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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Livermore, California

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OF THE $\text{LiH } ^1\Sigma^+$ EXCITED STATE

A. M. Karo

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A. M. Karo

Lawrence Radiation Laboratory, University of California
Livermore, California

ABSTRACT

Detailed consideration is given to some properties of the first excited electronic state. Following the analysis proposed by Mulliken, SCF LCAO-MO coefficients are used to obtain qualitative information about the electron distribution. Comparison is made with earlier work with respect to the description of the excited state in terms of the interacting configurations. In addition to the excited-state dipole moment, the effective electric moment between the ground and excited states is also calculated. From this, the oscillator strength for the first allowed transition is computed as a function of the internuclear distance.

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I. INTRODUCTION

In an early extensive treatment by Mulliken¹ of the low-lying electronic states of simple heteropolar diatomic molecules, the alkali metal hydrides were examined in detail because of interest in the unusual form of the $A\ ^1\Sigma^+$ potential curves. In particular, attention was given to the excited $^1\Sigma^+$ state of LiH. The shape of the potential curve was accounted for, in the absence of good molecular wave functions, by an approximate perturbation treatment between the homopolar $Li(^2S)\cdot H$ state and the completely ionic Li^+H^- state. A subsequent analysis by Rosenbaum² showed that there should be sufficient interaction between these two configurations around 9 au to predict unequivocally dissociation to $Li(^2P) + H$. Both treatments emphasized the predominant Li^+H^- character of the excited molecular wave function at internuclear distances somewhat greater than the equilibrium separation.

Recent calculations have resulted in good wave functions for the first excited state over a range of internuclear distances from 2 to 8 au.³ In terms of the curvature around the minimum, the position of the minimum, and the dissociation energy associated with the potential curve, it appears very likely that the wave functions obtained are quite adequate for describing the excited state. Other than describing the characteristics of the potential curve, however, only brief mention has been given in these recent papers to the excited state.

In the present paper the discussion is extended by describing the excited state with respect to the interacting configurations. Results of both

¹R. S. Mulliken, Phys. Rev. 50, 1028 (1936).

²E. J. Rosenbaum, J. Chem. Phys. 6, 16 (1938).

³A. M. Karo and A. R. Olson, J. Chem. Phys. 30, 1232 (1959).

the determinantal AO and MO calculations are examined. The first method is more directly related to the early papers in which just such interacting configurations were considered. The second method provides a different sort of insight into the nature of the excited state, by considering the charge distribution among the available configurations and the MO's. The dipole moment of the excited state is also evaluated, as well as the matrix element of the dipole moment operator between the ground and excited states.

II. ELECTRON-POPULATION ANALYSIS

Recent descriptions of electron populations in molecules have been largely based on the scheme proposed by Mulliken⁴ for SCF LCAO-MO calculations. The popularity of this sort of analysis is, no doubt, in large part due to the resulting graphic illustrations of hybridization, charge localization within the molecule, and electron promotion by configuration interaction (CI). If the usefulness of this type of description can be demonstrated in small molecules, its popularity can be expected to increase as attention is turned to the rigorous calculation of larger systems and, in particular, to organic structures.

The electron populations of the ground states of LiH and HF were analysed in detail in a preceding paper.⁵ There, caution was emphasized because the bonding properties of the orbitals in HF were found to be very sensitive to the choice of Slater or Hartree-Fock basis functions. At the same time, however, a more promising indication was also noted in that the use of the better basis orbitals gave results in closer agreement with experiment.

⁴R.S. Mulliken, J. Chem. Phys. 23, 1833, 1841 (1955).

⁵A.M. Karo, J. Chem. Phys. 31, 182 (1959).

The use of Hartree-Fock lithium functions in the present case permits somewhat more confidence in the population analysis. Because the lithium 2s and 2p orbitals can be adequately described by relatively few exponential functions, it is also probable that the picture presented will remain essentially unchanged for other recent LiH calculations⁶ where the basis functions are orthonormal sets of exponential orbitals.

Definitions of the gross and total atomic populations and of the subtotal and total overlap populations have been given in earlier reports for single-determinant wave functions⁴ and for multi-configuration wave functions.⁵

The enumeration of the determinantal AO and MO configurations ϕ_r is given in Table I. These configurations represent, as usual, completely normalized antisymmetric products (Slater determinants) of the given AO's or MO's (AP AO's or AP MO's). The 1s, 2s, and 2p AO's on lithium and the 1s AO on hydrogen are represented by s, S, p₀, and h, respectively. Overlap integrals between the AO's have been given previously.³

Table II lists the coefficients a_r for the expansion of several normalized molecular wave functions Ψ in terms of the ϕ_r . It is apparent that for Ψ 's composed of AP AO configurations ϕ_2 is the limiting configuration at large values of r, in agreement with the analysis of Rosenbaum. For both the ground and the excited states the dominant configurations are ϕ_1 , ϕ_2 , and ϕ_3 . A clearly defined analogous trend has not yet developed among the AP MO configurations, although one expects the limiting configuration to be ϕ_6 . However, it is necessary to consider the changing character of the MO's with internuclear distance, as well as the weights of the configurations. Population analysis allows both factors to be taken into consideration.

⁶Miller, Friedman, Hurst, and Matsen, J. Chem. Phys. 27, 1385 (1957); A.C. Hurley, J. Chem. Phys. 28, 532 (1958).

TABLE I. Enumeration of configurations, ϕ_r .

(a) Determinantal AO configurations	
$\phi_1:$	$\frac{1}{\sqrt{2}} \left[s(\alpha)s(\beta)S(\alpha)h(\beta) - s(\alpha)s(\beta)S(\beta)h(\alpha) \right]$
$\phi_2:$	$\frac{1}{\sqrt{2}} \left[s(\alpha)s(\beta)p_0(\alpha)h(\beta) - s(\alpha)s(\beta)p_0(\beta)h(\alpha) \right]$
$\phi_3:$	$s(\alpha)s(\beta)h(\alpha)h(\beta)$
$\phi_4:$	$s(\alpha)s(\beta)S(\alpha)S(\beta)$
$\phi_5:$	$\frac{1}{\sqrt{2}} \left[s(\alpha)s(\beta)S(\alpha)p_0(\beta) - s(\alpha)s(\beta)S(\beta)p_0(\alpha) \right]$
$\phi_6:$	$s(\alpha)s(\beta)p_0(\alpha)p_0(\beta)$
(b) Determinantal MO configurations	
$\phi_1:$	$1\sigma(\alpha)1\sigma(\beta)2\sigma(\alpha)2\sigma(\beta)$
$\phi_2:$	$\frac{1}{\sqrt{2}} \left[1\sigma(\alpha)1\sigma(\beta)3\sigma(\alpha)4\sigma(\beta) - 1\sigma(\alpha)1\sigma(\beta)3\sigma(\beta)4\sigma(\alpha) \right]$
$\phi_3:$	$1\sigma(\alpha)1\sigma(\beta)3\sigma(\alpha)3\sigma(\beta)$
$\phi_4:$	$1\sigma(\alpha)1\sigma(\beta)4\sigma(\alpha)4\sigma(\beta)$
$\phi_5:$	$\frac{1}{\sqrt{2}} \left[1\sigma(\alpha)1\sigma(\beta)2\sigma(\alpha)3\sigma(\beta) - 1\sigma(\alpha)1\sigma(\beta)2\sigma(\beta)3\sigma(\alpha) \right]$
$\phi_6:$	$\frac{1}{\sqrt{2}} \left[1\sigma(\alpha)1\sigma(\beta)2\sigma(\alpha)4\sigma(\beta) - 1\sigma(\alpha)1\sigma(\beta)2\sigma(\beta)4\sigma(\alpha) \right]$

TABLE II. Coefficients for the configuration terms for several excited-state molecular wave functions (a_r for values of r_0).

(a) Determinantal AO configurations									
Config- uration	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
ϕ_1	0.84756	0.76801	0.72318	0.68026	0.64218	0.54606	0.37972	0.20649	0.09435
ϕ_2	0.85582	0.85753	0.84668	0.83063	0.82034	0.82698	0.87058	0.91662	0.95201
ϕ_3	0.19633	0.15036	0.13186	0.12286	0.12540	0.14819	0.17328	0.17386	0.14320
ϕ_4	0.11595	0.05633	0.02266	-0.00466	-0.01793	-0.02177	-0.01525	-0.00829	-0.00467
ϕ_5	0.10822	0.06577	0.04747	0.03283	0.02372	0.01421	0.00863	0.00517	0.00414
ϕ_6	-0.03599	-0.03550	-0.02299	-0.00874	0.00031	0.00581	0.00532	0.00116	-0.00037
ϕ_1	0.81738	0.76211	0.73040	0.69676	0.66095	0.55996	0.38717	0.20935	0.09562
ϕ_2	0.76609	0.79508	0.80716	0.81280	0.81455	0.82799	0.87180	0.91649	0.95164
ϕ_3	0.20242	0.16496	0.14478	0.13129	0.13010	0.14928	0.17341	0.17391	0.14323
ϕ_1	0.62141	0.62014	0.61375	0.59605	0.56289	0.44519	0.27192	0.13261	0.05841
ϕ_2	0.91994	0.92016	0.91715	0.91383	0.91579	0.94098	0.97818	0.99517	0.99914
(b) Determinantal MO configurations									
Config- uration	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
ϕ_1	0.06578	0.07659	0.08776	0.10784	0.13904	0.23900	0.37947	0.47064	0.46516
ϕ_2	0.25441	0.26442	0.27276	0.28503	0.29667	0.30214	0.24784	0.13114	-0.01923
ϕ_3	0.17030	0.17952	0.18802	0.20096	0.21692	0.25002	0.27601	0.28501	0.28830
ϕ_4	-0.02967	-0.03298	-0.03795	-0.04744	-0.06208	-0.11402	-0.20535	-0.30829	-0.37998
ϕ_5	-0.94912	-0.94362	-0.93826	-0.92901	-0.91599	-0.87588	-0.80495	-0.71304	-0.62351
ϕ_6	0.01554	0.02185	0.02798	0.03793	0.05211	0.09437	0.16818	0.27677	0.40865

A comparison of the excited-state functions in terms of the energy is made in Table III. The single-configuration wave functions exhibit correct general behavior. Marked improvement occurs in the 2-term function because of s, p hybridization. Thus, in contrast with earlier predictions,^{1,2} the strongest interaction is between the two nonpolar configurations, ϕ_1 and ϕ_2 , the Li^+H^- state contributing relatively little over the range of r considered here.

The distribution of the electron population among the AO's is shown in Table IV, where the single determinant (SD) $\Psi = \phi_5$ is compared with the 6-term Ψ (CI). The configuration ϕ_5 remains the lowest excited state between 2 and 8 au, although it should eventually transform to the atomic states, $\text{Li}(^2\text{S}) + \text{H}$, corresponding to the dissociated molecular ground state. From the usual MO correlation diagrams it is seen that the 3σ and 4σ MO's change, respectively, to the lithium 2s and 2p AO's, so that the configuration corresponding to the excited state of the molecule at large r is ϕ_6 . It can also be seen that CI allows for the promotion of electrons from the 2s to the 2p AO, or, equivalently, from the 3σ to the 4σ MO (cf. Table V(a)).

The electron distribution among the configurations, given in Table V(b), indicates, also, that ϕ_5 is by far the most important configuration up to 5 or 6 au. As r increases, the shift of population is expected to be from ϕ_5 to ϕ_6 and is just becoming strongly evident at 8 au. In any case, the limiting behavior of the excited state is by no means as well delineated in the SCF MO method as in the determinantal AO calculation. In addition, since both 6-term wave functions are nearly equivalent in terms of the energy and dipole moment, the population analysis does not give a quantitatively true picture of the charge distribution at large r , although the qualitative trends are correct.

TABLE III. Excited-state energies (ry).^a

r_0	Determinantal AO configurations				Determinantal MO configurations	
	(1-term Ψ : ϕ_2)	(2-term Ψ : ϕ_1, ϕ_2)	(3-term Ψ : ϕ_1, ϕ_2, ϕ_3)	(6-term Ψ)	(1-term Ψ : ϕ_5)	(6-term Ψ)
2.0	0.25530	0.33486	0.32598	0.30734	0.40253	0.30640
2.6	0.08384	0.16383	0.15747	0.15167	0.25545	0.15160
3.0	0.04219	0.11829	0.11295	0.11087	0.21879	0.11089
3.5	0.02572	0.09217	0.08727	0.08665	0.20051	0.08671
4.0	0.02882	0.08177	0.07652	0.07610	0.19789	0.07618
5.0	0.05523	0.08102	0.07323	0.07285	0.21539	0.07291
6.0	0.08712	0.09551	0.08500	0.08480	0.25222	0.08483
7.0	0.10578	0.10782	0.09785	0.09779	0.29579	0.09780
8.0	0.11869	0.11911	0.11263	0.11261	0.35595	0.11262

^aEnergies are relative to the separated, unexcited neutral atoms taken to be zero on the energy scale.

TABLE IV. Gross atomic populations, $N(p_k)$.

r		$N(1s)$	$N(2s)$	$N(2p)$	$N(H)$
2.0	SD	1.9936	0.6568	0.5767	0.7729
	CI	1.9936	0.6779	0.6085	0.7200
2.6	SD	1.9986	0.6948	0.5887	0.7179
	CI	1.9986	0.7105	0.6208	0.6701
3.0	SD	1.9994	0.7250	0.5924	0.6832
	CI	1.9994	0.7370	0.6245	0.6391
3.5	SD	1.9997	0.7584	0.5870	0.6549
	CI	1.9997	0.7664	0.6200	0.6139
4.0	SD	1.9998	0.7859	0.5717	0.6426
	CI	1.9998	0.7897	0.6065	0.6040
5.0	SD	2.0000	0.8299	0.5236	0.6465
	CI	2.0000	0.8150	0.5617	0.6233
6.0	SD	2.0000	0.8671	0.4615	0.6714
	CI	2.0000	0.7954	0.5053	0.6993
7.0	SD	2.0000	0.9022	0.3842	0.7136
	CI	2.0000	0.7335	0.4789	0.7876
8.0	SD	2.0000	0.9351	0.2980	0.7669
	CI	2.0000	0.6640	0.5257	0.8103

TABLE V. Total atomic populations.

(a) Electron distribution among the MO's									
	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
1 σ	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
2 σ	0.9097	0.9026	0.8965	0.8877	0.8804	0.8903	0.9642	1.0280	0.9885
3 σ	1.0236	1.0248	1.0254	1.0251	1.0212	0.9835	0.8617	0.6881	0.5554
4 σ	0.0667	0.0726	0.0781	0.0872	0.0984	0.1262	0.1740	0.2839	0.4561
(b) Electron distribution among the configurations, ϕ_r									
	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
N(ϕ_1)	0.0173	0.0235	0.0308	0.0465	0.0773	0.2285	0.5760	0.8860	0.8655
N(ϕ_2)	0.2589	0.2797	0.2976	0.3250	0.3520	0.3652	0.2457	0.0688	0.0015
N(ϕ_3)	0.1160	0.1289	0.1414	0.1615	0.1882	0.2500	0.3047	0.3249	0.3325
N(ϕ_4)	0.0035	0.0043	0.0058	0.0090	0.0154	0.0520	0.1687	0.3802	0.5775
N(ϕ_5)	3.6033	3.5617	3.5213	3.4522	3.3561	3.0687	2.5918	2.0337	1.5550
N(ϕ_6)	0.0010	0.0019	0.0031	0.0058	0.0109	0.0356	0.1131	0.3064	0.6680

Subtotal and total overlap populations are given in Table VI. The effective overlap populations $n(i;CI)$ for the MO's and the total overlap populations n are plotted in Fig. 1. With respect to the overlap populations, the chief effect of CI comes from electron promotion from the non-bonding 3σ MO to the strongly antibonding 4σ MO. Thus, the total overlap decreases markedly, although the energy around the minimum is lowered more than 0.1 ry.

Of considerable interest is the correlation observed here (and also seen previously⁵) between the shape of the total overlap curve as a function of internuclear distance and the calculated potential curve. This correlation has been emphasized by plotting the potential curve for the excited state in Fig. 1. Not only does the minimum of the potential curve correspond to the region of maximum overlap, but also the broad behavior of the minimum is reproduced in the dependence of the overlap on internuclear distance.

Table VII gives the overlap distribution among the MO's and the configurations. Values of $n(i)$ are based on total occupancy of the MO's ($N(i) = 2$), and the values for $n(i;CI)$ are the actual or "effective" bonding strengths of the MO's allowing for CI. As was found for the ground state, the bond in the excited state over the whole range of r considered is primarily due to the bonding 2σ electrons. In distributing the overlap population among the configurations, it was found, for the ground state, that ϕ_1 is the only bonding configuration. Here, ϕ_5 is the principal bonding configuration, with ϕ_1 contributing considerably at larger distances.

TABLE VI. Subtotal overlap populations, $n(p_k, q_l)$.

r		n(1s, H)	n(2s, H)	n(2p, H)	n(total overlap)
2.0	SD	-0.0692	0.0745	0.2112	0.2165
	CI	-0.0748	-0.0356	0.1285	0.0181
2.6	SD	-0.0220	0.1194	0.2202	0.3176
	CI	-0.0246	0.0114	0.1191	0.1059
3.0	SD	-0.0099	0.1292	0.2294	0.3487
	CI	-0.0112	0.0273	0.1206	0.1367
3.5	SD	-0.0036	0.1250	0.2373	0.3587
	CI	-0.0041	0.0340	0.1242	0.1541
4.0	SD	-0.0013	0.1118	0.2397	0.3502
	CI	-0.0015	0.0333	0.1271	0.1589
5.0	SD	-0.0002	0.0791	0.2287	0.3077
	CI	-0.0002	0.0291	0.1257	0.1546
6.0	SD	0.0000	0.0498	0.2015	0.2513
	CI	0.0000	0.0317	0.1071	0.1388
7.0	SD	0.0000	0.0273	0.1640	0.1913
	CI	0.0000	0.0299	0.0601	0.0900
8.0	SD	0.0000	0.0128	0.1227	0.1355
	CI	0.0000	0.0207	0.0089	0.0296

FIG. 1. Partial and total overlap populations for LiH, as a function of CI and internuclear distance.

TABLE VII. Overlap populations.

		(a) Overlap population distribution among the MO's								
		2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
n(i):	1 σ	0.0160	0.0035	0.0014	0.0006	0.0003	0.0001	0.0000	0.0000	0.0000
	2 σ	0.4692	0.6509	0.7025	0.7135	0.6904	0.5980	0.4808	0.3612	0.2537
	3 σ	-0.0683	-0.0228	-0.0080	0.0027	0.0094	0.0172	0.0218	0.0214	0.0174
	4 σ	-5.2862	-4.9522	-4.4960	-3.7748	-3.0497	-1.9036	-1.1770	-0.7256	-0.4413
n(i; CI):	1 σ	0.0160	0.0035	0.0014	0.0006	0.0003	0.0001	0.0000	0.0000	0.0000
	2 σ	0.2134	0.2938	0.3149	0.3167	0.3039	0.2662	0.2318	0.1857	0.1254
	3 σ	-0.0349	-0.0117	-0.0041	0.0014	0.0048	0.0085	0.0094	0.0074	0.0048
	4 σ	-0.1764	-0.1797	-0.1755	-0.1645	-0.1501	-0.1201	-0.1024	-0.1030	-0.1006
		(b) Overlap population distribution among the configurations, ϕ_r								
		2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
n(ϕ_1)		0.0021	0.0038	0.0054	0.0083	0.0134	0.0342	0.0692	0.0800	0.0549
n(ϕ_2)		-0.1723	-0.1737	-0.1674	-0.1532	-0.1338	-0.0861	-0.0355	-0.0060	-0.0001
n(ϕ_3)		-0.0015	-0.0006	-0.0002	0.0001	0.0005	0.0011	0.0017	0.0017	0.0014
n(ϕ_4)		-0.0046	-0.0054	-0.0065	-0.0085	-0.0118	-0.0247	-0.0496	-0.0690	-0.0637
n(ϕ_5)		0.1950	0.2828	0.3069	0.3096	0.2938	0.2360	0.1628	0.0973	0.0527
n(ϕ_6)		-0.0006	-0.0010	-0.0015	-0.0022	-0.0032	-0.0058	-0.0098	-0.0139	-0.0156

III. DIPOLE MOMENTS

From a naïve viewpoint, the early prediction that the excited state is characterized at intermediate values of r by the Li^+H^- configuration leads to the expectation of a negative dipole moment. On the contrary, the moment at nearly every stage of approximation considered here turns out to be positive and large, out to 6 au. The decrease in the moment at larger distances represents only a relatively small contribution from the Li^+H^- configuration. This result is in agreement with the relatively low weight given to the Li^+H^- term in the total wave function.

Dipole moment integrals, not given previously, are listed in Table VIII. Table IX presents the compiled dipole moment results for the excited state functions that have been discussed. The best dipole moment values for both Σ states are plotted in Fig. 2 to emphasize the change in the moment during the transition. Although neither one of the nonpolar AO configurations, ϕ_1 and ϕ_2 , considered separately, gives a positive moment from 2 to 8 au, the best linear combination results in a moment that compares well with the 6-term Ψ . Results for the 3-term Ψ indicate that the effect of including the Li^+H^- configuration is more noticeable at distances greater than 6 au.

The MO configuration ϕ_5 is a good approximation to the excited state at small values of r , and here the computed moment is in partial agreement with that calculated from the 6-term Ψ . The transformation of ϕ_5 to neutral atomic states on dissociation can be associated with the decreasing value of the moment at 7 and 8 au.

The apparent dipole moment, based on the gross atomic charges, is also given in Table IX. Near the equilibrium distances, the results agree

TABLE VIII. Dipole moment integrals.

	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
$\int s(r \cos \theta) h d\tau$	0.10850	0.07649	0.05770	0.03913	0.02578	0.01056	0.00414	0.00158	0.00060
$\int S(r \cos \theta) h d\tau$	-0.89954	-1.06522	-1.13357	-1.17301	-1.16725	-1.05608	-0.87281	-0.67401	-0.49408
$\int h(r \cos \theta) h d\tau$	1.99973	2.60049	3.00044	3.49908	3.99695	4.99972	6.01831	6.99503	7.98666
$\int s(r \cos \theta) p_0 d\tau$	0.10243	0.10243	0.10243	0.10243	0.10243	0.10243	0.10243	0.10243	0.10243
$\int S(r \cos \theta) p_0 d\tau$	-2.37356	-2.37356	-2.37356	-2.37356	-2.37356	-2.37356	-2.37356	-2.37356	-2.37356
$\int h(r \cos \theta) p_0 d\tau$	1.29225	1.51157	1.63721	1.75962	1.83795	1.86279	1.74339	1.53258	1.28344

TABLE IX. Computed dipole moments (in Debye units).

r_0	Determinantal AO configurations			Determinantal MO configurations		Apparent moment, $r_0 Q(H)$	
	(2-term Ψ)	(3-term Ψ)	(6-term Ψ)	(1-term Ψ)	(6-term Ψ)	SD	CI
2.0	5.071	5.359	5.139	5.535	5.133	1.154	1.423
2.6	5.077	5.126	4.999	5.922	5.001	1.863	2.179
3.0	5.049	4.981	4.907	6.198	4.909	2.415	2.751
3.5	4.953	4.783	4.758	6.542	4.761	3.068	3.433
4.0	4.742	4.491	4.496	6.850	4.500	3.632	4.025
5.0	3.817	3.418	3.436	7.290	3.441	4.490	4.786
6.0	2.147	1.392	1.397	7.447	1.403	5.009	4.583
7.0	0.857	-0.357	-0.360	7.266	-0.354	5.093	3.778
8.0	0.252	-0.908	-0.911	6.608	-0.906	4.738	3.857

MUL-7025

FIG. 2. Dipole moments for the ground and excited states of LiH, as a function of internuclear distance.

with the exact calculation. Elsewhere, there is only qualitative agreement. In general, it has been found that the sign of the apparent moment is correct but that not much confidence should be placed in the magnitude.

IV. DIPOLE STRENGTH OF THE $^1\Sigma^+ - ^1\Sigma^+$ TRANSITION

Experimental values of the dipole moment have not yet been reported for either the ground or the excited state. A related experimental quantity is the dipole derivative at the equilibrium internuclear separation. A comparison between calculated and experimental values reported by Norris and Klemperer⁷ showed reasonable agreement with respect to sign and order of magnitude.

Another possibility for comparison is the effective electric moment of the transition. The matrix element of the dipole moment between the two $^1\Sigma^+$ states,

$$R^{10} = e \int \Psi_1 \bar{r} \Psi_0 d\tau,$$

can be easily computed theoretically and compared with the experimental integrated absorption coefficient by means of the relation

$$\int k_\nu d\nu = \frac{8\pi^3 \nu_{10}}{3hcN_0} |R^{10}|^2, \quad (1)$$

where N_0 is the number of atoms per cm^3 in the ground state. Experimental results may also be given in terms of the oscillator strength,

$$f^{10} = \frac{8\pi^2 mc \nu_{10}}{3he^2} |R^{10}|^2, \quad (2)$$

where m and e are the mass and charge of the electron, respectively.

Table X gives values for the effective electric moment of the transition R^{10} (in units of 10^{-18} esu-cm) and for the oscillator strength f^{10} at

⁷W.G. Norris and W. Klemperer, J. Chem. Phys. 28, 749 (1958).

TABLE X. Computed electric moments and oscillator strengths.

	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0	∞
R^{10}	2.370	2.825	3.065	3.363	3.754	4.865	6.103	6.505	6.355	6.030
f^{10}	0.072	0.100	0.112	0.121	0.132	0.165	0.211	0.237	0.245	0.254

each internuclear distance. There are several reasons why the intensity of this transition is expected to be relatively strong with f values between 0.1 and 1. In the first place, high-intensity transitions are usually associated with parallel transitions ($\Delta\Lambda = 0$). The example here is closely related to a class of transitions that Mulliken has termed charge-transfer spectra.⁸ Characterizing this type of transition is electron promotion from bonding to non-bonding or antibonding orbitals. In other words, some aspects of charge resonance appear in the transition, as can be seen from the change in sign of the dipole moment or, more qualitatively, from the change in the gross atomic populations.

The variation of the electric moment with internuclear distance over the range involved is assumed small in the quantum-mechanical formulation of the Franck-Condon principle.⁹ Earlier work on H_2^{10} showed the theory to be in disagreement with experiment and indicated that the r variation of the electric moment could not be disregarded. A large change of the moment with r , but in the opposite direction, occurs here also, although not so pronounced in the important region between 2.6 and 4.0 au.

⁸R. S. Mulliken, J. Chem. Phys. 7, 20 (1939).

⁹G. H. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 199.

¹⁰H. M. James and A. S. Coolidge, Phys. Rev. 55, 184 (1939).

Unfortunately, experimental values for the transition probabilities do not appear to be in the literature. It would be interesting to compare such results with the computed values of Table X in the event that dipole moments for the ground and excited states are not forthcoming in the near future. A reasonable check with respect to these off-diagonal elements of the dipole moment would give more confidence in the computed diagonal elements.

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