A calculation of the electron affinity of the lithium molecule

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Using the equation-of-motion method, an electron affinity of 0.90 eV was computed for the Li_2 molecule. This value is larger than the results of other calculations and is also larger than the experimental electron affinity of the lithium atom. A prediction of the stable ground state for Li_2^- is a result of our calculation. Using some experimental data and the calculated Li_2 electron affinity within a Born–Haber cycle, an approximate dissociation energy of Li_2^- can be obtained. SCF-level potential energy curves have been calculated for Li_2 and Li_2^- as well as spectroscopic constants which give qualitatively good agreement with available experiment results. A comparison between properties of Li_2^- and Li_2^+ is also discussed.

I. INTRODUCTION

The lithium molecule has received substantial attention in recent years.[1] Because this molecule is one of the smallest diatomics of chemical interest and because no experimental determination of the electron affinity has been found, Li_2 presents an excellent opportunity for theoretical study to yield valuable new predictions. Calculations on the anion of the lithium molecule are not as numerous as those on the neutral species; in fact, it has been shown that for a minimal basis set Roothaan's SCF equations for an open shell species,[2] within the traditional iteration procedure, can give rise to an oscillatory solution.[3] These and other problems associated with the solution of the SCF equations have been discussed in a recent publication.[3]

The method used for calculating the electron affinity of the lithium molecule in this work is the equation-of-motion (EOM) method which has been developed and implemented by Simons *et al.*[4] This research group has published a series of papers comparing the results of the EOM method with experimental results.[5–8] The EOM formalism contains all second order perturbation corrections with most of the third order terms and some shifted denominators. The reader is referred to Ref. 4 for details of the method.

II. CALCULATIONS

The EOM method discussed in Ref. 4 requires as input the results of an SCF calculation on the closed-shell parent, Li_2. These SCF results were obtained using the Harris DIATOM program, which was run on the University of Utah Univac 1108 computer. The basis set was formed by starting with a basis for the lithium atom reported by Clementi.[9] To this set of Slater-type functions we added one full set of diffuse p functions and another set of p_τ type functions. The basis was then optimized to give the maximum value for the electron affinity of Li_2. Based upon our experience on other molecules, we find that this procedure of optimization leads to the best balanced description of the parent (Li_2) and the anion (Li_2^-).

During the optimization, the need for a more diffuse $2s$ function became apparent. The first three $2p$ functions on each lithium atom were optimized together as a set. After attempting to optimize the p_σ and s orbitals to yield the maximum value for the electron affinity, we added another set of diffuse p_τ functions whose exponents were then optimized. All optimization was performed at 5.3 bohr, which is near our computed equilibrium bond length of Li_2. The resulting basis set is shown in Table I.

The results of this optimization gave a vertical electron affinity of 0.80 eV for Li_2 at $R = 5.3$ bohr.

III. RESULTS AND DISCUSSION

A. Potential energy curves for Li_2 and Li_2^-

An SCF-level potential energy curve was calculated for Li_2 with the optimized basis set described above. The total SCF energy resulting in this calculation is higher than that previously reported by Das.[10] The total Li_2 SCF energy obtained by optimizing for the largest electron affinity is -14.863280 hartree with a corresponding equilibrium bond length of 5.29 bohr. Reference 10 reports an energy of -14.90260 hartree with a bond length of 5.07 bohr, which compares well with the experimental bond length of 5.051 bohr.[11]

A potential energy curve was calculated for Li_2^- by using Eq. (1),

TABLE I. The optimized 20 STO basis set for Li_2 and the coefficients for the occupied orbitals at 5.3 bohr[a]; $E = -14.86325$.

Orbital	ζ	$C_{1\sigma}$	$C_{2\sigma}$	$C_{3\sigma}$
$1sLi$	2.4739	0.63248	0.63664	-0.07663
$1sLi'$	2.4739	0.63687	-0.63224	-0.07663
$1s'Li$	4.6925	0.07906	0.07974	-0.02727
$1s'Li'$	4.6925	0.07968	-0.07919	-0.02727
$2sLi$	0.3523	0.00004	-0.00752	0.19206
$2sLi'$	0.3523	-0.00001	0.00752	0.19208
$2s'Li$	1.0287	-0.00016	-0.00232	0.56164
$2s'Li'$	1.0287	-0.00017	0.00232	0.56164
$2s''Li$	1.6350	0.00501	0.00573	-0.26926
$2s''Li'$	1.6350	0.00505	-0.00570	-0.26926
$2p_\sigma Li$	0.4066	-0.00054	-0.00352	0.18068
$2p_\sigma Li'$	0.4066	0.00057	-0.00352	-0.18068
$2p_\tau Li$	0.4066	0.0	0.0	0.0
$2p_\tau Li'$	0.4066	0.0	0.0	0.0
$2p_{\tau'} Li$	0.6449	0.0	0.0	0.0
$2p_{\tau'} Li'$	0.6449	0.0	0.0	0.0

[a]The asymmetry in the coefficients is due to convergence criteria problems.
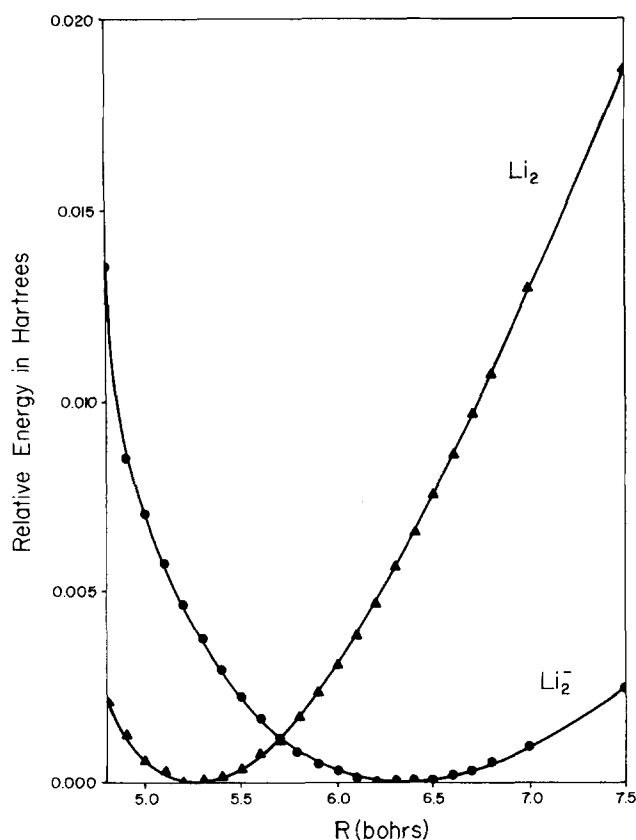
FIG. 1. Potential energy curves for Li_2, ▲, and Li_2^-, •, shifted by the energy minima of the potential curves. $E_{Li_2}(R_e)$ $= -14.863280$; $E_{Li_2^-}(R_e) = -14.896417$.

$$E_{Li_2} - (R) = E_{Li_2}(R) - E. A._{(vert)}(R) , \qquad (1)$$

where $E_{Li_2^-}(R)$ is the bond-length-dependent energy of the anion (Li_2^-); $E_{Li_2}(R)$ is the bond-length-dependent energy of the parent (Li_2) calculated in this work; and E. A._{(vert)}(R) is the bond-length-dependent vertical electron affinity of Li_2 from the EOM theory. This procedure gave a minimum energy of $- 14.896417$ hartree at 6.30 bohr for Li_2^- which can be compared with a recent valence bond calculation that yielded a value of $- 14.8701$ hartree at 6.242 bohr. [12]

The Li_2 and Li_2^- potential curves are shown in Fig. 1. These curves demonstrate that the potential energy well is much broader for the negative ion than for the neutral species. This would be expected in view of the fact that the 4σ orbital into which the "extra" electron is being added is an antibonding orbital. The very large change in the bond length is consistent with the decrease in the bond order from one to one-half, especially in such a small molecule. Because both potential curves are of SCF quality, one should not expect to be able to extract quantitative information from them, especially at large R values. However, the equilibrium internuclear distances and vibrational frequencies obtained from the curves for the purposes of this paper should be reasonably ($\pm 10\%$) reliable.

B. Spectroscopic and thermodynamic parameters

The spectroscopic parameters of Li_2 and Li_2^- were determined by least-squares fitting a parabola to the bottom of the respective potential curves. The results of this calculation are given in Table II.

The dissociation energy of Li_2^- was calculated from Eq. (2),

$$D_{0_{L i_2^-}} = D_{0_{L i_2}} + E. A._{L i_2(thermo)} - E. A._{Li} , \qquad (2)$$

where $D_{0_{L i_2}}$ is the chemical dissociation energy of Li_2; E.A._{L i_2(thermo)} is the thermodynamic electron affinity; and E.A._{Li} is the electron affinity of lithium atom. The dissociation energy of Li_2 was obtained from the experimental determination of Velasco et al. [13] The electron affinity for atomic Li has also been determined experimentally. [14] The thermodynamic electron affinity appearing in Eq. (2) was obtained from the calculated Li_2 and Li_2^- potential curves by making harmonic zero-point energy corrections to the difference in the minimum electronic energies. This procedure results in a predicted thermodynamic electron affinity of 0.90 eV and a calculated $D_{0_{L i_2^-}}$ of 1.31 eV. The weakest step in the procedure used to compute this D_0 is the use of our computed thermodynamic electron affinity of Li_2. We estimate this error to be ± 0.2 eV. The other quantities appearing in Eq. (2) were taken from accurate experimental data.

C. EOM-Koopmans' theorem comparison

In a previous paper, [6] the relation between Koopmans' theorem and the EOM results was discussed for BeH^-. As in this earlier work, it appears that this Koopmans defect is a slowly varying function of internuclear distance in the Li_2–Li_2^- system. The difference between the lowest unoccupied molecular orbital (LUMO) energy and the EOM result is shown in Fig. 2 as a function of R. Although this difference is relatively insensitive to variations in internuclear distance, it does not appear to be as linear as was previously reported for another system. [6] One reason for this difference is probably the rather small range of internuclear distances studied in the earlier work.

D. The ground state of Li_2^- and the electron affinity of Li_2

The ground state of Li_2^- has been reported by Linnett et al. to be $a^2\Pi_u$. [15] In the Linnett calculations, the $^2\Pi_u$ state is more stable than the $^2\Sigma_u^+$ state by 0.016 hartree (0.44 eV). We find in this work that the $^2\Sigma_u^+$ state is more stable than the $^2\Pi_u$ by 0.6 eV at 5.3 bohr, based

TABLE II. Molecular properties for Li_2 and Li_2^-.

Parameter	Unit	Li_2^j(calc)	Li_2^j(exptl)	Li_2^-(calc)
R_e	a.u.	5.29	5.051[a]	6.30
K_e	dyn/cm×10^{-4}	2.112		0.7849
ν_e	cm^{-1}	319.7	351.43[a]	195.9
D_e	eV		$1.026 \pm .006$[b]	1.31
E.A._{(vert)}	eV	0.80		
I.P.	eV			1.06
E.A._{(thermo)}	eV	0.90		

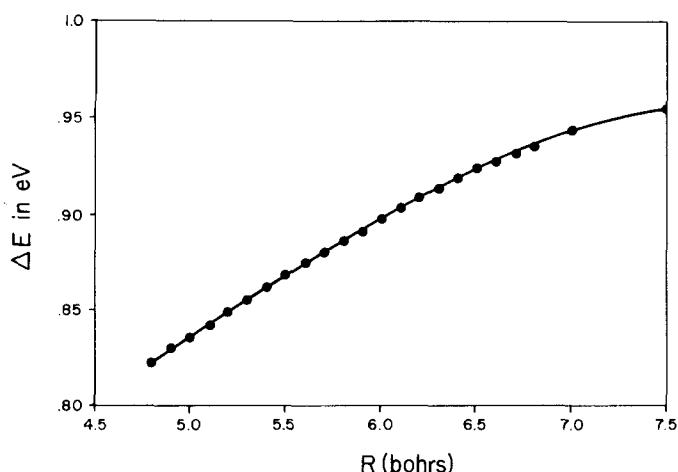[a]G. Herzberg, Ref. 11.   [b]R. Velasco et al., Ref. 13.

FIG. 2. Difference between EOM and LUMO energy.

upon a difference of optimized vertical electron affinities for the two states. Using the vertical electron affinities obtained from the above potential curves, the calculated vibrational frequency of Li_2^-, and the measured frequency of Li_2, we compute a thermodynamic electron affinity of Li_2 of 0.90 eV. This value is substantially larger than the 0.27 eV reported by Linnett[15] for the $^2\Pi_u$ state of Li_2^-. A calculation of the vertical photodetachment energy of Li_2^- can also be achieved from the above mentioned potential energy curves. For this quantity we obtain a value of 1.06 eV.

IV. GENERAL DISCUSSION

It is very interesting to make use of the results of the present calculations to compare the bonding and spectroscopic parameters of Li_2^+ and Li_2^-, both of which have a bond order of one-half. Calculations on Li_2^+ give a fundamental frequency of 254.7 cm^{-1},[16] which is not very different from the fundamental frequency of Li_2^- determined in this work (195.9 cm^{-1}). Several values of the dissociation energy of Li_2^+ have been tabulated by Wahl et al., in Ref. 16. One of the more recent values (1.31 eV)[17] is identical to our computed dissociation energy.

By comparing these spectroscopic parameters for Li_2^+ and Li_2^- to those of the neutral molecule, we see that Li_2 has a stronger bond (larger ω_e, shorter R_e) than the ions; however, both of the ions are more stable (larger D_0) than the neutral Li_2. The positive and negative ions have very similar bond lengths (both ~ 6 bohr) which are 1 bohr longer than that of the neutral. This is in line with the difference in bond order between the neutral and its ions. The fact that the ions have a larger dissociation energy may be related to the long-range ion–atom interaction. A set of minimal-basis valence bond calculations[12] on Li_2, Li_2^+, and Li_2^- provides data which tend to support our findings. In Ref. 12, the resulting dissociation energies of Li_2, Li_2^+, and Li_2^- are 0.76 eV, 1.06 eV, and 0.92 eV, respectively.

V. CONCLUDING REMARKS

Previous calculations have shown how well the EOM method has succeeded in obtaining electron affinities of molecules in cases where experimentally determined values were known.[5,6] This indicates that by applying the EOM method valuable predictions can be made. From this work, we obtain a prediction that the $^2\Sigma_u^+$ ground state of Li_2^- is stable with respect to dissociation and electron loss. We find that the ground state of Li_2^- is a species which should be as stable to dissociation as Li_2^+. The overlap of the $v = 0$ Li_2 and Li_2^- vibrational wavefunctions is so small that we conclude that the vertical electron affinity and photodetachment measurements should give significantly different values for this system. Furthermore, we have found the Li_2–Li_2^- system to be very interesting because the large change in internuclear separation in going from Li_2 to Li_2^- is accompanied by a decrease in vibrational frequency and an increase in dissociation energy. Such a seemingly anomalous situation also occurs in going from Li_2 to Li_2^+.

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