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Configuration Interaction in the Lithium Hydride Molecule. I. A Determinantal AO Approach*

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Numerical Hartree-Fock lithium orbitals and a $1s$ exponential hydrogen orbital have been used as basis functions for determining eigenfunctions for the LiH molecule. The calculations were carried out for both the ground electronic state and the first excited electronic state at nine internuclear distances. A configuration interaction treatment was superimposed on the valence-bond, ground-state calculation. Determinantal functions were constructed for the states of the system, the Hamiltonian matrix calculated between these states, and the corresponding secular determinant solved for the eigenvalues and corresponding eigenvectors. The total molecular energy, binding energy, and dipole moment were determined as functions of the internuclear distance. Where possible, comparison is made with experiment and with other theoretical work.

I. INTRODUCTION

THE following paper is based on a valence-bond (VB) calculation of the electronic structure of LiH. The complete Hamiltonian for the system of interacting charges has been used, and all electrons have been included. One of the purposes of this work has been to treat the molecular system over a wide range of internuclear distances, evaluating all integrals by a uniform procedure which is extendible to polyatomic molecules.

The VB approach, based on the early work of Heitler and London,¹ was developed and extended as a general, formal procedure by Slater² and Pauling.³ The non-orthogonality difficulties which arise have been reconsidered recently by McWeeny⁴ and Slater,⁵ who have shown the possibility of transforming the method to an orthogonal basis. In the present case an alternate scheme developed by Löwdin has been used.

In general, one-electron orbitals characteristic of the atomic components (AO's) are used as basis functions. The molecular eigenfunction is then approximated by a suitably chosen combination of antisymmetrized products (AP's) of the AO's. The choice of an AP representation of a molecular configuration results in correlation of the spatial distribution of electrons with like spin. A generalization of the scheme is necessary to describe adequately the electrons of unlike spin. Proceeding from the single configuration representation of the ground state, one can construct a better ap-

proximation to the true eigenfunction by considering a linear combination of those configurations of proper symmetry and multiplicity which can be formed from the basis set of AO's. The use of complete sets of basis functions and all configurations allows, in principle, an exact solution of the eigenvalue problem.

Earlier, less extensive calculations on the LiH molecule were carried out by Fischer⁶ and by Tomita and Fukui,⁷ where single-term exponential orbitals were chosen for the basis set. More recent VB treatments include the work of Kastler⁸ on HF and Matsen *et al.*⁹ on LiH. The procedures followed in the present paper are similar in that we have essentially used a configuration interaction (CI) treatment superimposed on the ground-state VB calculation. Determinantal functions were constructed for the states of the system, the Hamiltonian matrix calculated between these states, and the secular determinant solved for the eigenvalues and corresponding eigenvectors. In this manner the molecular eigenfunctions for LiH have been evaluated for both the ground state and the first excited state at nine internuclear distances. The total molecular energy, binding energy, and dipole moment consequently have been determined as functions of the internuclear distance.

II. METHOD OF CALCULATION¹⁰

The eigenvalue problem in the present case involves the usual expression for the Hamiltonian operator

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,a} (Z_a/r_{ia}) + \sum_{i,j} (1/r_{ij}) + (Z_a Z_b / r_{ab}), \quad (1)$$

where the indices i and j refer to the four electrons, and

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¹ W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

² J. C. Slater, *Phys. Rev.* **37**, 481 (1931); **38**, 1109 (1931).

³ L. Pauling, *J. Am. Chem. Soc.* **53**, 1367, 3225 (1931); **54**, 988, 3570 (1932); etc.

⁴ R. McWeeny, *Proc. Roy. Soc. (London)* **A223**, 63, 306 (1954); **A227**, 288 (1955).

⁵ J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology (April 15, 1955), p. 5.

⁶ I. Fischer, *Arkiv Fysik*, **5**, 349 (1952).

⁷ K. Tomita and K. Fukui, *Progr. Theoret. Phys.* **10**, 362 (1953).

⁸ D. Kastler, *J. chim. phys.* **50**, 556 (1953).

⁹ Miller, Friedman, Hurst, and Matsen, *J. Chem. Phys.* **27**, 1385 (1957).

¹⁰ Atomic units are used throughout. a_0 = unit of length = 0.5293 Å. Rydberg = unit of energy = 13.602 eV.

the indices a and b to the two nuclei with nuclear charges Z_a and Z_b , respectively.

The ground state and the excited states are formed from Slater determinants (linear combinations of determinants where necessary) of appropriate symmetry and multiplicity. The Slater determinants represent AP's of the occupied AO's. The AO's which were used are the numerical Fock-Petrashen $1s$, $2s$, and $2p$ lithium functions, $P_{nl}(r)$,¹¹ and a normalized Slater $1s$ hydrogen function:

$$\begin{aligned} s &\equiv (1s)_{Li} = (1/4\pi)^{1/2} P_{1s}(r), \\ S &\equiv (2s)_{Li} = (1/4\pi)^{1/2} P_{2s}(r), \\ p_0 &\equiv (2p_0)_{Li} = (3/4\pi)^{1/2} P_{2p}(r) \cos\theta, \\ p_{\pm} &\equiv (2p_{\pm})_{Li} = (3/8\pi)^{1/2} P_{2p}(r) \sin\theta e^{\pm i\varphi}, \\ h &\equiv (1s)_H = (1/\pi)^{1/2} e^{-r'}. \end{aligned} \quad (2)$$

It was necessary to interpolate the lithium functions in some places to obtain values on a finer mesh, and the functions were also smoothed to five places or better. The nonorthogonality of the hydrogen orbital with respect to the lithium functions was included without approximation throughout the calculation.

Löwdin has worked out the expressions for matrix elements between Slater determinants involving an arbitrary number of nonorthogonal functions.¹² Following his notation, for a matrix element between two N -electron determinants,

$$U = (N!)^{-1} \det(u_1 u_2 \cdots u_k \cdots)$$

and

$$V = (N!)^{-1} \det(v_1 v_2 \cdots v_l \cdots),$$

we have

$$\begin{aligned} H_{UV} &= \int U^* \Omega_{op} V(dx) = \Omega_0 D_{UV} \\ &+ \sum_{k,l} \{k | \Omega_1 | l\} D_{UV}(k | l) + \sum_{k_1 < k_2} \{k_1 k_2 | \Omega_{12} | l_1 l_2\} \\ &\quad \times D_{UV}(k_1 k_2 | l_1 l_2), \end{aligned} \quad (3)$$

where

$$\begin{aligned} \{k | \Omega_1 | l\} &= \int u_k^*(x_1) \Omega_1 v_l(x_1) dx_1, \\ \{k_1 k_2 | \Omega_{12} | l_1 l_2\} \\ &= \int u_{k_1}^*(x_1) u_{k_2}^*(x_2) \Omega_{12} v_{l_1}(x_1) v_{l_2}(x_2) dx_1 dx_2. \end{aligned} \quad (3a)$$

D_{UV} is the overlap determinant defined for the "nonorthogonality" integrals,

$$\int u_k^*(x_1) v_l(x_1) dx_1,$$

associated with the sets of functions forming the Slater

determinants, and $D_{UV}(k | l)$ and $D_{UV}(k_1 k_2 | l_1 l_2)$ are the first- and second-order (signed) minors. Ω_0 represents the nuclear repulsion term in the Hamiltonian operator, Ω_1 the one-electron terms, and Ω_{12} the two-electron terms. The summations are over rows, k , and columns, l , of the Löwdin determinants; the integrations are carried out over the electronic space-spin coordinates.

All integrals were evaluated numerically on the MIT digital computer Whirlwind using programs written by F. J. Corbató.¹³ The two-center one- and two-electron integrals were obtained by the procedure of expanding the hydrogen orbital about the lithium center, a method analogous to that of Barnett and Coulson¹⁴ and Lundquist and Löwdin.¹⁵ As programmed by Corbató the expansion in general form for a normalized Slater AO is

$$\begin{aligned} r \chi_{nlm}(k, r') &= \sum_{j=|m|} (2j+1) \alpha_j (nlm | k | r_0 | r) P_j^{|m|}(\cos\theta) \\ &\quad \times (e^{im\varphi}/(2\pi)^{1/2}), \end{aligned} \quad (4)$$

where

$$\begin{aligned} \chi_{nlm}(k, r') &= \{[(2k)^{2n+1}/(2n)!]^{1/2} r'^{n-1} \exp(-kr')\} \\ &\quad \times \left\{ \left[\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_j^{|m|}(\cos\theta') \frac{e^{im\varphi'}}{(2\pi)^{1/2}} \right\}. \end{aligned} \quad (4a)$$

The expansion functions α_j are appropriate combinations of spherical Bessel functions of half-integer order and imaginary argument. The spherical polar coordinates (r, θ, φ) and (r', θ', φ') refer, respectively, to the origin and to the center displaced by the distance r_0 . The radial integrations involved, then, the numerical lithium functions and the appropriate α functions and were performed using Simpson's rule on a 73-point mesh. In general, the accuracy of the integrals was controlled by the error inherent in the integration method, so that the integrals are rounded to five places in the appendix. The angular integrations were considered separately and combined with the radial integrals.

The one-center lithium kinetic energy integrals were obtained by transforming the Laplacian operator to a product of gradient operators

$$-\int u_k^*(x_1) \nabla^2 v_l(x_1) dx_1 = \int \nabla u_k^*(x_1) \cdot \nabla v_l(x_1) dx_1 \quad (5)$$

by means of Green's theorem, thus requiring but one numerical differentiation of each function. In evaluating these integrals a redefinition of the radial func-

¹³ F. J. Corbató, J. Chem. Phys. **24**, 452 (1956); Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, April 15, 1956, p. 33.

¹⁴ M. P. Barnett and C. A. Coulson, Trans. Roy. Soc. (London) **A243**, 221 (1951).

¹⁵ P. O. Löwdin and S. O. Lundquist, Arkiv Fysik **3**, 147 (1951).

¹¹ V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion **8**, 547 (1935).

¹² P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

TABLE I. Configuration interaction in lithium.

Configurations ^a (² S)	a_r	$E(\text{ry})$	Configurations ^a (² P)	a_r	$E(\text{ry})$	$\Delta E(^2P-^2S)^b$
$\phi_1: s(\alpha)s(\beta)S(\alpha)$	0.999993	-14.865470	$\phi_1: s(\alpha)s(\beta)p_+(\alpha)$	0.999991	-14.730180	0.135290
$\phi_2: s(\alpha)S(\alpha)S(\beta)$	0.001046		$\phi_2: S(\alpha)S(\beta)p_+(\alpha)$	-0.002547		
$\phi_3: (1/\sqrt{3})[s(\alpha)p_-(\alpha)p_+(\beta)$ $-s(\alpha)p_-(\beta)p_+(\alpha)$ $-s(\alpha)p_0(\alpha)p_0(\beta)]$	0.003579		$\phi_3: (1/\sqrt{6})[2s(\beta)S(\alpha)p_+(\alpha)$ $-s(\alpha)S(\alpha)p_+(\beta)$ $-s(\alpha)S(\beta)p_+(\alpha)]$	0.003054		
$\phi_4: (1/\sqrt{3})[S(\alpha)p_-(\alpha)p_+(\beta)$ $-S(\alpha)p_-(\beta)p_+(\alpha)$ $-S(\alpha)p_0(\alpha)p_0(\beta)]$	0.000935	-14.865544	$\phi_4: (1/\sqrt{2})[s(\alpha)S(\alpha)p_+(\beta)$ $-s(\alpha)S(\beta)p_+(\alpha)]$	-0.001378		
			$\phi_5: (1/\sqrt{2})[p_+(\alpha)p_-(\alpha)p_+(\beta)$ $-p_+(\alpha)p_0(\alpha)p_0(\beta)]$	0.000672	-14.730305	0.135239

^a The ordering of electrons must be preserved.^b Experimental value=0.135815 ry (Moore, 1949).

tions proposed by Freeman and Löwdin¹⁶ was used as an aid to greater numerical accuracy.

The standard variational treatment of the CI problem results in a secular determinant which must be solved for the eigenvalues and eigenvectors. One thus obtains the eigenfunctions in terms of the best linear combinations of those configurations included in the calculation. The eigenvalue problem can be defined in terms of the total molecular energy or the dissociation energy. A significant amount of analytic cancellation in evaluating the matrix elements is obtained for the latter case, and this procedure has been followed here. The secular equations for Li and LiH were solved on Whirlwind using programs written by Meckler¹⁷ and refined by Corbató.¹⁸

III. CONFIGURATION INTERACTION IN LITHIUM AND LITHIUM HYDRIDE

The selection of a set of one-electron AO's means that single configuration atomic and molecular wave functions can be only approximations to the wave functions representing the actual electron distribution in these systems. A better approximation is possible by considering a linear combination of the configurations of proper symmetry and multiplicity obtainable from the basis set of AO's,

$$\Psi = \sum_r a_r \phi_r, \quad (6)$$

and applying to the undetermined coefficients a_r the usual variational treatment for minimizing the energy. Because the number of possible configurations increases enormously with the number of unoccupied orbitals available, one is forced to consider only those configurations which would be expected to interact appreciably.

¹⁶ A. J. Freeman and P. O. Löwdin, Phys. Rev. **111**, 1212 (1958).

¹⁷ A. Meckler, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1954, p. 16.

¹⁸ F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January 15, 1955, p. 33.

Lithium

In computing the dissociation energy one subtracts from the total molecular energy the energies of the separated atoms. To do this unambiguously the same set of basis functions should be used for the atomic and the molecular calculations.¹⁹ That is, when CI has been included in the molecule, a consistent treatment of the atomic energies would include CI to the same extent. However, the approximation of using only the ground-state configurations to represent the separate atoms is reasonable if the effect of CI is as small as that shown for Li.

Using the 1s, 2s, and 2p Li AO's the possible determinantal functions ϕ were found with the symmetry of the ground state (²S), and also, as an additional calculation, functions were set up with the symmetry of the first excited state (²P). Appropriate combinations of these were formed which describe eigenstates of the spin and orbital angular momentum operators. These configurations are listed in Table I. Also listed are the eigenvectors corresponding to the lowest eigenvalues obtained from diagonalizing the Hamiltonian (CI) matrices.²⁰ In both cases the improvement in the energy from CI with the states available is seen to be negligible. The calculated atomic energy of lithium is 99.43% of the experimental value (cf. Table IX).

Valence-Bond Calculation

The ground-state configuration of LiH can be represented by a VB description in which there is a filled, tightly bound lithium 1s shell and a covalent bond describing the pairing of the 2s lithium electron

¹⁹ One allows the energy to be minimized with respect to any variation parameters built into the set of basis functions. These parameters are functions of the internuclear distance, but the effort involved in readjusting them is sufficiently great that many calculations (including this) have used parameters characteristic of the individual atoms, i.e., "free" AO's.

²⁰ The configurations enumerated as products and combinations of products in Tables I and II are to be understood as representing completely normalized Slater determinants. The coefficients explicitly included in the tables are those required to make the configurations eigenstates of the spin operator.

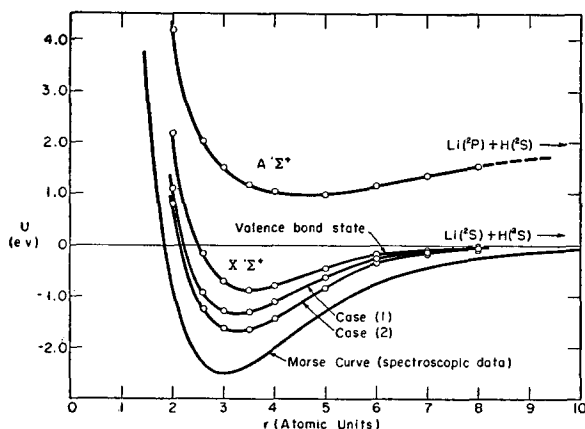


FIG. 1. Comparison of calculated potential curves for LiH.

with the $1s$ hydrogen electron. The VB method possesses an inherent advantage at large distances in describing correctly the asymptotic behavior of the system. Improvements on this simple description, considered in detail in the following sections, include the introduction of ionic terms by means of CI and additional electron correlation by means of hybridization. The potential energy curve for the VB state is shown as a function of internuclear distance in Fig. 1.

Lithium Hydride

CI in the molecule was considered in several stages. At 3 au CI was carried out among all the states obtained by using the lithium $1s$ and $2s$ AO's and the hydrogen $1s$ AO. Three states, the covalent VB configuration and two ionic configurations, Li^+H^- and Li^-H^+ , occur with the lithium $1s$ shell filled. Three more states result when one or both lithium $1s$ electrons are promoted to higher orbitals. These configurations ϕ and three others used later when the lithium $2p_0$ AO was included, are listed in Table II. Table III lists the improvement in the binding energy as each configuration was added.²¹ The very slight improvement in the energy from mixing in configurations where one or both lithium $1s$ electrons were promoted justified excluding them in extending the CI treatment to other internuclear distances. The potential curve for the ground state, from

TABLE II. Enumeration of configurations ϕ_r .

ϕ_1 : $(1/\sqrt{2})[s(\alpha)s(\beta)S(\alpha)h(\beta) - s(\alpha)s(\beta)S(\beta)h(\alpha)]$
ϕ_2 : $s(\alpha)s(\beta)h(\alpha)h(\beta)$
ϕ_3 : $s(\alpha)s(\beta)S(\alpha)S(\beta)$
ϕ_4 : $(1/\sqrt{2})[s(\alpha)S(\alpha)S(\beta)h(\beta) - s(\beta)S(\alpha)S(\beta)h(\alpha)]$
ϕ_5 : $(1/\sqrt{2})[s(\alpha)S(\beta)h(\alpha)h(\beta) - s(\beta)S(\alpha)h(\alpha)h(\beta)]$
ϕ_6 : $S(\alpha)S(\beta)h(\alpha)h(\beta)$
ϕ_7 : $(1/\sqrt{2})[s(\alpha)s(\beta)p_0(\alpha)h(\beta) - s(\alpha)s(\beta)p_0(\beta)h(\alpha)]$
ϕ_8 : $(1/\sqrt{2})[s(\alpha)s(\beta)S(\alpha)p_0(\beta) - s(\alpha)s(\beta)S(\beta)p_0(\alpha)]$
ϕ_9 : $s(\alpha)s(\beta)p_0(\alpha)p_0(\beta)$

²¹ Results are tabulated in terms of binding energies which were obtained directly by solving the secular equations. Total molecular energies may be computed by adding to the binding energies the calculated atomic energies = $-(14.865470 + 0.5)$ ry.

TABLE III. Binding energy.^a

Sequence of configurations interacting	D_e (ry)	D_e (ev)
ϕ_1	-0.051633	-0.70231
ϕ_2	-0.091612	-1.24611
ϕ_3	-0.094054	-1.27932
ϕ_4	-0.094054	-1.27932
ϕ_5	-0.094054	-1.27932
ϕ_6	-0.094057	-1.27937

^a $r = 3\text{au}$.

the interaction of configurations ϕ_1 , ϕ_2 , and ϕ_3 , is shown in Fig. 1 (case 1). Table IV summarizes the result of representing the calculated values of the potential energy by a Morse curve. The fit was made most accurately to the four points nearest the minimum. The computed molecular constants, obtained from the analytic function, are also tabulated.

The possibility of one or both electrons outside the closed shell occupying the lithium $2p_0$ orbital was considered. Three configurations, ϕ_7 , ϕ_8 , and ϕ_9 , were formed and mixed with states ϕ_1 , ϕ_2 , and ϕ_3 . The corresponding potential curve is given in Fig. 1 (case 2). These results were fitted with a Morse curve as indicated in Table V and molecular constants evaluated.

In Table VI the coefficients a_r which result in the lowest electronic energy for the molecule are listed for the six configuration terms of the total molecular wave function. As anticipated, the VB configuration predominates as the internuclear separation increases, with a corresponding decrease in the importance of all the ionic states. The excited VB configuration ϕ_7 is weighted most heavily near the equilibrium separation of the nuclei.

In Table VII the binding energy is tabulated for the nine internuclear distances in the same manner as in Table III, so that the effect of successively increasing the number of configurations may be seen. Thus, at

TABLE IV. Morse curve for the ground electronic state (lithium $1s$, $2s$; hydrogen $1s$ functions).

r_0 (au)	$U(r)$ (ev) (computed)	$U(r)$ (ev) (fitted Morse curve)	Δ (ev)
2.0	1.1018	1.0053	-0.0965
2.6	-0.9309	-0.9306	0.0003
3.0	-1.2793	-1.2830	-0.0037
3.5	-1.2912	-1.2885	0.0027
4.0	-1.1071	-1.1065	0.0006
5.0	-0.6364	-0.6766	-0.0402
6.0	-0.2545	-0.3719	-0.1174
7.0	-0.1254	-0.1958	-0.0704
8.0	-0.0618	-0.1010	-0.0392

Fitted Morse curve: $U(r) = 1.324[e^{-0.682(r-3.238)} - 1]^2 - 1$

Computed molecular constants: ω_e $1.165 \times 10^3 \text{ cm}^{-1}$
 $D_e = 1.324 \text{ ev}$
 $r_e = 3.238 \text{ au}$

TABLE V. Morse curve for the ground electronic state (lithium $1s$, $2s$, $2p_0$; hydrogen $1s$ functions).

r_0 (au)	$U(r)$ (ev) (computed)	$U(r)$ (ev) (fitted Morse curve)	Δ (ev)
2.0	0.8072	0.7200	-0.0872
2.6	-1.2461	-1.2462	-0.0001
3.0	-1.6167	-1.6221	-0.0054
3.5	-1.6372	-1.6321	0.0051
4.0	-1.4283	-1.4287	-0.0004
5.0	-0.8460	-0.9193	-0.0733
6.0	-0.3368	-0.5339	-0.1971
7.0	-0.1467	-0.2966	-0.1499
8.0	-0.0662	-0.1611	-0.0949

Fitted Morse curve: $U(r) = 1.669 \{ [e^{-0.632(r-3.245)} - 1]^2 - 1 \}$

Computed molecular constants: $\omega_e = 1.212 \times 10^3 \text{ cm}^{-1}$
 $D_e = 1.669 \text{ ev}$
 $r_e = 3.245 \text{ au}$

each internuclear distance is shown the binding energy resulting from the interaction of two through six configurations added in order proceeding down the column. The first entry is the value for the VB state. Except for $r=2$ au, the configurations are listed in order of increasing energy. Interaction among the first three configurations gives nearly the final result for the potential energy.

IV. s, p HYBRIDIZATION

The covalent configurations, ϕ_1 and ϕ_7 , interact very strongly. A "hybrid" VB configuration may be constructed by using a hybrid lithium orbital, formed as

an undetermined linear combination of the $2s$ and $2p_0$ orbitals, which is substituted for the $2s$ orbital in ϕ_1 . This hybrid configuration is then expanded in terms of the two covalent states for which the CI problem has been solved and for which the eigenvectors have been found. At each distance the eigenvectors are equated to the coefficients of the expanded hybrid VB state yielding the best linear coefficients for the hybrid orbital.

Figure 2 shows the potential energy curve resulting from the interaction of the two covalent configurations and is, of course, the same as that obtained for the hybrid configuration. The potential curves for the VB state ($\gamma_2=0$) and for the complete CI treatment (case 2) are given for reference. Table VIII tabulates the coefficients of the hybrid orbital, and Fig. 3 shows the % $2p_0$ character in the hybrid orbital as a function of the internuclear distance. Since LiH dissociates into $\text{Li}(^2S)$ and $\text{H}(^2S)$, the amount of s, p hybridization should become very small at large internuclear separations.

V. EXCITED ELECTRONIC STATES

The ground-state configuration for LiH in Mulliken's notation is given as $(1s\sigma)^2(2s\sigma)^2$ corresponding to a $^1\Sigma^+$ state. The lowest excited electronic configuration is $(1s\sigma)^2(2s\sigma)(2p\sigma)$ which gives rise to an observed $^1\Sigma^+$ state, possessing a very broad minimum ($\omega_e=234.4 \text{ cm}^{-1}$) occurring at 4.9052 au and 3.286 ev above the ground state ($T_e=26509.6 \text{ cm}^{-1}$).²² Since the ground state and first excited state have the same symmetry,

TABLE VI. Coefficients for the configuration terms of the total ground-state molecular wave function.

Configuration	a_r for values of r_0								
	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
ϕ_1	0.66035	0.69738	0.71159	0.72380	0.74280	0.81115	0.90758	0.96964	0.99155
ϕ_7	-0.35374	-0.36568	-0.37546	-0.38024	-0.37426	-0.32986	-0.22559	-0.11598	-0.05011
ϕ_2	-0.35814	-0.28750	-0.24675	-0.21564	-0.19764	-0.17265	-0.12941	-0.08124	-0.04547
ϕ_3	0.14454	0.09924	0.06930	0.04048	0.02153	0.00319	-0.00347	-0.00246	-0.00138
ϕ_8	-0.09254	-0.07551	-0.05770	-0.03802	-0.02380	-0.00935	-0.00260	-0.00234	-0.00167
ϕ_9	0.03619	0.03569	0.03060	0.02390	0.01847	0.01295	0.00951	0.00740	0.00496

TABLE VII. Binding energy (ry) as a function of the internuclear distance and the states used in the configuration interaction.

Sequence of configurations interacting	D_e for values of r_0			Sequence of configurations interacting	D_e for values of r_0					
	2.0	2.6	3.0		3.5	4.0	5.0	6.0	7.0	8.0
ϕ_1	0.16050	-0.01229	-0.05163	ϕ_1	-0.06402	-0.05839	-0.03421	-0.01305	-0.00699	-0.00377
ϕ_7	0.11994	-0.05308	-0.09158	ϕ_7	-0.10075	-0.08924	-0.05043	-0.01833	-0.00821	-0.00401
ϕ_2	0.07069	-0.08511	-0.11519	ϕ_2	-0.11877	-0.10435	-0.06204	-0.02468	-0.01073	-0.00484
ϕ_3	0.06422	-0.08827	-0.11680	ϕ_3	-0.11936	-0.10453	-0.06204	-0.02468	-0.01073	-0.00484
ϕ_8	0.06357	-0.09072	-0.11821	ϕ_8	-0.11944	-0.10462	-0.06213	-0.02475	-0.01078	-0.00484
ϕ_9	0.05934	-0.09161	-0.11886	ϕ_9	-0.12036	-0.10500	-0.06220	-0.02476	-0.01078	-0.00486

²² G. H. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 341, 546.

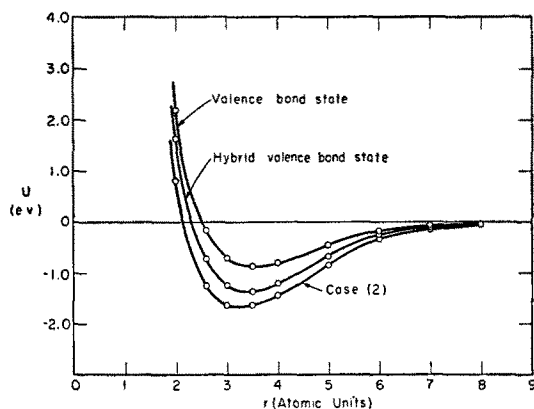


FIG. 2. Comparison of calculated potential curves for LiH.

and since the CI scheme has included configurations similar to the lowest excited state, the next to lowest eigenvalue of the secular determinant should be a fair approximation to this state.

The calculated potential curve for the first excited state *A* is given in Fig. 1. The calculated separation of the minima, T_e is 2.66 eV or 21459 cm^{-1} . Because of the departure of the potential curve from the conventional form for which a Morse function is satisfactory, it was more convenient to fit the points near the minimum to Dunham's power series expression,²³

$$U(r) = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots), \quad (7)$$

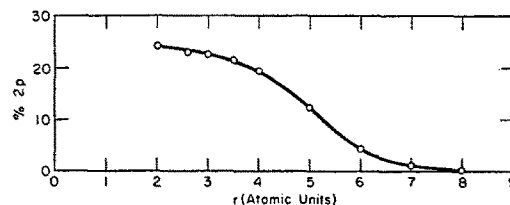
where

$$\xi = (r - r_e)/r_e.$$

A four-term fit to the values of $U(r)$ at $r = 3.5, 4.0, 5.0$, and 6.0 au gave $a_0 = 0.5929$; three-term fits to the values at $3.5, 4.0$, and 5.0 and at $3.5, 4.0$, and 6.0 gave $a_0 = 0.6305$ and 1.027 , respectively. These results for a_0 correspond to values of ω_e ranging from 232.2 cm^{-1} ($a_0 = 0.5929$) to 305.6 cm^{-1} ($a_0 = 1.027$). The constant derived by Mulliken from band spectra is 243 cm^{-1} ($a_0 = 0.65$).²⁴ The general spread obtained here indicates slightly more curvature, but the qualitative agreement is good. In agreement with an earlier analy-

TABLE VIII. Hybrid orbital coefficients.^a

r_0 (au)	γ_1	γ_2	% $2p_0$
2.0	0.86990	-0.49323	24.328
2.6	0.87728	-0.47998	23.038
3.0	0.88044	-0.47416	22.483
3.5	0.88612	-0.46346	21.480
4.0	0.89745	-0.44112	19.459
5.0	0.93621	-0.35144	12.351
6.0	0.97742	-0.21129	4.464
7.0	0.99492	-0.10067	1.013
8.0	0.99906	-0.04341	0.188

^a $\phi_{\text{Hyb}} = \gamma_1 S + \gamma_2 p_0$.²³ J. L. Dunham, Phys. Rev. **41**, 721 (1932).²⁴ R. S. Mulliken, Phys. Rev. **50**, 1028 (1936).FIG. 3. *s,p* hybridization in LiH as a function of internuclear distance.

sis by Rosenbaum,²⁵ it appears quite certain that the excited state will dissociate to $\text{Li}(^2P) + \text{H}(^2S)$.

VI. DIPOLE MOMENT CALCULATION

The dipole moment corresponding to the ground-state molecular wave function Ψ was evaluated at each internuclear distance. Taking the origin of coordinates to be at the lithium nucleus with the positive z direction toward the hydrogen nucleus, the instantaneous value of the dipole moment is given by

$$\mu = -e \sum_{i=1}^4 r_i \cos \theta_i + er_0, \quad (8)$$

where $r_i \cos \theta_i$ is the z coordinate of the i th electron, and r_0 is the internuclear distance. The average value of the dipole moment is then given by

$$\bar{\mu} = \int \Psi^* \mu \Psi dx_1 \cdots dx_4 = \sum_{r,s} a_r^* a_s \int \phi_r^* \mu' \phi_s dx_1 \cdots dx_4 + er_0, \quad (9)$$

where

$$\mu' = -e \sum_{i=1}^4 r_i \cos \theta_i \quad (9a)$$

and Ψ is given by Eq. (6). The coefficients a_r and configurations ϕ_r are those given in Table VI. With the definition

$$\mu_{rs}' = \int \phi_r^* \mu' \phi_s dx_1 \cdots dx_4 \quad (10)$$

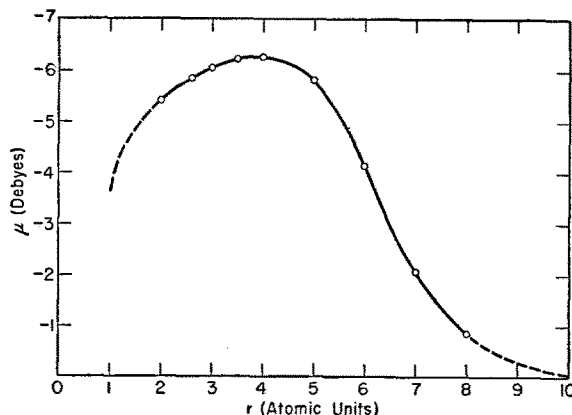


FIG. 4. Dipole moment for LiH as a function of internuclear distance.

²⁵ E. J. Rosenbaum, J. Chem. Phys. **6**, 16 (1938).

TABLE IX. Calculated and experimental total energies (ry).

State	Calculated	Free atoms		Calculated	Molecule	
		Experimental ^a	Ratio		Experimental ^b	Ratio
$X^1\Sigma^+$	15.86554	15.95594	0.9943	15.98824	16.14087	0.9905
$A^1\Sigma^+$	15.73031	15.82012	0.9943	15.79269	15.89930	0.9933

^a C. E. Moore, "Atomic energy tables," Natl. Bur. Standards Circ. No. 467 (1949), Vol. I.^b Value for D_e taken from R. Velasco, Can. J. Phys. **35**, 1204 (1957).

TABLE X. Calculated and experimental molecular constants.

State	Configurations interacting	D_e (ev)	Ratio (calc/obs)	r_e (au)	ω_e (cm ⁻¹)	$y(D)^a$
$X^1\Sigma^+$	ϕ_1	0.871	0.3463	3.50	...	-0.89
	ϕ_1, ϕ_7	1.365	0.5427	3.40	...	-5.41
	ϕ_1, ϕ_2, ϕ_3	1.324	0.5264	3.238	1165	-3.61
	$\phi_1, \phi_2, \phi_3, \phi_7, \phi_8, \phi_9$	1.669	0.6635	3.245	1212	-6.05
	experimental ^b	2.5154		3.014	1406	...
$A^1\Sigma^+$	$\phi_1, \phi_2, \phi_3, \phi_7, \phi_8, \phi_9$	0.8487	0.7884	4.90	232-306	3.44
	experimental ^b	1.0765		4.905	234.4	...

^a Calculated at 3 au for the $X^1\Sigma^+$ state; at 5 au for the $A^1\Sigma^+$ state.^b See reference b, table IX.

and the fact that the coefficients a_r are real, one obtains the expression used in the calculation

$$y = \sum_r a_r^2 y_{rr}' + 2 \sum_{r < s} a_r a_s y_{rs}' + e r_0. \quad (11)$$

Expansion of y_{rs}' in terms of one-electron integrals parallels exactly the treatment of the one-electron part of the Hamiltonian matrix in Sec. II.

The dipole moment calculated in this way is negative for the ground state, indicating that the charge distribution is shifted toward the proton. It is plotted as a function of the internuclear distance in Fig. 4. A similar calculation for the dipole moment of the excited state near the minimum gave a positive value of 3.44 debyes.

VII. DISCUSSION AND COMPARISON WITH EXPERIMENT

At the present stage of atomic and molecular calculations total energies are, in general, computed to somewhat better than 99% of the experimental values. Except for the simplest systems, such as H_2 and LiH , the differences between the calculated and observed total energies will then be larger than the binding energies. It is, of course, cancellation of error between the molecular and corresponding atomic systems that allows reasonable estimates to be obtained for a number of molecular constants.

The calculated and experimental atomic and molec-

ular energies for LiH at the equilibrium distance are summarized in Table IX. Derived molecular constants are summarized and compared in Table X. Agreement with the recent calculations using Slater AO's by Matsen *et al.*⁹ and by Hurley²⁶ is satisfactory.

Although a large fraction of the remaining difference between experimental and calculated molecular energies is associated with electron correlation in the nearly spherically symmetric closed inner shells, the electronic charge distribution is still somewhat poorly determined for the purpose of obtaining good values of the rather sensitive dipole moment. The moment calculated at 3 au is $-6.0525D$ and agrees with similar calculations.²⁷ Other values previously reported are $-3.50D$ ²⁸ and $-4.05D$.²⁹ These differences are not unreasonable for this type of calculation. The dipole moment shows the expected dependence on internuclear distance, and the recent work of Norris and Klemperer³⁰ indicates that the derivative at the equilibrium distance is of the correct sign and magnitude.³¹

²⁶ A. C. Hurley, J. Chem. Phys. **28**, 532 (1958).²⁷ Hurst, Miller, and Matsen, J. Chem. Phys. **26**, 1092 (1957).²⁸ M. Adamov, Zhur. Fiz. Khim. **23**, 1172 (1949).²⁹ W. Klemperer and J. Margrave, J. Chem. Phys. **20**, 527 (1952).³⁰ W. G. Norris and W. Klemperer, J. Chem. Phys. **28**, 749 (1958).³¹ The ratio, $\theta = [\mu_e / (d\mu/dr)_e r_e]$, defined by Norris and Klemperer was found from their measurements to be $+1.5 \pm 0.3$ and was compared with the value of $+4.5$ obtained from the present calculation. Improvements in the calculation could decrease the dipole moment or increase the value of the derivative thereby reducing the discrepancy considerably.

The choice of AO's characteristic of the separated atoms as basis functions for the molecule is more valid at the larger internuclear distances. The calculated equilibrium distance is 10% greater than the observed and is directly attributable to this. If one were to use sets of AO's perturbed by the molecular environment at each internuclear distance, the relatively greater improvement in the molecular energy at smaller distances would move the minimum inward.

The two CI treatments, with and without the $2p_0$ orbital, converge to nearly the same values of the molecular energy as the internuclear distance increases. This is in agreement with the decrease of s, p hybridization. As shown in the atomic CI problem of Sec. III, the importance of the $2p_0$ function must become very small. It is evident that a much larger set of basis functions should be used for effective CI at larger distances (e.g., inclusion of d and f orbitals on lithium; p and d orbitals on hydrogen). Radial correlation and, to some extent, angular correlation have been treated by means of the AO's and configurations used, but correlation associated with the azimuthal angle φ has been largely neglected since only orbitals of σ symmetry were chosen.

VIII. CONCLUSIONS

The practicability of considering intermediate range interactions (at two or three times the equilibrium distance) by conventional molecular schemes has been demonstrated. The VB CI description, as contrasted with MO treatments, does not provide a convenient representation of one-electron orbitals characteristic of the molecule. However, although it is not the natural method for orbital energies, it is an equivalent alternative procedure for determining the molecular eigenfunctions associated with the Hamiltonian and hence the total molecular energies for the eigenstates. Dissociation energies and the moments of the electron distribution are not difficult to calculate once the molecular wave function is known. At large internuclear distances where the atomic aspects of molecular structure predominate, the VB description seems less artificial and proceeds naturally to the correct situation as the molecule dissociates.

The orthogonality problem inherent in the VB treatment can be handled with Löwdin's formalism. Unfortunately, the evaluation of the overlap determinants and the associated single and double minors rapidly gets out of hand for more than 4 or 5 electron systems. The operations, however, are of such a nature that machine programming is possible for the deter-

mination of the matrix elements, as well as the integrals and the secular determinants.

For the present case the choice of Hartree-Fock AO's over simple analytic functions results chiefly in better total energies because of similarities in the orbitals. For heavier molecules the choice of Hartree-Fock AO's would be increasingly important.

An SCF LCAO-MO treatment of LiH using the same basis set of Hartree-Fock AO's has been completed and will be reported in a second paper.

ACKNOWLEDGMENTS

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APPENDIX³²

TABLE IA. One-center integrals.

One-electron integrals: $(u_k/\Omega_1/v_l) = \int u_k^*(1)\Omega_1 v_l(1)dx_1$			
(s/s)	1.00000	$[s/(1/r)/s]$	2.68449
(S/s)	0.00000	$[S/(1/r)/s]$	0.27275
(S/S)	1.00000	$[S/(1/r)/S]$	0.34550
(p/p)	1.00000	$[p/(1/r)/p]$	0.26499
(h/h)	1.00000	$[h/(1/r)/h]$	1.00000
$[s/-(\Delta/2)/s]$	3.61037		
$[S/-(\Delta/2)/s]$	0.69533		
$[S/-(\Delta/2)/S]$	0.20834		
$[p/-(\Delta/2)/p]$	0.14100		
$[h/-(\Delta/2)/h]$	0.50000		
Two-electron integrals: $(u_{k_1}v_{l_1}u_{k_2}v_{l_2}) = \int u_{k_1}^*(1)v_{l_1}(1)\Omega_2 u_{k_2}^*(2)v_{l_2}(2)dx_1dx_2$			
$s s s s$	1.64978	$p S p s$	-0.00492
$S s s s$	0.12216	$p S p S$	0.04403
$S s S s$	0.01412	$p p s s$	0.26411
$S S s s$	0.32298	$p p S s$	0.00101
$S S S s$	0.00278	$p p S S$	0.20881
$S S S S$	0.23448	$p p p p$	0.20403
$p s p s$	0.00294	$h h h h$	0.62500

³² Integrals are in atomic units = 2 ry.

TABLE IIA. Two-center integrals.

One-electron integrals: $(u_k \Omega_1 v_l) = \int u_k^*(1)\Omega_1 v_l(1)dx_1$									
	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
(h/s)	0.24765	0.14903	0.10445	0.06613	0.04144	0.01595	0.00604	0.00227	0.00085
(h/S)	-0.53434	-0.50141	-0.46932	-0.42210	-0.37115	-0.27160	-0.18769	-0.12411	-0.07932
(h/p)	0.44962	0.49562	0.50598	0.50073	0.48017	0.41181	0.33017	0.25213	0.18579
$[h/-(\Delta/2)/s]$	0.03493	-0.00084	-0.00798	-0.00951	-0.00805	-0.00422	-0.00187	-0.00077	-0.00031
$[h/-(\Delta/2)/S]$	-0.05182	-0.05431	-0.04797	-0.03526	-0.02582	-0.00923	-0.00431	-0.00212	0.00281
$[h/-(\Delta/2)/p]$	0.11689	0.10922	0.09785	0.07853	0.06416	0.03641	0.02590	0.00864	0.00339
$[h/(1/r)/s]$	0.33138	0.18998	0.12998	0.08037	0.04947	0.01857	0.00692	0.00257	0.00095
$[h/(1/r)/S]$	-0.18650	-0.16662	-0.14885	-0.12533	-0.10276	-0.06523	-0.03927	-0.02280	-0.01290
$[h/(1/r)/p]$	0.17053	0.16696	0.15791	0.14253	0.12517	0.09110	0.06290	0.04191	0.02725
$[h/(1/r)/h]$	0.47253	0.37698	0.33003	0.28454	0.24958	0.19995	0.16666	0.14286	0.12500
$[s/(1/r')/s]$	0.49987	0.38453	0.33332	0.28571	0.25000	0.20000	0.16667	0.14286	0.12500
$[S/(1/r')/s]$	0.00216	0.00037	0.00010	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000
$[S/(1/r')/S]$	0.29593	0.27859	0.26443	0.24549	0.22658	0.19216	0.16409	0.14203	0.12473
$[p/(1/r')/s]$	0.02245	0.01457	0.01120	0.00832	0.00639	0.00410	0.00285	0.00209	0.00160
$[p/(1/r')/S]$	-0.09275	-0.10004	-0.09978	-0.09563	-0.08891	-0.07285	-0.05771	-0.04540	-0.03596
$[p/(1/r')/p]$	0.28854	0.28414	0.27729	0.26541	0.25109	0.21970	0.18951	0.16333	0.14174
$[h/(1/r')/s]$	0.15876	0.07368	0.04424	0.02355	0.01267	0.00376	0.00115	0.00036	0.00012
$[h/(1/r')/S]$	-0.31899	-0.30501	-0.28263	-0.24631	-0.21139	-0.14503	-0.09815	-0.05994	-0.03685
$[h/(1/r')/p]$	0.34170	0.35704	0.35084	0.32889	0.30424	0.24231	0.19098	0.13470	0.09628
Two-electron integrals: $(u_{k_1}v_{l_1}u_{k_2}v_{l_2}) = \int u_{k_1}^*(1)v_{l_1}(1)\Omega_{12}u_{k_2}^*(2)v_{l_2}(2)dx_1dx_2$									
	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
$h s s s$	0.26846	0.15526	0.10665	0.06619	0.04085	0.01539	0.00575	0.00214	0.00079
$h s S s$	0.01362	0.00762	0.00515	0.00315	0.00192	0.00071	0.00026	0.00010	0.00004
$h s S S$	0.07699	0.04611	0.03222	0.02033	0.01271	0.00487	0.00184	0.00069	0.00026
$h s p s$	0.00283	0.00174	0.00122	0.00077	0.00048	0.00018	0.00007	0.00003	0.00001
$h s p S$	-0.00526	-0.00360	-0.00266	-0.00177	-0.00114	-0.00046	-0.00018	-0.00007	-0.00003
$h s p p$	0.06522	0.03923	0.02747	0.01737	0.01087	0.00418	0.00158	0.00059	0.00022
$h s h s$	0.05453	0.01876	0.00897	0.00350	0.00135	0.00019	0.00003	0.00000	0.00000
$h s S s$	-0.19471	-0.17113	-0.15187	-0.12717	-0.10387	-0.06564	-0.03942	-0.02286	-0.01292
$h S S s$	0.00019	0.00002	-0.00001	-0.00003	-0.00002	-0.00001	-0.00001	0.00000	0.00000
$h S S S$	-0.13961	-0.12728	-0.11625	-0.10088	-0.08520	-0.05693	-0.03564	-0.02129	-0.01229
$h S p s$	-0.00416	-0.00387	-0.00347	-0.00288	-0.00230	-0.00136	-0.00075	-0.00040	-0.00021
$h S p S$	0.02675	0.02901	0.02874	0.02690	0.02398	0.01704	0.01088	0.00645	0.00362
$h S p p$	-0.12770	-0.11941	-0.11093	-0.09827	-0.08462	-0.05845	-0.03753	-0.02281	-0.01331
$h S h s$	-0.05384	-0.02889	-0.01810	-0.00965	-0.00496	-0.00121	-0.00027	-0.00006	-0.00001
$h S h S$	0.10869	0.09722	0.08523	0.06846	0.05229	0.02706	0.01244	0.00524	0.00207
$h p s s$	0.16985	0.16657	0.15765	0.14237	0.12507	0.09107	0.06289	0.04190	0.02725
$h p S s$	0.00102	0.00065	0.00046	0.00030	0.00019	0.00007	0.00003	0.00001	0.00000
$h p S S$	0.11551	0.12243	0.12120	0.11490	0.10514	0.08137	0.05851	0.04003	0.02648
$h p p s$	0.00625	0.00543	0.00479	0.00398	0.00323	0.00203	0.00122	0.00072	0.00041
$h p p S$	-0.03694	-0.03905	-0.03902	-0.03747	-0.03463	-0.02688	-0.01897	-0.01250	-0.00786
$h p p p$	0.11079	0.12004	0.12061	0.11643	0.10837	0.08629	0.06333	0.04387	0.02918
$h p h s$	0.04882	0.02906	0.01934	0.01107	0.00609	0.00169	0.00044	0.00011	0.00003
$h p h S$	-0.10273	-0.10452	-0.09835	-0.08565	-0.07061	-0.04228	-0.02241	-0.01088	-0.00494
$h p h p$	0.10411	0.11657	0.11660	0.10938	0.09700	0.06706	0.04100	0.02293	0.01202
$h h s s$	0.46641	0.37517	0.32923	0.28417	0.24920	0.19983	0.16717	0.14280	0.12479
$h h S s$	0.00469	0.00177	0.00089	0.00037	0.00015	0.00002	0.00000	0.00000	0.00000
$h h S S$	0.27832	0.26305	0.25123	0.23536	0.21939	0.18878	0.16317	0.14143	0.12434
$h h p s$	0.01453	0.01158	0.00970	0.00770	0.00614	0.00406	0.00285	0.00209	0.00160
$h h p S$	-0.07217	-0.08058	-0.08252	-0.08165	-0.07827	-0.06721	-0.05518	-0.04420	-0.03541
$h h p p$	0.26186	0.25868	0.25398	0.24547	0.23510	0.20993	0.18464	0.16052	0.14020
$h h h s$	0.13009	0.06552	0.04084	0.02244	0.01229	0.00372	0.00115	0.00036	0.00012
$h h h S$	-0.24751	-0.23450	-0.21847	-0.19383	-0.16769	-0.11762	-0.07821	-0.04957	-0.03056
$h h h p$	0.24833	0.26349	0.26249	0.25224	0.23587	0.19249	0.14839	0.10906	0.07807