Lawrence Berkeley National Laboratory

Recent Work

Title

POTENTIAL ENERGY SURFACES FOR $H + Li_2 \rightarrow LiH + Li$ GROUND STATE SURFACE FROM LARGE SCALE CONFIGURATION INTERACTION

Permalink

<https://escholarship.org/uc/item/3q40d483>

Authors

Siegbahn, Per
Schaefer, Henry F.

Publication Date

1974-10-01

POTENTIAL ENERGY SURFACES FOR $H + Li_2 \rightarrow LiH + Li$
GROUND STATE SURFACE FROM LARGE SCALE
CONFIGURATION INTERACTION

Per Siegbahn and Henry F. Schaefer III

October, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

POTENTIAL ENERGY SURFACES FOR $H + Li_2 \rightarrow LiH + Li$
GROUND STATE SURFACE FROM LARGE SCALE CONFIGURATION INTERACTION

Per Siegbahn* and Henry F. Schaefer III**

Department of Chemistry and Lawrence Berkeley Laboratory[†]

University of California, Berkeley, California 94720

October 1974

* Miller Fellow.

** Alfred P. Sloan Fellow.

[†] Work performed under the auspices of the U.S. Atomic Energy
Commission.

ABSTRACT

Ab initio electronic structure calculations have been performed to determine the HLi_2 potential energy surface. A contracted gaussian basis set was employed: $\text{H}(5s\ 1p/3s\ 1p)$, $\text{Li}(8s\ 3p/4s\ 3p)$. In addition to self-consistent-field (SCF) wave functions, full configuration interaction (CI) was carried out for the three valence electrons. For general geometry (point group C_s) the CI included 5175 configurations. For the diatomic molecules Li_2 and LiH , these methods yield dissociation energies within 5 kcal/mole of experiment, and accurate spectroscopic constants are also predicted. The minimum on the HLi_2 CI potential surface occurs for an isosceles triangle structure with $r(\text{H-Li}) = 1.72\ \text{\AA}$ and on LiHLi bond angle of 95° . This minimum lies 22.4 kcal/mole below the separated products $\text{LiH} + \text{Li}$. The linear HLiLi minimum is much shallower, lying only 4.2 kcal/mole below the products. The much simpler single configuration SCF calculations yield qualitatively similar results. Furthermore, these features of the surface are quite analogous to those predicted for $\text{F} + \text{Li}_2$ by Pearson and coworkers. The angular dependence of the surface between the C_{2v} and $C_{\infty v}$ extremes is discussed. The "electron jump" from covalent HLi_2 to ionic H^-Li_2^+ is seen to be much more gradual than was the case for FLi_2 . The electronic structure is described using a natural orbital analysis of the most important configurations in the wave function.

Introduction

Lee, Gordon and Herschbach¹ have reported crossed molecular beam studies of the reactions of H and D atoms with K₂, Rb₂, and Cs₂. From their results a number of important qualitative conclusions were drawn. For example, only a small fraction of the available energy appeared in product translation. Thus it seems likely that either the alkali hydride product MH is vibrationally and/or rotationally excited or the alkali atom M must be electronically excited. In addition, Lee, Gordon and Herschbach¹ concluded that there is an anisotropic reaction probability for H + M₂, with $\text{M} \overset{\text{H}}{\text{---}} \text{M}$ configurations more likely to lead to reaction.

The hydrogen atom plus alkali dimer reactions are of interest to theoreticians first because of the opportunity for fruitful interaction with experiment and second because these systems are among the simplest for which the dynamics frequently must be described in terms of more than a single potential energy surface.^{2,3} For the simplest such reaction at thermal energies only a single channel is energetically open⁴:

However, under the conditions utilized by Lee et al., namely ~ 10 kcal/mole of H or D atom translational energy and 6 ± 3 kcal/mole of alkali dimer vibrational excitation, a second pathway is possible⁵:

From either an experimental or theoretical viewpoint, then, it will be of great interest to determine the relative importance of these two competing reaction pathways. Herschbach's work, though not definitive, suggested the former path (1) to be the dominant one.

The potential beauty of a theoretical treatment of this reaction lies in the opportunity to study the product energy distribution as a function of initial conditions. While the molecular beam experimentalist will do splendidly to study this reaction under one particular set of circumstances, we are free to study it under whichever circumstances appear most interesting. For example, the ratio of $\text{LiH} + \text{Li}$ to $\text{LiH} + \text{Li}^*$ can be studied as a function of H atom translational energy or as a function of Li_2 vibrational energy. Even if the $\text{LiH} + \text{Li}^*$ pathway is shown to be unimportant, the partitioning⁶ of the available energy into translation, vibration, and rotation of $\text{LiH} + \text{Li}$ should be interesting.

The potential surfaces required for a thorough study are those arising from $\text{LiH} + \text{Li}({}^2\text{S})$ and $\text{LiH} + \text{Li}({}^2\text{P})$. For general geometry (C_s symmetry), three of these surfaces will be of ${}^2\text{A}'$ irreducible representation and one of ${}^2\text{A}''$. Although our primary concern in the present theoretical study is with the accurate determination of the ground state ${}^2\text{A}'$ surface, a later paper will describe a series of more modest calculations on the excited

state surfaces. In this research both self-consistent-field (SCF) and large scale configuration interaction (CI) techniques have been used. In addition to providing a sound starting point for detailed dynamical (specifically, classical trajectory⁷) studies, it is of interest to compare our ab initio results with the semi-empirical diatomics-in-molecules calculations⁸ of Companion⁹ for HLi_2 . This is particularly important since the discussion of Lee and co-workers¹ makes several references to Companion's work.

Theoretical Approach

It is clear that no ab initio calculation can surpass the limitations placed on it by the chosen basis set.¹⁰ The present work began with the $\text{H}(4s)$ and $\text{Li}(8s)$ primitive gaussian basis sets of van Duijneveldt.¹¹ These were contracted to $\text{H}(4s/2s)$ and $\text{Li}(8s/4s)$ to provide maximum flexibility in the valence region. This basis was supplemented by functions roughly optimized in our CI studies of the Li_2 and LiH molecules. For hydrogen, a diffuse s function ($\alpha = 0.05$) was added to describe the H^- character in LiH . A set of p functions (p_x, p_y, p_z) were then added as hydrogen polarization functions. The lithium basis was augmented by three uncontracted sets of 2p functions. The entire basis is seen in Table I.

The relative adequacy of our basis may be examined by comparison of self-consistent-field results with known near-Hartree-Fock

energies. For the 2S ground state of the Li atom, the present basis set yielded an SCF energy of -7.43162 hartrees, compared to the Hartree-Fock limit,¹² -7.43273 hartrees. We also computed the SCF energy of the 2P excited state to be -7.35378 hartrees, or 2.15 eV above the ground state. Experimentally, the $^2S - ^2P$ separation is 1.85 eV.⁵ For the H atom, an energy of -0.49931 hartrees was found, as opposed to the exact result, -0.5 hartrees. Our computed SCF energy at a bond distance of 3.025 bohrs was -7.98459 hartrees, to be compared with Cade and Huo's near Hartree-Fock energy¹³ of -7.98731 hartrees. Finally, for Li_2 at $r(Li-Li) = 5.07$ bohrs, we obtained $E = -14.86912$ hartrees, compared to the value of -14.87159 hartrees obtained by Das¹⁴ using a large basis set of Slater functions. In conclusion it appears that the SCF potential surface obtained for $H Li_2$ using the basis set of Table I should be no more than 0.005 hartrees ≈ 3 kcal/mole above the true Hartree-Fock potential surface.

The present theoretical approach begins with single configuration SCF calculations on $H Li_2$. For linear $H-LiLi$ approaches, the lowest potential surface will be of $^2\Sigma^+$ symmetry, with SCF configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma \quad (3)$$

This same configuration will be dominant for large $H Li-Li$ separations. However, when the Li atom is in its 2P state, the corresponding Σ and Π electronic states correspond to electron configurations

$$1\sigma^2 2\sigma^2 3\sigma^2 5\sigma \quad (4)$$

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi \quad (5)$$

For C_{2v} approaches and large H-Li₂ separation, the lowest potential surface should be of 2A_1 symmetry, with electron configuration

$$1a_1^2 1b_2^2 2a_1^2 3a_1 \quad (6)$$

This configuration correlates for $D_{\infty h}$ geometries Li-H-Li with

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g \quad (7)$$

However, it must be noted that Companion⁹ found the lowest total energy to occur for a ${}^2\Sigma_u^+$ state, corresponding predominantly to the electron configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u \quad (8)$$

Note that for C_{2v} geometries, configuration (8) becomes

$$1a_1^2 1b_2^2 2a_1^2 2b_2 \quad (9)$$

For general geometry (C_s point group) the lowest potential surface should be of irreducible representation ${}^2A'$ and in most regions be well-described by the single configuration

$$1a'^2 2a'^2 3a'^2 4a' \quad (10)$$

The three states generated by bringing a 2P Li atom up to ground state LiH are described by electron configurations

$$1a'^2 2a'^2 3a'^2 5a' \quad (11)$$

$$1a'^2 2a'^2 3a'^2 1a'' \quad (12)$$

$$1a'^2 2a'^2 3a'^2 6a' \quad (13)$$

The wave functions (3) - (13) give the simple molecular orbital description of the electronic states of primary interest in the present work.

Following the SCF calculations, full valence (outer 3 electrons) configuration interaction (CI) was carried out. The theoretical method used was developed and programmed by one of us (P.S.), and is specific to full CI for systems with three valence electrons.¹⁵ This same method is currently being applied to the H_3 potential surface.¹⁶

Briefly the method combines the diagonalization procedure with the construction of the Hamiltonian matrix. If perturbation theory is used, a perturbation function $\phi^{(k)}$ is calculated in iteration k with components in a configuration basis

$$C_i^{(k)} = \frac{1}{H_{00}^o - H_{ii}^o} \sum_{j=1}^N V_{ij} C_j^{(k-1)} - \sum_{m=0}^{k-1} \epsilon_{k-m} C_i^{(m)} \quad (14)$$

where the usual perturbation splitting $H = H_0 + V$ is made, ϵ are perturbation energies and N is the number of configurations in the basis set. The perturbation energies obtained in iteration

k are given by¹⁵

$$\begin{aligned}\epsilon_{2k-1} &= \langle \phi^{(k-1)} | V | \phi^{(k-1)} \rangle - \sum_{m=1}^{k-1} \sum_{n=1}^{k-1} \epsilon_{2k-1-m-n} \langle \phi^{(m)} | \phi^{(n)} \rangle \\ \epsilon_{2k} &= \langle \phi^{(k)} | V | \phi^{(k-1)} \rangle - \sum_{m=1}^k \sum_{n=1}^{k-1} \epsilon_{2k-m-n} \langle \phi^{(m)} | \phi^{(n)} \rangle\end{aligned}\quad (15)$$

The perturbation functions may now simply be added and normalized to give the final wave function and the perturbation energies added to give the final energy. More efficiently the secular equation can be solved in terms of the perturbation functions where the matrix elements of V are given by

$$\langle \phi^{(p)} | V | \phi^{(q)} \rangle = \epsilon_{p+q+1} + \sum_{k=1}^p \sum_{l=1}^q \epsilon_{p+q+1-k-l} \langle \phi^{(k)} | \phi^{(l)} \rangle \quad (16)$$

This is the procedure used here, and the unperturbed Hamiltonian H^0 was chosen to give orbital energies in the denominator in (14). This is easily achieved by setting

$$H_0 = \sum_{i=1}^N |i\rangle \alpha_i \langle i| \quad (17)$$

where α_i are sums of orbital energies.

The main computational problem in this procedure is the calculation of the vector $\underline{\sigma}$ with components

$$\sigma_i^{(k)} = \sum_{j=1}^N v_{ij} c_j^{(k-1)} \quad (18)$$

When this vector is calculated only minor extra work is required to obtain the quantities (14), (15), and (16). The special CI-method used here updates the components $\sigma_i^{(k)}$ directly from the molecular integrals through

$$\Delta\sigma_i^{(k)} = A \cdot (ab|cd) \cdot c_j^{(k-1)} \quad (19)$$

where $(ab|cd)$ are two-electron integrals and A are coupling coefficients. By using (19) instead of (16) directly, the explicit construction of the Hamiltonian matrix is avoided. Instead only a sequential reading of the molecular integrals is needed. The adaptation and the special modifications of the original method¹⁷ for the case of full CI for three valence electrons has been discussed elsewhere.¹⁵

Reactants and Products

Our SCF and CI results for the diatomic molecules Li_2 and LiH are seen in Table II. Let us turn first to the dissociation energies D_e . Although the predicted CI dissociation energies are certainly in reasonable agreement with experiment, the errors are nevertheless of the order of 5 kcal/mole. Since we have used a fairly large basis and coupled it with full valence CI, it is clear that a significantly more accurate prediction (say, to

within 1 kcal/mole) will be difficult to achieve. These results also reinforce our feeling that the goal of most theoretical studies of potential energy surfaces should be to qualitatively pin down only those parts of the surface not amenable to experimental determination. Then, available experimental diatomic molecule potential curves should be incorporated semi-empirically into the final potential surface. In the present case, for example, it makes little sense to adopt an ab initio potential curve for LiH that is known to be in error by 4.3 kcal/mole at the minimum. Note however that the predicted exothermicity is 32.7 kcal/mole, in close agreement with experiment,⁴ 31.7 ± 0.7 .

For LiH, the predicted r_e is $0.013 \text{ \AA}$ larger than experiment, and for Li_2 the difference is even greater, $0.04 \text{ \AA}$. Especially the latter difference is greater than expected¹⁸ from this calibre of calculation. However, the shallow nature of both potential curves makes the determination of r_e - either from theory or experiment - rather difficult. For LiH, the calculations have been carried further, via CI including all single and double excitations with respect to both core and valence orbitals. The bond distance r_e predicted in this way is $1.600 \text{ \AA}$, or only $0.005 \text{ \AA}$ greater than experiment. Thus it would appear that for LiH, the core correlation energy has a noticeable effect on the predicted bond distance.

The remaining spectroscopic constants ω_e , B_e , $\omega_e x_e$, and α_e were obtained in a manner analogous to that used by experimentalists. That is, after numerically solving the vibrational Schrödinger

equation, the constants were obtained from the theoretical $\Delta G_v + 1/2$ levels, as discussed by Lie, Hinze, and Liu.¹⁹ This procedure guarantees a valid comparison with experiment, and Table II shows indeed that reasonable agreement is found. Particularly noteworthy are the 3.8% (Li_2) and 1.2% (LiH) errors in the theoretical ω_e values for the two molecules. Except for the $\text{LiH } B_e$ value, the CI results are seen to provide improved (relative to SCF) agreement with experiment.

Potential Minima

The most obviously important features of the HLi_2 surface which have not been determined experimentally are the various constrained potential minima. The diatomics-in-molecules work of Companion concluded that the absolute minimum for HLi_2 occurs for a $D_{\infty h}$ structure of $^2\Sigma_u^+$ symmetry, lying 20.7 kcal/mole below separated $\text{Li} + \text{LiH}$. From their experiments and qualitative theoretical arguments, Lee, Gordon, and Herschbach¹ concluded that the most typical reactive encounters occur roughly broadside, i.e., in the vicinity of the C_{2v} approach.

Table III summarizes the present results for the different constrained minima considered. In agreement with Companion,⁹ the $^2\Sigma_u^+$ state is found to be the $D_{\infty h}$ ground state. However, Table III show the $^2\Sigma_g^+$ minimum to lie only 1.1 kcal/mole higher. The most compelling evidence against the validity of the diatomics-in-molecules model is our prediction that the true equilibrium geometry of HLi_2 occurs

for a C_{2v} geometry (95° bond angle) and the lowest electronic state is not of 2B_2 symmetry, but rather of 2A_1 symmetry. The fact that the deepest well (22.4 kcal/mole) is of 2A_1 symmetry is significant since ground state H approaches ground state Li_2 on this surface. Thus the deep potential well is directly accessible to $H + Li_2$ collisions. If, on the other hand, the collision complex were a 2B_2 state, hypothetical C_{2v} collisions could not reach it, although C_s encounters would allow access to the well.

For the extreme opposite approach, linear $H-Li-Li$, a rather small well of only 4.2 kcal/mole was found. This is quite similar to the $F + Li_2$ surface, which previous less exhaustive studies²⁰ predicted to have an $F-Li-Li$ well of 4 kcal/mole, but an well of 34 kcal/mole. Although the $H + M_2$ and $X + M_2$ systems both form ionic triatomic radicals, fluorine is so much more ionic than hydrogen that such close similarities are a bit surprising. The stronger nature of the $F-Li_2$ bond is of course consistent with its more ionic character. Finally, we note that even though the $H + M_2$ and $X + M_2$ potential surfaces have qualitative similarities, the much heavier mass of the halogen atom X may give rise to large dynamical differences,²¹ and hence to qualitatively different experimental observations for the two families of reactions.

The intermediate case, , yields an attractive energy only 0.4 kcal/mole greater than that for linear $H-Li-Li$. This suggests that the deep well for the C_{2v} approach ($\theta = 90^\circ$) may

greatly diminish as one moves even slightly away from the directly broadside approach. In that case, the 22.4 kcal/mole minimum might have little dynamical significance. To test this possibility, the three additional calculations shown in Table IV were carried out. There it is seen that the deep well is fairly broad, being more than 15 kcal/mole deep everywhere within $\pm 20^\circ$ of the C_{2v} approach. Thus complex formation could conceivably be a factor in the dynamics of the $H + Li_2$ reaction, and nearly broadside collisions will lead most often to such an HLi_2 complex. However, the experiments¹ on this family of reactions do not show complex formation, presumably due to the large exothermicity.

Table III also shows the single configuration SCF approximation to give a qualitatively reasonable description of the surface in the region of the complex. This tends to confirm one's intuitive feeling,²⁰ that although the SCF approximation is not reasonable for repulsive surfaces,²² it may be quite useful in describing attractive surfaces such as $F + Li_2$ and $H + Li_2$.

Companion's diatomics-in-molecules (DIM) study concentrated on $Li-H-Li$ geometries, and hence allows us to fill in only that entry in Table III. However, in more recent but unpublished work, she has explored the $H + Li_2$ surface in detail.²³ Her unpublished results are the DIM results seen in Table III. Companion has pointed out that none of the DIM calculations to date have employed 2p orbitals on Li. Hence it is not unreasonable to expect refined future DIM calculations to provide better agreement with the ab

initio results. Furthermore, it should be emphasized that there are no adjustable parameters in Companion's DIM procedure: It is based strictly on the most accurate available diatomic potential curves. By taking some of these curves as adjustable parameters it should be possible to obtain a simple but accurate form for the HLi_2 potential surface.

The Electron Jump Region

In a simple picture, at large H-Li₂ separations, the reactants approach on the covalent potential surface arising diabatically from $^2S_g H + ^1\Sigma_g^+ Li_2$. However, at some smaller separation, the diabatic $H^- Li_2^+$ surface becomes lower, and an electron jump²⁴ is said to occur at the point of crossing of these two diabatic²⁵ surfaces. In an adiabatic representation, such as results automatically from large scale CI calculations like ours, there will be an avoided intersection between the two surfaces. Although we have calculated only the lower surface, the position of the electron jump (or closest approach of the two surfaces avoiding each other) should be apparent from a rather abrupt change in the nature of the ground state surface.

To further our discussion of the electron jump, separate calculations have been carried out for H^- and Li_2^+ . For H^- , the calculation comparable to our HLi₂ CI is a full CI. The total energy obtained was -0.51532 hartrees, corresponding to an electron affinity of 0.44 eV. For comparison, the exact²⁶ electron affinity is 0.754 eV. For Li_2^+ , the comparable calculation is a simple SCF treatment, and yields a total energy of -14.71246 hartrees at $r_e(Li-Li) = 5.908$ bohrs = 3.13 Å. The increase in bond length relative to neutral Li₂ is consistent with the long bond lengths²⁷ (3.08 and 3.18 Å) of the $C^1\Pi_u$ and $D^1\Pi_u$ Rydberg states of Li₂. In addition, the predicted dissociation energy of Li_2^+ is 27.9 kcal/mole, compared to experiment,^{27,28}

~ 33 kcal/mole. The important point is that the calculations do predict Li_2^+ to have a larger dissociation energy than Li_2 , and the difference is very nearly correct. Finally, we note that the asymptotic energy difference between $\text{H} + \text{Li}_2$ and $\text{H}^- + \text{Li}_2^+$ is 105.6 kcal, compared to experiment,²⁶⁻²⁸ ~ 100 kcal/mole. Thus we expect the position of the electron jump to be fairly reliably predicted from the present calculations.

Table V shows a few points on the minimum energy path for the collinear $\text{H} + \text{Li}_2$. There it is seen that the optimum Li-Li separation changes quite gradually as the H atom approaches. The Li-Li separation seems to change least slowly at $r(\text{H-Li}) \sim 5.5$ bohrs, and hence this is as close as one can come to identifying the position of the collinear electron jump. This is in sharp contrast to the $\text{F} + \text{Li}_2$ system, where the Li-Li separation changes rather abruptly. This is just another indication that the HLi_2 complex is less ionic than FLi_2 . For C_{2v} approaches, a similar situation is seen in Table VI. That is, although the electronic structure changes from covalent to ionic as the reactants come together, the change is a gradual one. This would seem to imply that the two lowest potential surfaces avoid each other rather broadly in the region of the electron jump or avoided intersection. However, the second potential surface must be calculated explicitly to enable a definitive statement on this subject.

Some related data are the Mulliken populations (obtained from the SCF wave functions only) at the various constrained

equilibrium geometries

In the first three geometries (those most likely to be sampled during $\text{H} + \text{Li}_2$ collisions) the number of electrons assigned to hydrogen is 1.56 ± 0.01 . This result is consistent with the broadly avoided intersection of the two lowest potential surfaces. Thus although HLi_2 is indeed ionic, the degree of ionicity is much less than for the hypothetical $\text{H}^- \text{Li}_2^+$.

Qualitative Pictures of the Surface

In light of a) the essential correctness of the SCF approximation

in the region of the potential minimum, and b) the simplicity and computational speed of the SCF procedure, it was decided to carry out additional SCF calculations to provide contour maps for two especially interesting regions of the HLi_2 ground state potential surface.

Figure 1 shows the potential surface for a fixed Li-Li separation of 5.27 bohrs, the SCF equilibrium bond distance of Li_2 . This contour map shows clearly the energetic favoring of the C_{2v} potential minimum. Note that energies in this figure are given relative to separated $\text{H} + \text{Li}_2$. Figure 2, on the other hand, depicts the potential surface for the approach of Li to a rigid LiH molecule. Although this contour map is unsymmetrical, one can nevertheless see that the potential minimum corresponds roughly to an isosceles or C_{2v} structure.

As discussed earlier, there are definite differences between the SCF and CI surfaces for ground state HLi_2 . However, these differences are quantitative and not likely to be clearly visible in contour diagrams comparable to our Figures 1 and 2.

Electronic Structure Considerations

Since full configuration interaction was carried out for the three valence electrons, the natural orbitals obtained by diagonalization of the first-order reduced density matrix are the exact valence natural orbitals for the chosen basis set. Thus the natural orbitals generated from our wave functions are of particular interest.

Table VII gives occupation numbers for the most important natural orbitals of HLi_2 . In each case the description of the electronic

structure is qualitatively similar to the molecular orbital or Hartree-Fock picture. Among the SCF-occupied orbitals, the greatest deviation is for the $2a_1$ orbital of $H + Li_2$. This is of course the $2\sigma_g$ orbital of the isolated Li_2 molecule. The depletion of the $2a_1$ occupation number is seen to be due primarily to the $4a_1$, $5a_1$, $1b_1$, and $2b_2$ orbitals, none of which is occupied in the Hartree-Fock model. By comparison, the single configuration picture seems to provide a more accurate description of the equilibrium molecule. Such a conclusion is questionable however, since Table III shows that

has 2.2 kcal/mole more correlation energy than separated $H + Li_2$.

Table VIII gives the coefficients c_i (in each wavefunction) which are greater than 0.04. Note that $\sum_i c_i^2 = 1$. These results also imply that correlation is most important for separated $H + Li_2$. Shown in both Tables VII and VIII is the fact that the electronic structures of $HLi + Li$ and $H-Li-Li$ (the linear minimum) are very similar. This is of course reasonable since the geometries are very similar and the linear minimum lies only 3.5 kcal/mole below separated $HLi + Li$.

Additional information not given in the Tables concerns the effectiveness of the natural orbitals in reducing the size of the CI expansion. For example, for $H + Li_2$, in terms of the canonical SCF orbitals, there are 29 configurations with CI coefficient greater than 0.01. In terms of the natural orbitals, only 5 such important configurations remain. Actually this result is expected since, for separated $H + Li_2$, we have in reality a two-electron correlation

problem, involving the two valence electrons of Li_2 . As is well known²⁹ and can in fact be proven,³⁰ for two-electron systems a drastic reduction in configurations is achieved using natural orbitals.

A genuine test of the effectiveness of natural orbitals may be made for the equilibrium geometry. In that case, the canonical orbitals yield 72 configurations with $c_i \geq 0.01$, whereas natural orbitals reduce this number to 25. Similarly, for the linear minimum, the use of natural orbitals reduces the number of configurations with $c_i \geq 0.01$ from 65 to 19. Thus, even though for many-electron systems the desired properties of natural orbitals cannot be proven, for HLi_2 they do substantially simplify the form of the CI wave function.

Acknowledgments

We thank Dr. William A. Lester, Dr. Bowen Liu, Professor Dudley Herschbach, and Professor Yuan T. Lee for helpful discussions. This research was supported in part by the National Science Foundation, under Grant GP-41509X.

REFERENCES

1. Y. T. Lee, R. J. Gordon, and D. R. Herschbach, J. Chem. Phys. 54, 2410 (1971).
2. R. K. Preston and J. C. Tully, J. Chem. Phys. 54, 4297 (1971); J. Chem. Phys. 55, 562 (1971).
3. C. W. Bauschlicher, S. V. O'Neil, R. K. Preston, H. F. Schaefer, and C. F. Bender, J. Chem. Phys. 59, 1286 (1973).
4. We take the dissociation energies $D_0(^7\text{Li}_2) = 25.8 \pm 0.7$ kcal/mole and $D_0(^7\text{Li}^1\text{H}) = 56.0$ kcal/mole from A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (Chapman and Hall, London, 1968). The zero point energies of 0.5 kcal/mole (Li_2) and 2.0 kcal/mole (LiH) may be found in B. Rosen, Spectroscopic Data Relative to Diatomic Molecules (Pergamon Press, Oxford, 1970). Thus the exothermicity based on D_0 's is 30.2 ± 0.7 kcal/mole, while the classical exothermicity (obtained from the D_e values) is 31.7 ± 0.7 kcal/mole.
5. The $^2\text{S} - ^2\text{P}$ excitation energy for the Li atom is 42.6 kcal/mole. See C. E. Moore, "Atomic Energy Levels", Nat. Bur. Std. (U.S.) Circ. No. 467 (1949).
6. R. D. Levine and R. B. Bernstein, Disc. Faraday Soc. 55, 100 (1973).
7. D. L. Bunker, Methods in Computational Physics 10, 287 (1971).
8. F. O. Ellison, J. Am. Chem. Soc. 85, 3540 (1963).
9. A. L. Companion, J. Chem. Phys. 48, 1186 (1968).
10. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Massachusetts, 1972).

11. F. B. van Duijneveldt, RJ 945, December, 1971 (IBM Research Laboratory, San Jose, California, 95193).
12. C. Roetti and E. Clementi, J. Chem. Phys. 60, 3342 (1974).
13. P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).
14. G. Das, J. Chem. Phys. 46, 1568 (1967).
15. P. Siegbahn, in Proceedings of the Conference "Quantum Chemistry - The State of the Art", to be published.
16. P. Siegbahn and B. Liu, to be published.
17. B. Roos, Chem. Phys. Letters, 15, 153 (1972).
18. H. F. Schaefer, in Critical Evaluation of Chemical and Physical Structural Information, Editors D. R. Lide and M. A. Paul (National Academy of Sciences, Washington, D.C., 1974).
19. G. C. Lie, J. Hinze, and B. Liu, J. Chem. Phys. 59, 1887 (1973).
20. P. K. Pearson, W. J. Hunt, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 58, 5358 (1973).
21. J. C. Polanyi, Accounts of Chemical Research, 5, 162 (1972).
22. C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, Science, 176, 1412 (1972).
23. A. L. Companion, to be published.
24. J. L. Magee, J. Chem. Phys. 8, 687 (1940); M. Polanyi, Endeavor 8, 3 (1949).
25. F. T. Smith, Phys. Rev. 179, 111 (1969).
26. C. L. Pekeris, Phys. Rev. 126, 1470 (1962).
27. R. F. Barrow, N. Travis, and C. V. Wright, Nature 187, 141 (1960).
28. P. J. Foster, R. E. Leckenby, and E. J. Robbins, J. Phys. B 2, 478 (1969).
29. H. Shull and P. O. Löwdin, J. Chem. Phys. 30, 617 (1959).

30. R. McWeeny and B. T. Sutcliffe, Methods of Molecular Quantum Mechanics (Academic Press, New York, 1969).

TABLE I. Basis set for SCF and CI calculations on the H Li_2 potential surface. Primitive gaussian functions are of the form $A e^{-\alpha r^2}$ for s functions and $B x e^{-\alpha r^2}$ for p_x functions. A and B are normalization constants, and the p_y and p_z functions are defined in an analogous manner.

Hydrogen

<u>Type</u>	<u>Exponent α</u>	<u>Coefficient</u>
s	13.0134	0.019678
	1.96250	0.137952
	0.444569	0.478313
	0.121953	1.0
	0.05	1.0
p	0.4	1.0

Lithium

<u>Type</u>	<u>Exponent α</u>	<u>Coefficient</u>
s	647.084	0.002125
	97.1551	0.016164
	22.0827	0.077505
	6.17666	0.246890
	1.92119	0.471834
	0.630596	1.0
	0.072548	1.0
	0.028118	1.0
p	0.9	1.0
	0.18	1.0
	0.064	1.0

TABLE II. Predicted and experimental spectroscopic constants for Li_2 and LiH .

	<u>SCF</u>	<u>CI</u>	<u>Experiment</u> ^a
<u>Li_2</u>			
D_e (kcal/mole)	3.9	21.0	26.3 ± 0.7
r_e (Å)	2.788	2.708	2.67
ω_e (cm^{-1})	337.2	338.0	351.3
B_e (cm^{-1})	0.6186	0.6548	0.6729
$\omega_e x_e$ (cm^{-1})	1.84	2.71	2.56
α_e (cm^{-1})	0.00538	0.00643	0.00719
<u>LiH</u>			
D_e (kcal/mole)	33.6	53.7	58.0
r_e (Å)	1.607	1.608	1.595
ω_e (cm^{-1})	1429	1389	1406
B_e (cm^{-1})	0.7406	7.398	7.515
$\omega_e x_e$ (cm^{-1})	20.9	24.1	23.2
α_e (cm^{-1})	0.191	0.219	0.213

^aReference 4.

TABLE III. Geometries and energies E relative to separated LiH
+ Li for several constrained equilibrium forms of H Li₂.

	$\begin{array}{c} r \quad r \\ \text{Li} \text{---} \text{H} \text{---} \text{Li} \end{array}$		
	DIM	SCF	CI
$2\Sigma_u^+$			
$r \text{ (Å)}$	1.71	1.69	1.70
$E \text{ (kcal/mole)}$	-20.2	-10.6	-13.9
$2\Sigma_g^+$			
$r \text{ (Å)}$	1.71	1.62	1.63
$E \text{ (kcal/mole)}$	+32.9 ^a	-10.2	-12.8
	$\begin{array}{c} r_1 \quad r_2 \\ \text{H} \text{---} \text{Li} \text{---} \text{Li} \end{array}$		
	DIM	SCF	CI
$r_1 \text{ (Å)}$	1.6	1.62	1.63
$r_2 \text{ (Å)}$	3.2	3.39	3.32
$E \text{ (kcal/mole)}$	-5.8	- 3.5	- 4.2

^a Not a minimum on the DIM potential surface. Furthermore, there appears to be no minimum nearby.

Table III (continued).

r_1 (Å)	2.2	2.30	2.28
r_2 (Å)	3.2	3.03	2.96
E (kcal/mole)	-6.5	- 3.0	- 4.6

	DIM	SCF	CI
r_1 (Å)	1.58	1.17	1.16
r_2 (Å)	2.67	2.52	2.53
E (kcal/mole)	+22.5	-20.2	-22.4

TABLE IV. Angular dependence of the H Li_2 potential minimum. For $\theta = 0^\circ, 45^\circ$, and 90° , the total energy has been minimized with respect to r_1 and r_2 . For $\theta = 60^\circ, 70^\circ$, and 80° , the optimum r_1 and r_2 values have been estimated.

θ	r_1 (bohrs)	r_2 (bohrs)	E (kcal/mole)
0°	6.27	3.08	- 4.2
45°	5.59	3.05	- 4.6
60°	5.34	3.06	- 9.7
70°	5.16	3.10	-15.2
80°	4.98	3.17	-20.1
90°	4.79	3.25	-22.4

TABLE V. Minimum energy path for collinear $H + Li_2 \rightarrow H Li + Li$ in the electron jump region. Bond distances are in bohrs and energies given relative to infinitely separated $H + Li_2$. The last point represents the equilibrium geometry of $H Li Li$.

r (H-Li)	r (Li-Li)	E (kcal/mole)	
∞	5.12	0.0	Reactants
6.0	5.34	- 2.3	
5.5	5.69	- 6.2	
5.0	5.91	-12.4	
4.0	6.13	-27.6	
3.08	6.27	-36.8	Minimum

TABLE VI. A few points on the minimum energy path for equilateral $H + Li_2$. r (H-M) is the distance between the H atom and the midpoint of the Li_2 bond. Distances are in bohrs and energies are given relative to infinitely separated $H + Li_2$. The last point is the equilibrium geometry of $H Li_2$.

<u>r (H-M)</u>	<u>r (Li-Li)</u>	<u>E (kcal/mole)</u>	
∞	5.12	0.0	Reactants
6.0			
5.0	4.94	-18.0	
4.0	4.71	-33.8	
3.0	4.75	-49.6	
2.19	4.79	-55.0	Minimum

TABLE VII. Natural orbital occupation numbers for several stationary points on the Li_2H ground state potential energy surface. In general, only orbitals with coefficients greater than 0.0005 are included.

$\text{H} + \text{Li}_2$		C_{2v} Minimum		$\text{HLi} + \text{Li}$		Linear Minimum H-Li-Li	
$1a_1$	2.000	$1a_1$	2.000	1σ	2.000	1σ	2.000
$2a_1$	1.820	$2a_1$	1.947	2σ	2.000	2σ	2.000
$3a_1$	1.000	$3a_1$	0.993	3σ	1.945	3σ	1.942
$4a_1$	0.055	$4a_1$	0.018	4σ	1.000	4σ	0.997
$5a_1$	0.035	$5a_1$	0.010	5σ	0.032	5σ	0.031
		$6a_1$	0.003	6σ	0.008	6σ	0.009
$1a_2$	3×10^{-5}	$1a_2$	6×10^{-5}			7σ	0.001
				1π	0.014	8σ	0.001
$1b_1$	0.055	$1b_1$	0.009			1π	0.014
$1b_2$	2.000	$2b_1$	0.003			2π	0.003
$2b_2$	0.035					3π	0.001
		$1b_2$	2.000				
		$2b_2$	0.012				
		$3b_2$	0.003				

TABLE VIII. Dominant configurations in the wave functions for Li_2H at several points on the potential energy surface.

Only configurations with coefficients greater than 0.04 are included. The doubly-occupied inner shell orbitals are not explicitly referred to.

		C_{2v} Minimum		Linear Minimum	
$\text{H} + \text{Li}_2$				$\text{HLi} + \text{Li}$	
				H-Li-Li	
$2a_1^2 3a_1$	0.954	$2a_1^2 3a_1$	0.984	$2\sigma^2 3\sigma$	0.986
$2a_1^2 \rightarrow 4a_1^2$	0.166	$2a_1^2 \rightarrow 4a_1^2$	0.086	$2\sigma^2 \rightarrow 4\sigma^2$	0.126
$2a_1^2 \rightarrow 1b_1^2$	0.166	$2a_1^2 \rightarrow 2b_2^2$	0.068	$2\sigma^2 \rightarrow 1\pi^2$	0.084
$2a_1^2 \rightarrow 5a_1^2$	0.132	$2a_1^2 \rightarrow 5a_1^2$	0.061	$2\sigma^2 \rightarrow 5\sigma^2$	0.063
$2a_1^2 \rightarrow 2b_2^2$	0.132	$2a_1^2 \rightarrow 1b_1^2$	0.057		
		$2a_1 3a_1 \rightarrow 2b_2 3b_2$	0.041		
				$2\sigma^2 3\sigma$	0.985
				$2\sigma^2 \rightarrow 4\sigma^2$	0.120
				$2\sigma^2 \rightarrow 1\pi^2$	0.083
				$2\sigma^2 \rightarrow 5\sigma^2$	0.063

Figure Captions

Figure 1. Contour map of one part ($r(\text{Li-Li})$ fixed at 5.27 bohrs) of the SCF potential surface for HLi_2 . Distances from the Li_2 bond midpoint are given in bohrs. The contours are labeled in kcal/mole relative to separated $\text{H} + \text{Li}_2$.

Figure 2. Contour map for the part of the HLi_2 potential surface with $r(\text{LiH})$ held fixed at 3.04 bohrs. Distances relative to the midpoint of the LiH bond are given in bohrs. Contours are labeled in kcal/mole relative to separated $\text{LiH} + \text{Li}$.

Li + Rigid Li H

XBL7410-4436

Fig. 1

H + Rigid Li_2

XBL7410-4437

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720