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FOREWORD

Howard S. Taylor is Assistant Professor of Chemistry at the University of Southern California, Los Angeles, California.

ABSTRACT

15785 Author

The potential energy curve of the lowest lying triplet sigma state of lithium hydride has been computed by a variational technique. Linear combinations of products of two center molecular orbitals were used to approximate the wave function. All linear and nonlinear parameters are minimized and open shell techniques are utilized. The triplet state is shown to be of a repulsive nature. Author

I. INTRODUCTION

In recent years interest on the nature of the lowest-lying triplet state of lithium hydride (LiH) has arisen in connection with molecular beam experiments. These methods have been very successful in measuring the dipole moment and other properties of an ever-growing number of bound states of small molecules. In particular, the bound state of LiH has been studied in great detail by beam techniques (Ref. 1). Since experimental facility had been gained with LiH, it was hoped that certain low-lying excited states would be bound states and therefore would be amenable to study by beam techniques. The question of the nature of the lowest-lying triplet state arose out of this situation. One might guess, using a model that "shrinks" the lithium electrons into the lithium nucleus, by analogy to the hydrogen molecule, that the lowest-lying triplet state is repulsive. This guess is borne out by the calculation reported below.

II. METHOD OF COMPUTATION

The method of computation used in this work has been discussed in detail in a number of previous papers by the author and F. E. Harris (Ref. 2 and 3). For this reason only a brief resume of the method is given here. The spatial wave function is a linear combination of a product of two centered molecular orbitals, which are combined with spin functions in an open shell manner. At each internuclear distance, R, the calculation is repeated until enough data is available to minimize the nonlinear parameters of the wave function by a least squares method. Final parameters are verified by a grid-type pattern search described in Ref. 2.

The one-electron, two-center-molecular orbital used in this calculation is

$$\chi_a(i) = \xi_i^{\eta_a}\, \eta_i^{m_a} \left[(\xi_i^2 - 1)(1 - \eta_i^2)\right]_{\exp} (-\delta_a \xi_i - \zeta_a \eta_i - i\nu_a \phi_i) \tag{1}$$

where ξ_i, η_i, and ϕ_i are the standard prolate elliptical coordinates and n_a, m_a and ν_a are integers, the first two being restricted to positive numbers. δ_a and ζ_a can be any number but δ_a must be positive. The advantages of such a function as (1) are discussed in Ref. 2. The three spin functions used as a triplet spin basis are*

$$\begin{aligned}
\Theta_1(1234) &= \frac{1}{\sqrt{6}}(\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \beta\beta\alpha\alpha) \\
\Theta_2(1234) &= \frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - 2\beta\beta\alpha\alpha) \\
\Theta_3(1234) &= \frac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\beta\alpha)
\end{aligned} \tag{2}$$

*$\alpha\beta\beta\alpha$ implies $\alpha(1)\,\beta(2)\,\beta(3)\,\alpha(4)$, etc.

The spatial configurations are each products of four different functions of type (1). We shall denote a four-electron spatial configuration by Φ_i. The M configuration wave function corresponding to the Kth root of the secular determinant can be denoted by

$$\Psi_K(1234) = a\left\{\sum_{j=1}^{m}\sum_{i=1}^{3} C_{ji}^{k}\, \Phi_j\, \Theta_i\right\} \tag{3}$$

where a is the four-electron antisymmetrizer. The Φ_j's as used in this notation are discussed in the next section and reported in detail in Table 1. The coefficients listed in Table 2 are the normalized coefficients which reflect the true importance of the ji space-spin configuration. They are related to the C_{ji}^{k} of Eq. (3) by the formula

$$C_{ji}^{k'} = \frac{C_{ji}^{k}\,(S_{jj})^{1/2}}{\sum_i \sum_j \sum_{j'} (C_{ji}^{k}\, C_{j'i}^{k'}\, S_{jj'})} \tag{4}$$

The $S_{jj'}$'s are given in Table 3. The lowest root of the secular equation was minimized since we are seeking the energy of the lowest state of a particular irreducible representation of the LiH molecule.

Table 1. Nonlinear parameters of the configurations

au	δ	ζ	N	M	μ	δ	ζ	N	M	μ
Configuration I										
1	1.6656	1.5633	0	0	0	1.0820	0.8609	0	0	0
2	3.2804	3.3059	0	0	0	2.0907	1.9819	0	0	0
4	6.5751	6.5924	0	0	0	4.1605	4.0765	0	0	0
6	9.8468	9.8811	0	0	0	6.1978	6.1367	0	0	0
8	13.1180	13.1850	0	0	0	8.2547	8.1862	0	0	0
10	16.3960	16.4909	0	0	0	10.3095	10.2406	0	0	0
1	0.4290	0.4611	1	0	0	0.3471	−0.3471	0	0	0
2	0.5530	0.8093	1	0	0	1.0982	−1.0982	0	0	0
4	0.9720	1.2057	1	0	0	2.0163	−2.0163	0	0	0
6	1.4896	1.2092	1	0	0	2.9961	−2.9961	0	0	0
8	1.9743	1.3987	1	0	0	3.9947	−3.9947	0	0	0
10	2.4025	1.6823	1	0	0	4.9992	−4.9992	0	0	0
Configuration II										
1	1.7178	1.5618	0	0	0	1.1553	0.7453	0	0	0
2	3.1628	3.1689	0	0	0	2.2286	1.4598	0	0	0
4	6.5523	6.8249	0	0	0	4.4090	4.3800	0	0	0
6	10.1857	9.7620	0	0	0	6.3889	6.5902	0	0	0
8	13.5320	13.4925	0	0	0	9.0046	8.8351	0	0	0
10	16.4055	16.1357	0	0	0	11.0030	10.9285	0	0	0
1	0.5635	0.3930	0	1	0	0.1786	−0.1786	0	0	0
2	1.2651	1.3156	0	1	0	0.2970	−0.2970	0	0	0
4	3.5935	1.7891	0	1	0	1.9733	−1.9733	0	0	0
6	5.2758	3.4829	0	1	0	2.9338	−2.9338	0	0	0
8	7.3009	5.2618	0	1	0	3.9327	−3.9327	0	0	0
10	8.3484	7.4705	0	1	0	4.9549	−4.9549	0	0	0
Configuration III										
1	1.9689	1.9590	0	0	1	1.9615	1.9929	0	0	−1
2	3.9234	3.9138	0	0	1	3.9072	3.9844	0	0	−1
4	7.8355	7.8224	0	0	1	7.7989	7.9758	0	0	−1
6	11.7242	11.7197	0	0	1	11.6628	12.0045	0	0	−1
8	15.6530	15.6424	0	0	1	15.5748	15.9910	0	0	−1
1	0.4636	0.3637	1	0	0	0.3581	−0.3581	0	0	0
2	0.5535	0.6159	1	0	0	1.0338	−1.0338	0	0	0
4	0.9301	1.1414	1	0	0	1.9822	−1.9822	0	0	0
6	1.4248	1.1229	1	0	0	2.9933	−2.9933	0	0	0
8	1.8789	1.2821	1	0	0	3.9984	−3.9984	0	0	0

Table 2. The normalized linear coefficients $c_{ij}^{k\prime}$

au	k=	$c_{11}^{k\prime}$	$c_{12}^{k\prime}$	$c_{13}^{k\prime}$	$c_{21}^{k\prime}$	$c_{22}^{k\prime}$	$c_{23}^{k\prime}$	$c_{31}^{k\prime}$	$c_{32}^{k\prime}$	$c_{33}^{k\prime}$
1	1	2.0907506E-02	2.0309496E-02	7.8632422E-01	−3.6216563E-03	2.7555642E-05	−2.6521580E-01	−2.2636042E-05	−8.0505176E-06	−3.1873110E-02
2	1	−2.4518799E-03	5.7521631E-03	9.3957639E-01	−1.3541970E-03	−2.2564370E-02	−1.0383468E-01	−7.2602161E-06	−1.0390233E-06	−3.3138448E-02
4	1	9.0163162E-05	9.7125126E-04	1.0213075E-00	−1.9018879E-04	−3.4372698E-03	5.9328860E-02	−2.1364196E-07	−6.8278990E-07	−3.3291084E-02
6	1	3.4782538E-06	5.8418507E-04	1.0292123E-00	−2.1969915E-06	−4.2099758E-03	6.9540968E-02	−7.5449182E-08	−3.0793269E-06	−3.3271776E-02
8	1	1.1544897E-05	1.3741418E-03	1.0293125E-00	−8.9871763E-07	−6.2355719E-03	6.7122955E-02	−4.0238513E-08	−3.3643601E-06	−3.3242184E-02
10	1	5.0582343E-06	1.1963224E-03	1.0360885E-00	1.8886869E-06	−2.2846543E-03	7.9828988E-02			
1	2	2.2290000E-01	1.6880366E-01	1.4549421E-00	7.5329992E-02	2.0673370E-01	1.5772190E-00	1.7830509E-05	5.0595414E-06	−5.6822528E-03
2	2	6.8929937E-02	3.8669070E-02	7.2490768E-01	1.6626111E-02	2.6134545E-01	1.1499645E-00	1.6160747E-05	−2.0349031E-06	−3.6716697E-03
4	2	−1.6196219E-02	−1.0763133E-01	−3.8086727E-01	−2.2151310E-02	−8.9680669E-01	−1.8230465E-00	−5.4880139E-07	−2.6276342E-05	−3.2136136E-03
6	2	−3.6386829E-03	−1.2601727E-01	−4.6216350E-01	−1.3449190E-03	−9.9840350E-01	−1.9300027E-00	−9.2349938E-07	−3.8433001E-05	−3.6214737E-03
8	2	−1.7533057E-03	−1.5506051E-01	−4.9949659E-01	−5.1137136E-04	−1.0003093E-00	−1.9571357E-00	−3.7079563E-07	−3.1598133E-05	−3.6011659E-03
10	2	−6.2012402E-04	−1.4929221E-01	−5.5944083E-01	−2.1457423E-04	−1.0350625E-00	−2.0289191E-00			
1	3	1.2035175E-00	9.5380638E-01	3.7178948E-01	1.9966525E-01	8.0019063E-01	3.8564319E-02	3.2288260E-05	1.1585387E-05	−2.0117571E-03
2	3	5.8721258E-02	8.7726412E-02	2.2495748E-01	6.9818449E-02	1.0176033E-00	−1.2344900E-01	9.3372194E-07	−1.2019396E-05	1.0129367E-03
4	3	2.1253283E-02	1.0593328E-00	−1.1815518E-03	−6.9538431E-03	9.5506663E-02	−2.1086777E-01	2.5706265E-06	8.9117177E-05	−1.9692188E-03
6	3	−9.7969414E-03	1.0871566E-00	−9.1361705E-03	−3.0267121E-03	1.8479282E-01	−1.7491341E-01	−1.3255031E-06	1.2523172E-04	−2.2160656E-03
8	3	−2.3400095E-03	1.0837619E-00	−8.5275160E-03	−5.6943608E-04	1.7267411E-01	−1.9232862E-01	−2.5057965E-07	1.1569265E-04	−2.3295279E-03
10	3	−3.9306661E-04	1.0921105E-00	−1.0860140E-02	−1.0066528E-04	1.9778860E-01	−1.6441468E-01			
1	4	3.3065878E-01	1.9242321E-01	1.6018011E-01	−5.0960029E-01	−6.4564563E-01	1.3303827E-01	7.8830971E-05	5.0320925E-05	−3.3500419E-03
2	4	4.0627810E-01	4.9466279E-01	1.2788168E-01	−5.8013593E-01	3.2907927E-02	1.0958661E-02	5.3452808E-05	3.7554833E-05	−2.2446450E-03
4	4	9.9423279E-01	4.2803316E-02	4.0347346E-03	2.1832862E-01	2.9135904E-02	2.4785224E-02	9.9408493E-05	9.7384794E-07	−4.3612199E-06
6	4	1.0438691E-00	4.2162309E-02	−1.4697621E-04	2.5240935E-01	4.2998934E-03	−7.3883099E-03	1.4027963E-04	4.6196881E-06	−7.7674162E-05
8	4	1.0752076E-00	1.5805350E-02	−9.8150649E-05	2.2380078E-01	1.4248996E-03	−3.3995118E-03	1.2338938E-04	1.5799219E-06	−3.4470121E-05
10	4	1.1070920E-00	4.9622290E-03	−5.9717086E-05	2.4771518E-01	4.2827179E-04	−1.0823271E-03			
1	5	7.3471250E-01	4.0072401E-01	7.6097554E-02	9.8027934E-01	−3.8229653E-01	1.0881853E-01	1.9590520E-05	2.8763855E-05	−1.5010805E-03
2	5	8.7395670E-01	1.1881183E-01	6.6125202E-02	5.6951097E-01	−1.5855363E-01	1.0248039E-01	5.4466977E-05	1.5203792E-05	−1.5384882E-03
4	5	5.4095378E-02	3.0829611E-01	2.4244429E-02	−1.5284470E-01	2.4291614E-00	1.8214892E-00	2.6730683E-06	−1.0359256E-05	2.5998040E-03
6	5	1.1415968E-02	3.6388099E-01	2.2399699E-02	4.3534979E-04	2.4889153E-00	1.8133586E-00	6.6589829E-07	8.4894584E-06	3.0065492E-03
8	5	5.1152935E-03	4.1250584E-01	1.1356851E-01	−1.7843234E-04	2.7014674E-00	2.0799518E-00	−7.0220874E-08	−1.9537902E-05	3.9797418E-03
10	5	1.9602403E-03	4.6061637E-01	1.8190438E-01	−1.2996178E-04	2.8615038E-00	2.2639145E-00			
1	6	−1.2127607E-01	−1.2475347E-00	−1.0017829E-01	−5.1009426E-01	−3.3282696E-01	−1.6054493E-02	2.0594149E-05	−3.4492339E-05	−1.0511473E-04
2	6	−3.2094729E-01	1.0148335E-00	5.6585732E-02	7.6486749E-01	1.2424788E-01	−3.3707472E-03	−4.2858400E-05	6.5130102E-05	−2.4562201E-04
4	6	−1.2834697E-01	2.1047012E-01	9.8618269E-03	9.7897154E-01	6.2088599E-01	4.7052552E-01	−1.4606131E-05	−3.5102908E-06	8.2452641E-04
6	6	5.2407709E-02	1.2311989E-02	3.0354028E-04	1.0139579E-00	1.5348773E-02	9.3744589E-03	1.6876067E-05	5.6627072E-07	3.9073071E-07
8	6	2.6166684E-01	4.4906626E-03	3.8730973E-04	1.0836492E-00	7.1889886E-03	4.8684233E-03	−4.3925623E-05	−6.7144294E-07	2.0710768E-06
10	6	3.8909858E-01	2.1811471E-03	2.6654600E-04	1.1470255E-00	3.7275152E-03	2.6290764E-03			
1	7	−2.6221609E-05	3.9631510E-05	−3.0461935E-05	4.3506212E-05	1.3521467E-05	−2.6143851E-05	5.5642734E-01	−5.0621620E-01	−5.1202238E-04
2	7	−6.8014438E-05	6.3682853E-05	−1.6689043E-05	5.1097298E-05	2.2943287E-06	−2.1398567E-05	7.6805381E-01	−5.2855573E-01	−2.4493921E-04
4	7	−9.5895244E-05	2.5098966E-05	2.8720905E-06	−7.2513109E-06	4.0004653E-07	1.7614433E-06	9.4886056E-01	−2.7939782E-01	1.0090448E-05
6	7	−1.4627001E-04	1.2013747E-05	2.0354636E-06	−5.2138168E-05	6.3031125E-06	5.3663602E-06	9.9337857E-01	−9.1397473E-02	2.4187002E-05
8	7	−1.2112444E-04	2.0304446E-06	3.0740225E-07	1.9969984E-05	−9.9860047E-08	−9.3523490E-08	9.9965675E-01	−1.6637948E-02	4.7629580E-06
1	8	−5.3601757E-05	−4.2169641E-05	−5.7031232E-05	−9.8457946E-07	1.9198113E-05	−2.4172116E-05	1.4672088E-00	1.4852812E-00	−1.1478276E-03
2	8	−5.0008315E-05	−6.0219565E-05	−2.3477809E-05	−1.0118607E-05	8.3706366E-06	−1.4507270E-05	6.6083676E-01	8.6443098E-01	−3.9237176E-04
4	8	−3.1183225E-05	−8.9883538E-05	−1.0709029E-05	−3.2754400E-07	−4.1742238E-06	−7.7583695E-06	3.1831746E-01	9.6104069E-01	−6.5961239E-05
6	8	1.7300093E-05	1.4397307E-04	2.2428080E-05	6.2073454E-06	7.9448984E-05	6.4300255E-05	−1.1794724E-01	−9.9617217E-01	2.7218768E-04
8	8	3.2246644E-06	1.2232720E-04	1.8811147E-05	−7.5165259E-07	−5.4756434E-06	−5.3926606E-06	−2.8947777E-02	−9.9993733E-01	3.0313402E-04
1	9	6.5554047E-03	4.6427984E-03	3.4736666E-02	4.2521445E-04	1.3634447E-05	1.1944230E-03	1.9697988E-03	1.4464291E-03	9.9946620E-01
2	9	2.2912924E-03	1.7871274E-03	3.3991570E-02	−2.9285274E-04	−9.5902319E-04	1.0884498E-03	4.4768212E-04	2.0992589E-04	9.9943967E-01
4	9	−3.7692601E-05	7.9809052E-04	3.2721488E-02	−5.0036315E-04	−9.6409471E-03	−9.4273843E-03	1.1430360E-05	6.6346334E-05	9.9943485E-01
6	9	1.1971794E-05	8.8198340E-04	3.2500833E-02	6.2526369E-06	−1.0835137E-02	−1.0521835E-02	8.0816160E-06	2.7352231E-04	9.9943275E-01
8	9	4.7840838E-06	3.7097660E-04	3.1964186E-02	2.9841429E-06	−1.4166498E-02	−1.3550213E-02	4.0173894E-06	3.0348891E-04	9.9943013E-01

Note: E-02 = 10^{-2}

Table 3. The *H* and *S* matrices

au	k =	$S_{11}{}^k$	$S_{12}{}^k$	$S_{13}{}^k$	$S_{21}{}^k$	$S_{22}{}^k$	$S_{23}{}^k$	$S_{31}{}^k$	$S_{32}{}^k$	$S_{33}{}^k$
1	1	−3.3304E-01	9.9456E-00	1.8160E-01	1.2175E-00	−5.7094E-01	−2.1962E-00	−1.0692E-03	5.4764E-04	−4.7900E-02
1	2	...	−1.3786E-01	4.6594E-00	1.4740E-00	1.6726E-00	−1.2938E-00	2.4419E-04	−3.2856E-04	−1.4732E-02
1	3	...	...	−1.6505E-02	−2.1586E-00	2.3913E-00	4.2024E-01	8.2964E-04	−3.4221E-04	7.2051E-01
1	4	...	...	...	−9.9890E-01	−9.6611E-02	5.0323E-01	1.3896E-04	−6.1336E-05	6.0339E-03
1	5	...	...	...	...	−1.3045E-00	−5.4077E-01	3.3133E-05	3.6287E-05	−1.3072E-02
1	6	...	...	...	...	...	−1.7381E-01	−3.6228E-04	1.5156E-04	−1.8340E-01
1	7	...	...	...	...	...	...	1.8767E-00	−1.0571E-00	1.8962E-04
1	8	...	...	...	...	...	...	...	1.0994E-00	−5.5267E-05
1	9	...	...	...	...	...	...	...	...	4.2083E-01
2	1	−8.1197E-03	−4.4110E-04	4.2558E-03	4.6617E-05	−4.0944E-04	3.6280E-04	−1.1464E-07	5.9415E-09	−3.4160E-06
2	2	...	−7.4020E-03	4.3602E-03	6.6187E-04	3.4053E-04	−3.4238E-04	−4.7820E-11	−8.8452E-08	−3.5943E-06
2	3	...	...	−1.5641E-01	−4.4257E-04	−3.8226E-03	1.1299E-02	4.5504E-08	4.9583E-09	2.1817E-04
2	4	...	...	...	−2.3884E-04	−1.0235E-05	6.4757E-05	7.6959E-09	−1.6751E-12	3.4929E-07
2	5	...	...	...	...	−9.4470E-04	−1.5210E-04	−2.3561E-09	8.0877E-09	−6.0437E-06
2	6	...	...	...	...	...	−3.2195E-03	−1.4663E-08	1.6213E-09	−1.5714E-05
2	7	...	...	...	...	...	...	5.8276E-05	−7.5060E-06	3.2660E-09
2	8	...	...	...	...	...	...	...	5.2891E-05	4.1768E-10
2	9	...	...	...	...	...	...	...	...	5.3101E-05
4	1	−1.2552E-06	4.6710E-08	9.0102E-09	−2.1473E-11	−1.0418E-10	2.9998E-10	−8.3446E-12	3.1517E-13	−2.6168E-12
4	2	...	−1.7469E-06	9.7574E-07	3.4996E-10	1.1155E-08	−1.1498E-08	2.9719E-13	−9.0875E-12	−2.9052E-10
4	3	...	...	−3.2202E-05	−1.6693E-10	−3.8774E-08	6.1170E-08	6.7980E-14	1.0166E-12	1.5479E-08
4	4	...	...	...	−2.7400E-12	−7.7814E-13	1.9851E-12	−4.2100E-16	2.0467E-15	3.4957E-14
4	5	...	...	...	...	−3.7294E-10	4.7528E-10	−4.0849E-16	5.5779E-14	1.7728E-11
4	6	...	...	...	...	...	−6.8035E-10	1.8874E-15	−5.5054E-14	−3.0782E-11
4	7	...	...	...	...	...	...	1.3453E-09	−4.9406E-11	9.3152E-16
4	8	...	...	...	...	...	...	...	1.3211E-09	8.5437E-15
4	9	...	...	...	...	...	...	...	...	1.4031E-09
6	1	−3.1140E-09	1.0063E-10	−9.0776E-12	7.6245E-13	−1.1266E-13	1.4425E-13	−1.4894E-14	4.1420E-16	8.8845E-16
6	2	...	−4.7283E-09	3.1065E-09	5.0513E-14	3.9060E-11	−3.9570E-11	4.1504E-16	−1.7268E-14	−4.7365E-13
6	3	...	...	−8.5528E-08	−6.6006E-15	−1.3852E-10	2.1506E-10	−1.0699E-17	3.3817E-15	2.1035E-11
6	4	...	...	...	−3.5636E-15	−6.1446E-17	7.6101E-17	−7.6621E-19	1.9768E-19	6.7732E-19
6	5	...	...	...	...	−1.3797E-12	1.7199E-12	−3.0547E-19	1.0305E-16	3.1984E-14
6	6	...	...	...	...	...	−2.4196E-12	4.6545E-19	−1.1093E-16	−5.4933E-14
6	7	...	...	...	...	...	...	9.5388E-13	−2.4375E-14	−1.5409E-19
6	8	...	...	...	...	...	...	...	9.4498E-13	2.2732E-17
6	9	...	...	...	...	...	...	...	...	1.0065E-12
8	1	−5.1869E-11	7.2979E-13	−1.8203E-14	1.6804E-14	−2.2664E-16	2.1717E-16	−1.4183E-16	1.7869E-18	1.0356E-18
8	2	...	−8.1001E-11	5.5283E-11	1.0533E-17	5.9294E-13	−6.2992E-13	1.7900E-18	−1.6831E-16	−5.0300E-15
8	3	...	...	−1.4846E-09	−6.2697E-19	−2.0796E-12	3.5604E-12	−1.4577E-20	3.6754E-17	2.1837E-13
8	4	...	...	...	−7.8438E-19	−3.9098E-21	3.8754E-21	7.6412E-20	1.8731E-23	3.7906E-23
8	5	...	...	...	...	−1.8232E-14	2.4809E-14	−4.7077E-22	1.1028E-18	2.8820E-16
8	6	...	...	...	...	...	−3.6772E-14	4.1724E-22	−1.0195E-18	−5.4505E-16
8	7	...	...	...	...	...	...	5.9387E-15	−7.1930E-17	−1.0565E-22
8	8	...	...	...	...	...	...	...	5.9392E-15	1.5378E-19
8	9	...	...	...	...	...	...	...	...	6.3697E-15

Table 3. (Cont'd)

au	k =	$S_{11}{}^k$	$S_{12}{}^k$	$S_{13}{}^k$	$S_{21}{}^k$	$S_{22}{}^k$	$S_{23}{}^k$	$S_{31}{}^k$	$S_{32}{}^k$	$S_{33}{}^k$
10	1	−2.6731E-12	1.2248E-14	−7.8126E-17	3.8565E-15	−3.5452E-18	3.1720E-18			
10	2	...	−4.2110E-12	2.8966E-12	−1.3604E-19	1.0782E-13	−1.1603E-13			
10	3	...	...	−7.7986E-11	−4.5996E-22	−3.7612E-13	6.8060E-13			
10	4	...	...	...	−3.4661E-18	4.0124E-23	−3.2702E-23			
10	5	...	...	...	...	−1.1073E-14	1.5293E-14			
10	6	...	...	...	...	...	−2.3018E-14			
6	6	...	...	...	...	...	3.5658E-13	0	0	0
6	7	...	...	...	...	...	...	2.6459E-13	−6.9940E-15	0
6	8	...	...	...	...	...	...	...	2.5964E-13	0
6	9	...	...	...	...	...	...	...	...	2.5470E-13
8	1	1.2754E-11	−1.6221E-13	2.3337E-15	−7.6437E-15	4.1111E-17	−3.4382E-17	0	0	0
8	2	...	1.7560E-11	−7.0211E-12	−1.2366E-18	−1.1475E-13	9.9919E-14	0	0	0
8	3	...	...	1.7880E-10	7.6976E-20	2.6601E-13	−4.4349E-13	0	0	0
8	4	...	...	...	2.5001E-17	1.7947E-22	−3.1032E-22	0	0	0
8	5	...	...	...	...	3.6669E-15	−4.1538E-15	0	0	0
8	6	...	...	...	...	...	5.5714E-15	0	0	0
8	7	...	...	...	...	...	...	1.5845E-15	−1.9423E-17	0
8	8	...	...	...	...	...	...	...	1.5707E-15	0
8	9	...	...	...	...	...	...	...	...	1.5570E-15
10	1	6.6981E-13	−2.7876E-15	1.0105E-17	−1.5353E-15	6.5450E-19	−4.9856E-19			
10	2	...	9.2805E-13	−3.7169E-13	5.2603E-20	−2.0766E-14	1.8383E-14			
10	3	...	...	9.4772E-12	4.0684E-23	4.8375E-14	−8.5260E-14			
10	4	...	...	...	1.2853E-17	−1.3999E-23	8.7861E-24			
10	5	...	...	...	...	2.1334E-15	−2.4918E-15			
10	6	...	...	...	...	...	3.4200E-15			
1	1	5.5076E-00	−1.9567E-00	−1.8801E-00	−1.5894E-01	5.9584E-02	1.5028E-01	0	0	0
1	2	...	2.5073E-00	−4.6055E-01	−2.3622E-01	−2.7463E-01	1.5553E-01	0	0	0
1	3	...	...	1.6171E-01	2.1955E-01	−2.4397E-01	−4.0716E-00	0	0	0
1	4	...	...	...	1.6605E-01	1.2497E-02	−5.1379E-02	0	0	0
1	5	...	...	...	...	2.0846E-01	3.5940E-02	0	0	0
1	6	...	...	...	...	...	1.7308E-00	0	0	0
1	7	...	...	...	...	...	...	1.2187E-00	−7.1752E-01	0
1	8	...	...	...	...	...	...	...	7.1133E-01	0
1	9	...	...	...	...	...	...	...	...	2.0397E-01
2	1	1.5252E-03	2.4027E-05	−4.6742E-04	−6.2116E-06	5.5477E-05	−6.6199E-05	0	0	0
2	2	...	1.4096E-03	−4.8718E-04	−1.1071E-04	−6.3364E-05	3.8998E-05	0	0	0
2	3	...	...	1.6165E-02	4.8493E-05	−4.0899E-04	−1.1931E-03	0	0	0
2	4	...	...	...	4.4150E-05	1.5390E-06	−7.5450E-06	0	0	0
2	5	...	...	...	...	1.4213E-04	3.0538E-06	0	0	0
2	6	...	...	...	...	...	3.7823E-04	0	0	0
2	7	...	...	...	...	...	...	2.1966E-05	−3.3411E-06	0
2	8	...	...	...	...	...	...	...	1.9604E-05	0
2	9	...	...	...	...	...	...	...	...	1.7241E-05

Note: E-02 = 10^{-2}

Table 3. (Cont'd)

au	$k =$	$H_{11}{}^k$	$H_{12}{}^k$	$H_{13}{}^k$	$H_{21}{}^k$	$H_{22}{}^k$	$H_{23}{}^k$	$H_{31}{}^k$	$H_{32}{}^k$	$H_{33}{}^k$
4	1	2.8097E-07	−1.0110E-08	−9.3052E-10	−3.8763E-11	9.0628E-12	−4.8383E-11	0	0	0
4	2	...	3.5613E-07	−1.1842E-07	−6.8822E-11	−2.0008E-09	1.7660E-09	0	0	0
4	3	...	...	3.7165E-06	2.0390E-11	4.7321E-09	−7.3234E-09	0	0	0
4	4	...	...	...	9.6711E-13	7.0802E-14	−3.0316E-13	0	0	0
4	5	...	...	...	...	6.8856E-11	−7.6162E-11	0	0	0
4	6	...	...	...	...	...	1.0088E-10	0	0	0
4	7	...	...	...	...	...	...	3.9733E-10	−1.5955E-11	0
4	8	...	...	...	...	...	...	...	3.8605E-10	0
4	9	...	...	...	...	...	...	...	...	3.7477E-10
6	1	7.4175E-10	−2.1613E-11	1.1534E-12	−3.7624E-13	1.8089E-14	−2.2577E-14	0	0	0
6	2	...	1.0002E-09	−3.8813E-10	−1.0385E-14	−7.2659E-12	6.1832E-12	0	0	0
6	3	...	...	1.0152E-08	8.2878E-16	1.7336E-11	−2.6363E-11	0	0	0
6	4	...	...	...	2.2759E-15	9.0592E-18	−1.1250E-17	0	0	0
6	5	...	...	...	...	2.5815E-13	−2.7659E-13	0	0	0

Note: E-02 = 10^{-2}

III. RESULTS OF THE COMPUTATION

As Fig. 1 and Table 4 show, the potential curve of the lowest-lying $LiH^3\Sigma$ state is repulsive. The normalized coefficients show that the spin function, Θ_3, is by far the most important function at $R = 1$ au. Θ_3 becomes the only important spin function at larger R. The normalized coefficients also show that the configuration that has one electron with $n = 1$, $m = \nu = 0$ and all other electrons with $n = m = \nu = 0$ (denoted configuration 1) is the most important and determines the electron density. The parameters of configuration I were varied to 0.0125 at all R. The second configuration in importance (as determined by the normalized coefficient) is the one in which one electron has $m = 1$, $n = \nu = 0$ and all other electrons with $n = m = \nu = 0$ (called configuration II). The third configuration is one that correlates angularly the inner electrons. (See Ref. 4 for a discussion of such configurations.) This term (configuration III) has two electrons with π type molecular orbitals with n's and m's set to zero except for the outer electron which has an $n = 1$. The nonlinear parameters of configurations II and III were minimized by doing two configuration calculations using configurations I and II and I and III. In both these calculations the parameters of II or III respectively were varied to 0.0125 while those of I were held fixed at their optimal values, as determined in a one-configuration calculation. A single three-configuration run was then done at each R using the best nonlinear parameters obtained for each configuration. An attempt at simultaneous minimization of all parameters indicated that the improvement in energy would be negligible, and this procedure was abandoned. Table 1 shows that the nonlinear parameters of all configurations vary smoothly with internuclear distance.

The result for infinite internuclear separation was to be reported in a paper by the author and F. E. Harris on the ground state of lithium hydride (Ref. 5). The energy at infinite nuclear separation, for similar type configurations is -7.9474 au.

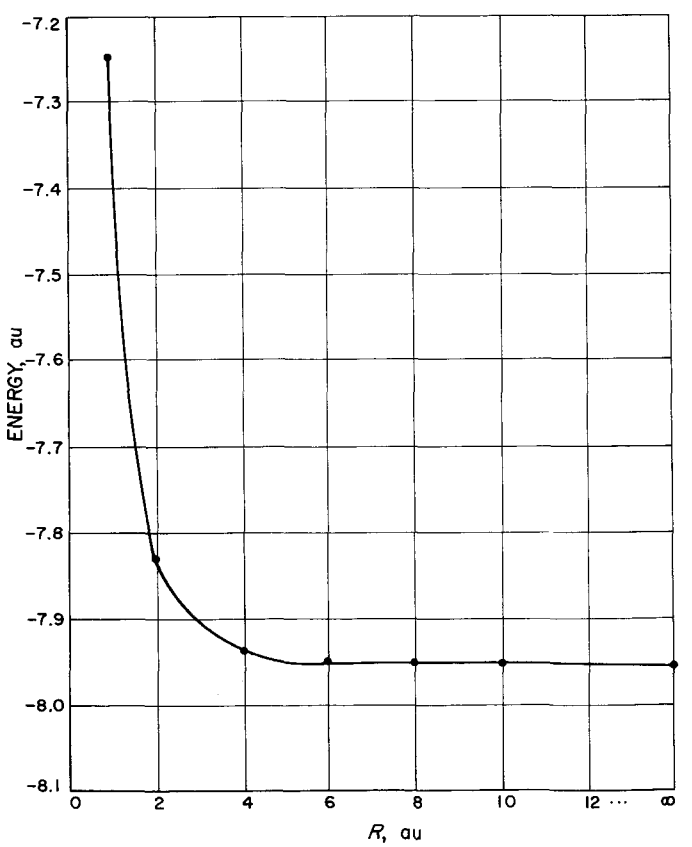

Fig. 1. The lowest-lying energy curve of a LiH triplet sigma state three-configuration result

Table 4. Potential energy of the lithium hydride triplet sigma state as a function of internuclear distance[a]

R	Configuration[b]	—E
1.00	I	7.2118003
1.00	I + II	7.2335268
1.00	I + III	7.2247045
1.00	I + II + III	7.2460374
2.00	I	7.8050098
2.00	I + II	7.8135024
2.00	I + III	7.8187989
2.00	I + II + III	7.8271397
4.00	I	7.9151768
4.00	I + II	7.9222628
4.00	I + III	7.9290367
4.00	I + II + III	7.9360476
6.00	I	7.9254986
6.00	I + II	7.9336651
6.00	I + III	7.9393251
6.00	I + II + III	7.9473932
8.00	I	7.9290752
8.00	I + II	7.9376573
8.00	I + III	7.9428960
8.00	I + II + III	7.9513831
10.00	I	7.9296209
10.00	I + II	7.9385613

[a]All energies are in atomic units.
[b]See the text or Table 1 for the form of configurations I, II, and III.

It will be noted in Fig. 1 and the tables, that at $R = 10$ au a π-π type configuration is not reported. The reason for this is that the optimal parameters of this configuration were too large for our programs to handle (i.e., δ or $\zeta > 18$). Our final $R = 10$ point was obtained by noting that the effect of adding configuration III to I and II at $R = 6$ and 8 was to lower E by 0.014 au. Figure 1 shows that this value moves the $R = 10$ point down to exactly where one would expect it to be from the smaller R and separated atom results.

If the results for configuration I in Table 1 are compared to the analagous results for the ground state, a very interesting point can be observed (Ref. 4), viz. that the parameters of the most important configuration indicated that the inner lithium atom orbits were unaffected by the formation of a molecule; that the orbit that came from the hydrogen atom remained almost completely centered on the hydrogen atoms and that the 2S lithium orbit formed the bond. For the triplet state the three orbits that did not form the bond in the ground state have almost exactly the same parameters in the triplet system as in the singlet system. This of course implies that the inner electrons on the lithium atom are again unaffected. The only difference between the singlet and the triplet is that the orbit that was the 2S lithium orbit at infinite separation in the former[a] was a displaced orbit with its maximum density between the two nuclei thereby forming a bond, while on the latter it remains centered on the lithium atom and at short distances even is polarized away from the hydrogen center. The transition from the bonding singlet state to the repulsive triplet state then appears as a one-electron excitation from a one-electron bonding orbit to a one-electron atom-centered orbital, the rest of the molecule remaining essentially unchanged. This result comes from the free and independent variation of the parameters and was not built in by guessing the parameters using this model.

In the ground state the important configurations were of the type used in the triplet state except that in the former a π-π configuration correlating the 1S hydrogen orbit with the 2S lithium orbit was important. In the latter this configuration was tried but failed to improve the energy even to 0.0001 au. The discussion of the previous paragraph clearly explains why this is so. In the triplet state the 2S lithium orbit and the 1S hydrogen orbit are simply not near enough to each other to correlate strongly.

These results suggest that a possible simplification in the treatment of excited states is to try to take advantage of the cancellations inherent in a calculation of the excitation energy due to the invariance of most of the orbits from state to state[b]. It is immediately seen that such approaches must take care to consider the one-electron orbital change as well as the changes in correlation that occur in such single-electron excitations.

Configurations correlating inner and outer orbits were tried but as in the ground state, this "intershell" correlation failed to yield any significant lowering of the energy. Also notable is the fact that configuration II yielded 0.014 au lowering of the energy at almost all intermediate distances in the triplet as well as the ground state problem and the atomic problem. This indicates the constant pairwise additivity of correlation energies of similar orbits. These observations are a further confirmation of the physical ideas upon which Sinanoglu based his "Many Electron Theory of Atoms and Molecules" (Ref. 6). The results of this paper also indicate that the Sinanoglu theory might trivially predict the singlet-triplet excitation energy in LiH as, in Sinanoglu's language, the sum of the difference in the Hartree Fock energy of the two states (which by a Koopman-type theorum could be just the difference in the orbital energies of the orbits that actually are effected) plus the E_{ij} correlation energy for the outer electrons in the LiH ground state. All other orbital and correlation energies remain the same and cancel.

[a]The orbit that goes to the 2S Li at infinite separation is termed the 2S Li orbit; the orbit that goes to the 1S H orbit at infinite separation, the 1S H orbit, etc.

[b]Such an idea had been suggested to the author by R. Sahni in a private conversation.

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