

# Valence bond description for the ground state and several low-lying excited states of LiH

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## Abstract

The potential energy curves of the ground and four singlet low-lying excited states of LiH were calibrated using the bonded tableau unitary group approach (BTUGA). The results show that the ground and the first excited states can be described quite well by only three bonded tableaux, namely

$$\begin{vmatrix} \text{Li}1s & \text{Li}1s \\ \text{Li}2s & \text{H}1s \end{vmatrix}, \begin{vmatrix} \text{Li}1s & \text{Li}1s \\ \text{Li}2p_z & \text{H}1s \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} \text{Li}1s & \text{Li}1s \\ \text{H}1s & \text{H}1s \end{vmatrix}$$

Of these three bonded tableaux, the first two consist of the covalent bond between the atomic orbital H1s and the hybrid atomic orbitals of Li2s and Li2p<sub>z</sub>, while the last one corresponds to the ionic structure Li<sup>+</sup>H<sup>-</sup>. Further analyses showed that, compared with the covalent structures, the ionic structure Li<sup>+</sup>H<sup>-</sup> contributes less to the binding energy and the dipole moment of the ground state of LiH. This result differs from that based on MO theory. Our results clearly indicate that an electron will transfer from lithium to hydrogen in the range 5.0–7.0 a.u., which explains the so-called “harpoon” mechanism in the molecular-beam dynamics. A detailed and successful valence bond explanation for the variation curve of the dipole moment  $\mu$  with respect to the distance  $R$  for the first excited state is also presented. There are two opposite effects, namely the contribution from the ionic structure Li<sup>+</sup>H<sup>-</sup> and the non-equivalent sp hybridization of the atomic orbitals on lithium, which make the dipole moment of the first excited state vary with  $R$  and lead the direction of  $\mu$  to reverse at approximately 6.0 a.u. A brief discussion of the other three excited states is given.

## Introduction

Heitler and London's successful quantum mechanical calculation on the hydrogen molecule [1] was a great step forward in the interpretation of the nature of the binding force between atoms. Based only on their idea that a chemical bond is formed by means of the overlap of two atomic orbitals (AOs), the classical valence bond (VB) theory was established and developed. Pauling [2]

and Wheland [3] made a remarkable contribution to qualitative VB theory because they proposed and developed many concepts such as resonance, hybridization and electronegativity, which have been used by chemists for nearly 60 years to elucidate the relationship between the structures and properties of molecules by using an imaginable chemical picture. This type of chemical picture proposed by classical VB theory has greatly affected the development of theoretical chemistry. Nevertheless, it should be remembered that classical VB theory is mainly interested in the molecular structures and properties of ground

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states. In the case of quantitative calculation, however, owing to the non-orthogonality between bonding AOs, the antisymmetry requirement leads to the well-known  $N!$  problem, which is a formidable obstacle to the evaluation of matrix elements. Recently, stimulated by computer science, modern VB approaches have begun to arouse chemists' interest again [4–7]. Although the VB approach at the *ab initio* level can be applied only to some small systems (less than 12 active electrons [8]), at present, the bridge between primitive VB concepts and quantitative results is being built.

While molecular static properties relate to the ground state of a molecule, the spectroscopic phenomena and chemical processes heavily involve the behaviours of the excited states. The independent particle model (IPM), which performs well in describing ground states, in many cases fails to reproduce accurately the observed data concerning excitation processes and cannot even qualitatively predict the dissociation behaviour of a molecule. Recently, several theoretical models based on CI, Green's function and polarization propagator, many-body perturbation theory, coupled cluster theory, etc. have been used to study the excited states successfully and profoundly [9]. The coincidence between the results obtained with these methods and experimental values has reached the state of the art. Nevertheless, the large-scale configurations involved in the calculation not only confuse our intuitive understanding of excited states, but also converge slowly. Obviously, this has far-reaching significance for studies using modern VB approaches. For example, resonance theory succeeds in describing the ground states of conjugated molecules, and thus it is of interest to know what characteristics it has in describing excited states. As an early attempt, Hurley [10] made semiempirical calculations on the excited states of some hydrides where molecular basis functions were designated by the states of the atoms or ions involved. Goddard and co-workers [11,12] optimized the orbitals of GVB functions

to discuss the bonding mechanism of many molecules and, moreover, used a simple schematic representation of the GVB orbitals to depict how molecular states are formed by the interaction between atoms. A modern VB approach, namely spin-coupled VB (SCVB) theory, has been developed and applied by Cooper and co-workers [5,13]. When delocalized AOs, or so-called "overlap-enhanced AOs" are used as in the GVB method, just one structure configuration can describe states very well. Recently, Zhang and Li [14,15] proposed a simple spin-free VB method which is called the "bonded tableau unitary group approach" (BTUGA). Simultaneously, McWeeny [16,17] also claimed to use the standard projection operator  $e_{11}$  to generate VB structure functions. In view of the idea of adopting bonded tableaux (BTs) as the state functions of a system, whilst these state functions can describe corresponding resonance structures, BTUGA is much closer to classical conceptions and ideas than are other many-body theories. Thus, by using BTUGA to calculate the ground and excited states of some systems, we hope that we can use quantitative results to test and explain some conjectures and conclusions about classical VB theory and to understand excited states having different VB pictures.

As the smallest heteronuclear diatomic molecule, LiH has been studied extensively both experimentally and theoretically, [18–28]. Because many data on LiH have been accumulated, this molecule has always been investigated with new calculation methods as a test molecule. The early theoretical work [18–22] concentrated mainly on the ground state and its properties, e.g.  $\mu$ . For example, Palke and Goddard [22] employed the GVB method to discuss the bonding picture of the ground state of LiH. Using the MCSCF procedure, Docken and Hinze [24] carefully investigated five valence states,  $X^1\Sigma^+$ ,  $A^1\Sigma^+$ ,  $B^1\Pi$ ,  $^3\Sigma^+$  and  $^3\Pi$  of LiH, and they showed for the first time that the  $B^1\Pi$  state is a very weakly bound state theoretically. Because the spectroscopy of the three lowest singlet states was quite well understood, Partridge

and Langhoff [25] undertook extensive CI calculations on the  $X^1\Sigma^+$ ,  $A^1\Sigma^+$  and  $B^1\Pi$  states of LiH, using a  $22\sigma 12\pi 7\delta$  function Slater basis set. The calculated dissociation energies were very near to the experimental values and the properties such as dipole moments and electronic transition moments were fully analysed.

In the present study we used BTUGA to compute the ground and four lowest-lying singlet states of LiH. The emphasis was on the bonding picture of each state, and the origins of the variation in dipole moment with respect to the bond length were shown. In the following, we briefly describe the method of calculation, and report and discuss the results obtained.

### Methodology

In the BTUGA, a BT represents a state wavefunction of a system, in other words, a BT  $\phi(k)$  can describe a VB structure, so the true wavefunction of a molecular system can be expressed as a superimposition of all possible BTs, namely

$$\psi_i = \sum_{k=1}^M C_{ik} \phi(k) \quad (1)$$

where a BT  $\phi(k)$  is defined as

$$\phi(k) = A_k e_{11}^{[\lambda]} \phi_0(k) = \begin{vmatrix} u_1 & u_2 \\ u_3 & u_4 \\ \cdot & \cdot \\ u_{2i-1} & u_{2i} \\ \cdot & \cdot \end{vmatrix} \quad (2)$$

In eqn. (2),  $A_k$  is a normalization constant and  $u_i$  is a one-electron basis function, while  $e_{11}^{[\lambda]}$  is a standard projection operator defined as

$$e_{11}^{[\lambda]} = (f_N/N!)^{1/2} \sum_P D_{11}^{[\lambda]} P \quad (3)$$

where  $[\lambda] = [2^{1/2N-S} 1^{2S}]$  is an irreducible representation of permutation group  $S_N$ ,  $D_{11}^{[\lambda]}$  is the matrix element of the standard representation  $[\lambda]$  of the permutation  $P$ ,  $N$  is the number of electrons, and  $S$  is spin quantum number of the

system. In fact, a BT  $\phi(k)$  corresponds to a VB structure where two AOs  $u_{2i-1}$  and  $u_{2i}$  overlap to form a bond (if  $u_{2i-1} = u_{2i}$ , the “bond” is a lone pair of electrons). For a system with  $N$  electrons, if  $m$  ( $m \geq N/2$ ) AOs  $\chi_i$  are assumed to form an one-electron basis set  $\{\chi_i, i = 1, 2, \dots, m\}$ , an initial function  $\phi_0(k)$  can be defined as

$$\phi_0(k) = u_1(1)u_2(2) \dots u_N(N) \quad (4)$$

where  $u_j$  belongs to  $\{\chi_i\}$ , and a  $\chi_i$  cannot appear in  $\phi_0(k)$  more than twice. The number of canonical bonded tableaux is

$$\begin{aligned} M &= (2S+1)[(m+1)!]^2 / [(m+1)(N/2-S)! \\ &\quad \times (m-N/2+S+1)!(N/2+S+1)! \\ &\quad \times (m-N/2-S)!] \end{aligned} \quad (5)$$

For a four-electron system, where  $S = 0$ , a BT can be expanded as

$$\begin{aligned} \phi(k) &= \frac{\sqrt{3}}{12} A_k \sum_{a,b,c,d}^4 (3\delta_{c+d,3} + 3\delta_{c+d,7} - 1) \\ &\quad \times u_a(1)u_b(2)u_c(3)u_d(4) \end{aligned} \quad (6)$$

where  $\delta_{c+d,3}$  and  $\delta_{c+d,7}$  are Kronecker functions,  $a$ ,  $b$ ,  $c$  and  $d$  are the integer indexes ranging from 1 to 4.

By calculating the overlap matrix element  $S_{kl}$ , hamilton matrix element  $H_{kl}$ , and the solution of secular equation  $|H - \Delta S| = 0$ , the molecular state energy  $E_i$  and, correspondingly, a set of coefficients  $\{C_{ik}\}$  can be deduced. The structural weight of a BT  $\phi(k)$  in the state  $\psi_i$  can be defined as

$$T_i(k) = \sum_{l=1}^M C_{ik} C_{il} S_{kl} \quad (7)$$

Thus the condition of normalization is

$$\sum_{k=1}^M T_i(k) = 1 \quad (8)$$

As the calculation procedure introduced above is

quite similar to traditional CI method, this procedure can be called the “BT interaction” (BTI) [29].

## Results and discussion

### Basis set and AO integrals

Split valence basis sets give better results for quantities such as total energies than do minimal basis sets. However, they have a relative lack of VB meaning because in VB theory one AO should be described by one basis function or by a linear combination of several functions. Moreover, our focus here is not on the accuracy of molecular energies but on understanding the molecular behaviour, and we wish to give a VB picture for such understanding. Thus we used the minimal basis set STO-6G with a p polarization function imposed on H, i.e. the total number  $m$  of basis orbitals for LiH is 9. The orbital exponents were optimized roughly, i.e. 1.00 for 1s and the polarization function on H, and 2.69, 0.65 and 0.77 for 1s, 2s and 2p respectively on Li. When  $S=0$ , the number  $M$  of full BTs is 540. In the following discussion, for simplicity, the Arabic numerals 1 to 9 are used to represent the AOs H 1s, H  $p_x$ , H  $p_y$ , H  $p_z$ , Li 1s, Li 2s, Li 2 $p_x$ , Li 2 $p_y$ , and Li 2 $p_z$  respectively. The GAUSSIAN 80 program [30] was used to calculate the AO integrals.

### Potential curves and dissociation energies

The calculated total energies for the ground and four low-lying excited states using full BTs are presented in Table 1, while the corresponding potential curves are depicted in Fig. 1 where X, A, B, C and D represent the ground and the first to fourth excited states respectively.

For the ground state, the calculated results show that the minimum point of the potential curve is at  $R = 3.066$  a.u., which is quite close to the experimental value of 3.014 a.u., and at this

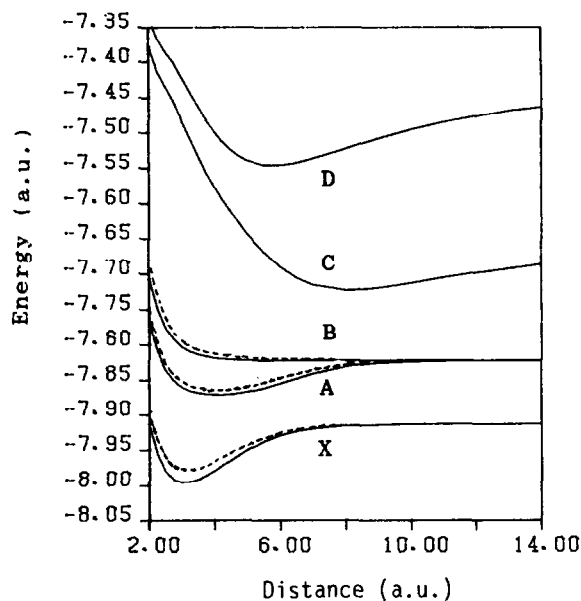


Fig. 1. Potential energy curves of the ground and excited states.

point the total energy of LiH is  $-7.996562$  a.u. (the Hartree–Fock (HF) energy is  $-7.967145$  a.u.). There is some discrepancy between our calculated energy and the exact value of  $-8.070$  a.u. because our basis sets are so limited; however, our calculated dissociation energy of the ground state is approximately 90% of the experimental value (see Table 2). In order to investigate the convergence of BTs, we calculated the total energy using 15 bonded tableaux the absolute coefficients of which in the full wavefunction are larger than 0.01. The energy found is  $-7.995639$  a.u., which accounts for 96.9% of the correlation energy (here the correlation energy is defined as the difference between the HF and full BTI energies). Moreover, when Li 1s is frozen the total number of BTs is reduced to only 36 and the total energy is  $-7.994948$  a.u. In the ground state wavefunction, three BTs play the main role.

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

The total energy calculated with these three BTs

Table 1  
Electronic energies (a.u.) of LiH

R (a.u.)	State				
	X	A	B	C	D
2.00	-7.913799	-7.770175	-7.707327	-7.378198	-7.336280
2.25	-7.956630	-7.810522	-7.749250	-7.413179	-7.366544
2.50	-7.980512	-7.835708	-7.775751	-7.434298	-7.384884
2.75	-7.992318	-7.851326	-7.792536	-7.455560	-7.400553
3.00	-7.996393	-7.860848	-7.803146	-7.480649	-7.421074
3.25	-7.995534	-7.866425	-7.809905	-7.507091	-7.442699
3.50	-7.991647	-7.869639	-7.814351	-7.532403	-7.463216
3.75	-7.985874	-7.871244	-7.817248	-7.555457	-7.481925
4.00	-7.979028	-7.871796	-7.819227	-7.576227	-7.498540
4.25	-7.971654	-7.871581	-7.820530	-7.595139	-7.512698
4.50	-7.964128	-7.870735	-7.821429	-7.612616	-7.524202
4.75	-7.956842	-7.869381	-7.822018	-7.628783	-7.533015
5.00	-7.949910	-7.867529	-7.822445	-7.643862	-7.539332
5.50	-7.938112	-7.862494	-7.822931	-7.669959	-7.545859
6.00	-7.929309	-7.855946	-7.823134	-7.690537	-7.546238
6.50	-7.923322	-7.848681	-7.823234	-7.705603	-7.542796
7.00	-7.919570	-7.841714	-7.823242	-7.715590	-7.537042
8.00	-7.915871	-7.831322	-7.823198	-7.723294	-7.522828
9.00	-7.914580	-7.826362	-7.823164	-7.720574	-7.508436
10.00	-7.914081	-7.824363	-7.823143	-7.713645	-7.495750
11.00	-7.913913	-7.823493	-7.823132	-7.705944	-7.485195
12.00	-7.913862	-7.823205	-7.823125	-7.698792	-7.476573
13.00	-7.913840	-7.823122	-7.823118	-7.692485	-7.469491
14.00	-7.913824	-7.823089	-7.823120	-7.687012	-7.463547
100.00	-7.912876	-7.821026	-7.821026	-7.604201	-7.370580

is  $-7.978865$  a.u., which accounts for 39.8% of the correlation energy. In fact, the sum of the structural weights of these three BTs is around 1.00 over the whole range of  $R$ , so the potential curve of the ground state can be described quite well using these three BTs (see the dashed line for state X in

Table 2  
Comparison of calculated and experimental dissociation energies ( $\text{kcal mol}^{-1}$ )<sup>a</sup>

State	Present work	Ref. 25	Exp.
X	52.48	57.10	58.01
A	31.89	25.85	24.82
B	1.37	0.81	0.82
C	74.77	—	—
D	110.47	—	—

<sup>a</sup> For each state the energy at  $R = +\infty$  as its zero point.

Fig. 1). Of these three BTs,

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

describe the covalent bonds between H 1s and Li 2s and between H 1s and Li 2P<sub>z</sub>, respectively, while

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

describes the ionic structure resulting from the transfer of an electron from the lithium atom to the hydrogen atom. Thus, the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

represents the weight of the ionic structure in the LiH molecule. Further discussion regarding the weights of the BTs and their effects are discussed

further in the next section. It is generally claimed [13] that the ground states  $\text{Li}(1s^2 2s; ^2S) + \text{H}(^2S)$  and  $\text{Li}(1s^2 2p; ^2P) + \text{H}(^2S)$  give rise to weak covalent bonds and the major part of the binding energy for LiH arises from the ionic states  $\text{Li}^+(^1S) + \text{H}^-(^1S)$ . In order to discuss the individual effects of the covalent and the ionic structures on the molecule LiH at the equilibrium distance  $R = 3.066$  a.u., we first made a calculation using three BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

then two BTI calculations by subtracting a BT. In this way, the increase of energy can be deduced and taken as the rough effect of the subtracted BT in LiH. The results show that the total energy will increase by 0.010418, 0.041473 and 0.016904 a.u., on subtracting

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

respectively. The sum of above values is 0.068795 a.u., which is near the value of the dissociation energy (0.065988 a.u.) calculated using three BTs. Therefore, the increment of energy primarily illustrates the contribution of a BT to the binding energy. We find that the ionic structure accounts for only about 16% of the binding energy of LiH, and the chief component in LiH is the covalent bond, not the ionic bond. In addition, the effect of the Li 2s AO on bonding is much larger than that of Li 2p<sub>z</sub>. Further proof of the dominant role of the covalent bond in the ground state of LiH is the individual energies of above three BTs. At  $R = 3.066$  a.u.,

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

is of the highest energy (i.e.  $-7.882674$  a.u.), while the energies of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

are  $-7.941692$  a.u. and  $-7.898953$  a.u. respectively. Also, the potential curve indicates that, when  $R$  becomes infinite, the ground state can be described by one BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}$$

which corresponds to two atomic states  $\text{Li}(1s^2 2s; ^2S) + \text{H}(1s; ^2S)$ . It is known that, in the HF calculation, LiH dissociates into  $\text{Li}^+$  and  $\text{H}^-$ .

The first excited state A of LiH is a weakly bound state. At  $R = 4.042$  a.u., the energy of this state reaches a minimum and the dissociation energy is  $31.89 \text{ kcal mol}^{-1}$ . This value is a little higher than the experimental result and Partridge and Langhoff's [25] value because we did not optimize the  $\zeta$  value of Li 2p over the whole range of  $R$ . The symmetry of the A state is the same as that of the ground state ( $^1\Sigma^+$ ), and in MO theory, this state is considered to be constructed by means of the excitation of an electron from the ground state to an antibonding MO. The potential curve calculated using three BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

coincides completely with that obtained by full BTI (see the dashed line for state A in Fig. 1). In fact, the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

is not noticeable, especially around the equilibrium position, so only

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

can give a good description of state A. Furthermore, the above conclusion sufficiently shows that the ionic structure contributes only a little to the binding energy of state A. The most intriguing phenomenon associated with the first excited state of LiH is the peculiar variation in its dipole moment. No satisfactory explanation is given for

this by MO theory; however, a successful VB explanation is possible and is given in the following section. State A will dissociate into the  $\text{Li}(^2\text{P}) + \text{H}(^2\text{S})$ . As the atomic state  $\text{Li}(^2\text{P})$  is triply degenerate, the interaction between  $\text{Li}(^2\text{P})$  and  $\text{H}(^2\text{S})$  can produce a doubly degenerate state  $\text{B}(^1\Pi)$  as well as state A.

Accurate experiment has shown that state B is a very weakly bound state with a dissociation energy of only  $0.82 \text{ kcal mol}^{-1}$ . Using the MCSCF procedure, Docken and Hinze [24] were the first to obtain a bound potential-energy curve for this state theoretically, but their calculated binding energy was only half the experimental value. Later, Partridge and Langhoff [25] used a  $22\sigma 11\pi 7\delta$  function Slater basis set to perform CI calculations and the resulting dissociation energy is in excellent agreement with the experimental result. Our potential-energy curve for state B shows that the minimum is around 6.70 a.u. However, the dissociation energy is  $1.37 \text{ kcal mol}^{-1}$ , which is larger than the experimental value. The reason for above result is that the orbital exponents were not optimized at infinite distance (namely atomic states). If the optimization is made, the value will be near to zero, owing to the limited basis sets. Obviously, the weak correlation between the Rydberg orbitals of lithium and hydrogen is the main reason for the very small binding energy. Nevertheless, in the present calculation no d or f basis sets were used. Analysis of the structural weights indicates that state B can be represented by one bonded tableau

$$\begin{vmatrix} 5 & 5 \\ 1 & 7 \end{vmatrix} \text{ or } \begin{vmatrix} 5 & 5 \\ 1 & 8 \end{vmatrix}$$

The potential-energy curve of one bonded tableau is shown in Fig. 1 (dashed line for state B).

The dissociation products of the third singly excited state are  $\text{H}^-(^1\text{S})$  and  $\text{Li}^+(^1\text{s})$ . It can be conjectured that the strong interaction between ions will result in a large dissociation energy. Our calculated results show that the equilibrium position of state C is at  $R = 8.10 \text{ a.u.}$  and the dissociation energy is  $74.77 \text{ kcal mol}^{-1}$ . In the

terms of VB theory, as of  $\text{H}^-$  and  $\text{Li}^+$  approach one another the electron cloud of  $\text{H}^-$  becomes greatly polarized towards  $\text{Li}^+$ . Such polarization can be depicted as the mixing of the empty orbitals  $\text{Li } 2\text{s}$  and  $\text{Li } 2\text{p}$  into  $\text{H } 1\text{s}$ . As a result, a reasonable description of state C can be reached using a complex BT

$$\begin{vmatrix} \chi(\text{Li } 1\text{s}) & \chi(\text{Li } 1\text{s}) \\ \chi(\text{H } 1\text{s}) + \lambda_1\chi(\text{Li}) & \chi(\text{H } 1\text{s}) + \lambda_1\chi(\text{Li}) \end{vmatrix}$$

where  $\chi(\text{Li})$  represents the  $\text{Li } 2\text{s}$  and  $\text{Li } 2\text{p}$  AOs, and  $\lambda_1$  is a mixing coefficient which varies with  $R$ . This complex BT can be used to explain the whole potential-energy curve of state C quite well. At the equilibrium point, two simple BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

are sufficient to describe state C and their structural weights are 0.8967 and 0.0712, respectively; correspondingly,  $\lambda_1$  for the complex BT is 0.0397.

As the dissociation products for state D are  $\text{H}^+$  and  $\text{Li}^-$ , its dissociation energy is as high as  $110.47 \text{ kcal mol}^{-1}$ . The treatment of state D is similar to that of state C. We can also construct a complex BT for this state:

$$\begin{vmatrix} \chi(\text{Li } 1\text{s}) & \chi(\text{Li } 1\text{s}) \\ \chi(\text{Li}) + \lambda_2\chi(\text{H } 1\text{s}) & \chi(\text{Li}) + \lambda_2\chi(\text{H } 1\text{s}) \end{vmatrix}$$

The potential-energy curve reaches its minimum at  $R = 5.79 \text{ a.u.}$  At this position, the contribution to state D is mainly five BTs,

$$\begin{vmatrix} 5 & 5 \\ 6 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 4 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 7 & 7 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 8 & 8 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 9 & 9 \end{vmatrix}$$

the structural weights of which are 0.7493, 0.1208, 0.0281, 0.0281 and 0.0162 respectively.

#### Further VB description for the ground and four low-lying excited states

The electron transfer process in the ground state of  $\text{LiH}$  and the peculiar phenomenon of the dipole moment variation with  $R$  in the first excited state are two very interesting problems. In

this section we attempt to present distinct VB pictures for the ground state and the first excited state.

In the preceding section we mentioned that the potential-energy curves of the ground state and the first excited state can be described quite well by only three BTs. Thus, we consider that the construction of the VB pictures for these states can be done using these three BTs. As a result of full BTI calculation, the structural weights of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

in the ground state and first excited state wavefunctions were calculated using Eq. (7). In order to understand the results more clearly, the structural weight versus distance curve for the ground state is shown in Fig. 2. It can be seen that the contribution of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}$$

is the dominant one for  $R > 7.00$  a.u. For  $R < 7.00$  a.u., as the hydrogen and lithium atoms

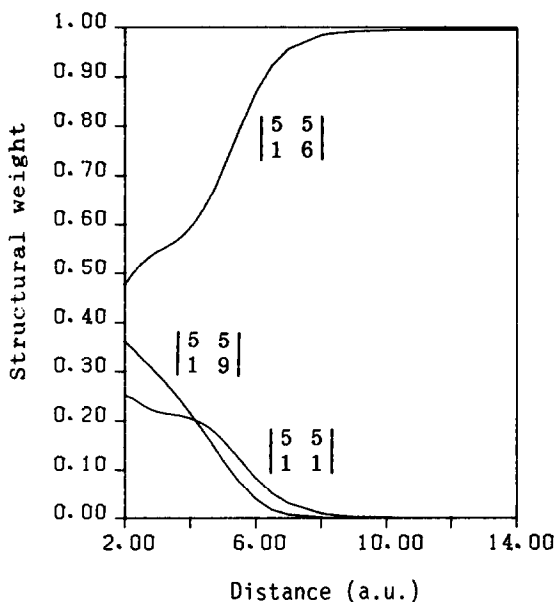


Fig. 2. The structural weights of the three BTs in the ground state.

come closer together the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}$$

decreases sharply while the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

increases steeply at almost the same rate. These results illustrate the phenomenon of hybridization between the Li2s and Li2p<sub>z</sub> AOs and the non-equivalent sp<sup>x</sup> hybridization will occur when the internuclear distance decreases to less than 7.00 a.u. The value of  $x$  is simply the ratio of the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}$$

to that of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}.$$

The relationship between  $x$  and the distance  $R$  is illustrated in Fig 3; it can be easily seen that  $x$  varies almost linearly with  $R$ . In the ground state the

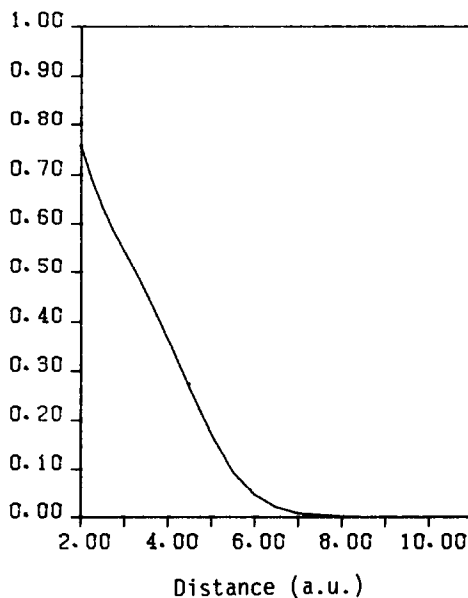


Fig. 3. Variation in the coefficient of hybridization  $x$  with the interatomic distance  $R$ .



hybridization is positive and thus the electron density of the lithium atom moves towards the hydrogen atom. In this way the covalent bond between hydrogen and lithium is strengthened. The third BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

illustrates the interaction between the ions  $\text{Li}^+$  and  $\text{H}^-$  and represents the ionic structure of the molecule  $\text{LiH}$ . In the variation of the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

with respect to  $R$ , there is a very apparent transition between 5.0 and 7.0 a.u., which indicates the occurrence of electron transfer. This phenomenon underlies the harpoon mechanism which was found in the molecular beam reaction experiment, and 7.0 a.u. is a critical point because the harpoon occurs below this point. The harpoon mechanism is a very important phenomenon in molecular beam dynamics, and our VB calculation reveals that VB theory can describe the electron transfer process much more directly and clearly than can MO theory.

The molecular dipole moment is due to both the atomic polarization and the ionic structure. The latter gives rise to the dipole moment caused by the real transfer of electrons. Figure 4 shows the variation of the dipole moment of the ground and the first two excited singlet states with respect to  $R$ . One argument for the view that the ground state of  $\text{LiH}$  is mainly ionic is its very high dipole moment. As for the  $\text{LiH}$  molecule

$$\mu = \mu_x + \mu_y + \mu_z = \mu_z \quad (9)$$

in order to discriminate between the two kinds of dipole moment, we define the dipole moment weight of a BT  $\phi(k)$  for the total dipole moment of the state  $\psi_i$  as

$$\mu_i(k) = \sum_{l=1}^M C_{ik} C_{il} [S_{kl} \mu_N - \langle \phi(k) | z | \phi(l) \rangle] \quad (10)$$

where  $\mu_N$  is the dipole moment resulting from the

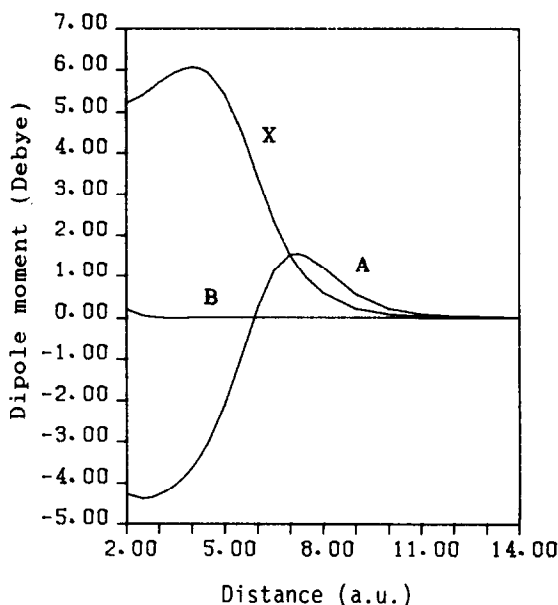


Fig. 4. Theoretical dipole moment functions for states X, A and B.

nuclei. At  $R = 3.066$  a.u., we calculate the dipole moment of the ground state using three BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

and the result is 5.597 D compared with the experimental value of 5.828 D, while the dipole moment weights of the BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

are 2.0813, 1.9105 and 1.6054 D respectively. Thus the contribution to the molecular dipole moment resulting from the polarization of the AOs on lithium accounts for as much as 71%, and the contribution from the ionic structure accounts for only 29%, although the dipole moment of the ionic structure  $\text{Li}^+\text{H}^-$  is 7.8801 D.

For the first excited state, the variation in  $\mu$  with respect to  $R$  (see Fig. 4) is relatively important. For  $R < 6.00$  a.u., the negative pole of the dipole moment is on lithium and MO theory holds that the state is predominantly  $\text{Li}^-\text{H}^+$ . In the region of

6.00–10.00 a.u., however, the negative pole is on the hydrogen side and according to MO theory this state switches character to become  $\text{Li}^+\text{H}^-$ . As one of two sources of the dipole moment is the polarization of atomic orbitals, it is inappropriate to express the direction of the dipole moment using forms such as  $\text{Li}^-\text{H}^+$  and  $\text{Li}^+\text{H}^-$ . We suggest that forms such as  $\text{Li}^{(-)}\text{H}^{(+)}$  should be used to show the negative and positive poles of the dipole moment. Although a detailed calculation of the dipole moment for state A has been made, regrettably, no explanation that is both reasonable and intuitively correct has been proposed.

Figure 5 shows the variation in the structural weights of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

with respect to the interatomic distance  $R$ . Because the sum of the structural weights of these three BTs is near 1.00 over the whole range of  $R$ , there is no noticeable contribution from the structure  $\text{Li}^-\text{H}^+$  according to VB theory. In

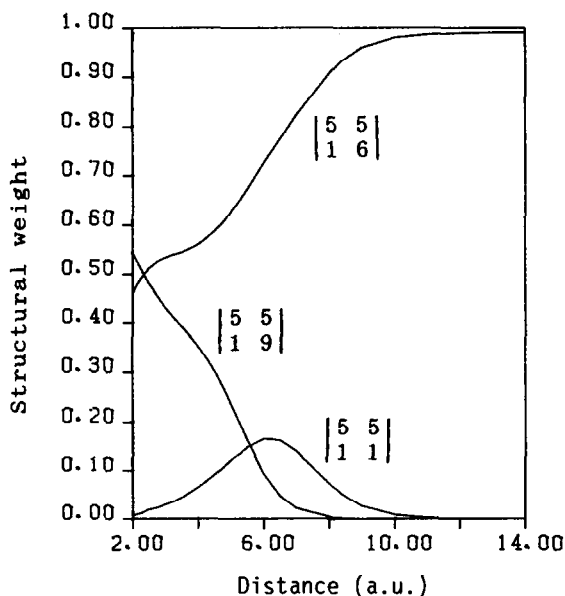


Fig. 5. The structural weights of three BTs in the first excited state.

contrast to  $\text{Li}^-\text{H}^+$ , the structure  $\text{Li}^+\text{H}^-$  corresponding to the BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

has a limited effect at around  $R = 6.00$  a.u. The curve for this BT (Fig. 5) is quite interesting. Below  $R = 6.20$  a.u., as  $R$  decreases the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

increases and reaches its maximum at  $R = 6.2$  a.u.; however, for  $R < 6.2$  a.u., the structural weight decreases with  $R$ . Considering that around  $R = 6.0$  a.u. the direction of the dipole moment will reverse, we propose that the BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

has a key effect on this reversion. The intersection between the  $T$ - $R$  curve of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

and that of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

also happens around 6.0 a.u. Let us consider the situations of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

further. As  $R$  decreases, the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}$$

gradually decreases while that of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

increases. Like the results for the ground state, these results indicate hybridization of the  $\text{Li}2s$  and  $\text{Li}2p_z$  AOs. However, in the first excited state wavefunction these two BTs are out of

phase and the hybridization makes the electron density on the lithium atom move away from the hydrogen atom. The higher the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

the more the electron density moves. In this way the polarization of lithium makes the dipole moment present the property of  $\text{Li}^{(-)}\text{H}^{(+)}$ . However, the ionic structure  $\text{Li}^+\text{H}^-$  corresponding the BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

makes the dipole moment present the property of  $\text{Li}^{(+)}\text{H}^{(-)}$ . In brief, the two contrary effects, namely the polarization of the lithium atom and the electron transfer from lithium to hydrogen are the primary reasons for the peculiar shape of the  $\mu$ - $R$  curve for the first excited state. For  $R > 6.0$  a.u., the effect of  $\text{Li}^{(+)}\text{H}^{(-)}$  is larger than for  $\text{Li}^{(-)}\text{H}^{(+)}$ , so the negative pole of the dipole moment is on the hydrogen atom. Conversely, the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

is larger than that of

$$\begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix}$$

For  $R < 6.0$  a.u., the strengthening of the atomic polarization of lithium and the decrease in the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

indicate that the effect of  $\text{Li}^{(-)}\text{H}^{(+)}$  is gradually increased relative to that of  $\text{Li}^{(+)}\text{H}^{(-)}$ , so the

direction of the dipole moment of the LiH molecule inverts and the negative pole is now on the side of the lithium atom. It is worth emphasizing again that there is no contribution from the ionic structure  $\text{Li}^-\text{H}^+$ .

It should be mentioned that the results calculated using only three BTs

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

coincide with the above results.

As state B can be described by one BT,

$$\begin{vmatrix} 5 & 5 \\ 1 & 7 \end{vmatrix} \text{ or } \begin{vmatrix} 5 & 5 \\ 1 & 8 \end{vmatrix},$$

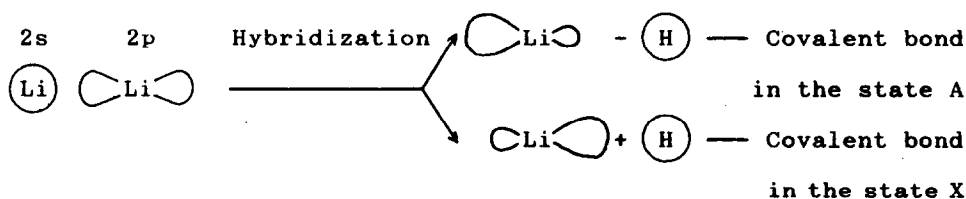
which corresponds to an unpolarized covalent bond, the dipole moment of state B is near to zero over the whole range of the interatomic distance. This conclusion is the same as that reached from MO calculations. States C and D express the interactions  $\text{Li}^+ + \text{H}^-$  and  $\text{Li}^- + \text{H}^+$  respectively. As  $R$  decreases, the dipole moments decrease. However, the direction of the dipole moment remains unchanged.

## Conclusion

The potential-energy curves of the ground and the first excited states of LiH can be described well by three BTs,

$$\begin{vmatrix} 5 & 5 \\ 1 & 6 \end{vmatrix}, \begin{vmatrix} 5 & 5 \\ 1 & 9 \end{vmatrix} \text{ and } \begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix},$$

where the first two BTs consist of the covalent bond between the H 1s AO and the hybridized atomic orbitals  $sp^x$ . The formation of the covalent bonds can be depicted as:



In the ground state, the covalent bond between the hydrogen and lithium atoms contributes about 84% to the binding energy. The structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

in the ground-state wavefunction shows a transition between  $R = 5.0$  and  $7.0$  a.u., which indicates there is electron transfer from lithium to hydrogen in this range of  $R$ . In general, the dipole moment is due to both the ionic structure and atomic polarization. Although atomic polarization leads to the dipole moment, it cannot be simply assumed that there is an electron transfer process. Only the ionic structure can indicate a true transfer of electrons. At the equilibrium of the ground state, the structural weight of the ionic structure accounts for about 1/5 of the dipole moment and thus the ionic structure contributes only 29% to the molecular dipole moment, and the dipole moment mainly results from the atomic polarization of lithium due to non-equivalent  $sp$  hybridization. For the first excited state, as the lithium and hydrogen atoms approach one another the structural weight of

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

increases, reaching a maximum at  $R = 6.2$  a.u. and then decreasing. This result is the fundamental key to explaining the shape of the dipole moment  $\mu$  versus distance  $R$  curve. The atomic polarization of lithium leads to a  $\text{Li}^{(-)}\text{H}^{(+)}$  type dipole moment, but the ionic structure corresponding to the BT

$$\begin{vmatrix} 5 & 5 \\ 1 & 1 \end{vmatrix}$$

leads to a  $\text{Li}^{(+)}\text{H}^{(-)}$  type dipole moment. For  $R > 6.2$  a.u., the effect of the ionic structure is larger than that of the polarization, and thus the dipole moment is of the  $\text{Li}^{(+)}\text{H}^{(-)}$  type. However, as  $R$  decreases the effect of the ionic structure decreases and the effect of atomic polarization increases, so the direction of the dipole moment is

reversed, i.e.  $\text{Li}^{(-)}\text{H}^{(+)}$ . However, there is no contribution from the ionic structure  $\text{Li}^{-}\text{H}^{+}$ .

Within VB theory, excitation from the ground to the first excited states can be interpreted as the electronic excitation between two non-equivalent  $sp$  hybridized AOs on the lithium atom.

The second excited state is a degenerate state which can be described by

$$\begin{vmatrix} 5 & 5 \\ 1 & 7 \end{vmatrix} \text{ or } \begin{vmatrix} 5 & 5 \\ 1 & 8 \end{vmatrix}.$$

Obviously the  $1s$  and  $\text{Li}\pi$  AOs cannot overlap for a bonding state. Experiment shows that this state is weakly bonded (a binding energy of only  $0.82 \text{ kcal mol}^{-1}$ ), mainly due to the correlation between the outer  $pdf$  AOs of hydrogen and lithium. The reasoning for states C and D is relatively simple because two states are formed by  $\text{Li}^{+} + \text{H}^{-}$  and  $\text{Li}^{-} + \text{H}^{+}$  respectively.

### Acknowledgements

This research is a State Major Key Project for Basic Researches and was also supported by the National Natural Science Foundation of China.

### Note added in proof

The referee questioned our result that  $\text{LiH}$  is chiefly covalent and suggested that this is merely a basis-set artefact. Although we suspect that the use of a large basis set would not change this conclusion qualitatively, we will test the result in the near future. We thank the referee for his suggestions.

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