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The Low Electronic States of Simple Heteropolar Diatomic Molecules

II. Alkali Metal Hydrides*

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Some discussion of the nature of the V level in H_2 and M_2 is first given, then the alkali hydrides are taken up. The upper electron state involved in the one well-known band system of each of the molecules LiH, NaH, and KH is a V state. The exceptional form of its potential energy curve (shown by the abnormal band spectrum constants) can be explained satisfactorily if we suppose that the observed N and V curves result from the strong interaction of two zero approximation curves, one of atomic (M·H), the other of ionic (M^+H^-) character. The situation is analyzed in detail for LiH. It is shown that the V state of LiH, while of only partially ionic character near its minimum, goes over at somewhat larger r values into the pure ionic (Li^+H^-) curve. The N state of LiH is strongly polar near its minimum, but finally goes over into a pair of neutral atoms with increasing r. It is concluded that the "additivity" theorem for homopolar bond energies is not fulfilled in MH (nor in MX; cf. III). This conclusion is forced by the otherwise unaccountably small dissociation energy of diatomic MH. N and V levels of the molecules BeH^+, ZnH^+ and the like are identified. In CuH, AgH and AuH, the presence of d electrons is considered responsible for a lack of close analogy to MH.

1. H_2 MOLECULE

THE present paper is the second[1] in a series of three. It is devoted primarily to the diatomic alkali hydrides MH. Incidentally to an understanding of this type some discussion of H_2 and M_2 is needed.

Quantum-mechanical calculations on the normal states (N) of H_2, M_2 and MH have appeared in a number of papers.[2–5] The calculations were first made using atomic orbitals (Heitler-London method), corresponding in the case of H_2 to the electron configuration $1s\cdot 1s$. Later the usefulness in H_2 of a small ionic admixture (H^+H^- and H^-H^+, corresponding to perturbation of the $1s\cdot 1s$, ${}^1\Sigma^+_g$ approximate N state by the $1s^2$, ${}^1\Sigma^+_g$ approximate Z state: cf. Paper I and its Table I) was pointed out.[5] A similar admixture can be used in M_2, but is unimportant.

Later the advantages of the molecular orbital approximation were shown,[3, 4, 6] and, in the case of H_2,[3] of the related but much more accurate whole-molecule approximation (cf. Paper I, near end of Section 2).

By similar methods, the course of the $U(r)$ curve of the T state of H_2 has been calculated theoretically and also approximately checked experimentally.[7] Our knowledge of the T states of M_2 and MH is purely theoretical (cf. Paper I, Tables I, II). According to the Heitler-London method, the $U(r)$ curve of the T state should rise steadily with decreasing r from an asymptote corresponding to unexcited atoms. It should, however, according to the method of molecular orbitals, remain below the $U(r)$ curve of the V state at least for small r (cf. Paper I, end of Section 6).

Our principal interest here centers on the V states. Empirically, the lowest energy stable excited state of H_2 and M_2 is a ${}^1\Sigma^+_u$ state ordinarily designated as the "B" state. The only definitely known excited state of MH is likewise a ${}^1\Sigma^+$ state. These states are here identified as more or less ionic V states corresponding to the specifications in Paper I. In M_2, however, it appears that the ionic characteristics are nearly lacking, and the B states are perhaps better classified as incipient than as actual V states.

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* For a preliminary account, cf. R. S. Mulliken, Phys. Rev. **49**, 881A (1936).

[1] R. S. Mulliken, Phys. Rev. this issue, paper I.

[2] For a good general survey of the H_2 problem, cf. L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Publishing Co., 1935). In this survey, however, the states $T\,{}^3\Sigma^+_u$ and $V\,{}^1\Sigma^+_u$ are erroneously labeled ${}^3\Sigma^-_u$ and ${}^1\Sigma^-_u$ (pp. 353–4). In regard to H_2, M_2, and MH, cf. also J. H. Van Vleck and A. Sherman, "The Quantum Theory of Valence," Rev. Mod. Phys. **7**, 167 (1935), especially Sections 11, 16.

[3] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933) on H_2; H. M. James, J. Chem. Phys. **2**, 794 (1934) on Li_2.

[4] E. Hutchisson and M. Muskat, Phys. Rev. **40**, 340 (1932), Heitler-London method; J. H. Knipp, J. Chem. Phys. **4**, 300 (1936), essentially molecular orbital method.

[5] J. C. Slater, Phys. Rev. **35**, 514 (1930).

[6] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935), and references given there.

[7] Cf. H. M. James, A. S. Coolidge and R. D. Present, J. Chem. Phys. **4**, 187 (1936).

Some band spectrum and derived $U(r)$ curve data on the N and V states of H_2 and of typical examples of M_2 and MH are given in Table I; some other relevant data are given in Table III of Paper I. It will be noted that the V states are more or less abnormal, especially in MH. As will be shown below, these abnormalities can be given a reasonable explanation in accord with expected characteristics of V states.

As compared with most of the excited states of H_2, the state V has an unusually large r_e and small ω_e. Also, the potential energy curve approaches its asymptote unusually slowly with increasing r; and this asymptote, considering the large r_e and small ω_e, is unusually high above the minimum of the curve. These last features are exactly what should be found for a $U(r)$ curve derived from $H^+ + H^-$. This can be seen by referring, for example, to a figure given by the writer, showing the $U(r)$ curves of H_2.[8] In this figure, the V state is represented by a (partially Morse) curve which probably represents a tolerably good approximation to the actual $U(r)$ curve near $r = r_e$ and at larger r values. If in the same figure one plots a Coulomb curve $U(r) = A - e^2/r$, this runs fairly close to the Morse curve from 3A to 6A, but it is a little steeper; it intersects the Morse curve at about 4A, running above it for larger and below it for smaller r. [The Coulomb curve can be sketched in on the figure from the following points: 2.97 ev at 1A, 10.12 ev at 2A, 12.50 ev at 3A, 13.70 ev at 4A, 14.41 ev at 5A, 14.89 ev at 6A.]

The suggestion that the V state is of H^+H^- character was first made by Pauling;[9] it was further analyzed by Kemble and Zener.[10] Quantum-mechanical calculations by Zener and Guillemin,[11] while somewhat inconclusive in this respect, indicated that the V state is at least partially of H^+H^- character. Other calculations have also been made on this state;[2] most recently by Present,[12] using the whole-molecule approximation. As will be shown below, Present's results also give indications of H^+H^- character.

In view of calculations like those of Present, yielding close approximations to the exact wave functions, it might be thought superfluous further to consider other rougher approximations, e.g., that based on H^+H^-. Such consideration is, however, needed in the present papers because of the insight it gives into the forms of the wave

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[8] R. S. Mulliken, Rev. Mod. Phys. **4**, 46 (1932): Fig. 46.

[9] L. Pauling, Chem. Rev. **5**, 204 (1928).

[10] Cf. E. C. Kemble and C. Zener, Phys. Rev. **33**, 512 (1929).

[11] C. Zener and V. Guillemin, Jr., Phys. Rev. **34**, 999 (1929).

[12] R. D. Present, J. Chem. Phys. **3**, 122 (1935).

TABLE I. *Some band spectrum data and derived potential energy curve constants.*

Molecule and State	Band spectrum data				$U(r)$ curve constants				
	ω_e cm^{-1}	$x_e\omega_e$ (both cm^{-1})	α_e	B_e	r_e (A)	D_e (ev)	a_0 (ev)	a_1	a_2
H_2, N	4450	130.7	3.32	60.95	0.74	4.72	9.88	−1.66	+2.00
V	1358	19.97	1.196	19.99	1.29	3.56	2.85	−1.68	2.85
Li^7_2, N	351.4	2.590	0.00708	0.672	2.67	1.16	5.66	−1.92	2.03
V	255.5	1.603	0.00519	0.497	3.12	1.26	4.04	−1.89	2.33
Li^7H, N	1405.7	23.20	0.2132	7.513	1.59	2.68±0.2	8.13	−1.86	2.58
V	234.4	−28.95	−0.0783	2.819	2.59	1.25±0.2	0.65	−0.87	6.74
KH, N	983	14.40	0.0673	3.407	2.24	1.97±	8.75	−1.95	1.93
V	240	−7.01	−0.0527	1.311	3.61	1.17±	1.36	+0.23	3.63

Notes. Coefficients a_0, a_1, a_2 are those in the expansion $U(r) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdots)$, where a_0 (in cm^{-1}) $= \omega_e^2/4B_e$; $a_1 = -(1 + \alpha_e\omega_e/6B_e^2)$; $a_2 = (5/4)a_1^2 - (2/3)x_e\omega_e/B_e$. Cf. J. L. Dunham, Phys. Rev. **41**, 721 (1932); also I. Sandeman, Proc. Roy. Soc. Edinburgh **55**, Part I, 72 (1935), where the constants for state N of H_2 are calculated. For state V of H_2, C. R. Jeppesen's values of ω_e, $x_e\omega_e$, etc. have been used (Jeppesen, Phys. Rev. **44**, 165 (1933)). The coefficients a_1, a_2 for LiH are those recently computed by Crawford and Jorgensen (Phys. Rev. **49**, 11 (1936)). The other values of a_0, a_1, and a_2 have been computed by the writer. All data on r_e, ω_e, $x_e\omega_e$, α_e, and B_e, except those on H_2, may be found in the tables given by H. Sponer, *Molekülspektren, I and II* (J. Springer, Berlin, 1935 and 1936); note supplementary tables in both I and II; for state N of Li_2, Sponer erroneously gives the value of $2x_e\omega_e$ in place of that of $x_e\omega_e$. Values of D_e are dissociation energies in electron volts for dissociation of a completely nonvibrating molecule to give products as indicated in Table I of Paper I; the values for LiH are based on a careful extrapolation of the levels of the N states as given by F. H. Crawford in a letter to the writer; *in Fig. 1, somewhat smaller D_e values* (but within the likely error of the extrapolation) *have been used.* In the values of ω_e, $x_e\omega_e$, etc. in Table I, the Dunham corrections have not been made except in the case of state N of H_2; they are not always negligible, but are so for our purposes.

functions and their change with r, especially in connection with a comparative study of H_2 and other molecules where the whole-molecule approximation calculation is more difficult and has not yet been carried out.

As noted above, the V state $U(r)$ curve near $r=4A$ has almost exactly the energy one calculates for H^+H^- assuming pure Coulomb attraction between H^+ and H^-. This is just what one might expect. For smaller r values, however, deviations due to the following two modifying causes are to be expected: (1) resonance of H^+H^- with H^-H^+; (2) repulsive forces arising when the H^+ appreciably penetrates the H^- wave function. The first effect should begin to be important at larger r values than the second. On setting up the resonance integrals (cf. discussion of $H_{ii'}$ for LiH near end of Section 3), one sees that the energy change due to (1) should be about proportional to the overlapping of two H^- $1s$ orbitals, one around each nucleus. Estimating the radius of H^- for strong overlapping as 1.4A (cf. Section 3), it appears that the resonance effect should be appreciable, but not very strong, at $r=4A$. It should cause a splitting of the Coulomb curve of H^-H^+, H^+H^- into an upper (Z, ${}^1\Sigma^+{}_g$) and a lower (V, ${}^1\Sigma^+{}_u$). Thus it tends to push V below the Coulomb curve. The effect of penetration of H^+ into H^-, on the other hand, should tend to raise V above the Coulomb curve, and should presumably become strong by the time r is reduced to 2A.

Actually, in harmony with the preceding considerations, the V curve of H follows the Coulomb curve fairly closely down to about 3A, but then begins to run higher and higher relative to the latter. The necessity of this behavior is easily understood also in terms of the molecular orbital approximation, which becomes increasingly valid for decreasing r. According to this (cf. Paper I, Table I), state V for medium r is $\sigma_g\sigma_u$, ${}^1\Sigma^+{}_u$, becoming $\sigma_g 2p\sigma_u$ and finally $1s\sigma_g 2p\sigma_u$ for smaller r (united-atom orbitals). The configuration $\sigma_g 2p\sigma_u$ demands that the V curve shall be higher than that of, for example, $\sigma_g 2s\sigma_g$, ${}^1\Sigma^+{}_g$. In order to satisfy this requirement, the V curve must swing away from the Coulomb curve and rise far above the latter as r decreases.

Examination of the figure mentioned above shows that the large r_e and small ω_e of state V can be understood as an incidental consequence of this process. So long as the atomic orbital approximation holds fairly well, the V curve tends to be of the Coulomb type. Under this influence, in the range from 2.0 to 1.5A, it descends well below the minimum of the $\sigma_g 2s\sigma_g$ curve. Near 1.3A the molecular orbital approximation $\sigma_g 2p\sigma_u$ apparently begins to be dominant and the atomic orbital approximation $\mathbf{1s}^2$ to lose its force, allowing the curve to swing upward. The large r_e may be considered a somewhat fortuitous result of this transition from the dominance of the one approximation to that of the other. If the atomic orbital dominance had been arrested either sooner or less soon, r_e would have been smaller.

Another point of view which is probably simultaneously valid is that the long down-swing of the V state $U(r)$ curve below those of other stable excited states is connected with the fact that it shares with the T state the molecular orbital configuration $\sigma_g\sigma_u$. Now there is a region of medium r values where the σ_u molecular orbital differs markedly from the united atom orbital $2p\sigma_u$ which it approximates for small r; and the difference is such that σ_u has relatively lower energy. As a result, both T and V states have, for medium r values, lower energy than other excited states. For small r values, where σ_u approximates $2p\sigma_u$, they both take their place among the 2-quantum states. For large r values, where all molecular orbital approximations fail, T and V behave more and more according to separated atom requirements.

In his whole-molecule approximation calculation of the wave function of state V, which was made only for $r=1.28A$ (equal to r_e of state V), Present found the r_{12} terms (r_{12}=interelectronic distance) to be relatively large, and seemed to have some difficulty in explaining this (reference, 12, p. 126 and footnote 18). It seems to the writer, however, that these relatively large r_{12} terms may be taken as a confirmation of the expected pronounced H^+H^- character of the wave function at $r=r_e$. If the wave function is nearly $a(H^+H^-+H^-H^+)$ for large r and nearly $\sigma_g 2p\sigma_u$ for small r, the r_{12} terms would be expected to be comparatively large for large r, but to fall to normal proportions (i.e., comparable with those in the whole-atom approximation for $1s2p$, ${}^1P$ of the He atom) for small r. For $r=r_e$ one would expect an intermediate case. Extension of Present's calculations to other r values than r_e should be of considerable interest, since according to the present interpretation, one may anticipate that the r_{12} terms will be found relatively to decrease for $r<r_e$ and to increase for $r>r_e$.

According to the foregoing discussion, one might be led to expect that for large r values state V would follow more and more nearly a pure Coulomb curve, dissociating finally into $H^+ + H^-$. There is, however, as is well known, a possible complication.

From $H(1s)$ plus $H(2s, 2p)$, there must arise, among other states, two ${}^1\Sigma^+_u$ states, which may be described by the electron configurations $1s\cdot 2q^+\sigma$ and $1s\cdot 2q^-\sigma$, where $2q^+\sigma = (2s\sigma + 2p\sigma)/2^{\frac{1}{2}}$ and $2q^-\sigma = (2s\sigma - 2p\sigma)/2^{\frac{1}{2}}$ (using the symbols $2s$, $2p$ etc. as short-hand for wave functions). Proceeding as in Section 4 and Table III of Paper I, we find $r_c = 5.4\text{A}$ as the r value at which the Coulomb $U(r)$ curve of H^+H^- tends to cross the $U(r)$ curves of $1s\cdot 2q^+\sigma$ and $1s\cdot 2q^-\sigma$, assumed horizontal.

Now, however, an extrapolation of the known vibrational levels of state V leads to an energy of dissociation which checks rather well with dissociation into $H(1s) + H'(2s, 2p\sigma)$ and not into $H^+ + H^-$. While such an extrapolation is not conclusive, since the observed levels do not go up to an energy closely approaching that for r_c, it has been generally accepted (cf., e.g., the writer's figure mentioned above[8]). This would imply that the H^+H^-, ${}^1\Sigma^+_u$ curve fails effectively to cross the $1s\cdot 2q^+\sigma$ and $1s\cdot 2q^-\sigma$ ${}^1\Sigma^+_u$ curves, but interacts with them to give modified $U(r)$ curves such that the V curve goes over continuously into $H(1s) + H(2\sigma)$.

In view of the large value of r_c, however, it appears uncertain whether or not the interaction integral near r_c is large enough to make this point of view sensible (cf. the very similar case, discussed in Section 3, of the V state of LiH, where the Li^+H^- curve tends to cross the $Li'(2p\sigma)\cdot H(1s)$ curve at $r_c = 5.1\text{A}$, noting that the $2p\sigma$ orbital of Li′ is nearly identical with that of H here). It appears quite possible that it might turn out to be more sensible to draw the $U(r)$ curve of state V as crossing the other two ${}^1\Sigma^+_u$ curves at r_c, and going up to dissociate into $H^+ + H^-$. An investigation of the high vibrational energy levels of state V would be of interest in this connection.

For values of $r < r_c$ the H^+H^- curve must fall below those of $1s\cdot 2q^+\sigma$ and $1s\cdot 2q^-\sigma$, because of the Coulomb attraction involved in the former. In this range, state V should at first be nearly pure H^+H^-.[10] In the neighborhood of $r = r_e$ of state V, however, where the atomic-orbital approximation based on H^+H^- should be beginning to fail badly in convergence (cf. Section 5 of Paper I), one would expect a considerable admixture of $1s\cdot 2q^-\sigma$ (and $1s\cdot 2q^+\sigma$?),—and other ingredients,—in the atomic-orbital-approximation wave function of V, in harmony with the results of Zener and Guillemin.[11]

2. M_2 Molecules

Empirically (cf. Table I, and Table III of Paper I), the B states of M_2 appear analogous to that of H_2, but there are several differences. In particular, r_e is much larger because of the larger sizes of the atoms involved, yet r_c for crossing of M^+M^- by $M'(np\sigma)\cdot M(ns)$ is smaller than the r_c of H_2 calculated for crossing of H^+H^- by $H'(2s, 2p\sigma)\cdot H(1s)$. Relative to the sizes of the atoms or ions, this r_c is thus *much* smaller than in H_2.

Further consideration indicates that this calculated r_c really has little significance, because the M^+M^- ${}^1\Sigma_u{}^+$ curve can no longer be nearly a pure Coulomb curve at this r. One may estimate that the radius, e.g., of the Li^- ion is several times that of the H^- ion (roughly proportional to n^2, where n = principal quantum number). If the radius of H^- for pronounced overlapping is 1.4A (cf. Section 3), then at the calculated r_c of 4.5A for Li_2, the Li^+ ion in Li^+Li^- must already have strongly penetrated the Li^- ion, making the energy much higher than the Coulomb value $A - e^2/r$. Resonance of Li^+Li^- with Li^-Li^+ must of course also exist, tending to lower the energy, but there are also repulsions between K shells of the Li atoms, tending to raise it. On the whole, there seems to be little doubt on this score that the Li^+Li^- curve at $r = 4.5\text{A}$ and all the more so at $r = r_e$ of state B (3.12A for Li_2), would lie rather far above the pure Coulomb curve.

The actual energy of state B at $r = r_e$ is found, however, to be very nearly as low as for a pure Coulomb curve of M^+M^-, i.e., relatively much lower even than in H_2. According to the preceding paragraph, this cannot be taken to mean that the actual wave function is nearly pure M^+M^- but, on the contrary, indicates that it must be mainly something else. There are two lines of evidence which indicate the nature of the wave function.

In the first place, Heitler-London calculations by Furry[13] for Li_2 have succeeded in duplicating fairly well the empirical characteristics (D_e, r_e, and ω_e) of the B state by using the pure atomic orbital configuration $2s \cdot 2p\sigma$ (dissociation into $^2S+^2P$). However, such a calculation is not conclusive, in view of the usual roughness of Heitler-London approximations.

Strong support is nevertheless given to the electron configuration $ns \cdot np\sigma$ for state B of M_2 by a study of the size of Λ-doubling in the rotational levels of the C state. This is a $^1\Pi$ state to which the atomic orbital configuration $ns \cdot np\pi$ should be assigned (with dissociation, like the B state, into $^2S+^2P$). To be sure, the Heitler-London calculations of Furry[13] on the C state of Li_2 show rather poor agreement with experiment, casting doubt on the goodness of Heitler-London approximations here and in general. Nevertheless the Λ-doubling coefficients q_0 for the $C\,^1\Pi_u$ states of Li_2 and Na_2 show almost perfect agreement with values of q_0 calculated on the basis of a relation of "pure precession" between the states $B\,^1\Sigma^+{}_u$ and $C\,^1\Pi_u$;[14] the agreement is especially notable in view of the fact that q_0 is about fifteen times as large for Li_2 as for Na_2. This agreement constitutes strong evidence that the wave functions of states B and C differ only in the substitution of $np\sigma$ in the one for $np\pi$ in the other. Taken together with the Heitler-London calculation on $2s \cdot 2p\sigma$ for Li_2, they tend to indicate that the wave function of state B in terms of atomic orbitals is of $ns \cdot np\sigma$ character without much M^+M^- or other admixture.

For small r values, the lowest energy $^1\Sigma^+{}_u$ state must be one of the kind we have called V, with an electron configuration $\sigma_g\sigma_u$ (same as for state T) in terms of molecular orbitals. There can be no reasonable doubt that state B goes over into this for small r values. State B of M_2 may then be classified as a V state, or possibly as an incipient V state. According to the results of the preceding paragraphs, it differs apparently from most V states in not having a large ionic component in its wave function, and in the fact that it does not even try to go over into two ions on dissociation.

It is not entirely clear just how good, relatively, are the atomic orbital approximation $ns \cdot np\sigma$ and the molecular orbital approximation $\sigma_g\sigma_u$ at $r=r_e$ of state V. Furry's evidence that the Heitler-London calculation is poor for the $^1\Pi_u$ state of Li_2, and a comparison of Heitler-London and molecular orbital calculations for state N of Li_2,[3] indicate that the molecular orbital approximation is the better at r_e of N and perhaps at r_e of V. If so, the amount of M^+M^- in the approximation using atomic orbitals may after all be considerable for $r=r_e$, but certainly not for large r values.

On the other hand, the Λ-doubling evidence seems at first to require the pure atomic orbital configuration. Still, it seems not at all impossible that a relation of "pure precession" might be fairly well preserved between the $B\,^1\Sigma^+{}_u$ and the $C\,^1\Pi_u$ states even if molecular orbital configurations were best for both; this is a point which requires further investigation. [In H_2, the Λ-doubling in the $C\,^1\Pi_u$ state again indicates[14] fulfillment of a relation of pure precession between this and the $B\,^1\Sigma^+{}_u$, i.e., V, state, but the result can be understood in terms of an approach to united atom configurations $1s2p\pi$ and $1s2p\sigma$, respectively. In M_2 the wave functions are surely remote from united-atom conditions.]

3. MH MOLECULES

The V states of MH are unique among all known states of diatomic molecules in having negative values for the band spectrum constants α_e and $x_e\omega_e$ (cf. Table I). Corresponding to this, the quantities $B_v=B_0-\alpha_e v+\cdots$ and $\omega_{v+\frac{1}{2}}\equiv G(v+1)-G(v)=\omega_e-2x_e\omega_e(v+1)$ increase with increasing v; each of them finally reaches a maximum, however, then decreases.

These unusual characteristics indicate, of course, that the V states of MH have $U(r)$ curves of quite unusual shape. The behavior of $\omega_{v+\frac{1}{2}}$ can be shown to mean that $U(r)$ at first rises on both sides of r_e faster than a parabola, while the behavior of B_v means that the $U(r)$ curve here has less asymmetry than such curves normally do. In all other known cases the asymmetry is sufficient to make α_e positive.

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[13] W. H. Furry, Phys. Rev. **39**, 1015 (1932); Phys. Rev. **43**, 361 (1933): excited states of Li_2.

[14] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 97 (1931).

The situation can be understood by expressing $U(r)$ in terms of a series expansion about r_e (cf. Table I, notes), and by plotting it (cf. Fig. 1). Several coefficients in this expansion for LiH have been determined by Crawford and Jorgensen from their very careful work on LiH and LiD. The first three coefficients, namely a_0, a_1, and a_2 are given for the states N and V of H_2, Li_2, LiH and KH in Table I.

It will be noted that the values of a_1 and a_2 remain fairly constant in the states listed (also for other diatomic molecules) except in the states V of MH. As for a_0, while this coefficient is more variable in general than a_1 and a_2, it will be noted that it is extraordinarily low for the V states of MH, especially LiH.

Theoretically as well as empirically, the V states of MH must obviously differ in some respects strongly from those of H_2 and M_2. In H_2 and M_2, we have a homopolar V, ${}^1\Sigma^+{}_u$ state containing the ionic terms A^+B^- and A^-B^+ in equal proportions in its wave function; and the latter is excluded by symmetry from any admixing with the wave function of the atomic type $(A \cdot B)$ normal state N, ${}^1\Sigma^+{}_g$. In MH, on the other hand, we might expect a strongly polar V, ${}^1\Sigma^+$ state because $M^+ + H^-$ is very much lower in energy than $M^- + H^+$ (cf. Table III of Paper I) so that M^+H^- should predominate greatly over M^-H^+ in the wave function. The considerations advanced in Section 6 of Paper I, however, indicate that state V must be less polar than state N.

If for the moment we neglect minor disturbing elements, there can be little doubt that the following statement is essentially correct: the observed N and V states of MH represent the results of an interaction between two first approximation ${}^1\Sigma^+$ $U(r)$ curves, the one homopolar and derived from unexcited neutral atoms, the other ionic and heteropolar, derived from $M^+ + H^-$. As we shall see, this makes easily understandable the unusual shape of the $U(r)$ curve of state V.

Since the substances MH are known to form ionic NaCl-type crystal lattices, and to give H^- ions on electrolysis, it would seem reasonable to expect that state N is mainly ionic and state V mainly homopolar, as in MX. From the general chemical standpoint, also, one would say that H is much more electronegative than M, so that MH (in its N state) should be strongly polar. Again, according to the writer's scale of "absolute electroaffinity,"[15] MH should have a polarity comparable with that of HF. No more than a rough qualitative significance should be attached to this prediction, however, since the scale is not really applicable in a case like the present, where $M^+ + H^-$ lies near $M + H$, with $M^- + H^+$ far above.

From here on, we shall consider mainly LiH as a typical example of MH, since more experimental data are available than for other MH.

Before going further, we should notice one, at first innocent looking, fact which really is perhaps just as anomalous as the unusual form of the V state $U(r)$ curve. This fact is the value of the dissociation energy of state N. Although the $U(r)$ curve of N is entirely normal in *form* so far as we know, its D_e value is inexplicably low as judged by the empirical "additivity" theorem for the energies of normal homopolar bonds.

If this theorem holds, then, as Pauling has pointed out, the dissociation energy D_e (usually D_0 is considered, but D_e is more accurate) of any molecule AB should be equal to or greater than the average of the dissociation energies of the molecules A_2 and B_2; and the quantity Δ, where Δ is given by

$$\Delta = D_e(AB) - \tfrac{1}{2}[D_e(A_2) + D_e(B_2)], \qquad (1)$$

should be some sort of measure of the degree of polarity of the bond.[15, 16] In particular, $\Delta = 0$ should correspond to the case of a pure homopolar bond, provided the additivity theorem holds. (This statement really defines the additivity theorem.) A pure homopolar bond is that type of bond which occurs when A and B are of equal "electronegativity" or "electroaffinity;" it is obviously realized when A and B belong to the same element, but should also be approximately realizable for various other atom pairs. Pauling found by a study of $\Delta^{\frac{1}{2}}$ values that he could assign a number of atoms A and B approximately to places on an empirical electronegativity scale; this fact implies that the homopolar additivity theorem is approximately valid for all such atom pairs AB.

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[15] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934); **3**, 573 (1935).

[16] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

In the case of LiH, however, one finds (cf. Table I),

$$\Delta = 2.68 \pm 0.2 - \tfrac{1}{2}[4.72 + 1.16] = -0.26 \pm 0.2.$$

If anything, D_e is probably somewhat less than 2.68 volts for LiH, making Δ probably about -0.4; the value 2.68 ± 0.1 or ± 0.2 is that obtained by Crawford from the band spectrum data on the vibrational levels of state N (cf. Table I, notes). If Δ is negative, the additivity theorem certainly has failed; even if it is zero, which is about the extreme upper limit experimentally allowable, we are in a dilemma. Pauling and Yost, noting that Δ is approximately zero, concluded that diatomic LiH is nonpolar.[17]

This conclusion, however, is hard to swallow, in view of the considerations given above, according to which one would expect LiH (in its N state) to be strongly polar. Some of the objections to nonpolarity of LiH may be put more specifically as follows. If state N is pure nonpolar (structure Li·H), then state V must be pure polar (Li^+H^-). This is in violent contradiction to the theorem given in Section 6 of Paper I. Further, it fails to explain the unusual shape of the $U(r)$ curve of state, V: a pure Li^+H^- curve could not have such a shape. Moreover, it would be astonishing if the two curves (Li^+H^- and Li·H) do not interact appreciably; judging from other known cases (cf. III for some of these), as well as from perturbation theory considerations, a strong interaction, giving a large Δ for state N if the additivity theorem holds, would be expected.

Nevertheless something must be abnormal. On due consideration one finds that, if one assumes *failure of the additivity rule*, everything else follows expectation. As we shall find in Paper III, this assumption has support from the case of molecules MX, where spectroscopic data make it very reasonable to suppose that the additivity rule fails completely. Further (see below), failure of additivity allows a more reasonable location for the T state $U(r)$ curve of LiH in Fig. 1 than would be predicted if additivity holds.

On the other hand, Heitler-London calculations (cf. James' critical study[2, 3]) on Li_2, LiH and H_2, neglecting inner shells in the cases of Li_2 and LiH, and necessarily assuming a pure homopolar bond in LiH, obey the additivity rule fairly well (calculated values 2.87 ev for H_2, 1.09 ev for Li_2, 2.30 ev for LiH). To be sure, James has shown[3] that inclusion of inner shell terms modifies the result for Li_2 very considerably; presumably LiH would also be decidedly affected. But if the effect is about half as large for LiH as for Li_2, as one would surmise, the additivity theorem would still hold fairly well. On the whole, these Heitler-London considerations, although not conclusive, tend decidedly to support the validity of the homopolar additivity rule for LiH. But other considerations weigh strongly in favor of its failure.

In view of the unusual assumption which seems required to explain it, it is obviously essential to be quite sure that the experimental D_e value is well founded. Actually, there seems to be no reasonable doubt that the value given above is experimentally correct to within an amount that is far too small to allow a Δ of the order of magnitude (about 2 ev, giving about 4.5 or 5 ev for D_e) that one would expect if the homopolar additivity law held and if the Δ were related in a normal way to the expected polarity.

In the first place, Crawford and Jorgensen have followed the vibrational levels of state N of LiH up to $v=6$, and find the energy of all the observed levels to be capable of representation with great accuracy by a simple formula of the type

$$\omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 + y_e\omega_e(v+\tfrac{1}{2})^3.$$

In view of the smoothness of fit of the formula to the observed levels, which moreover already extend over a range of about 1 electron volt, it appears that extrapolation of the formula to estimate D_e should be relatively reliable. Experience with other molecules indicates that the extrapolated value should be nearly correct (Crawford gives 2.68 ± 0.1 or ± 0.2 ev), and if not, that the true value is more likely to be smaller than larger.

A supporting line of argument is the following. It is readily verified that the following equation is correct (all quantities are assumed reduced to 0°K):

$$D_{\mathrm{MH}} = Q + S_{\mathrm{M}} + \tfrac{1}{2}D_{\mathrm{H}_2} - S_{\mathrm{MH}} \tag{2}$$

Here the D's refer to dissociation energies from $v=0$, Q is the energy of reaction (solid $M+H_2$ gas$\rightarrow$solid MH), and the S's are sublimation energies. The quantities Q, S_{M}, and D_{H_2} are known ($D=4.45$ ev for H_2, $Q=0.91$ ev for LiH, 0.52 ev for NaH, KH, and $S_{\mathrm{M}}=1.44$, 1.14, and 0.93 ev for Li, Na, K).[18] If data on S_{MH} existed, we could get good values of D_{MH}. Conversely, if we use band spectrum values of D_{MH}, we can get values of S_{MH}.

Inserting the above values of Q, S_{M}, and D_{H_2} in Eq. (2), we find for $D_{\mathrm{MH}}+S_{\mathrm{MH}}$ the following:

$$D_{\mathrm{MH}}+S_{\mathrm{MH}}: \text{LiH, 4.59 ev; NaH, 3.92 ev; KH, 3.60 ev.} \tag{3}$$

These obviously give upper limits for D_{MH}. If in (3) we insert the band spectrum values for D_{MH} (cf. Table I), first subtracting the zero point energy included in the latter, we get

$$S_{\mathrm{MH}}: \text{LiH, 1.99 ev; NaH, 1.75 ev; KH, 1.59 ev.} \tag{4}$$

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[17] L. Pauling and D. M. Yost, Proc. Nat. Acad. Sci. **18**, 414 (1932).

[18] Cf. J. Sherman, Chem. Rev. **11**, 93 (1932) for sources of data.

These values are fairly reasonable, considering that the solids MH have the same type of crystal structure as the salts MX, and that they apparently have a similar degree of volatility if we may judge from the fact that in work on the absorption band spectra of MH vapor, experimenters mention that the solid was heated to 600–900°C in order to obtain sufficient absorption. Similar or even somewhat lower temperatures have been used in investigating MX vapors. For salts MX, the values of S_{MX} are in the neighborhood of 1.9–2.4 ev.[18]

Further, in a quantum-mechanical calculation based on the use of molecular orbitals, and including the effects of the Li inner electrons but not of the r_{12} terms, Knipp[4] arrives at a value of about 2.0 ev for D_e of LiH. This of course supports the band spectrum value, and again indicates a negative Δ. Finally, as we shall see below, a consideration of the behavior of the V state $U(r)$ curve at large r values strongly indicates a value of about 2.5 ev for D_e of state N.

Extension of Knipp's calculations to a complete whole-molecule approximation calculation, by revealing the relative size of the r_{12} terms (cf. Section 1, above), should throw light on the polarity of the wave function of state N. Even better for this purpose in some respects would be an explicit calculation of the dipole moment.

We may now turn to an examination of the $U(r)$ curves of the N and V states of LiH, in order to see if we can determine how they may be related to the hypothetical Li·H and Li$^+$H$^-$ curves. Each curve can be plotted in the neighborhood of its r_e by using the series expansion in powers of ξ. By estimating the mode of convergence of the series, the curves can be extended over a somewhat wider range of r values (full line parts of N and V curves in Fig. 1). Outside this range, uncertain extrapolations or else other new considerations must be used (dashed line parts of N and V in Fig. 1).

After plotting the known parts, with the vertical distances between them determined accurately from the band spectrum, it remains to fix the positions of these relative to the energy of Li+H. If D_e of N (or V) were accurately known, this could be done at once. Using the approximate D_e of Crawford (2.68 ev), the curves were first approximately located. Next the energy levels of Li(^2P)+H and of Li$^+$+H$^-$ relative to Li(^2S)+H were located. Then the $U(r)$ curve corresponding to Coulomb attraction of Li$^+$ and H$^-$ was computed (cf. Eq. (4) and Table III of Paper I). It is found that this crosses the Li(^2P)+H horizontal at $r_c=5.1$A and the Li(^2S)+H horizontal at $r_c=3.1$A. This Li$^+$H$^-$ curve, modified by adding a repulsion term (cf. Eq. (6)) is shown dotted in Fig. 1; the modified curve is practically the same as the pure Coulomb curve for, say, $r>3.5$A.

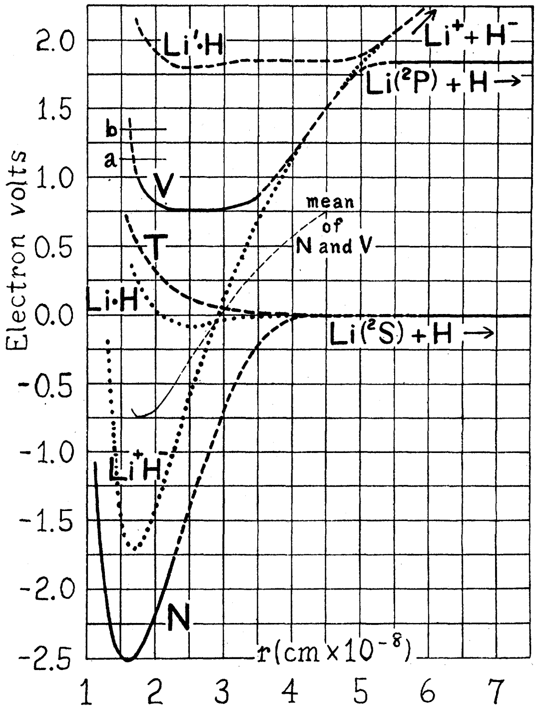

FIG. 1. $U(r)$ curves of N, T and V states of LiH. Experimentally established parts are shown by full heavy lines. Dashed parts represent estimates, except for state V, where the right hand side of the curve goes into an Li$^+$H$^-$ Coulomb curve, which should be fairly accurate. The absolute heights of V and N relative to each other are accurately known, from the band spectrum, but their heights relative to Li+H have been fixed only by making the experimentally established part of the V curve extrapolate smoothly into the Li$^+$H$^-$ curve. Dotted curves marked Li$^+$H$^-$ (cf. Eq. (6)) and Li·H are two hypothetical illustrative curves whose resonance according to Eq. (7*a*) would give the curves N and V, if the resonance intensity is as given by the main curve of Fig. 2. At the top right of the figure is indicated the effect of a weak resonance (cf. Fig. 2) between the Li$^+$H$^-$ and the Li(^2P)·H, $^1\Sigma^+$ curve near their calculated crossing point, causing crossing to be avoided and giving two new curves as shown. Dashed curve marked Li$'$·H shows possible course of $^1\Sigma^+$ curve of $np\sigma_{\mathrm{Li}}\cdot 1s_{\mathrm{H}}$ character (form doubtful!). Three further predicted curves derived from Li(^2P)+H (cf. reference 19) are omitted. According to Knipp's recent calculations,[4] the T curve is probably considerably higher than is here shown.

Dismissing the negligible possibility that the N and V curves might cross, the former must dissociate to Li+H, while the latter must go over into the Li^+H^- curve for large r. On examining the plot, one sees that in order that the observed (full line) part of the V curve shall go over as smoothly as possible into the Li^+H^- curve, a slightly smaller value of D_e for state N than the 2.68 ev value of Table I must be assumed. If we use 2.68 volts, the V curve actually crosses the Li^+H^- curve within the range where its form is definitely known from the experimental data. A slightly smaller value, 2.52 ev, gives a smooth transition, and has been used in constructing Fig. 1. In this way we arrive at what appears to be a fairly reliable value of D_e of N. At the same time we establish beyond much question the course of the $U(r)$ curve of state V for large r values.

This fitting of the V state curve, somewhat beyond its r_e, to the Li^+H^- curve, gives at once an explanation of the most striking anomalies of the V curve, namely the unusual values of the coefficients a_1 and a_2, provided we momentarily take for granted the unusually low value of a_0, which corresponds to unusual flatness of the V state curve near $r=r_e$.

In ordinary $U(r)$ curves, which can be approximated by Morse functions, the left side of the curve ($r<r_e$) rises faster than the parabola to which the bottom of the curve approximates, while the right side rises more slowly than the parabola. Moreover, in ordinary cases, the slowing down near the right side more than makes up for the speeding up near the left side so that the vibration frequency $c\omega_{v+\frac{1}{2}}$ decreases with increasing v. Such $U(r)$ curves have a pronounced asymmetry, of which the coefficient a_1 is a chief index.

The abnormally small a_1 for state V of LiH, indicating abnormally little asymmetry, the unusually large a_2, and the $\omega_{v+\frac{1}{2}}$ increasing at first with v, all mean that the right hand side of the $U(r)$ curve for this state rises much more steeply, relatively to the left hand side, than is usual. Now this can be accounted for very well as a result of the pulling up of the right hand side of the $U(r)$ curve of state V as it goes over into the Li^+H^- Coulomb-type curve (see Fig. 1). The latter rises much more steeply, at r values in the here important neighborhood of 3.5–4A, than would an ordinary curve involving dissociation into neutral atoms (cf., e.g., the dashed part of the $U(r)$ curve for state N).

It is interesting to note at what height on the V state curve the maximum of $\omega_{v+\frac{1}{2}}$ comes. The energy for this is indicated in Fig. 1 by the line marked a; the line marked b denotes the position of the highest vibrational level of state V which has been observed so far. The occurrence of a maximum value of $\omega_{v+\frac{1}{2}}$ and of B_v is easily understood in terms of the shape of the V curve.

We may pause here to refer to the data on KH (NaH also is probably similar, cf. Table I). KH shows less extreme behavior than LiH in respect to a_0 and a_2, more extreme behavior for a_1 (reversal of the usual *sign*, indicating that the V curve at first actually rises less steeply on the inner than on the outer side). One can see how this could happen if the right side of the V curve is jammed more tightly against its M^+H^- asymptote curve than is true in LiH. Without going into detail, one can appreciate that such a change might well occur as a result of the different ionization potential and size of the K as compared with the Li atom.

Returning to LiH, let us consider further how the observed N and V curves might result from the interaction of two hypothetical zero-approximation curves, the one pure Li·H, the other pure Li^+H^- in character. First we may seek to use crystal structure data in estimating the form of the Li^+H^- curve (cf. Section 4 of Paper I). In so doing, the constants β and n of a Born-type formula were first determined so as to agree with the known lattice energy and grating spacing in LiH.[18] Assuming the same β and n for diatomic LiH, we have

$$Li^+H^-: U(r)=4.65-14.30/r+9.387/r^{4.12}, \quad (5)$$

where r is in A and energy is in ev. Eq. (5) gives $r_e=1.375$A and $U(r_e)=-3.22$ ev; that is, it gives r_e considerably less and $U(r_e)$ lower than for the actual curve of state N. Obviously this will not do, since the pure Li^+H^- curve must be everywhere above the actual N curve. Eq. (5) should, however, give us some idea of the value of n, and tends to indicate that the actual pure Li^+H^- curve goes relatively low. Since we cannot readily determine how it actually goes, the following plausible equation for a pure Li^+H^- curve has been arbitrarily assumed for purposes of illustration:

$$\mathrm{Li^+H^-}: U(r)=4.65-14.30/r+17.95/r^{4.08}. \quad (6)$$

Eq. (6) has been plotted as the dotted curve marked $\mathrm{Li^+H^-}$ in Fig. 1. Obviously this curve, although dubious for small r values, should be nearly correct for large r values (say, $r>3.5\mathrm{A}$).

For the Li·H curve, it would be logical to use the results of an accurate Heitler-London calculation, especially for the larger r values. Instead, however, we have, for purposes of illustration, *assumed* the dotted Li·H curve shown in Fig. 1. The form of this has been determined largely by the requirement that it shall go over into the Li+H horizontal as $r\rightarrow\infty$, and by the fact that for small r values, *for a given assumed* $\mathrm{Li^+H^-}$ *curve*, its form is specified by perturbation theory (energy interval $V-\mathrm{Li\cdot H}$ must be at least roughly equal, at each r, to interval $\mathrm{Li^+H^-}-N$). There is, to be sure, great arbitrariness in the form of the Li·H curve even for small r, but this is not independent of the arbitrariness in the $\mathrm{Li^+H^-}$ curve, i.e., if the one is assumed, the other approximately follows. For medium r values, where there is uncertainty as to the form of the N curve, there is independent arbitrariness in the form of the Li·H curve, but not very much if one requires a smooth interpolation between small and large r.

Given the Li·H, the $\mathrm{Li^+H^-}$, and the V curves, it was possible, using the approximate perturbation theory relation just noted, to construct the dashed portion of the N curve, which should be regarded for the present as merely illustrative. The N and V curves now being given, a *median* curve marked "mean of N and V" could be drawn; this is useful in subsequent perturbation theory considerations. The median of N and V is obviously also, by perturbation theory, at least roughly the same as the median of the $\mathrm{Li^+H^-}$ and Li·H curves. In connection with the dashed part of the N curve, it should be stated that this runs above the corresponding Morse curve;[19] for example, the latter is still about 0.3 ev below its asymptote at 4A, where the N curve in Fig. 1 is already very close to the asymptote.

We may now consider these curves in relation to perturbation theory. Neglecting possible disturbances due to $\mathrm{Li^-H^+}$, $\mathrm{Li(^2\mathit{P})\cdot H}$, or other excited states, let us consider just the mutual perturbation of the hypothetical Li·H and $\mathrm{Li^+H^-}$ curves to give the real N and V curves. According to perturbation theory, the following relation exists,[20] for any r:

$$[(\tfrac{1}{2})(E_V-E_N)]^2=[(\tfrac{1}{2})(H_a-H_i)]^2/(1-S^2)+(H_{ai}-SX)^2/(1-S^2)^2. \quad (7)$$

Here E_V and E_N are the energies of states V and N, H_a and H_i are those of Li·H and $\mathrm{Li^+H^-}$, X is the mean of H_a and H_i; while H_{ai} and S are given by

$$H_{ai}=\int\psi(\mathrm{Li\cdot H})H\psi(\mathrm{Li^+H^-})d\tau;$$
$$S=\int\psi(\mathrm{Li\cdot H})\psi(\mathrm{Li^+H^-})d\tau. \quad (8)$$

Each of the quantities E_V, E_N, H_a, H_i, H_{ai} is a function of r, and all should be negative.

As an approximation leading to results which should be qualitatively correct, and adequate for our purposes, we may neglect S in Eq. (7), and obtain[10]

$$[(\tfrac{1}{2})(E_V-E_N)]^2=[(\tfrac{1}{2})(H_a-H_i)]^2+H_{ai}^2. \quad (7a)$$

The quantity H_{ai} can now be plotted, approximately, as a function of r by using data on E_V-E_N and H_a-H_i read from Fig. 1 and solving Eq. (7*a*) for H_{ai}. The results, shown in Fig. 2, are of a reasonable character. Examination of Eq. (8) indicates that H_{ai} should be more or less proportional to the overlapping integral $\int\psi(2s_{\mathrm{Li}})\psi(1s_{\mathrm{H^-}})dv$. This should be fairly large for small r values, having perhaps a maximum at $r=0$, or perhaps having two maxima, then falling off exponentially with increasing r. On decreasing r from large values, H_{ai} should first become large at an r value where $\psi(2s_{\mathrm{Li}})$ and $\psi(1s_{\mathrm{H^-}})$ begin to overlap strongly. Taking the radius of $2s_{\mathrm{Li}}$ for strong overlap as half the r_e(2.67A) of $\mathrm{Li_2}$, and estimating the corresponding radius of $\mathrm{H^-}$ as 1.4A from the Li−H distance in crystalline LiH,[18] we get $2.67/2+1.4=2.7\mathrm{A}$ as such an r value. H_{ai} in Fig. 2 seems to agree reasonably well with what one might expect from the foregoing considerations.

Thus it is seen that the two plausible illustrative curves $\mathrm{Li^+H^-}$ and Li·H assumed in Fig. 1, together with an H_{ai} of reasonable character,

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[19] Cf. R. S. Mulliken, Rev. Mod. Phys. **4**, 2 (1932) for $\mathrm{H_2}$, $\mathrm{M_2}$, MH, $\mathrm{X_2}$ potential energy curves.

[20] Cf., e.g., R. S. Mulliken, J. Chem. Phys. **3**, 578 (1935), Eq. (11).

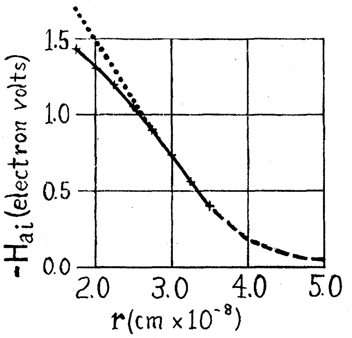

FIG. 2. Values of interaction integral $\int\psi(\mathrm{Li\cdot H})H\psi(\mathrm{Li^+H^-})d\tau$ necessary to account for N and V curves of Fig. 1 by resonance between hypothetical Li·H and $\mathrm{Li^+H^-}$ curves of Fig. 1, assuming Eq. (*7a*). The main curve in Fig. 2 (full and dashed lines) corresponds to the dotted curves in Fig. 1. The dotted curve in Fig. 2 shows how H_{ai} is modified if the left sides of the dotted curves of Fig. 1 are both replaced by a common curve coinciding with the left side of the median curve "mean of N and V" shown in Fig. 1.

suffice to account for the observed shapes of the N and V curves of LiH. The highly unusual form of the V curve and the highly normal form of the N curve are simultaneously obtained without difficulty.

It is now desirable to see how the $\mathrm{Li^+H^-}$ and Li·H curves, and the H_{ai} curve, may be varied while preserving the N and V curves unchanged. The simplest variation is obtained if we raise the part of the $\mathrm{Li^+H^-}$ dotted curve to the left of its crossing with the Li·H dotted curve, and simultaneously and equally lower the left-hand part of the Li·H curve, until these parts of the two curves coincide along the median curve, making $H_a=H_i=(E_V+E_N)/2$; to the right of their original intersection point, we leave both dotted curves unchanged. [By a slight smoothing, the resulting discontinuities in slope at the intersection point can be removed without appreciably altering other things.] With the foregoing assumption, we have $-H_{ai}=(E_V-E_N)/2$ everywhere in the left-hand region. The H_{ai} curve so obtained is indicated by the dots in Fig. 2. It is readily seen that this represents the upper limit of possible H_{ai} values for the given N and V curves.

Another variation of the $\mathrm{Li^+H^-}$ and Li·H curves is obtained by *interchanging* the left-hand sides of the dotted curves in Fig. 1, leaving the right-hand sides undisturbed. [With a little smoothing, the new curves take plausible forms, with the $\mathrm{Li^+H^-}$ curve wholly above the Li·H curve.] This variation gives the same H_{ai} curve as the first case.

From the foregoing discussion, the effects of still other variations can readily be estimated. Attention should perhaps be called to the fact that if the $\mathrm{Li^+H^-}$ and Li·H curves are made to approach the N and V curves more closely than is the case in the range included in the above three variations, H_{ai} of Fig. 2 drops, at first slowly, then rapidly.

Among the three variations just considered, and others, one somewhat similar to the first appears probable according to the considerations brought up early in this section. The N state of LiH would then be predominantly polar, and the V state predominantly nonpolar, in agreement with electronegativity and related ideas and with the theorem at the end of Section 6 of Paper I.

Another argument in favor of this variation is that, with an Li·H $^1\Sigma^+$ curve as shown in Fig. 1, the corresponding Li·H $^3\Sigma^+$ curve, representing the T state, would be expected according to Heitler-London considerations to take a form about like that shown by the heavy dashed line marked T in Fig. 1. This T curve lies below the V curve in a reasonable way from the standpoint of the molecular orbital approximation, according to which T and V have the same electron configuration (cf. Table I of Paper I). As $r\rightarrow0$, T and V should go, respectively, into the $1s^22s2p$, ^3P and ^1P states of the Be atom, of which the former lies 2.54 ev below the latter. In Fig. 1, T is shown as being only 1 ev below V at r equal to r_e of state N, where the molecular orbital approximation ought presumably to hold fairly well. It is hard to believe that T could be much higher than this, and one might even expect it to be lower, as was indicated in a figure once published by the writer.[19]

Publication of the details[4] of Knipp's calculations on LiH shows, however, that the foregoing ideas must be modified somewhat. Knipp has calculated a value for the energy of state T at $r=r_e$ of N (1.59A). Knipp's value, which is an *upper limit*, is 1.89 ev above the energy of $\mathrm{Li}(^2S)+\mathrm{H}$. Knipp states that this value should be correct within a few tenths of an ev. Making a reasonable allowance corresponding to this statement, one gets about 1.6 ev as an estimate of the height of T at $r=1.59$A. This is approximately the same as the energy of state V at this r value, according to Fig. 1. It thus appears that the T curve is about 1 ev higher for $r=1.59$A than is shown in Fig. 1, the difference going to zero, however, as $r\rightarrow\infty$. It appears possible that the T curve may run somewhat above the V curve over a range of r from 1.6A to perhaps about 2.2A.

According to Heitler-London considerations, the Li·H curve should be pushed down, as compared with the dotted curve in Fig. 1, by roughly the same amount that the T curve, in accordance with the preceding considerations, is raised above the dashed T curve in Fig. 1. This would bring the Li·H dotted curve nearly down to the median curve in Fig. 1, making it more reasonable from the standpoint of Heitler-London calculations; at the same time the dotted Li^+H^- curve would have to be brought up nearly to the median curve. On the whole, this state of affairs, which will be seen to correspond approximately to the "second variation" discussed above, seems reasonably in agreement with all the various considerations advanced above, including serious failure of the homopolar additivity rule. The relatively high location of the T state curve, however, indicates that the molecular orbital approximation cannot be so very good here until r gets below r_e of N; but it should be recalled that we have used Eq. (7*a*) instead of the more accurate Eq. (7) in arriving at this conclusion.

Before concluding this section, something should be said about a possible disturbing effect of the $Li(^2P)\cdot H$ curve on the other curves. $Li(^2P)+H$ should give rise to four states,[19] of the types $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$, of which the last two need not concern us. From the Heitler-London approach, one would expect the $^1\Sigma^+$ and $^3\Sigma^+$ curves to be very similar to those obtained from $Li(^2S)+H$. If the latter $^1\Sigma^+$ and $^3\Sigma^+$ curves should be about as shown (marked Li·H and T) in Fig. 1, then the $Li(^2P)\cdot H$, $^1\Sigma^+$ ought to follow a horizontal course down to small r, and then behave about as shown by the dashed curve marked Li′·H in Fig. 1; the $^3\Sigma^+$ curve should then be a little higher. Under such circumstances, no very pronounced interaction would be expected between the Li′·H and Li·H curves, nor any large interaction with the inner part of the Li^+H^- curve, so that our previous neglect of such effects will not have been serious. If, however, Li·H had a deep minimum, then strong interaction between the Li′·H $^1\Sigma^+$ and the Li·H $^1\Sigma^+$ and Li^+H^- curves would have had to be considered, also between the Li′·H, $^3\Sigma^+$ and the T curve. In any case, the actual Li′·H curves would be prevented from coming down much lower than is indicated in Fig. 1.

It is of interest to inquire whether the $U(r)$ curve of state V will effectively cross the Li′·H $^1\Sigma^+$ curve at the calculated $r_c=5.1$A (cf. Table III of Paper I), or whether it will interact so strongly that state V will in effect dissociate into $Li(^2P)+H$, as is commonly assumed. This depends on the magnitude of a suitable H_{ai} at 5.1A. In Fig. 2, H_{ai} for Li·H and Li^+H^- has been extrapolated according to an exponential law (dashed part of curve) out to 5A. Assuming the extrapolation to be correct, and to be approximately applicable also for interaction of Li′·H with Li^+H^-, as seems reasonable, we can calculate the effects at r_c by an equation like Eq. (7). The results are as indicated by the two dashed curves in the top right-hand corner of Fig. 1. According to these, it looks as if the V state perhaps does effectively dissociate into $Li(^2P)+H$. It would be of some interest to make actual calculations of H_{ai} to determine whether this is nearly correct. Experimental investigation of the high vibrational levels of state V would also be of interest in this connection (note that levels up to the height b in Fig. 1 have already been reached).

Finally, we may ask whether Li^-H^+ can make any important contribution to the wave functions of V and N. Interactions of Li^-H^+ with Li·H and Li^+H^- would be determined largely by integrals $H_{ai'}$ and $H_{ii'}$ similar to H_{ai} of Eq. (8). Of these, $H_{ai'}$ should probably be relatively small, being roughly proportional to $\int\psi(1s_{\mathrm{H}})\psi(2s_{\mathrm{Li}-})dv$, while $H_{ii'}$ should be larger, being roughly proportional to $\int\psi(1s_{\mathrm{H}-})\psi(2s_{\mathrm{Li}-})dv$, but not so large as H_{ai}, which involves $\int\psi(1s_{\mathrm{H}-})\psi(2s_{\mathrm{Li}})dv$. These conclusions are based on considerations of overlapping; this should be especially favorable between $2s_{\mathrm{Li}}$ and $1s_{\mathrm{H}-}$, which are approximately equal in size, less so between $2s_{\mathrm{Li}}$ and $1s_{\mathrm{H}}$ or $2s_{\mathrm{Li}-}$ and $1s_{\mathrm{H}-}$, least so between $1s_{\mathrm{H}}$ and $2s_{\mathrm{Li}-}$. That is, overlapping appears to be especially favorable in the case of H_{ai}. From this point of view, considering also the high energy of Li^-+H^+ at $r=\infty$ (Table III of Paper I), it is not to be expected that Li^-H^+ will enter largely into the wave functions of states V and N.

This conclusion has an indirect bearing on the question of the relative position of the Li^+H^- and Li·H curves in Fig. 1. If the Li^+H^- curve were above the Li·H curve for small r, then state V would be more polar than state N unless a large admixture of Li^-H^+ wave function were added to V to cut down its polarity in order to avoid a gross violation of the theorem at the end of Section 6 of Paper I. But as we have just seen, it seems impossible that $H_{ii'}$ is large enough to produce any such large admixture. Hence an arrangement with the Li^+H^- curve below the $Li\cdot H$ curve in Fig. 1 seems required.

4. Molecules CuH, AgH, AuH, Me^+H

Without going into details, attention may be called to the fact that for each of several molecules of the type $(MeH)^+$, namely those for Me = Be, Mg, Zn, Cd and Hg, the known electronic levels comprise just two $^1\Sigma^+$ states, exactly as in MH. There can be little doubt that these are analogous to N and V of MH. The state V, however, does not show pronounced abnormalities as in MH, although there seems to be some indication of a tendency in that direction, $x_e\omega_e$ (except in HgH^+) being unusually small, but still positive. The value of ω_e is considerably smaller in the V than in the N state, but there is no such great difference as in MH. The fact that these molecules are positive ions is enough to account for marked differences in their V states as compared with those of MH, since the peculiarities of the latter have been shown to result from a highly special situation which is not likely to be duplicated by chance with so different a charge distribution as here.

Brief consideration indicates that the N state of MeH^+ should dissociate into $Me^+(^2S)+H$ (analogous to $M+H$ of MH), and the V state probably to $Me^{++}+H^-$ (analogous to M^++H^-) if it succeeds in crossing the $Me^+(^2P)+H$ curve without too much interaction. Other details presumably resemble those in MH, although the analogy is apparently not very close.

In the case of AgH, there are again two known $^1\Sigma^+$ states; in CuH and AuH there are three each. Presumably one excited state in each case is somewhat similar to the V state in MH. There are, however, no obvious resemblances in the band spectrum data; $x_e\omega_e$ is in each case actually greater for the excited than for the N state, while ω_e shows no remarkable features. It will be noted (cf. Table III of Paper I) that A^++H^- lies higher in these molecules than in MH. State N is now doubtless predominantly nonpolar.

For the atoms Cu, Ag, Au (especially Cu, Au) there is a complication not present with the atoms M, namely the presence, near the surface, of d electrons. For this reason, in building up wave functions for the low $^1\Sigma^+$ states of these molecules, using atomic orbitals, we should consider not only $A(\cdots ns,\ ^2S)\cdot H$ and A^+H^-, but also $A(\cdots d\sigma d\pi^4 d\delta^4 ns^2,\ ^2D\Sigma)\cdot H$ and perhaps $A^+(\cdots d\sigma d\pi^4 d\delta^4 ns,\ ^1D\Sigma)H^-$ too. Using molecular orbitals, similar complications also arise. These complications, and the increased energy of A^++H^- above $A+H$, and the occurrence of $A(\cdots d^9ns^2,\ ^2D)+H$ in addition to $A(\cdots np,\ ^2P)+H$ as a possible dissociation outlet, suffice to explain the lack of superficial analogy of the excited $^1\Sigma^+$ states of CuH, AgH and AuH to those of MH. The lowest excited states in these molecules are probably mixtures of a V with other types of states, and thus probably are only *partially* analogous to the V states of MH and MeH^+; perhaps it is best not to use the label V at all in these cases.