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Per Siegbahn and Henry F. Schaefer III

October, 1974

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POTENTIAL ENERGY SURFACES FOR H + Li_2 → LiH + Li

GROUND STATE SURFACE FROM LARGE SCALE CONFIGURATION INTERACTION

Per Siegbahn[*] and Henry F. Schaefer III[**]
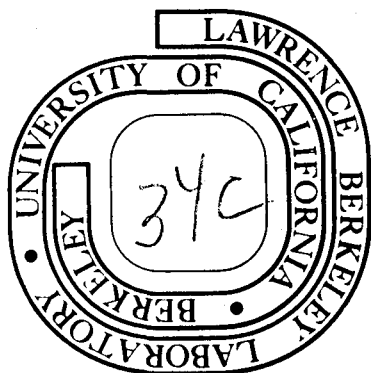
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October 1974

ABSTRACT

Ab initio electronic structure calculations have been performed to determine the HLi_2 potential energy surface. A contracted gaussian basis set was employed: H(5s 1p/3s 1p), 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(H-Li) = 1.72 Å and on LiHLi bond angle of 95°. This minimum lies 22.4 kcal/ mole below the separated products LiH + 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 F + 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 Herschbach[1] have reported crossed molecular

beam studies of the reactions of H and D atoms with K_2, Rb_2, and

Cs_2. 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 vibra-

tionally and/or rotationally excited or the alkali atom M must

be electronically excited. In addition, Lee, Gordon and Hersch-

bach[1] concluded that there is an anisotropic reaction probability

for H + M_2, with $M\overset{H}{\rule{1cm}{0.4pt}}M$ 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 des-

cribed 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 open[4]:

$$H + Li_2 \longrightarrow LiH(^1\Sigma^+) + Li(^2S) \qquad \Delta H = -30 \text{ kcal/mole} \qquad (1)$$
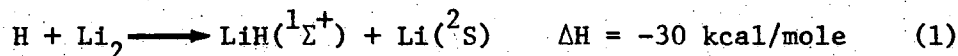
However, under the conditions utilized by Lee et al., namely

$\sim$ 10 kcal/mole of H or D atom translational energy and 6 ± 3

kcal/mole of alkali dimer vibrational excitation, a second

pathway is possible[5]:

$$H + Li_2 \longrightarrow LiH(^1\Sigma^+) + Li(^2P) \quad \Delta H = +12 \text{ kcal/mole} \quad (2)$$
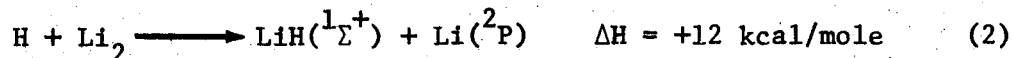
From either an experimental or theoretical viewpoint, then,
it will be of great interest to determine the relative im-
portance of these two competing reaction pathways. Herschbach's
work, though not definitive, suggested the former path (1) to
be the dominant one.

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 LiH + Li to LiH
+ Li* can be studied as a function of H atom translational
energy or as a function of Li_2 vibrational energy. Even if the
LiH + Li* pathway is shown to be unimportant, the partitioning[6]
of the available energy into translation, vibration, and rotation
of LiH + Li should be interesting.

The potential surfaces required for a thorough study are
those arising from LiH + Li(^2S) and LiH + Li(^2P). For general
geometry (C_s symmetry), three of these surfaces will be of $^2A'$
irreducible representation and one of $^2A''$. Although our primary
concern in the present theoretical study is with the accurate
determination of the ground state $^2A'$ 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 trajectory[7])

studies, it is of interest to compare our ab initio results with

the semi-empirical diatomics-in-molecules calculations[8] of

Companion[9] for HLi_2. This is particularly important since the

discussion of Lee and co-workers[1] 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 H(4s) and Li(8s) primitive gaussian basis sets

of van Duijneveldt.[11] These were contracted to H(4s/2s) and

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 ^{2}S gound 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 com-

puted the SCF energy of the ^{2}P excited state to be -7.35378

hartrees, or 2.15 eV above the ground state. Experimentally,

the ^{2}S - ^{2}P 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 energy[13] 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 Das[14] using a large basis set of Slater functions.

In conclusion it appears that the SCF potential surface obtained

for HLi$_2$ using the basis set of Table I should be no more than

0.005 hartrees $\approx$ 3 kcal/mole above the true Hartree-Fock potential

surface.

The present theoretical approach begins with single configuration

SCF calculations on HLi$_2$. For linear H-LiLi approaches, the lowest

potential surface will be of $^2\Sigma^+$ symmetry, with SCF configuration

$$1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 4\sigma \qquad\qquad (3)$$

This same configuration will be dominant for large HLi-Li separations.

However, when the Li atom is in its ^{2}P state, the corresponding Σ and

Π electronic states correspond to electron configurations

$$1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 5\sigma \qquad\qquad (4)$$

$$1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 1\pi \qquad\qquad (5)$$

For C_{2v} approaches and large $H-Li_2$ separation, the lowest potential surface should be of $^2A_1$ symmetry, with electron configuration

$$1a_1^2 \; 1b_2^2 \; 2a_1^2 \; 3a_1 \qquad\qquad (6)$$

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

$$1\sigma_g^2 \; 1\sigma_u^2 \; 2\sigma_g^2 \; 3\sigma_g \qquad\qquad (7)$$

However, it must be noted that Companion[9] found the lowest total energy to occur for a $^2\Sigma_u^+$ state, corresponding predominantly to the electron configuration

$$1\sigma_g^2 \; 1\sigma_u^2 \; 2\sigma_g^2 \; 2\sigma_u \qquad\qquad (8)$$

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

$$1a_1^2 \; 1b_2^2 \; 2a_1^2 \; 2b_2 \qquad\qquad (9)$$

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

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

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

$$1a'^2 \; 2a'^2 \; 3a'^2 \; 5a' \tag{11}$$

$$1a'^2 \; 2a'^2 \; 3a'^2 \; 1a'' \tag{12}$$

$$1a'^2 \; 2a'^2 \; 3a'^2 \; 6a' \tag{13}$$

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

$$c_i^{(k)} = \frac{1}{H_{oo}^\circ - H_{ii}^\circ} \sum_{j=1}^{N} V_{ij} c_j^{(k-1)} - \sum_{m=0}^{k-1} \varepsilon_{k-m} c_i^{(m)} \tag{14}$$

where the usual perturbation splitting $H = H_o + V$ 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 by[15]

$$\epsilon_{2k-1} = <\phi^{(k-1)}|v|\phi^{(k-1)}> - \sum_{m=1}^{k-1}\sum_{n=1}^{k-1} \epsilon_{2k-1-m-n}<\phi^{(m)}|\phi^{(n)}>$$

$$\epsilon_{2k} = <\phi^{(k)}|v|\phi^{(k-1)}> - \sum_{m=1}^{k}\sum_{n=1}^{k-1} \epsilon_{2k-m-n}<\phi^{(m)}|\phi^{(n)}> \qquad (15)$$

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

$$<\phi^{(p)}|v|\phi^{(q)}> = \epsilon_{p+q+1} + \sum_{k=1}^{p}\sum_{\ell=1}^{q} \epsilon_{p+q+1-k-\ell} <\phi^{(k)}|\phi^{(\ell)}> \qquad (16)$$

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

$$H_o = \sum_{i=1}^{N} |i>\alpha_i< i| \qquad (17)$$

where α_i are sums of orbital energies.

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

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

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

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

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 method[17] 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 experi-
mental 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 Å larger than experiment,
and for Li_2 the difference is even greater, 0.04 Å. Especially
the latter difference is greater than expected[18] 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 Å, or only 0.005 Å
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 note-

worthy are the 3.8% (Li_2) and 1.2% (LiH) errors in the theoretical

ω_e values for the two molecules. Except for the LiH B_e value,

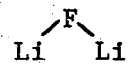the CI results are seen to provide improved (relative to SCF)

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 con-

cluded 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 Li + LiH.

From their experiments and qualitative theoretical arguments, Lee,

Gordon, and Herschbach[1] 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 simi-

lar to the $F + Li_2$ surface, which previous less exhaustive studies[20]

predicted to have an F–Li–Li well of 4 kcal/mole, but an $Li\overset{\diagup F\diagdown}{}Li$

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 quali-

tative 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, $Li\overset{H\diagdown}{\underset{45°}{\rule{1.5cm}{0.4pt}}}Li$, 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 ($\theta = 90°$) 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 ± 20° 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 experi-

ments[1] 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-Li$_2$ 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 jump[24] is said to
occur at the point of crossing of these two diabatic[25] 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
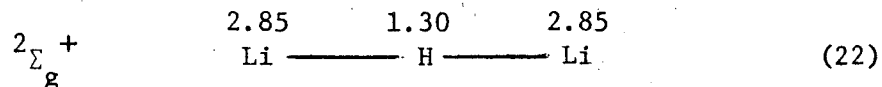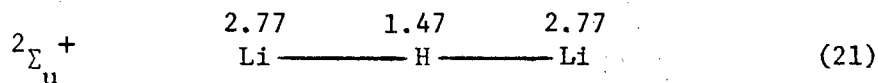be apparent from a rather abrupt change in the nature of the
ground state surface.

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 HLi$_2$ 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 exact[26]
electron affinity is 0.754 eV. For Li$_2^+$, the comparable cal-
culation 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 Li$_2$ is consistent
with the long bond lengths[27] (3.08 and 3.18 Å) of the C $^1\Pi_u$ and
D $^1\Pi_u$ Rydberg states of Li$_2$. In addition, the predicted dissociation
energy of Li$_2^+$ is 27.9 kcal/mole, compared to experiment,[27,28]

$\sim$ 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 $H + Li_2$ and $H^- + Li_2^+$ is 105.6 kcal, compared to experiment,[26-28] $\sim$ 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 $H + Li_2$. 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 $r(H-Li)$ $\sim$ 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 $F + Li_2$ 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

$$
\underset{H}{\overset{1.57}{\rule{0pt}{0pt}}}\underset{}{\overset{}{\text{———————}}}\underset{Li}{\overset{2.60}{\rule{0pt}{0pt}}}\underset{}{\overset{}{\text{————————}}}\underset{Li}{\overset{2.83}{\rule{0pt}{0pt}}} \tag{18}
$$

(19)

(20)

$$^2\Sigma_u^+ \qquad \underset{Li}{\overset{2.77}{}} \text{————} \underset{H}{\overset{1.47}{}} \text{————} \underset{Li}{\overset{2.77}{}} \tag{21}$$

$$^2\Sigma_g^+ \qquad \underset{Li}{\overset{2.85}{}} \text{————} \underset{H}{\overset{1.30}{}} \text{————} \underset{Li}{\overset{2.85}{}} \tag{22}$$
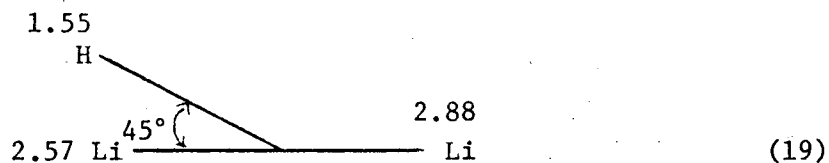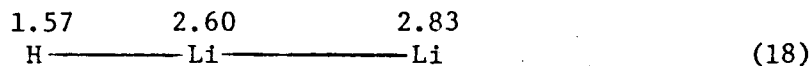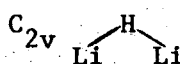
In the first three geometries (those most likely to be sampled during $H + Li_2$ collisions) the number of electrons assigned to hydrogen is 1.56 ± 0.01. This result is consistent with the broadly avoided intersection of the two lowest potential surfaces. Thus although HLi_2 is indeed ionic, the degree of ionicity is much less than for the hypothetical $H^- Li_2^+$.

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 $H + Li_2$. 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 $\overset{\displaystyle H}{\underset{\displaystyle Li \quad Li}{\diagup \diagdown}}$ molecule.

Such a conclusion is questionable however, since Table III shows that
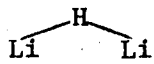
$\overset{\displaystyle H}{\underset{\displaystyle Li \quad Li}{\diagup \diagdown}}$ has 2.2 kcal/mole more correlation energy than separated

$H + Li_2$.

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 known[29] 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 $\underset{Li \quad Li}{\diagdown H \diagdown}$ 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

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4. We take the dissociation energies $D_o(^7Li_2) = 25.8 \pm 0.7$ kcal/mole
    and $D_o(^7Li\,^1H) = 56.0$ 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_o'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 $^2S - {}^2P$ excitation energy for the Li atom is 42.6 kcal/mole.
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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

Type	Exponent α	Coefficient
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

Type	Exponent α	Coefficient
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.

|	SCF	CI	Experiment[a]
__Li_2__			
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
__LiH__			
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

[a]Reference 4.

TABLE III. Geometries and energies E relative to separated LiH

+ Li for several constrained equilibrium forms of H Li$_2$.

$$\text{Li} \xrightarrow{r} \text{H} \xrightarrow{r} \text{Li}$$

	DIM	SCF	CI
$^2\Sigma_u^+$			
r (Å)	1.71	1.69	1.70
E (kcal/mole)	-20.2	-10.6	-13.9
$^2\Sigma_g^+$			
r (Å)	1.71	1.62	1.63
E (kcal/mole)	+32.9[a]	-10.2	-12.8

$$\text{H} \xrightarrow{r_1} \text{Li} \xrightarrow{r_2} \text{Li}$$

	DIM	SCF	CI
r_1 (Å)	1.6	1.62	1.63
r_2 (Å)	3.2	3.39	3.32
E (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).

H
r_1
45°
Li————————Li
r_2
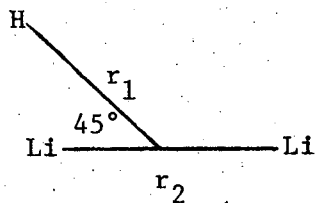
r_1 (Å)	2.2	2.30	2.28
r_2 (Å)	3.2	3.03	2.96
E (kcal/mole)	-6.5	- 3.0	- 4.6

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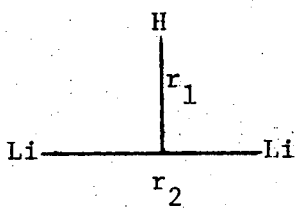
	DIM	SCF	CI
r_1 (Å)	1.58	1.17	1.16
r_2 (Å)	2.67	2.52	2.53
E (kcal/mole)	+22.5	-20.2	-22.4

TABLE IV. Angular dependence of the H Li$_2$ potential minimum. For

θ = 0°, 45°, and 90°, the total energy has been minimized

with respect to r_1 and r_2. For θ = 60°, 70°, and 80°,

the optimum r_1 and r_2 values have been estimated.
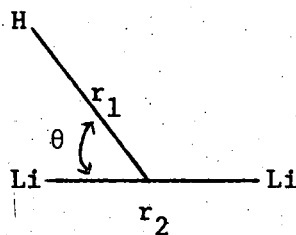
θ	r_1 (bohrs)	r_2 (bohrs)	E (kcal/mole)
0°	6.27	3.08	− 4.2
45°	5.59	3.05	− 4.6
60°	5.34	3.06	− 9.7
70°	5.16	3.10	−15.2
80°	4.98	3.17	−20.1
90°	4.79	3.25	−22.4

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 $H Li_2$.

r (H-M)	r (Li-Li)	E (kcal/mole)	
∞	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.
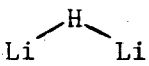
	$H + Li_2$	C_{2v} Minimum Li–H–Li		$HLi + Li$		Linear Minimum H–Li–Li	
$1a_1$ 2.000		$1a_1$ 2.000		1σ 2.000		1σ 2.000	
$2a_1$ 1.820		$2a_1$ 1.947		2σ 2.000		2σ 2.000	
$3a_1$ 1.000		$3a_1$ 0.993		3σ 1.945		3σ 1.942	
$4a_1$ 0.055		$4a_1$ 0.018		4σ 1.000		4σ 0.997	
$5a_1$ 0.035		$5a_1$ 0.010		5σ 0.032		5σ 0.031	
		$6a_1$ 0.003		6σ 0.008		6σ 0.009	
$1a_2$ 3×10^{-5}						7σ 0.001	
		$1a_2$ 6×10^{-5}		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.
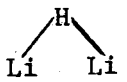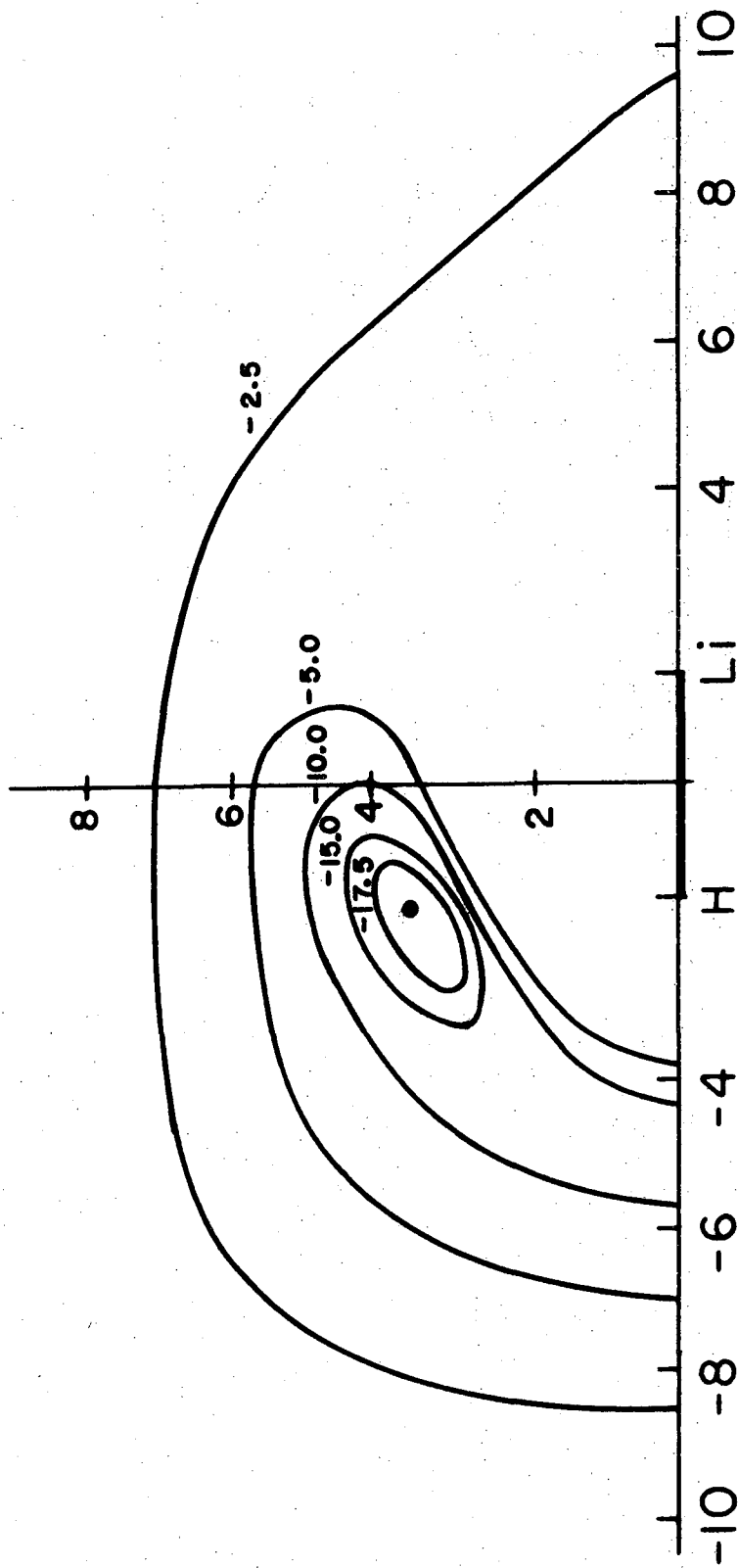
		C_{2v} Minimum				Linear Minimum	
H + Li_2		Li $\overset{H}{\diagdown}$ Li		HLi + Li		H-Li-Li	
$2a_1^2 \, 3a_1$	0.954	$2a_1^2 \, 3a_1$	0.984	$2\sigma^2 3\sigma$	0.986	$2\sigma^2 \, 3\sigma$	0.985
$2a_1^2 \rightarrow 4a_1^2$	0.166	$2a_1^2 \rightarrow 4a_1^2$	0.086	$2\sigma^2 \rightarrow 4\sigma^2$	0.126	$2\sigma^2 \rightarrow 4\sigma^2$	0.120
$2a_1^2 \rightarrow 1b_1^2$	0.166	$2a_1^2 \rightarrow 2b_2^2$	0.068	$2\sigma^2 \rightarrow 1\pi^2$	0.084	$2\sigma^2 \rightarrow 1\pi^2$	0.083
$2a_1^2 \rightarrow 5a_1^2$	0.132	$2a_1^2 \rightarrow 5a_1^2$	0.061	$2\sigma^2 \rightarrow 5\sigma^2$	0.063	$2\sigma^2 \rightarrow 5\sigma^2$	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				

Figure Captions

Figure 1. Contour map of one part (r(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 H + Li_2.

Figure 2. Contour map for the part of the HLi_2 potential

surface with r(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 LiH + Li.

Fig. 1

XBL7410-4436

H + Rigid Li$_2$

XBL7410-4437

Fig. 2