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Multi-body and stability considerations of small clusters of lithium

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In this paper the results of quantum-chemical calculations of the importance of multi-body effects (i.e. the deviations from pairwise additivity) for lithium are presented. In addition, we analyse the differences between the theoretical and recent experimental determinations of the stabilization energy of Li_3. The principal conclusions of this study are (1) multi-body effects are large for this system, (2) the experimental value of the stabilization energy of Li_3 is probably incorrect.

1. INTRODUCTION

Recently, much attention has been focused on the structure and stability of small clusters of metal atoms [1–8]. The understanding of the properties of such clusters is of signal importance in many areas, particularly dispersed metal catalysis. Many groups have chosen to forgo the explicit calculation of true stabilization and cohesion energies in their analyses of these systems and have adopted the pairwise additive approach for the prediction of geometric structures and stabilities. Burton has recently used the pair approximation to explain the existence of pentagonally shaped microcrystals of various metals [8]. These microcrystals are anomalous, in that the bulk metal structure cannot be directly generated from such a species. However, for these metallic systems the reliability of the pair approximation has not been assessed. Indeed, in other cases in which this approximation has been tested (e.g. $(H_2O)_3$, $LiFH_2O$) [9, 10] it has been found to be inadequate for some regions of their configurational space.

In addition, much attention has been placed on geometric structure and cohesion energies as a function of the number of atoms in the cluster [3–6]. These results indicate a general functional behaviour shown as curve *a* in figure 1. It is a monotonically decreasing function from $N=2$ to $N=\infty$ (the bulk metal). However, some recent observations on precipitation of colloidal particles formed in alkali halides containing excess metal seem to indicate that colloids containing less than a few hundred metal atoms are unstable with respect to the formation

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of metal dimers [7]. This type of behaviour could imply a functional dependence of the cohesion energy (E_c) on the number of atoms (N) as represented by curve *b* in figure 1. Notice, a maximum occurs in curve *b*, a qualitative difference from the other curve *a*. Fripiat *et al.* [4] recently noted a behaviour similar to curve *b* for Li in a series of SCF–Xα–SW calculations on Li clusters, but were unable to ascertain whether the effect was real or just an artifact of their calculational method. Pickup [6] has also noted this effect as a result of his diatomics in molecules, semi-empirical valence bond calculations on Li clusters. On the other hand, the experimental results of Wu [11] concerning the stabilization energy of Li_3 indicates an *a*-type behaviour for Li. The recent theoretical work on Li_3 by Kendrick and Hillier [12] suggests *b*-type behaviour for this species.

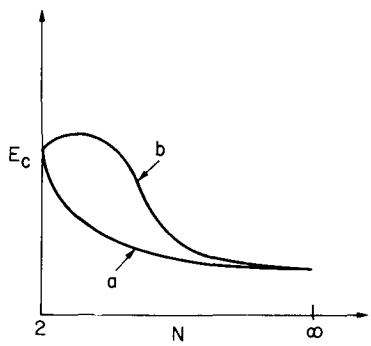

Figure 1. Two possible forms for the dependence of E_c on N.

In this paper we choose to analyse (in a rigorous, *ab-initio* manner) the lithium metal system because of its inherent simplicity and interesting physical characteristics. Kendrick and Hillier [12] have recently examined the Li_3 system in some detail. Our analysis differs from theirs in that our objectives are the examination of deviations from pairwise additivity and the elucidation of the origin of the apparent discrepancy between the theoretical and experimental values of the stabilization energy for Li_3. In the course of our work it was necessary to duplicate some of the earlier work of Kendrick and Hillier. When it is possible to compare the two sets of results the agreement is excellent.

With an eye to the resolution of our objectives, § 2 gives a brief outline of the general theoretical approach utilized in this work. Section 3 contains the multi-body effect analysis and § 4 presents the results of our study of the cohesion energy as a function of the number of atoms and the apparent experimental-theoretical disagreement for Li_3. In § 5 we discuss our results and speculate on their potential ramifications.

2. Theoretical framework

The results presented herein have been calculated using the method of Configuration Interaction (CI)†. We utilize this method, since it is well

† Any reader interested in a more detailed description of these techniques is referred to H. F. Schaefer's text on the electronic structure of atoms and molecules [13], or the chapter entitled " A General Approach to Configuration Interaction " by I. Shavitt in the recently published series on theoretical chemistry by Plenum Press [14].

known that conventional Hartree–Fock methods do not describe Li_n systems accurately [15]. Two Slater basis sets were used in our analysis. The first (BSI) contains four S-type and one P-type function on each atom (each P-type function consists of the x, y and z components). The S-type functions were taken from the compilation of Clementi and Roetti [16] and represents a double zeta quality basis. The P function was optimized on Li_2 via energy minimization at $R = 5{\cdot}28$ a.u., R being the Li–Li internuclear separation. BSI then, represents a double zeta plus polarization quality basis [13]. Basis set II (BSII) contains five S-type and two P-type functions on each atom. The S-type functions were taken from Clementi's [17] tabulation of atomic wave functions and represents a Hartree–Fock limit quality basis. The P-functions were also energy optimized on Li_2 at $R = 5{\cdot}28$ a.u. This basis is of the extended type [13]. Both basis sets are given in table 1 together with the energy predicted by each for the Li atom. Also given is the Hartree–Fock limit energy for the Li atom [16].

Several computational details to be noted are (1) BSI was used to search the potential energy surface of interest ; BSII was used to check the energies given by BSI at the BSI optimal geometries ; (2) in our CI calculations no excitations from the core orbitals (the 1S orbital on each centre) were permitted (they were always doubly occupied) and only symmetry-allowed single and double excitations from the valence orbitals were utilized. This core orbital freezing approximation was tested on Li_2 by doing a CI calculation in which *all* orbitals were available for excitation. Again, single and double excitations were used The stabilization energy obtained in this way was only ~ 4 kJ/mole below the frozen-core results, thus indicating this approximation to be reliable. The frozen-core restrictions led to the use of 32 space configurations on Li_2 (using BSI) and 78 space configurations using BSII. For Li_3 the $^2A_1$ state used 129 space configurations (BSI) and 330 space configurations (BSII). The $^2B_2$ state of Li_3 used 116 (BSI) and 306 (BSII) ; (3) since we are interested only in valence CI the proper atomic energies to use in the stabilization energy calculations (see § 3, the E(1) terms) are those given in table 1 ; and (4) to facilitate the analysis between differing geometrical forms C_{2v} symmetry was assumed for Li_3

Table 1. Basis-set information.

BSI (*a*)		BSII (*b*)	
Type	ζ	Type	ζ
1S	2·46167	1S	2·4758
1S	4·61679	1S	4·6878
2S	0·67198	2S	0·6183
2S	1·96299	2S	0·7500
2P	0·70730	2S	1·7710
		2P	0·8000
		2P	1·0000

(*a*) $E_{atom} = -7{\cdot}43270$ a.u. 1 a.u. $= 4{\cdot}3598$ aJ $= 2625{\cdot}47$ kJ mol^{-1}. Hartree–Fock limit is $-7{\cdot}43272$ a.u. [16].

(*b*) $E_{atom} = -7{\cdot}43272$ a.u.

with the coordinate axes shown in figure 2. The reference states chosen as the bases for the CI expansion were the $^2\Sigma_u^+$ for the linear form, the $^2B_2$ for the slightly non-linear geometries (the 3–1–2 angle being greater than 60°; see figure 2), the $^2E'$ for the equilateral triangle and the $^2A_1$ for the strongly non-linear geometries (the 3–1–2 angle being less than 60°). The $^2\Sigma_u^+$ state is the $^2B_2$ equivalent for the linear form and the $^2A_1$ and $^2B_2$ states become degenerate and equivalent to the $^2E'$ state in the equilateral form. Also, the $^2A_1$ state is lowest in energy for strongly non-linear geometries with the $^2B_2$ state lowest for slightly non-linear structures. Both states were found to have approximately the same energies at their respective minima, as noted previously [12].

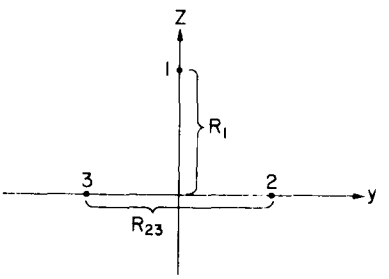

Figure 2. Li_3 geometry specification. The C_2 axis is taken to be the positive Z-axis.

3. Multi-body effects

The total stabilization energy (E_s) of the N atom, homonuclear system is defined as

$$E_s = E(1, 2, \ldots, N) - NE(1), \tag{1}$$

where $E(1, 2, \ldots, N)$ is the total energy of the N atom system and $E(1)$ is the total energy of an isolated atom. Thus, a complex which is stable with respect to dissociation into its component atoms will have an E_s which is negative. A common assumption in many-body theory is the pairwise additivity assumption; here, the stabilization energy of an N-body system is represented as the sum of two-body interactions. The assumption of pairwise additivity can be expressed formally as

$$E(s, 2) = \sum_{i<j} V(i, j). \tag{2}$$

Here, $E(s, 2)$ is a two-body stabilization energy,

$$V(i, j) = E(i, j) - 2E(1) \tag{3}$$

is the stabilization energy of the isolated pair i, j and $E(i, j)$ is the total energy of the isolated pair i, j. In general $E(s, 2)$ need not be the same as the total stabilization energy of the N-body system; accordingly, we may define an N-body stabilization energy (or deviation from pairwise additivity),

$$E(s, N) = E_s - E(s, 2). \tag{4}$$

The energy difference $E(s, N)$ defines the classical, non-additive contribution to the total stabilization energy of the system. We are interested in examining the case $N = 3$ for lithium.

As noted previously, the HF method does not yield correct values for stabilization energies for lithium systems. We find it is also unable to give reasonable $E(s, 2)$ values. For example, in the linear case for $R_{13} = R_{12} \approx 5{\cdot}54$ a.u. and $R_{23} \approx 11{\cdot}08$ a.u. HF predicts $V(1, 2) = V(1, 3) \approx -14{\cdot}23$ kJ mol^{-1} and $V(2, 3) \approx 145{\cdot}6$ kJ mol^{-1}. These values of $V(i, j)$ yield an $E(s, 2)$ of 117·1 kJ mol^{-1}, a result which is qualitatively incorrect inasmuch as it implies a negative $E(s, 3)$ whereas the CI result indicates $E(s, 3)$ is positive (see table 2).

Table 2. CI multi-body decomposition.

Source	Geometric type	E_s (*a*)	$E(s, 2)$	$E(s, 3)$	R_1 (*b*)	R_{23}
BSI	Isosceles	−111·7	−211·3	99·6	4·2	6·6
BSII	Triangle	−124·7	−233·9	109·2	4·2	6·6
KH (*c*)	($^2B_2$)	−123·0	—	—	4·4	6·0
BSI	Isosceles	−111·7	−216·7	105·0	5·4	5·1
BSII	Triangle	−121·8	−239·7	118·0	5·4	5·1
KH	($^2A_1$)	−123·0	—	—	5·2	5·1
BSI	Equilateral	−103·3	−226·8	123·4	4·9	5·6
BSII	Triangle	−118·4	−250·2	131·8	4·9	5·6
KH	($^2E'$)	−118·0	—	—	4·9	5·7
BSI	Linear	−94·1	−154·8	60·7	0·0	11·0
BSII	($^2\Sigma_u^+$)	−109·2	−171·1	61·9	0·0	11·0
KH		−106·7	—	—	0·0	11·0

(*a*) All energies are in kJ mol^{-1}.
(*b*) R_1 and R_{23} are defined in figure 2 and are in a.u. 1 a.u. = $0{\cdot}529167 \times 10^{-10}$ m.
(*c*) See reference [12].

The CI results we have obtained for various geometric forms of Li_3 are given in table 2. We find our E_s and equilibrium geometry results in good agreement with those of Kendrick and Hillier, except for small differences in the geometric parameters. These geometric discrepancies are understandable, since, for example, if we change R_{23} (in the $^2B_2$ isosceles triangle) to 6·2 a.u. (from its equilibrium value of 6·6 a.u. ; holding R_1 fixed at 4·2 a.u.), E_s changes by only 0·8 kJ mole. This is generally true for the entire surface and all states. The potential surface is very flat and the precise location of the absolute minima is not essential.

Further examination of the data in table 2 reveals immediately that the pairwise additivity approximation is *not* valid for this system. The $E(s, 3)$ terms are extremely large—indeed, in some cases they are as large (or larger) in magnitude than are the true stabilization energies. The multi-body effect can also be seen by an examination of what is the optimal triatomic geometry. If the pairwise additivity approximation was valid, one would expect the equilateral triangle to be the most stable conformer—it is not. The most stable conformers are the isosceles triangles ($^2B_2$ and $^2A_1$) with the equilateral triangle being at the

top of an energy barrier separating the isosceles triangle conformers. We speculate that the origin of this deviation from equilateral structure is a Jahn–Teller distortion [18].

The magnitude of the $E(s, 3)$ terms deserves further comment; they were found to be about an order of magnitude smaller in previous works [9, 10]. This is probably due to the strong overlap contributions present in these covalent systems, whereas in the previous work only electrostatic polarization interactions between closed-shell species were involved. This seems to imply that non-additivity effects from polarization are smaller than those from overlap even though the total stabilization energies in the prior work (~ -628 kJ mole for $LiFH_2O$) were much larger than those found here.

4. Stabilization and cohesion energies

The cohesion energy (E_c) of a cluster of N atoms is then defined in terms of the stabilization energy (equation 1) as

$$E_c = E_s/N. \tag{5}$$

Table 3 presents the results of our CI computations. Although the agreement among the various calculations is quite good, a basis-set dependence is noticeable when going from BSI to BSII. However, the E_c versus N curves are parallel. Thus BSI and BSII both predict a positive initial slope for the E_c versus N function.

Table 3. CI cohesion energies.

System	Source	E_s/kJ mol^{-1}	E_c/kJ mol^{-1} atom^{-1}	R/a.u. (*h*)
Li_2	BSI	−78·7	−39·4	5·13
	BSII	−87·0	−43·5	5·13
	D (*a*)	−95·4	−47·7	5·09
	KH (*b*)	−84·5	−42·3	5·17
	Y (*c*)	−79·9	−40·0	5·16
	Expt (*d*)	−99·6	−49·8	5·05
$Li_3(^2B_2)$	BSI	−111·7	−37·2	4·2, 6·6
	BSII	−124·7	−41·6	4·2, 6·6
	KH	−123·0	−41·0	4·4, 6·0
$Li_3(^2A_1)$	BSI	−111·7	−37·2	5·4, 5·1
	BSII	−121·8	−40·6	5·4, 5·1
	KH	−123·0	−41·0	5·2, 5·1
Li_3(expt)	Expt (*g*)	−172·8	−57·6	—

(*a*) See reference [15].
(*b*) See reference [12].
(*c*) See reference [19]. This is a valence-bond calculation.
(*d*) See reference [13], page 230, table III–28.
(*e*) Entries are R_1, R_{23}, where R_1 and R_{23} are defined in figure 2.
(*f*) Due to convergence problems in the Hartree–Fock calculation on the neutral species the +1 ion was used as the reference state in the CI.
(*g*) See reference [11].
(*h*) 1 a.u. $= 0{\cdot}529167 \times 10^{-10}$ m.

Although the Li_3 theoretical results agree quite well with each other, a rather large discrepancy exists between the theoretical and experimental information. Indeed, (as discussed in § 1) if we examine the E_c data we note a significant qualitative difference. We find the theory predicts the initial slope of the E_c versus N curve to be *positive*, whereas the experimental results indicate the initial slope is *negative*. In attempting to rectify this contradictory behaviour let us first examine the theoretical results.

Since we know the true result for Li_2 (from several experiments and various calculations) we can estimate the error in our theoretical results for Li_3 by means of a simple scaling technique. We note (for the E_s's) the ratio of experiment (Li_2) to BSI (Li_2) and BSII (Li_2) are 1·27 and 1·14, respectively. Applying these scaling factors to the Li_3 data we find E_s becomes $-141{\cdot}8$ kJ mol^{-1} (BSI) and $-142{\cdot}3$ kJ mol^{-1} ($^2B_2$; BSII) [3]. These values are still considerably different from $-172{\cdot}8$ kJ mol^{-1} (the experimental one) and they still predict the initial slope to be positive, although somewhat smaller.

The source of the possible discrepancy in the experimental result is not yet well understood. However, we have reviewed the experimental information [11] and have detected two possible causes for the theoretical/experimental differences. First, a temperature-independent ionization cross section (σ) for each species has been assumed in the determination of equilibrium constants for various reactions over a range of temperatures. This assumption is reasonable for Li_2. However, since the potential energy surface for Li_3 is quite flat, a Boltzmann distribution of conformers will be found at a given temperature. As the temperature changes so will the distribution. Since each conformer has a different ionization potential† the relative ionization cross section should change as the distribution of conformers changes and thus as the temperature changes. Therefore, the assumption of constant σ is probably not correct for Li_3. Our calculations show that with reasonable variations in σ with temperature one can obtain almost exact agreement between theory and experiment. Secondly, an incorrect, semi-empirical potential energy surface (which predicts the $^2A_1$ state to be lowest lying for all geometries) was used to calculate various thermodynamic quantities for Li_3 [20].

5. Conclusions and discussion

The primary conclusions of our work are (1) deviations from pairwise additivity are large, for $N=3$, thus implying that the pairwise additive approximation may not be valid for this system and (2) the initial slope of the E_c versus N curve is greater than zero, which implies that the experimental value for the E_s of Li_3 is probably incorrect.

Although the deviations from pairwise additivity are quite large (for Li_3) it may be that (in terms of geometrically dependent information) they will vanish in the thermodynamic limit‡. We postulate this behaviour for two reasons. The first is based on an analysis of the recent quantum-chemical and Monte Carlo work by Clementi and co-workers on H_2O [21]. For this system they

† The IP of the linear form is 7·00 aJ, the isosceles triangles are 6·65 aJ ($^2B_2$) and 6·60 aJ ($^2A_1$) and the equilateral triangle has an IP of 6·38 aJ. All IP's are calculated as $\Delta E_{CI} = E_{CI}(+1\text{ ion}) - E_{CI}(\text{neutral})$ using BSI at optimal geometries.

‡ That is, in the limit $N \to \infty$, $V \to \infty$, $(N/V) = \text{constant}$.

have calculated an essentially exact pair potential and have then used it to simulate the bulk liquid. They find, for geometrically dependent information (such as pair correlation functions, scattering curves, etc.) essentially exact agreement between pairwise additive potential theory and experiment—even though deviations from pairwise additivity are known to be significant for this system [9].

The second reason is rooted in the observation that for all conformers of Li_3 studied here, $E(s, 3)$ was always large, always had the same sign and varied only by a factor of slightly less than 2. This behaviour leads one to speculate that as the cluster size increases, $E(s, N)$ may become constant with respect to geometric structure change, thus allowing the structure to be determined by $E(s, 2)$. We are currently planning an examination of larger lithium clusters to see if this is the case.

Conclusion 2 can lead to some very interesting predictions in terms of the behaviour of larger atomic clusters The enthalpic condition for stability of a cluster of N atoms (stability with respect to decomposition to dimers or dimers plus an atom) is

$$E(1, 2, \ldots, N) < \frac{N}{2} E(1, 2)\,; \quad N_{\text{even}} \tag{6}$$

or

$$< \frac{N-1}{2} E(1, 2) + E(1)\,; \quad N_{\text{odd}}, \tag{7}$$

where $E(1, 2)$ is the equilibrium energy of the dimer and $E(1)$ is as defined previously. We can rewrite this condition as

$$E_c < E_c(\text{dimer})\,; \quad N_{\text{even}} \tag{8}$$

or

$$< \frac{N-1}{N} E_c(\text{dimer})\,; \quad N_{\text{odd}}. \tag{9}$$

A violation of this condition implies that (in the absence of other stabilizing effects) the enthalpic contribution to the dissolution process will be negative. Since the randomness of the system is also increasing (upon dissolution), this implies that the entropy change will be positive. Therefore, the free-energy change must be less than zero for this process. Thus, a violation of equation (8) or (9) corresponds to a sufficient condition for the spontaneous dissolution of atomic clusters.

A curve of the *b*-type (in figure 1 ; a positive initial slope) can violate these conditions. This implies that species which exhibit *b*-type behaviour may have some range of cluster sizes forbidden to them. Although lithium does not violate these conditions (for $N=3$) we present this discussion to point out that the qualitative behaviour needed to manifest this phenomenon is inherent in a physical system†.

Finally, we note that an electron in the box type of theory (developed by Libby [22] or Muth [7]) can also be utilized to examine cohesion energies and

† The non-existence of a range of cluster sizes for Pt has recently been documented by F. M. Dautzenberg and H. B. M. Wolters (1978, *J. Catalysis*, **51**, 26). It may be that it is a manifestation of *b*-type behaviour for Pt due to its S-like valence (analogous to Li). Studies are underway to ascertain if this is the case.

metal cluster stabilities. Indeed, these types of theories can even yield results in qualitative agreement with ours. However, the existence of arbitrarily constrained parameters in these theories reduces their utility, particularly when one notices that any theory used for the analysis of these systems needs to predict quite small differences for various properties (e.g., the small differences between E_c(dimer) and E_c(trimer) which allows the discrimination between *a* and *b*-type curves).

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References

[1] Schaefer, III, H. F., 1975, *J. chem. Phys.*, **62**, 4815.
[2] Baetzold, R., 1976, *Adv. Catalysis*, **25**, 1.
[3] Dykstra, C. E., Schaefer, III, H. F., and Meyer, W., 1976, *J. chem. Phys.*, **65**, 5141.
[4] Fripiat, J. G., Chow, K. T., Boudart, M., Diamond, J. B., and Johnson, K. H., 1975, *J. molec. Catalysis*, **1**, 59.
[5] Baetzold, R., and Mack, R., 1975, *J. chem. Phys.*, **62**, 1513.
[6] Pickup, B. T., 1973, *Proc. R. Soc.* A, **333**, 69.
[7] Muth, D. G., 1967, Ph.D. Thesis, University of Notre Dame.
[8] Burton, J. J., 1974, *Catalysis Rev.*, **9**, 209.
[9] Hankins, D., Moskowitz, J. W., and Stillinger, F. H., 1970, *J. chem. Phys.*, **53**, 4544.
[10] Kress, J. W., Clementi, E., Kozak, J. J., and Schwartz, M. E., 1975, *J. chem. Phys.*, **63**, 3907.
[11] Wu, C. H., 1976, *J. chem. Phys.*, **65**, 3181.
[12] Kendrick, J., and Hillier, I. H., 1977, *Molec. Phys.*, **33**, 635.
[13] Schaefer, III, H. F., 1972, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley).
[14] Shavitt, I., 1977, *Modern Theoretical Chemistry* (Plenum Press), Chap. 8.
[15] Das, G., 1967, *J. chem. Phys.*, **46**, 1568.
[16] Clementi, E., and Roetti, Carla, 1974, *Atom. Data nucl. data Tables*, **14**, 177.
[17] Clementi, E., 1965, *IBM Jl Res. Dev.*, Suppl., **9**, 39.
[18] Jahn, H. A., and Teller, E., 1937, *Proc. R. Soc.* A, **161**, 220.
[19] Yardley, R. N., and Balint-Kurti, G. G., 1976, *Chem. Phys.*, **16**, 287.
[20] Companion, A. L., Steible, D. J., and Starshak, A., 1968, *J. chem. Phys.*, **49**, 3637.
[21] Lie, G. C., Clementi, E., and Yoshimine, M., 1976, *J. chem. Phys.*, **64**, 2314.
[22] Libby, W. F., 1967, *J. chem. Phys.*, **46**, 399.