighbors as shown in Fig. 3 due to the high dimensionality of the system. The path is a closed loop in the six-dimensional space and its projection onto a two-dimensional plane rotates three times ($6\pi$) around the $D_{5h}$ symmetry point. It is interesting to calculate Berry’s phase associated with the geometrical transformation along the path and the fractional quantization of rotational motion. However, calculation of Berry’s phase is not simple for Li$_5$ because of its high dimensionality and the degeneracy at the $D_{5h}$ point.

In conclusion, the theoretical isotropic spin population indicates that the planar $C_{2v}(^{2}A_1)$ structure is more consistent with the EPR data than the $C_{2v}(^{2}B_1)$ trigonal bipyramid. Furthermore, the pseudorotation of the trigonal bipyramid is expected to be very slow due to the symmetry of the electronic wave function and the high potential barrier. A new pseudorotation path through a transition state at $C_{2v}(^{2}B_1)$ is proposed for the planar structure. The low potential barrier height probably permits rapid tunneling between extrema in the BO surface.

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**TABLE I.** Isotropic spin populations for Li$_3$. The experimental data are for the pseudorotating state.

| Method            | $^2B_2$  |            | $^2A_1$  |            |
|-------------------|----------|------------|----------|------------|
|                  | $p_1$    | $p_2$      | $p_{total}$ | $p_1$      | $p_2$      | $p_{total}$ |
| CEPA$^a$          | 0.02     | 0.35       | 0.72     | 0.22       | 0.19       | 0.60        |
| CI$^b$            | 0.05     | 0.28       | 0.60     | 0.31       | 0.14       | 0.60        |
| PW-PP-LDA$^c$     | 0.11     | 0.34       | 0.78     | 0.40       | 0.04       | 0.48        |
| Experiment$^d$    | –        | –          | (0.69)   | –          | –          | (0.69)      |
TABLE II. Comparison of calculated extremal geometries of Li_5. The cohesive energy $E_{\text{coh}}$ is in eV, relative energy to the $^2B_2$ state $\Delta E$ in eV, side length $R$ in a.u., and apex angle $\theta$ in degrees.

| Method      | $^2B_2$ | $^2A_1$ |
|-------------|---------|---------|
|             | $E_{\text{coh}}$ | $R$ | $\theta$ | $\Delta E$ | $R$ | $\theta$ |
| CEPA$^a$    | 0.50    | 5.23    | 72$^c$  | 0.010 | 5.69 | 54$^d$  |
| PP-LSD$^b$  | 0.49    | 5.53    | 73$^c$  | 0.00  | 5.1  | 52$^d$  |
| PW-PP-LDA$^c$ | 0.58  | 5.08    | 72$^c$  | 0.008 | 5.59 | 52$^d$  |
| Experiment$^d$ | 0.60  | 5.16    | 72$^c$  | 0.003 | 5.77 | 50$^d$  |

$^a$ Reference [8]  
$^b$ Reference [9]  
$^c$ This work  
$^d$ References [34] and [33]

TABLE III. Isotropic spin populations $\rho_i$ for Li_5. See Figs. 1(a) and 2(a) for the location of the $i$th nucleus.

| Structure | $\rho_1$ | $\rho_2$ | $\rho_3$ | $\rho_{\text{total}}$ |
|-----------|----------|----------|----------|-----------------------|
| $^2A_1$   | 0.05     | 0.17     | 0.17     | 0.72                  |
| $^2B_1$   | 0.03     | 0.27     | -0.03    | 0.53                  |
| Experiment|          |          |          | 0.71                  |

TABLE IV. Comparison of theoretical calculations for the low-energy geometries and cohesive energy of Li_5. $E_{\text{coh}}$ is in eV, and equilibrium bond distances in a.u. The atom numbers are defined in Figs. 1(a) and 2(a). for the $^2A_1$ and $^2B_1$ states, respectively.

| Method      | Structure | $E_{\text{coh}}$ | $R_{1-2}$ | $R_{1-3}$ | $R_{2-3}$ | $R_{1-2}$ |
|-------------|-----------|------------------|-----------|-----------|-----------|-----------|
| HF$^a$      | $^2A_1$   | 0.51             | 5.49      | 6.65      | 5.50      | 5.49      |
| CF$^a$      | $^2A_1$   | 0.74             | 5.44      | 5.54      | 5.56      | 5.54      |
| CF$^b$      | $^2A_1$   | 0.60             | 5.82      | 5.82      | 5.82      | 5.84      |
| PW-PP-LDA$^a$ | $^2A_1$ | 0.80             | 5.65      | 5.21      | 5.47      | 5.44      |

| Method      | Structure | $E_{\text{coh}}$ | $R_{1-2}$ | $R_{2-3}$ | $R_{1-3}$ | $R_{2-3}$ |
|-------------|-----------|------------------|-----------|-----------|-----------|-----------|
| CF$^b$      | $^2B_1$   | 0.56             | 5.31      | 6.41      | 5.90      | 6.20      |
| PW-PP-LDA$^a$ | $^2B_1$ | 0.85             | 4.81      | 5.43      | 5.38      | 5.58      |

$^a$ Reference [34]  
$^b$ Reference [17]  
$^c$ This work