Configuration Interaction in the Lithium Hydride Molecule. II. An SCF LCAOMO Approach

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Numerical Hartree-Fock lithium orbitals and a $1s$ exponential hydrogen orbital have been used as basis functions for a self-consistent field molecular orbital calculation of the electronic structure of the LiH molecule. The molecular orbitals were approximated as linear combinations of the atomic orbitals. Calculations were carried out at nine internuclear distances for both the ground state and the first excited state. Configuration interaction was included with the restriction that the 1σ molecular orbital remains filled. Comparison is made with the determinantal atomic orbital calculation reported in an earlier paper.

I. INTRODUCTION [1]

A DETERMINANTAL AO calculation of LiH has been described in a previous report,[2] hereafter referred to as I. A valence-bond configuration was chosen to represent the ground state, and a CI treatment was superimposed on this. It was found that, although the Löwdin formalism[3] provided a systematic method for handling determinantal functions composed of sets of nonorthogonal AO's, the problem of nonorthogonality remained one of the chief disadvantages.

The alternative Hund-Mulliken MO scheme[4] proceeds directly to form a set of orthonormal one-electron MO's. In a manner directly analogous to the *aufbauprinzip* in atomic structure, electrons are introduced into a nuclear environment and a set of MO's of successively higher orbital energy obtained. In principle, the best set of MO's obtainable from a single determinantal representation of the molecular wave function would result from solving a set of SCF integro-differential equations in direct correspondence with Hartree-Fock procedures for atomic systems. In practice, multicentered (multidimensional) numerical integration has proven a major difficulty.

In an important paper[5] Roothaan formulated the Hartree-Fock method for MO's approximated as LCAO's, and this procedure has turned out to be very popular and powerful for obtaining good solutions to molecular problems. A number of recent *ab initio*

calculations have been based on this scheme[6–11]; several included CI and evaluation of the molecular energy at more than one internuclear distance.

The present paper is based on the Roothaan procedure. SCF MO's are determined at nine internuclear distances. CI is introduced and the molecular energy, dissociation energy, and dipole moment are obtained as functions of the internuclear distance.

II. METHOD OF CALCULATION

The AO's forming the basis set are Hartree-Fock numerical lithium functions and a normalized Slater hydrogen $1s$ orbital and have been defined explicitly in I [Eq. (2)]. To evaluate the integrals between AO's the hydrogen orbital was expanded about the lithium nucleus by the method of Barnett and Coulson, Lundquist and Löwdin [references 14 and 15, and Eqs. (4) and (4a) of I]. The integrals are listed in I, Tables IA and IIA of the Appendix.

The determinantal AO approach and the SCF MO approach provide equivalent solutions of the eigenvalue problem when the set of AO's of the former case form the basis for an orthogonal set of MO's for the latter case and when CI is carried out among all possible configurations in both cases. The restricted CI which has been carried out here is such that the two approaches remain nearly equivalent. The result is a check on the internal consistency of the calculations.

The Roothaan procedure provides an approximate Hartree-Fock solution for a molecular system. One obtains a set of orthonormal MO's which minimize the energy of a single Slater deteriminant representing the ground-state molecular wave function. These MO's are formed as linear combinations of the chosen basis set of one-electron AO's:

$$\varphi_i = \Sigma_p c_{ip} u_p, \tag{1}$$

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[1] Abbreviations defined in I and used here are: AO, atomic orbital; LCAO, linear combination of atomic orbitals; MO, molecular orbital; SCF, self-consistent field; CI, configuration interaction. In the present paper SCF LCAO–MO's are abbreviated as SCF MO's for convenience.

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TABLE I. Molecular orbital coefficients.

MO	c_{ip}	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
1σ	c_{11}	0.995823	0.999103	0.999631	0.999847	0.999925	0.999979	0.999994	0.999998	0.999999
	c_{12}	0.004470	0.000518	−0.000012	−0.000091	−0.000057	−0.000067	−0.000116	−0.000156	−0.000162
	c_{13}	−0.004780	−0.003084	−0.002720	−0.002567	−0.002443	−0.002076	−0.001697	−0.001404	−0.001190
	c_{14}	0.016565	0.005940	0.003487	0.002265	0.001742	0.001176	0.000784	0.000511	0.000331
2σ	c_{21}	0.208550	0.113396	0.075146	0.045540	0.028021	0.010838	0.004172	0.001568	0.000557
	c_{22}	0.230174	0.292491	0.328847	0.360948	0.382230	0.408735	0.432739	0.456240	0.486274
	c_{23}	−0.167149	−0.184095	−0.204796	−0.227525	−0.243765	−0.263537	−0.269030	−0.261517	−0.241286
	c_{24}	−0.800631	−0.736362	−0.702165	−0.677573	−0.669679	−0.681458	−0.707050	−0.736786	−0.760565
3σ	c_{31}	−0.037798	−0.017957	−0.011519	−0.006903	−0.004251	−0.001508	−0.000360	0.000128	0.000296
	c_{32}	0.752666	0.741289	0.743195	0.752075	0.764147	0.789464	0.809265	0.824864	0.831991
	c_{33}	0.665646	0.666855	0.660135	0.645380	0.626386	0.582931	0.537011	0.483519	0.422447
	c_{34}	0.152008	0.129849	0.125553	0.128336	0.137902	0.168274	0.214075	0.274043	0.347343
4σ	c_{41}	−0.315291	−0.186583	−0.127407	−0.076807	−0.045518	−0.016057	−0.006103	−0.002710	−0.001524
	c_{42}	1.006762	0.942286	0.876948	0.786429	0.699031	0.554265	0.446086	0.358002	0.279075
	c_{43}	−0.988533	−1.016060	−1.010702	−0.986974	−0.956146	−0.902744	−0.875573	−0.875691	−0.894037
	c_{44}	1.246164	1.233294	1.200511	1.135303	1.058255	0.910698	0.789208	0.683955	0.586035

$$i\sigma = \sum_{p=1}^{4} c_{ip} u_p \qquad i = 1, \cdots, 4$$

$u_1 =$ lithium $1s$ $\qquad$ $u_3 =$ lithium $2p$

$u_2 =$ lithium $2s$ $\qquad$ $u_4 =$ hydrogen $1s$

TABLE II. Single determinant calculated energies (ry).

	2.0	2.6	3.0	3.5	4.0	5.0	6.0	7.0	8.0
Orbital energies: $\epsilon(1\sigma)$:	−4.907023	−4.932764	−4.958950	−4.987191	−5.011577	−5.051790	−5.079795	−5.100973	−5.109586
$\epsilon(2\sigma)$:	−0.640637	−0.629184	−0.610904	−0.582618	−0.551238	−0.491480	−0.438403	−0.396933	−0.363958
$\epsilon(3\sigma)$:	0.035600	0.021189	0.011757	0.001171	−0.008227	−0.026797	−0.042619	−0.058773	−0.072099
$\epsilon(4\sigma)$:	0.531794	0.562847	0.563403	0.533829	0.483794	0.371265	0.277110	0.199242	0.143615
Total electronic energy:	−18.779575	−18.235152	−17.951623	−17.662049	−17.425026	−17.059417	−16.787026	−16.585079	−16.426432
Nuclear repulsion energy:	3.000000	2.307692	2.000000	1.714286	1.500000	1.200000	1.000000	0.857143	0.750000
Total molecular energy:	−15.779575	−15.927460	−15.951623	−15.947763	−15.925026	−15.859417	−15.787026	−15.727936	−15.676432
− (H+Li atomic energy)[a]:	15.865470	15.865470	15.865470	15.865470	15.865470	15.865470	15.865470	15.865470	15.865470
Dissociation energy[b]:	0.085895	−0.061990	−0.086153	−0.082293	−0.059556	0.006053	0.078444	0.137534	0.189038

[a] Experimental value $= -15.95594$ ry.

[b] Experimental value $(D_e) = -0.18493$ ry.

where the linear coefficients, c_{ip}, are evaluated variationally and are solutions of the matrix equation

$$(\mathbf{H}+\mathbf{G})\mathbf{c}_i = \epsilon_i \mathbf{S}\mathbf{c}_i. \qquad (2)$$

The program for this process has been written by A. Meckler and R. K. Nesbet for the MIT digital computer, Whirlwind, and requires for input the one- and two-electron integrals and an initial estimate of the density matrix ρ $(\rho_{\lambda\nu} = \Sigma_i c_{\lambda i} c_{i\nu}{}^+)$. Equation (2) is evaluated iteratively, and the program accomplishes this by successive density matrix alterations and Hamiltonian matrix diagonalizations until a stationary density matrix is obtained. The final SCF c_{ip}, $\rho_{\lambda\nu}$, the one- and two-electron integrals transformed to the orthonormal SCF MO basis, and the one-electron energy parameters are obtained as output from the computer.
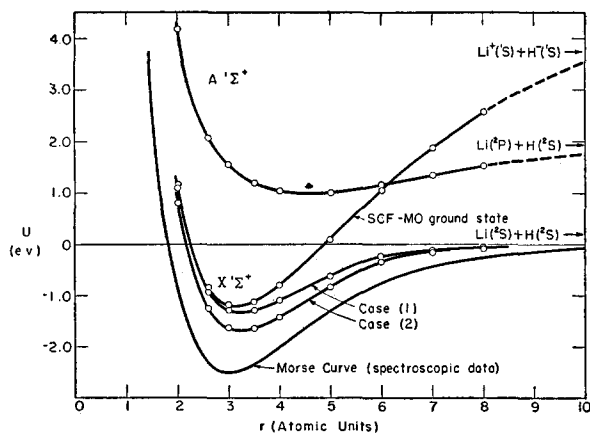

FIG. 1. Comparison of calculated potential curves for LiH.

III. BEST SINGLE DETERMINANT WAVE FUNCTION

The ground-state electronic configuration of LiH is described as $(1\sigma)^2(2\sigma)^2, {}^1\Sigma^+$. The orthonormal sets of MO's which solve Eq. (2) are listed in Table I for each internuclear distance. The 3σ and 4σ orbitals are unoccupied orthonormal MO's constructed by the computer program and are available for CI.

The orbital energies, the total molecular energy, and the dissociation energy are given for each internuclear distance in Table II. Calculation of the lithium atomic energy has been discussed in I.

The dissociation energy corresponding to the single configuration ground-state function is plotted with respect to internuclear distance in Fig. 1. The rapid deterioration of the MO method at larger distances is consistent with dissociation to $Li^+ + H^-$ instead of unexcited neutral atoms.

With the lithium nucleus taken to be at the origin, the dipole moment is given by

$$\mu = -e\int \phi^* \bar{r} \phi d\tau + er_0, \qquad (3)$$

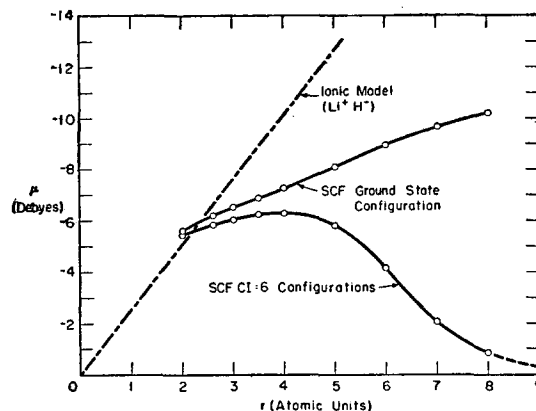where ϕ is the antisymmetrized product of the MO's

FIG. 2. Dipole moment for LiH as a function of the internuclear separation.

occupied in the ground state and r_0 is the internuclear separation. Figure 2 shows that the moment determined on the basis of the ground-state configuration overemphasizes the ionic character of the molecule at larger internuclear distances.

The negatives of the one-electron parameters approximate the ionization potentials of the molecule (Koopmans' theorem). At 3 au the predicted value of the ionization energy would be 8.31 ev. The ionization energy is thought to be about 8 ev.[12]

IV. CONFIGURATION INTERACTION

As previously discussed in I the method of superposition of configurations allows, in principle, an exact solution of the wave equation when complete sets of one-electron functions and all configurations are used. For practical reasons restricted sets of orbitals must be chosen and a judicious choice of configurations used as terms in the molecular wave function. The total molecular wave function is taken to be a linear combination of such configurations

$$\psi = \Sigma_r a_r \phi_r, \qquad (4)$$

and the energy is minimized with respect to the undetermined coefficients a_r.

For SCF MOs the leading term in the expression will be the ground-state single determinant function for which the multiplying coefficient will also be maximized. Therefore, compared to the determinantal AO method, for the first few terms of the series, convergence will

TABLE III. Enumeration of configurations ϕ_r.

ϕ_1: $(1\sigma_\alpha)(1\sigma_\beta)(2\sigma_\alpha)(2\sigma_\beta)$
ϕ_2: $(1/\sqrt{2})[(1\sigma_\alpha)(1\sigma_\beta)(3\sigma_\alpha)(4\sigma_\beta) - (1\sigma_\alpha)(1\sigma_\beta)(3\sigma_\beta)(4\sigma_\alpha)]$
ϕ_3: $(1\sigma_\alpha)(1\sigma_\beta)(3\sigma_\alpha)(3\sigma_\beta)$
ϕ_4: $(1\sigma_\alpha)(1\sigma_\beta)(4\sigma_\alpha)(4\sigma_\beta)$
ϕ_5: $(1/\sqrt{2})[(1\sigma_\alpha)(1\sigma_\beta)(2\sigma_\alpha)(3\sigma_\beta) - (1\sigma_\alpha)(1\sigma_\beta)(2\sigma_\beta)(3\sigma_\alpha)]$
ϕ_6: $(1/\sqrt{2})[(1\sigma_\alpha)(1\sigma_\beta)(2\sigma_\alpha)(4\sigma_\beta) - (1\sigma_\alpha)(1\sigma_\beta)(2\sigma_\beta)(4\sigma_\alpha)]$

[12] R. Velasco, Can. J. Phys. **35**, 1204 (1957).

TABLE IV. Coefficients for the configuration terms of the total wave function (ground state).

Configu-ration	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	0.98811	0.98659	0.98432	0.97942	0.97078	0.93471	0.85649	0.76020	0.69905
ϕ_2	−0.07310	−0.08143	−0.09068	−0.10727	−0.13171	−0.20463	−0.30291	−0.37497	−0.39204
ϕ_3	−0.02834	−0.03172	−0.03587	−0.04361	−0.05599	−0.09939	−0.18048	−0.28233	−0.38581
ϕ_4	−0.12048	−0.12442	−0.13126	−0.14449	−0.16201	−0.20033	−0.21570	−0.19244	−0.14744
ϕ_5	0.04799	0.05602	0.06429	0.07926	0.10323	0.18440	0.30834	0.40583	0.43202
ϕ_6	0.02605	0.01947	0.01564	0.01305	0.01414	0.02065	0.02247	0.00689	−0.01992

TABLE IVa. Coefficients for the configuration terms of the total wave function (excited state).

Configu-ration	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	0.06578	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

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

Sequence of configu-rations in-teracting	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	0.08589	−0.06199	−0.08615	−0.08229	−0.05956	0.00605	0.07844	0.13753	0.18904
ϕ_2	0.08266	−0.06598	−0.09082	−0.08808	−0.06693	−0.00625	0.05750	0.10411	0.14203
ϕ_3	0.08197	−0.06679	−0.09180	−0.08938	−0.06878	−0.01040	0.04718	0.07952	0.08937
ϕ_4	0.06022	−0.09047	−0.11761	−0.11875	−0.10258	−0.05587	−0.00859	0.02088	0.04064
ϕ_5	0.05958	−0.09134	−0.11869	−0.12026	−0.10488	−0.06194	−0.02450	−0.01076	−0.00471
ϕ_6	0.05901	−0.09167	−0.11890	−0.12040	−0.10504	−0.06222	−0.02476	−0.01078	−0.00485

be more rapid for internuclear distances near or smaller than the equilibrium separation.

Table III lists the configurations which have been considered. Electrons were not promoted from the 1σ orbital. The interaction between such highly excited configurations and the ground state can be shown by second-order perturbation theory to be negligible. Configurations ϕ_5 and ϕ_6 formed by excitation of a single electron from the ground state have no first-order interaction with the ground state (Brillouin's theorem). At larger internuclear distances the effect of interaction with the ground state through intermediate excited states becomes important, and such configurations as ϕ_5 and ϕ_6 cannot be neglected. In the present case to obtain a uniform treatment at each internuclear distance all configurations in Table III were used.

Tables IV and IVa list the coefficients a_r for the total molecular wave functions at each internuclear distance for both $^1\Sigma^+$ states. Table V gives the binding energy for the ground state at each internuclear distance as a function of the configurations considered in the inter-action. Tables VI and VIa give a comparison of the binding energies calculated in this paper and in I.

The resulting potential curves are plotted in Fig. 1. The ground state has been labeled "case (2)" because of the equivalence with case (2) in I. Case (1) ($2p$ orbitals omitted from the basis set) is shown for comparison.

The complete dipole moment is given by

$$\mu = -e \int \psi^* \bar{r} \psi d\tau + e r_0 \qquad (5)$$

and is shown as a function of the internuclear distance in Fig. 2. There is agreement to four or five places with the previous determinantal AO calculations. For the $^1\Sigma^+$ excited state μ was found to be $+3.44D$ at $r_0 = 5$ au in agreement with I.

V. DISCUSSION OF RESULTS

The range of internuclear distances for which the MO's have been obtained permits an examination of their change in character as the distance between the

nuclei changes. The description is more significant at the larger distances because of the choice of AO's which are characteristic of the free unperturbed atoms.

The MO correlation diagrams[13] indicate that in going from the situation of the united atom to the separated atoms, the 1σ MO would arise from a beryllium $1s$ AO and gradually transform to a lithium $1s$ AO. In the present case the 1σ MO is seen to be a nearly pure $1s$ function over the range of r considered. This accounts for the striking agreement between the CI results of the determinantal AO method and the present SCF MO method. We would expect the latter approach to give somewhat lower molecular energies since there is a small amount of mixing in of the lithium $1s$ orbital in the remaining MO's. This is noticeable at smaller internuclear distances where the $1s$ coefficient departs from unity in the 1σ MO (cf. Tables I, VI, and VIa).

The 2σ MO originates from a beryllium $2s$ AO and transforms to a hydrogen $1s$ function for the separated atoms. The 3σ MO is similarly associated with a beryllium $2p$ orbital and a lithium $2s$ orbital. The calculation has been carried out to sufficiently large internuclear distances so that trends are becoming evident, but a complete separation of the 2σ and 3σ MO's in terms of the hydrogen $1s$ and lithium $2s$ AO's has not yet taken place.

When CI is included, there is nearly exact agreement between the atomic and molecular energies and the molecular constants obtained by the present method and the previous determinantal AO method. The fact that the MO single determinant ground-state function does not correlate the electronic motion sufficiently is indicated by the rapidly rising values of the energy and dipole moment at larger distances. At infinite separation the single determinant energy, representing $Li^+ + H^-$, will be about 4.68 ev above that for the neutral atoms. In Fig. 2 the dipole moment is shown for a completely ionic model in order to illustrate the large ionic character of the single determinant dipole moment.

TABLE VI. Comparison of calculated ground-state binding energies (ev).

r_0 (au)	Determinantal AO CI method	SCF MO CI method	Δ
2.0	0.80717	0.80261	0.00456
2.6	−1.24609	−1.24691	0.00082
3.0	−1.61669	−1.61733	0.00064
3.5	−1.63717	−1.63768	0.00051
4.0	−1.42826	−1.42872	0.00046
5.0	−0.84601	−0.84629	0.00028
6.0	−0.33676	−0.33685	0.00009
7.0	−0.14669	−0.14665	−0.00004
8.0	−0.06616	−0.06602	−0.00014

[13] G. H. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 328.

TABLE VIa. Comparison of calculated excited-state energies (ev).[a]

r_0 (au)	Determinantal AO CI method	SCF MO CI method	Δ
2.0	4.1804	4.1677	0.0127
2.6	2.0630	2.0620	0.0010
3.0	1.5081	1.5084	−0.0003
3.5	1.1786	1.1795	−0.0009
4.0	1.0352	1.0362	−0.0010
5.0	0.9909	0.9918	−0.0009
6.0	1.1534	1.1539	−0.0005
7.0	1.3302	1.3303	−0.0001
8.0	1.5317	1.5318	−0.0001

[a] Energies are relative to the separated, unexcited neutral atoms taken as zero on the energy scale. At infinite separation, $H(^2S)+Li(^2P)$ is calculated to be 1.8395 ev above the ground state.

VI. CONCLUSIONS

The total molecular wave function ψ obtained in the present paper and in I are nearly equivalent. The use of an orthogonal set of one-electron MO's is a distinct advantage in the calculation itself. The single determinant ground-state configuration gives better results than the valence-bond configuration near the equilibrium separation, but it must be supplemented with CI at larger distances for meaningful results.

States formed by the excitation of a single electron from the ground state, which would be neglected at smaller internuclear separations, may not necessarily be omitted at larger distances (e.g., configuration ϕ_5 is required to obtain binding at 7 and 8 au). Criteria established by second-order perturbation theory are valid as a basis for neglecting other configurations.

The choice of the approach to be followed depends on the information which is sought. For a limited CI near the equilibrium distance the present method would probably be more favorable. It appears that in either case reasonable estimates can be obtained for a number of molecular constants. Another order of magnitude in the agreement between most quantum-mechanical calculations and experiment would appear to be required to obtain reliable chemical information. Within the present scheme this can result by allowing more variational flexibility in the AO's forming the basis set, by extending the basis set to include orbitals of higher angular momenta, and by allowing more configurations to interact.