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Alkali Hydride Molecules: Potential Energy Curves and the Nature of their Binding*

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INTRODUCTION

THE alkali hydrides form an interesting series of molecules. The peculiarities of their spectra have been discussed by Pearse.[1] The spectra of the alkali hydrides provide a good example of the similarity of the energy levels and band systems of molecules formed from atoms closely related in the periodic table. The potential energy curves of the ground states of these molecules are of special interest from the theoretical point of view because these molecules have very simple electronic configurations, and are formed from two atoms each possessing a single valence electron.

The first excited states of the alkali hydrides are known to show certain anomalous features, namely, the constants α_e and $\omega_e x_e$ are negative. Corresponding to this, the quantities $B_v = B_0 - \alpha_e v + \cdots$ and $\Delta G_{v+1/2} \equiv G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1)$ increase with increasing v; each of them finally reaches a maximum, then decreases.

The nature of the binding in the alkali hydrides has been a subject of considerable discussion during the last three decades. During the late twenties, the available evidence suggested an ionic binding in the alkali crystals (e.g., Zintl and Harder[2]), i.e., the crystal was believed to be formed of M^+ and H^- ions; where M denotes an alkali atom. This viewpoint was also carried over for alkali hydride gas molecules. However, in later years this view has undergone considerable modification.[3]

Mulliken's Work

We owe to Mulliken[4] the first detailed and critical discussion of the low electronic states of the alkali hydrides, their potential energy curves, and the nature of their binding. In order to facilitate the later discussions, we here summarize briefly the conclusions of Mulliken.

Mulliken[4] proposed that the unusual shape of the upper state ($A^1\Sigma^+$) potential curve can be understood by assuming that the two low states of an alkali hydride arise from the interaction between two $^1\Sigma^+$ states, one homopolar and derived from unexcited neutral atoms, the other ionic and derived from M^+ and H^-. Since, however, the excited state dissociates not into the ions, but usually, into $M(^2P)$ and $H(^2S)$ it is also necessary to assume a second similar interaction, between the $^1\Sigma^+$ state derived from $M(^2P)$ and $H(^2S)$ and the $^1\Sigma^+$ state of M^+ and H^-.

Figure 1 shows the potential curves for the lowest states of LiH, including the zero-approximation ionic and atomic curves (broken lines) based on the diagrams given by Mulliken[4] and Herzberg[5] and incorporating some recent experimental data due to Velasco.[6] For small r values, the zero-approximation ionic curve is the lowest, and therefore it appears rather certain that the ground state is predominantly ionic. Yet, on account of the strong interaction of the two states, the ground state dissociates into normal atoms. The first excited singlet state of LiH ($A^1\Sigma^+$ of Fig. 1 called V by Mulliken) has predominantly atomic character for small r values, but changes to ionic character for large r values where the potential curve coincides with the ionic curve Li^+H^-. On account of this rather sudden change from a weak atomic bond to a strong ionic bond the $\Delta G_{v+1/2}$ and B_v values of this state first increase to a maximum

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* The title of this paper follows the suggestions of K. Way, N. B. Gove and R. van Lieshout, Phys. Today **15**, No. 2, 22 (1962).

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[1] R. W. B. Pearse, Repts. Prog. in Phys. **5**, 249 (1939).

[2] E. Zintl and A. Harder, Z. Physik. Chem. **B14**, 265 (1931). For some recent evidence, see J. M. Bijvoet and K. Lonsdale, Phil. Mag. **44**, 204 (1953).

[3] Bibliographies for the properties of lithium hydride have been given by C. E. Messer (NYO-9470, Oct. 1960) and T. F. Davis (TID-3558) (unpublished).

[4] R. S. Mulliken, Phys. Rev. **50**, 1017, 1028 (1936).

[5] G. Herzberg, *Spectra of Diatomic molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951).

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

before the regular decrease sets in. The $A^1\Sigma^+$ state would lead to $\mathrm{Li}^+ + \mathrm{H}^-$ if it were not for a further intersection with the $^1\Sigma^+$ state arising from $^2P + {}^2S$.

The $C^1\Pi$ state has only recently been observed by Velasco.[6] It dissociates into $\mathrm{Li}(^2P) + \mathrm{H}(^2S)$ (as it does not interact with the ionic $^1\Sigma$ state).

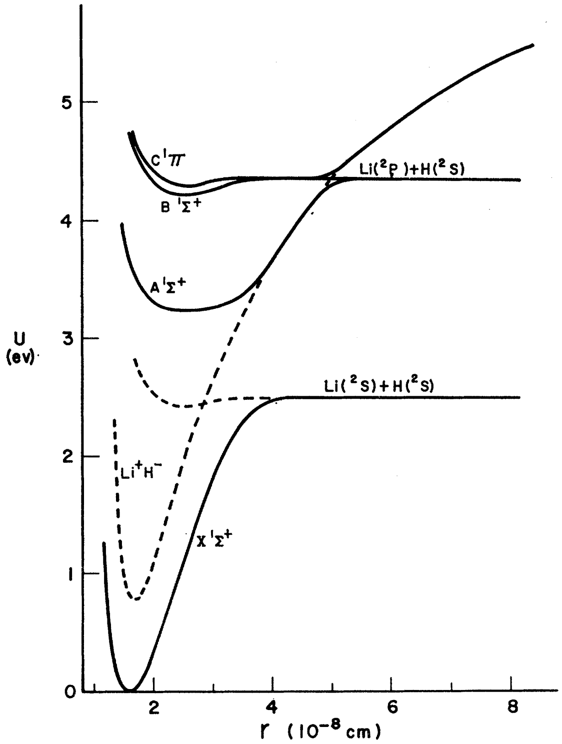

FIG. 1. Potential energy curves for the lowest states of LiH. The $B^1\Sigma^+$ curve has not yet been observed. The positions of the curves are only approximately quantitative.

The $B^1\Sigma$ state has not been observed as yet. Presumably, there would be another intersection with the $^1\Sigma^+$ state arising from $\mathrm{Li}(2^2S)$ and H and $B^1\Sigma$ state will dissociate into $\mathrm{Li}(2^2S)$ and H.

The method developed by Klein[7] and Rydberg[8] was applied by Rosenbaum[9] to construct the potential energy curve of the excited $A^1\Sigma^+$ state of LiH from the experimental data. The results were in accord with Mulliken's hypothesis.

Almy and Beiler[10] have constructed the potential energy curve for the excited state of KH, by the use of Klein's method and have found that the relative position of the atomic and ionic curves is in reasonable agreement with Mulliken's hypothesis.

In the case of CsH a good potential curve has not been constructed, but it has been shown by Almy and Rassweiler[11] by means of a power series curve that the upper state has about the predicted relation to the ionic curve.

IONIC POTENTIAL ENERGY CURVES

In the present paper we consider the applicability of a number of "ionic" potentials to the alkali hydrides, and later on we shall discuss the information available regarding the nature of the binding as obtained from classical models and quantum mechanical calculations.

The potentials considered have two features in common: All of them have the Coulombian attractive term $(-e^2/r)$, and all have two unknown constants. The two unknown parameters were determined by using the conditions

$$(dU/dr)_{r=r_e} = 0 \tag{1}$$

and

$$(d^2U/dr^2)_{r=r_e} = k_e\,, \quad \text{the force constant.} \tag{2}$$

Having fixed the potential energy curve, calculations were carried out for the rotational constant α_e, vibrational constant $\omega_e x_e$, and the ionic binding energy D_i for the different potentials. The method of calculating α_e and $\omega_e x_e$ has been explained in Varshni.[12]

We quote here the equations

$$\alpha_e = -[\tfrac{1}{3}Xr_e + 1]6B_e^2/\omega_e\,, \tag{3}$$

$$\omega_e x_e = [\tfrac{5}{3}X^2r_e^2 - Yr_e^2](W/\mu_A r_e^2)\,, \tag{4}$$

and

$$D_i = -U(r_e), \tag{5}$$

where

$$W = 2.1078 \times 10^{-16}\,, \quad \text{and}$$
$$X = U'''(r_e)/U''(r_e)$$
$$Y = U^{\mathrm{IV}}(r_e)/U''(r_e)\,.$$

The experimental data used, together with the sources, are recorded in Table I and are discussed below.

BORN-LANDÉ POTENTIAL

Many years ago, Born and Landé[13,14] used an inverse-power repulsive term in the potential energy function for alkali halide crystals. For gaseous ionic

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[7] O. Klein, Z. Physik **76**, 226 (1932).

[8] R. Rydberg, Z. Physik **73**, 376 (1931); **80**, 514 (1933).

[9] E. J. Rosenbaum, J. Chem. Phys. **6**, 16 (1938).

[10] G. M. Almy and A. C. Beiler, Phys. Rev. **61**, 476 (1942).

[11] G. M. Almy and M. Rassweiler, Phys. Rev. **53**, 890 (1938).

[12] Y. P. Varshni, Rev. Mod. Phys. **29**, 664 (1957); **31**, 839 (1959); See also D. Steele, E. R. Lippincott and J. T. Vanderslice, *ibid.*, **34**, 239 (1962).

[13] M. Born and A. Landé, Verhandl. Deut. Physik. Ges. **20**, 210 (1918).

[14] M. Born, Ann. Physik (Liepzig) **61**, 87 (1920).

TABLE I. Experimental values of the Molecular constants. Data for ω_e, r_e, α_e, and $\omega_e x_e$ were taken from Herzberg.[5] Sources of the D_e values are indicated.

Molecules	ω_e cm^{-1}	k_e (10^5 dyn/cm)	r_e (10^{-8} cm)	α_e cm^{-1}	$\omega_e x_e$ cm^{-1}	D_e kcal/mole	D_i kcal/mole
LiH	1405.65	1.0256	1.595	0.2132	23.20	58.01[a]	165.1
NaH	1172.2	0.78141	1.887	0.1353	19.72	49.0 ± 4.6[b]	150.3 ± 4.6
KH	985.0	0.56142	2.244	0.0673	14.65	44.3 ± 3.5[b]	127.2 ± 3.5
RbH	936.77	0.51485	2.367	0.072	14.15	40.5 ± 4.6[b]	119.6 ± 4.6
CsH	890.7	0.4674	2.494	0.057	12.6	42.8 ± 6.9[b]	115.4 ± 6.9

[a] R. Velasco, reference 6.
[b] Calculated from the D_0 values given by Gaydon, reference 36.

molecules, the Born–Landé potential may be written as

$$U = -e^2/r + b/r^n , \tag{6}$$

where b and n are constants. This potential was much used during the twenties for investigating ionic crystals. Krebs[15] applied Eq. (6) to LiH and NaH and in a later paper[16] discussed the nature of the binding of alkali hydrides in the gaseous state. Rice[17] has determined the value of n from the lattice energy data and has used it to calculate the binding energy of gaseous alkali hydrides. The above equation has also been employed by Mulliken[4] in discussing the nature of the binding in LiH.

It can be shown that for the potential (6),

$$n + 1 = k_e r_e^3/e^2 + 2 , \tag{7}$$

$$\alpha_e = \tfrac{1}{3}\,(n + 1)6B_e^2/\omega_e , \tag{8}$$

$$\begin{aligned} \omega_e x_e &= \tfrac{1}{3}\,(2n^2 + 19n + 26)W/\mu_A r_e^2 , \\ &= \tfrac{1}{3}\,\{2(n+1)^2 + 15(n+1) + 9\}W/\mu_A r_e^2 , \end{aligned} \tag{9}$$

and

$$D_i = (e^2/r_e)(1 - 1/n) . \tag{10}$$

The calculated values of α_e, $\omega_e x_e$ and D_i along with the percentage errors are recorded in Table II.

BORN–MAYER POTENTIAL

Quantum mechanical calculations of forces between ions showed that an inverse power repulsive term was not satisfactory. Born and Mayer[18] suggested that an exponential repulsive term was preferable and found it to be satisfactory for alkali halide crystals. In simplified form, their potential may be written

$$U = -e^2/r + Be^{-r/\sigma} , \tag{11}$$

where e in the first term represents the electronic charge and B and σ are constants. We are not happy to use "e" with two different meanings in the same equation. However, this practice is so common for ionic potentials that we hope there will not be any confusion.

TABLE II. Born–Landé potential (6). The figures in parentheses, below the calculated molecular constants, are percentage errors.

Molecules	n	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	2.8040	0.3055 (+43.3)	29.76 (+28.3)	134 (−18.8)
NaH	3.2760	0.1753 (+29.6)	22.41 (+13.6)	122.3 (−18.6)
KH	3.7499	0.1120 (+66.4)	17.80 (+21.5)	108.6 (−14.6)
RbH	3.9600	0.0966 (+34.2)	16.69 (+17.9)	104.9 (−12.3)
CsH	4.1431	0.0847 (+48.6)	15.70 (+24.6)	101 (−12.5)
Average % error		(44.4)	(21.2)	(15.4)

The necessary expressions for α_e, $\omega_e x_e$ and D_i have been given in a previous paper (Varshni and Shukla[19]). If Eq. (11) is applied to the alkali hydrides the calculated results along with the percentage errors have been tabulated in Table III.

WASASTJERNA POTENTIAL

Wasastjerna[20,21] has investigated two potential functions for the Na, K, Rb, and Cs halide crystals. The simpler of the two may be written

$$U = -e^2/r + Cr^7e^{-\beta r} , \tag{12}$$

where C and β are constants. The second one employs

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[15] A. Krebs, Z. Physik **80**, 134 (1933).

[16] A. Krebs, Z. Physik **81**, 1 (1933).

[17] O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), p. 249.

[18] M. Born and J. E. Mayer, Z. Physik **75**, 1 (1932).

[19] Y. P. Varshni and R. C. Shukla, J. Chem. Phys. **35**, 582 (1961).

[20] J. A. Wasastjerna, Soc. Sci. Fennica, Commentationes Phys.-Math. **8**, Nos. 20, 21 (1935).

[21] J. A. Wasastjerna, Phil. Trans. Roy. Soc. London **237**, 105 (1938).

TABLE III. Born–Mayer potential (11). The figures in parentheses, below the calculated molecular constants, are percentage errors.

Molecules	σ (10^{-8} cm)	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	0.4193	0.1362 (−36.1)	18.36 (−20.1)	153.5 (−7.0)
NaH	0.4413	0.0982 (−27.4)	15.17 (−23.1)	134.9 (−10.2)
KH	0.4724	0.0713 (+5.9)	12.87 (−12.2)	116.9 (−8.1)
RbH	0.4772	0.0639 (−11.2)	12.35 (−12.7)	112.1 (−6.3)
CsH	0.4849	0.0578 (+1.4)	11.83 (−6.1)	107.3 (−7.0)
Average % error		(16.4)	(14.8)	(7.7)

an extended form of the repulsive term of Eq. (12). Here we shall confine ourselves to Eq. (12).

For this equation, we have

$$\frac{k_e r_e^3}{e^2} + 2 = \frac{(\beta r_e - 7)^2 - 7}{\beta r_e - 7}, \tag{13}$$

which determines β, also

$$X = -\frac{1}{r_e}\left[\frac{(\beta r_e - 7)^3 - 27(\beta r_e - 7) - 14}{(\beta r_e - 7)^2 - 2(\beta r_e - 7) - 7}\right], \tag{14}$$

$$Y = \frac{1}{r_e^2} \times\left[\frac{(\beta r_e - 7)^4 - 42(\beta r_e - 7)^2 - 80(\beta r_e - 7) + 105}{(\beta r_e - 7)^2 - 2(\beta r_e - 7) - 7}\right], \tag{15}$$

and

$$D_i = \frac{e^2}{r_e}\left[1 - \frac{1}{\beta r_e - 7}\right] \tag{16}$$

The calculated values of α_e, $\omega_e x_e$, and D_i along with the percentage errors, are recorded in Table IV.

TABLE IV. Wasastjerna potential (12)

Molecules	$\beta r_e - 7$	β	α_e calc. cm^{-1} (% error)	$\omega_e x_e$ calc. cm^{-1} (% error)	D_i calc. kcal/mole (% error)
LiH	5.1605	7.6241	−0.3782	76.97 (+231.8)	167.9 (+1.7)
NaH	5.5396	6.6453	−0.1021	33.58 (+70.3)	144.3 (−4.0)
KH	5.9303	5.7622	−0.02093	19.09 (+30.3)	123.1 (−3.2)
RbH	6.1064	5.5371	−0.00582	16.27 (+15.0)	117.4 (−1.8)
CsH	6.2611	5.3172	+0.00281	14.34 (+13.8)	111.9 (−3.0)
Average % error					(2.7)

RITTNER POTENTIAL

A few years ago, Rittner[22] proposed a theory of the gaseous alkali halide molecules in which the molecule is treated as consisting of ions, each of which is polarized by the electrostatic field of the other. He obtained the following expression:

$$U = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} - \frac{c}{r^6} + A\exp(-r/\rho), \tag{17}$$

where α_1 and α_2 = polarizabilities of the ions, ρ and A = repulsion constants, and c = van der Waals' attraction constant.

Rittner's potential (17) has been found to be fairly successful for gaseous alkali halides.[19,22–24]

Klemperer and Margrave[25] tried to apply the potential (17) to the alkali hydrides. Using a value of $\alpha(\text{H}^-) = 1.80 \times 10^{-24}$ cm^3, they obtained satisfactory values for D_i. However, it was pointed out by Altshuller[26] that the value for the polarizability of H$^-$ ion employed by Klemperer and Margrave was not satisfactory. Altshuller[26] showed that if the theoretical value of $\alpha(\text{H}^-) = 14.6 \times 10^{-24}$ cm^3 calculated by Henrich[27] was employed, the Rittner model ran into a number of difficulties for alkali hydrides: The dipole moments were found to be negative, the new calculated binding energy of KH was some 100 kcal greater than the observed value. Altshuller traced these anomalies to the fact that Rittner has based his argument on a model of a diatomic molecule consisting of a point charge $+e$ at a distance a from a metal sphere of charge $-e$ of radius R, when $\alpha_1 \ll \alpha_2$, and applied the method of images. This model is satisfactory for the alkali halides, but this model is not satisfactory for the alkali metal hydrides because the condition that $a > R$ is not satisfied. If one assumes $R(\text{H}^-) = 2.08$ Å (Pauling[28]), then the condition is not satisfied for LiH and NaH. If an $\alpha(\text{H}^-) = 14.6 \times 10^{-24}$ cm^3 is employed in the expression $R = \alpha^{1/3}$, then $R(\text{H}^-) = 2.44$ Å and the condition is not satisfied by LiH, NaH, KH, or RbH, and is just barely satisfied by CsH.

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[22] E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951). The polarization terms were first deduced by M. Born and W. Heisenberg, Z. Physik **23**, 388 (1924).

[23] Y. P. Varshni, Trans. Faraday Soc. **53**, 132 (1957).

[24] K. S. Krasnov and V. G. Antoshkin, Zhur. Neorg. Khim. **3**, 1490 (1958); J. R. Rusk and W. Gordy, Phys. Rev. **127**, 817 (1962).

[25] W. A. Klemperer and J. L. Margrave, J. Chem. Phys. **20**, 527 (1952).

[26] A. P. Altshuller, J. Chem. Phys. **21**, 2074 (1953).

[27] L. R. Henrich, Phys. Rev. **62**, 545 (1942).

[28] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940 and 1948).

It may be that there is a considerable interpenetration of the large hydride ion by the alkali metal ion, which renders the ionic model inapplicable.

There have been a number of theoretical calculations of the polarizability of the H^- ion. We have summarized some of the results in Table V. Most values except those of Dalgarno and Stewart, are in the neighborhood of Henrich's value. In the present paper, we adopt Henrich's value.

TABLE V. The electronic polarizability of H^- as calculated by different workers.

$\alpha(H^-)$ (10^{-24} cm^3)	Reference
10.2	L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).
14.6	L. Henrich, Phys. Rev. **62**, 545 (1942).
16.1	R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).
13.4	R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957).
14.88	E. K. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957).
7.3 7.9	A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958).

In the following "Eq. (17a)" denotes Eq. (17) with $\alpha(H^-) = 1.80 \times 10^{-24}$ cm^3 and "Eq. (17b)" denotes Eq. (17), with $\alpha(H^-) = 14.6 \times 10^{-24}$ cm^3.

However, the fact that Klemperer and Margrave obtained satisfactory values of D_i by using $\alpha(H^-) = 1.80\,\text{Å}^3$ suggests an interesting possibility. Though on theoretical ground, Eq. (17a) appears to be not satisfactory, could it be that it is a semiempirical representation of the actual potential energy curve? To examine this point, calculations were carried out for α_e, $\omega_e x_e$, and D_i and the results are shown in Table VI. The necessary analytical expressions for calculating these quantities have been given elsewhere (reference 19). Equation (14) in reference 19 should read "Yr_e^2" instead of "Y".

TABLE VI. Rittner potential (17a), $\alpha(H^-) = 1.80$ Å^3.

Molecules	c 10^{-60} erg cm^6	ρ 10^{-8} cm	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	0.09265	0.3580	−0.1373	41.15 (+77.4)	165.6 (+0.3)
NaH	.5749	0.3965	+0.00532 (−96.1)	20.99 (+6.1)	141.9 (−5.6)
KH	2.648	0.4345	+0.0257 (−61.8)	15.13 (+3.2)	122.0 (−4.1)
RbH	4.460	0.4422	+0.0255 (−64.6)	14.09 (−0.4)	117.1 (−2.1)
CsH	7.629	0.4517	+0.0220 (−61.4)	13.44 (+6.7)	112.7 (−2.3)
Average			(71)[a]		(2.9)

[a] For four molecules only.

Equation (17b) is known to be unsuccessful in reproducing the D_i values. However, it is of interest to investigate whether it describes the shape of the potential energy curve in the neighborhood of r_e. Hence, calculations of α_e, $\omega_e x_e$, and D_i were carried out for the case of Eq. (17b) also and the results are recorded in Table VII.

TABLE VII. Rittner potential (17b), $\alpha(H^-) = 14.6$Å^3.

Molecules	c 10^{-60} erg cm^6	ρ 10^{-8} cm	α_e calc[a] cm^{-1}	$\omega_e x_e$ calc[b] cm^{-1}	D_i calc kcal/mole (% error)
LiH	0.7515	0.3196	−1.8143	986.6	236.6 (+43.3)
NaH	4.663	0.3565	−0.5585	286.1	183.2 (+21.9)
KH	21.48	0.3890	−0.2254	126.9	147.2 (+15.7)
RbH	36.17	0.3949	−0.1755	107.5	139.6 (+16.7)
CsH	61.88	0.4002	−0.1510	101.9	133.3 (+15.5)

[a] Percentage errors not given as the calculated values are negative.

[b] Percentage errors not given as the calculated values differ from the observed ones by large factors.

VS-I POTENTIAL

Recently, the authors[19] have found the following potential to be reasonably satisfactory for the alkali halides:

$$U = -e^2/r + P \exp(-kr^2) \quad \text{(VS-I)} \quad (18)$$

P and k are constants. We have examined this potential also for the alkali hydrides. The expressions for α_e, $\omega_e x_e$, and D_i are given in the above paper[19]; the calculated values along with the percentage errors are recorded in Table VIII.

TABLE VIII. VS-I potential (18).

Molecules	$x = 2kr_e^2$	k	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	4.8040	0.9442	−0.1222	22.80 (−1.7)	164.9 (−0.1)
NaH	5.2760	0.7409	−0.0148	14.75 (−25.2)	142.7 (−5.1)
KH	5.7499	0.5709	+0.0134 (−80.1)	11.36 (−22.5)	122.3 (−3.9)
RbH	5.9600	0.5319	+0.0182 (−74.7)	10.70 (−24.4)	116.8 (−2.3)
CsH	6.1431	0.4938	+0.0203 (−64.4)	10.14 (−19.5)	111.5 (−3.4)
Average			(73.1)[a]	(18.7)	(3.0)

[a] For three molecules only.

HELLMANN POTENTIAL

Some 25 years ago, Hellmann[29,30] introduced the following potential to represent the interaction between the valence electron and the core in an alkali atom:

$$U = -e^2/r + T(e^{-\lambda r}/r)\,, \tag{19}$$

where T and λ are constants. Since then it has been used for the electron-core interaction by a number of workers[31–35]. However, as far as we have been able to find, this potential has never been used before as the *interatomic* potential. We have found that such a potential yields satisfactory results for representing the shape of interatomic potential energy curves of alkali hydrides, at least in the neighborhood of the equilibrium internuclear distance.

The results can be conveniently expressed in terms of another parameter $y = \lambda r_e$

$$y^2/(y+1) = k_e r_e^3/e^2\,, \tag{20}$$

$$\alpha_e = \tfrac{1}{3}\,(y)6B_e^2/\omega_e\,, \tag{21}$$

$$\omega_e x_e = \tfrac{1}{3}\,(2y^2 + 18y + 9)W/\mu_A r_e^2\,, \tag{22}$$

and

$$D_i = [y/(y+1)]e^2/r_e\,. \tag{23}$$

The calculated results together with the percentage errors are tabulated in Table IX.

TABLE IX. Hellmann potential (19).

Molecules	y	λ 10^8 cm^{-1}	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	2.5199	1.5799 (−0.28)[a]	0.2024 (−5.1)	21.01 (−9.4)	149.1 (−9.7)
NaH	3.0277	1.6045 (+1.28)[a]	0.1241 (−8.3)	16.72 (−15.2)	132.3 (−12.0)
KH	3.5291	1.5727 (−0.73)[a]	0.0832 (+23.6)	13.83 (−5.6)	115.3 (−9.4)
RbH	3.7495	1.5841 (−0.01)[a]	0.0730 (+1.4)	13.17 (−6.9)	110.8 (−7.4)
CsH	3.9407	1.5801 (−0.27)[a]	0.0649 (+13.9)	12.53 (−0.6)	106.2 (−8.0)
Mean value of λ		1.5843			
Average % error			(10.5)	(7.5)	(9.3)

[a] These figures denote % deviation from the mean value.

ANOTHER POTENTIAL

Another potential which we have found to be reasonable is the following

$$U = -e^2/r + S(e^{-\eta r}/r^2)\,,\quad \text{(VS-II)} \tag{24}$$

where S and η are constants.

Applying the conditions (1) and (2) we obtain

$$t = \frac{k_e r_e^3}{e^2} + 2 = \frac{(\eta r_e + 2)^2 + 2}{(\eta r_e + 2)}\,. \tag{25}$$

We also obtain

$$\alpha_e = \left[\frac{(t-2)(\eta r_e + 2) - t + 4}{3(t-2)}\right]\frac{6B_e^2}{\omega_e}\,, \tag{26}$$

$$\omega_e x_e = \frac{2}{3}\left[\frac{(\eta r_e + 2)(t^3 + 3t^2 - 17t + 14) - 10t^2 + 42t - 34}{(t-2)^2}\right]\frac{W}{\mu_A r_e^2}\,, \tag{27}$$

$$D_i = \frac{e^2}{r_e}\left[1 - \frac{1}{\eta r_e + 2}\right]. \tag{28}$$

The calculated values of the above three molecular constants along with the percentage errors are given in Table X.

GRAPHICAL COMPARISON

Varshni[12] has shown that for three-constant potential energy functions, the quantities

$$-[\tfrac{1}{3}\,X r_e + 1] = F \tag{29}$$

$$[\tfrac{5}{3}\,X^2 - Y]r_e^2 = G \tag{30}$$

can be represented as functions of the Sutherland parameter Δ,

$$\Delta = k_e r_e^2/2D_e\,,$$

whence it is possible to compare the functions graphically.

An analogous method can be employed for six of the functions under consideration, viz., Born–Landé, Born–Mayer, Wasastjerna, VS-I, Hellmann, and VS-II potentials. In addition to Eqs. (29) and (30), we define a quantity H by

$$-U(r_e)[r_e/e^2] = H\,. \tag{31}$$

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[29] H. Hellmann, Acta Physicochim. U.R.S.S. **1**, 913 (1934); J. Chem. Phys. **3**, 61 (1935).

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[34] L. Szasz, Acta Phys. Acad. Sci. Hung. **6**, 307 (1957).

[35] J. Callaway, Phys. Rev. **112**, 322 (1958).

Table X. VS-II potential (24).

Molecules	ηr_e+2	η	α_e calc cm^{-1} (% error)	$\omega_e x_e$ calc cm^{-1} (% error)	D_i calc kcal/mole (% error)
LiH	3.1738	0.7359	0.2636 (+23.6)	25.56 (+10.2)	142.6 (−13.6)
NaH	3.7414	0.9228	0.1484 (+9.7)	19.00 (−3.7)	129.0 (−14.2)
KH	4.2829	1.0173	0.0945 (+40.4)	15.13 (+3.3)	113.5 (−10.8)
RbH	4.5173	1.0635	0.0816 (+13.3)	14.22 (+0.5)	109.3 (−8.6)
CsH	4.7193	1.0903	0.0718 (+26.0)	13.43 (+6.6)	105.0 (−9.0)
Average % error			(22.6)	(4.9)	(11.2)

TABLE XI. Expressions for F, G, and H for different potentials.

Potential	F	G	H
Born-Landé	$\frac{1}{3}t$	$\frac{1}{3}[2t^2+15t+9]$	$1-\dfrac{1}{(t-1)}$
Born-Mayer	$\frac{1}{3}t\left(\dfrac{t-3}{t-2}\right)$	$\dfrac{2}{3}\left[\dfrac{t^4+3t^3-30t^2+36t+18}{(t-2)^2}\right]$	$1-1/t$
Wasastjerna	$[(t-2)(t^2+28)^{1/2}+t^2$ $-4t-28]/6(t-2)$	$[(t^3+3t^2-80t+140)(t^2+28)^{1/2}$ $+t^4+3t^3-t^2-208t+1660]$ $/3(t-2)^2$	$1-\dfrac{2}{t+(t^2+28)^{1/2}}$
VS-I, Eq. (18)	$\dfrac{t^2-4t-2}{3(t-2)}$	$\dfrac{2t^4+5t^3-75t^2+122t+164}{3(t-2)^2}$	$1-1/(t+1)$
Hellmann	$\frac{1}{6}[(t-2)+(t^2-4)^{1/2}]$	$\frac{1}{3}[(t+7)(t^2-4)^{1/2}+t^2+7t-9]$	$1-2/[t+(t^2-4)^{1/2}]$
VS-II, Eq. (24)	$[(t-2)(t^2-8)^{1/2}+t^2$ $-4t+8]/6(t-2)$	$[(t^3+3t^2-17t+14)(t^2-8)^{1/2}$ $+t^4+3t^3-37t^2+98t-68]$ $/3(t-2)^2$	$1-\dfrac{2}{t+(t^2-8)^{1/2}}$
Experimental	$\alpha_e\omega_e/6B_e^2$	$\omega_e x_e(\mu_A r_e^2/W)$	$D_i r_e/e^2$

For these six functions F, G, and H can be represented in terms of another dimensionless parameter t, given by

$$k_e r_e^3/e^2+2=t \tag{32}$$

Then, the values of α_e, $\omega_e x_e$, and D_i are given by

$$\alpha_e=F(6B_e^2/\omega_e)\,, \tag{33}$$

$$\omega_e x_e=G(W/\mu_A r_e^2)\,, \tag{34}$$

$$D_i=H(e^2/r_e)\,. \tag{35}$$

The values given by Eqs. (33), (34), and (35) give the theoretical values of F, G, and H. The experimental values of these quantities are obtained by reversing Eqs. (33), (34), and (35)

$$F=\alpha_e\omega_e/6B_e^2\,, \tag{36}$$

$$G=\omega_e x_e\mu_A r_e^2/W\,, \tag{37}$$

$$H=D_i r_e/e^2\,. \tag{38}$$

The theoretical expressions of F, G, and H for the above mentioned functions are summarized in Table XI; the experimental values of these quantities have been shown in Table XII. F, G, and H have been plotted vs t in Figs. 2, 3, and 4, respectively. The experimental values (Table XII) have been shown as points.

TABLE XII. The experimental values of t, F, G, and H.

Molecules	t	F	G	H
LiH	3.8040	0.8849	24.683	0.793
NaH	4.2760	1.1004	32.174	0.854
KH	4.7499	.9518	34.394	0.859
RbH	4.9600	1.2325	37.476	0.852
CsH	5.1431	1.1530	37.202	0.866

DATA

The dissociation energy D_e values for NaH, KH, RbH, and CsH were obtained from the D_0 values listed by Gaydon[36] by correcting for the zero-point energy. The binding energy (or the ionic dissociation energy) D_i was calculated from the relation:

$$D_i = D_e + I - E,$$

where I is the ionization potential of the alkali atom (taken from Herzberg[37]), and E is the electron affinity of the hydrogen atom (taken from Pritchard[38]).

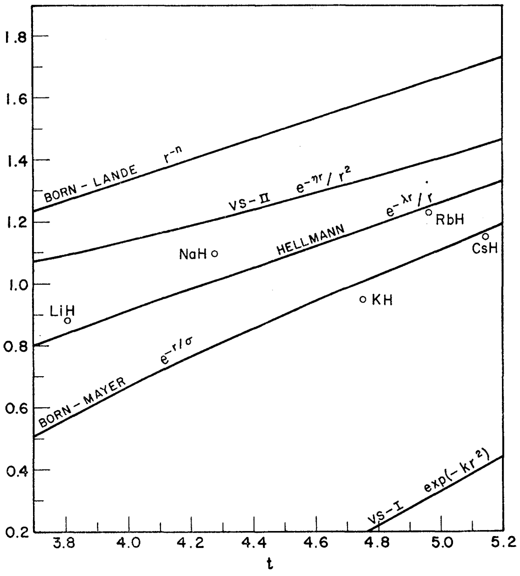

FIG. 2. F vs t. Experimental points are shown as open circles. The form of the repulsion term is also given by the side of the curves.

Table I shows that there are considerable uncertainties in the D_e (and consequently D_i) values of NaH, KH, RbH, and CsH (see also Somayajulu[39]). This fact should be borne in mind in considering the calculated values of D_i by the various functions.

DISCUSSION

We first discuss each function separately.

Born–Landé Potential (6)

(See Table II and Figs. 2, 3, and 4.)

α_e and $\omega_e x_e$: The calculated values are too high.

D_i : The calculated values are too low.

Thus we find that this equation is not satisfactory for alkali hydrides. However, it is interesting to note that for a particular constant (α_e, $\omega_e x_e$, or D_i) the percentage error is in the same direction, for all the molecules.

Born–Mayer Potential (11)

(See Table III and Figs. 2, 3, and 4).

α_e : The percentage error decreases rapidly from LiH to CsH.

$\omega_e x_e$: Broadly speaking, the negative percentage errors show a decreasing tendency as one passes from LiH to CsH.

D_i : The negative percentage errors are nearly the same ($\sim 8\%$) for all molecules.

For one of the molecules CsH this function appears to be reasonable as for this molecule the calculated values of all the three constants have low percentage errors.

Wasastjerna Potential (12)

(See Table IV and Fig. 4.)

α_e : For four of the molecules the calculated values are negative. For CsH, though the value is positive, it is only 1/20 of the observed value.

$\omega_e x_e$: The calculated values are very high, but the percentage error decreases rapidly from LiH to CsH.

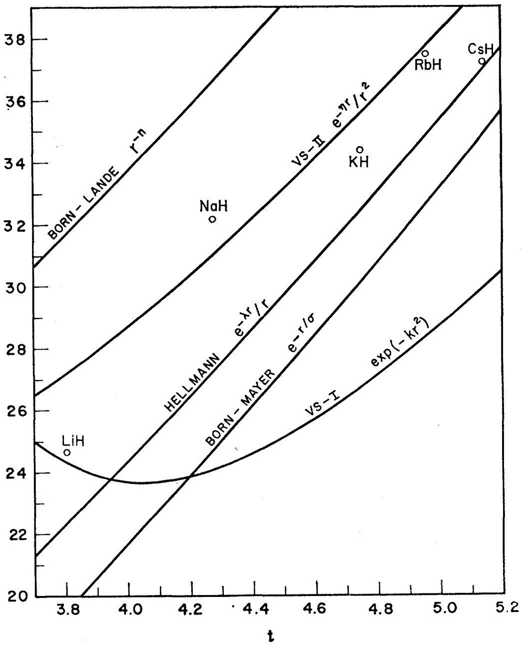

FIG. 3. G vs t. Experimental points are shown as open circles.

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[37] G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944).

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D_i : The calculated values are in excellent agreement with the observed ones. The average percentage error is only 2.7, which is of the same order of magnitude as the experimental uncertainties in the observed values.

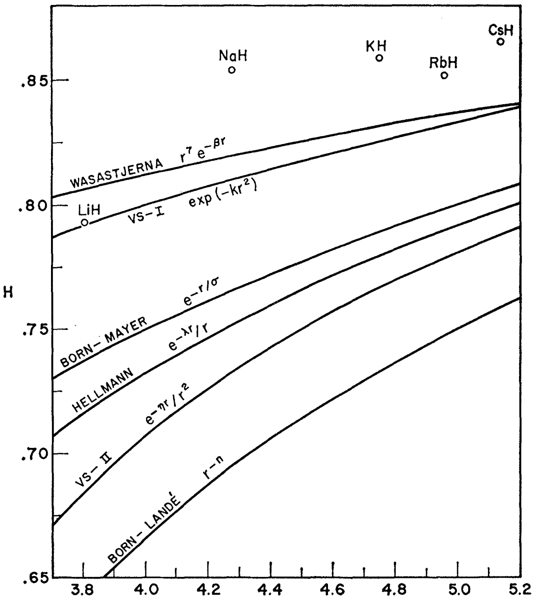

FIG. 4. H vs t. Experimental points are shown as open circles.

In this function we see the remarkable phenomenon that it is able to reproduce one of the constants (D_i) very successfully, but fails completely for the other two.

Rittner Potential (17a), $\alpha(H^-) = 1.80 Å^3$

(See Table VI.)

α_e : For LiH, the calculated value is negative; and for the other four molecules the calculated values are too small.

$\omega_e x_e$: Except for LiH, the percentage errors are reasonable.

D_i : The agreement between the observed and calculated values is satisfactory, as found earlier by Klemperer and Margrave.[25]

Rittner Potential (17b), $\alpha(H^-) = 14.6 Å^3$

(See Table VII.)

α_e : All the calculated values are negative, which is highly unsatisfactory.

$\omega_e x_e$: The calculated values are greater than the observed ones by a factor which varies between 42 to 8. Quite unsatisfactory.

D_i : Except for LiH, the calculated values are higher than the observed ones by about 15%, which is not as unsatisfactory as are the results for α_e and $\omega_e x_e$.

Thus we find that the use of $\alpha(H^-) = 14.6 Å^3$ in place of $\alpha(H^-) = 1.80 Å^3$ worsens the agreement. Perhaps one may interpret $\alpha(H^-) = 1.80 Å^3$ as the effective polarizability of the negative hydrogen ion in these molecules.

VS-I Potential (18)

(See Table VIII and Figs. 2, 3, and 4.)

α_e : For two of the molecules, LiH and NaH the calculated values are negative, which is contrary to observation. The calculated values for the other three molecules are ~1/4 of the observed values.

$\omega_e x_e$: Except for LiH, the calculated values are ~20% lower than the observed ones. The low error in the calculated value for LiH is a consequence of the fact that the (G,t) curve (see Fig. 3) goes through a minimum and again increases below $t \approx 4$.

D_i : The agreement between the observed and calculated values is satisfactory, though it may be noted that the calculated values, in all cases, are lower than the observed ones.

The constant k decreases as we go down the series. This function is another example of the fact that though a function may be successful for D_i, it may be a complete failure in reproducing other molecular constants. We have noted above that the Wasastjerna potential shows a similar behavior.

Hellmann Potential (19)

(See Table IX and Figs. 2, 3, and 4.)

α_e : The average percentage error is reasonable.

$\omega_e x_e$: There is reasonable agreement between the calculated and observed values. But it may be noted that the calculated values are smaller than the observed ones.

D_i : The calculated values are all lower than the observed ones by about 9%.

VS-II Potential (24)

(See Table X and Figs. 2, 3, and 4.)

α_e : The calculated values are too high.

$\omega_e x_e$: The average percentage error is the lowest amongst the potentials considered here.

D_i : The calculated values are about 10% lower than the observed ones.

The results by this potential may be compared with those by the Hellmann potential. For $\omega_e x_e$, (24) improves upon (19) but for α_e the average percentage error by (24) is nearly twice of that by (19). For D_i

also, the results by (24) are uniformly less satisfactory than those by (19).

COMPARATIVE DISCUSSION

Figures 2, 3, and 4 show the comparative behaviours of the Born–Landé, Born–Mayer, VS-I, Hellmann, and VS-II potentials. F and G curves for the Wasastjerna potential fall outside the figures.

We will find it more convenient to refer to these potentials by their repulsion terms which are r^{-n}, $e^{-r/\sigma}$, $e^{(-kr^2)}$, $e^{-\lambda r}/r$, and $e^{-\eta r}/r^2$. We notice in the (F,t) graph that the curves for these potentials fall in a certain order, i.e., r^{-n}, $e^{-\eta r}/r^2$, $e^{-\lambda r}/r$, $e^{-r/\sigma}$, $e^{(-kr^2)}$, and this order is maintained, at least when t is large, in the (G,t) and (H,t) graphs. A certain regularity can be readily seen in this order: $e^{-\lambda r}/r$ falls between the inverse power and the exponential. Also, $e^{-\eta r}/r^2$ falls between $e^{-\lambda r}/r$ and the inverse power. As if the increase of the exponent of r in the denominator has shifted the curve towards the inverse power. From these regularities it is possible to obtain a rough approximation for the behavior of some other type of simple repulsion terms. For example, it may be safely predicted that the curves for a repulsion term e^{-mr}/r^3 will lie between those for $e^{-\eta r}/r^2$ and r^{-n}, and that such a term will not be satisfactory for the alkali hydrides.

The question of a "universal" potential energy curve has been discussed in the literature.[12,40,41] In reference 12 the following question was raised: While it is not possible to have an exact "universal" Potential-energy function for *all* molecules, is it possible to have such a function for molecules with similar linkage, i.e. those belonging to the same molecular group? The present study sheds some light on this question. The Hellmann potential may be written as

$$U = \frac{e^2}{r}\left[-1 + \frac{e^{-\lambda(r-r_e)}}{\lambda r_e + 1}\right]. \tag{39}$$

Table IX shows that λ is a constant for all the five alkali hydrides to a good degree of accuracy; its mean value being 1.5843×10^8 cm^{-1}. We have already seen that the Hellmann curve is a good approximation to the shape of the actual alkali hydride curves in the neighborhood of r_e. Thus, we may say that Eq. (39) represents a "universal" potential energy curve for the alkali hydrides, in which r_e behaves as a scale factor. For quantitative significance, it is useful to qualify the accuracy of such a statement. In the present case we may say that the Hellmann curve reproduces molecular constants within 10% or less, and it is "universal" to that extent.

Figures 2, 3, and 4 show that even for a single molecule the same curve is not the best one for all the molecular constants. As an illustration, we may consider LiH: α_e of this molecule is best given by the Hellmann curve, while $\omega_e x_e$ and D_i are best by VS-I. For α_e (LiH), VS-I is extremely poor.

From the distribution of points, we also notice that it is not possible to find a single curve which will give least average errors for all the three constants for all the 5 molecules. For α_e we find the Hellmann curve gives the least errors; while for $\omega_e x_e$ VS-II is the best.

Three of the functions, viz., Born–Mayer, Hellmann, and VS-II give results which may be considered to be reasonable within a broad range. It is interesting to note that all of these give dissociation energies that are about 10% smaller than the observed ones; this is in agreement with Mulliken's theory.

In the past it has been customary to consider any function which has an attractive $[-e^2/r]$ term to be an ionic function, irrespective of the form of the repulsion term. The present study clearly brings out the very important effect of the repulsion term and the different behavior of the various functions, and one is led to the uncomfortable question as to which one (or ones) of these is to be considered as a truly "classical ionic" function?

We have discussed earlier[19] the question of the form of the repulsion term, and we had noted that the available evidence is not very clear. The present considerations also lead to a similar conclusion.

Comparison with the Experimental Potential-Energy Curve for LiH

Recently, Fallon, Vanderslice, and Mason[42] have obtained the potential energy curve for the ground state of LiH using the Rydberg–Klein–Rees method. Among the potentials examined by us, the Hellmann potential (19) appears to give the best over-all result. We shall compare the Hellmann curve with the curve obtained by Fallon *et al.* As the dissociation energy given by the Hellmann curve is too small, we have shifted the curve so as to coincide with the experi-

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mental one at $r = r_e$. Then for LiH, the Hellmann curve is

$$U = (116\,177/r)[-1 + 3.5306\, e^{-1.5799r}] + 52\,146\,, \tag{40}$$

where U is in cm^{-1} and r in Å. The two curves, i.e., the experimental one and the one represented by Eq. (40), have been shown in Fig. 5. The agreement between the two curves is satisfactory. However, to bring out the small differences between the two curves, we have shown (U[Eq. (40)] − U(expt)) vs r in Fig. 6. For $r < r_e$ the Hellmann curve is lower than the experimental curve, while for $r > r_e$, the reverse is the case. Also in the neighborhood of r_e, the agreement between the two curves is satisfactory, but as we go away from $r = r_e$ the differences between the two curves increase.

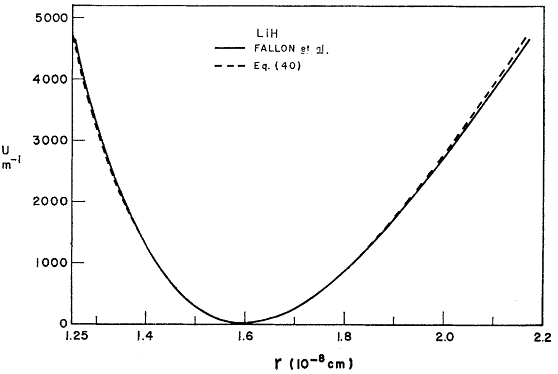

FIG. 5. Potential energy curves for the ground state of LiH. Continuous line shows the experimental curve obtained by Fallon, Vanderslice, and Mason[42]; broken line represents Eq. (40).

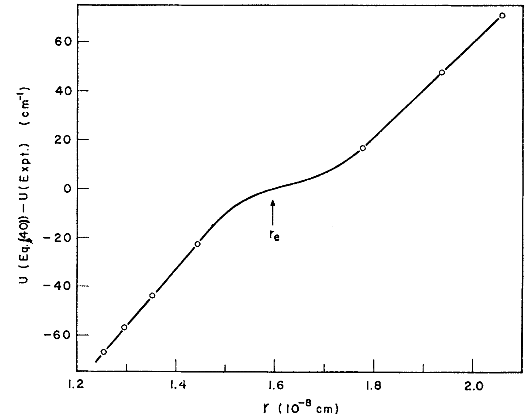

FIG. 6. (U[Eq.(40)] — U(expt)) for the ground state of LiH.

NATURE OF THE BINDING

An understanding of the nature of the binding in the alkali hydrides is of considerable interest. The binding in these molecules is believed to have a considerable amount of "ionic character." A very clear and critical discussion of the present status of the concept of partial ionic character has been recently given by Shull[43] (see also Mulliken[4]). In the following, we examine the available results on the alkali hydrides. These results also serve to illustrate the difficulties, present in a precise definition of the concept of partial ionic character, emphasized by Shull.[43]

Electronegativity and Dipole Moment Considerations

Pauling[28] noted early that alkali hydrides form an exception to his postulate of the additivity of normal covalent bonds, according to which the actual bond energies $D(A-B)$ between unlike atoms would always be greater than or equal to the arithmetic means of the corresponding symmetrical bond energies $D(A-A)$ and $D(B-B)$; the difference Δ defined as

$$\Delta = D(A-B) - \tfrac{1}{2}\{D(A-A) + D(B-B)\} \tag{41}$$

would never be negative. However, for alkali hydrides, Δ is found to be negative. This led Pauling[28] to formulate the postulate of geometric mean, according to which the quantity Δ' defined as

$$\Delta' = D(A-B) - \{D(A-A)D(B-B)\}^{1/2} \tag{42}$$

should always be greater than or equal to zero. Δ' is a measure of the ionic resonance energy of the unsymmetrical bond and it is found to be positive for alkali hydrides.

Recently, Allen[44] has suggested the reciprocal mean as a measure of the covalent bond energy and finds that it gives satisfactory results for the ionic resonance energy in alkali hydrides.

The concept of electronegativity has been reviewed and discussed by Pritchard and Skinner,[45] Howlett,[46] Batsanov,[47] and by Eczkowski and Margrave.[48] Lists of "best" electronegativity values have been given by Gordy and Thomas,[49] Little and

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TABLE XIII. Ionic characters as obtained by different methods.

	$\lvert x_A - x_B \rvert$[a]	$0.208(\Delta')^{1/2}$ Eq. (42)[b]	μ / er_e	I.C. Pauling Eq. (47)	I.C. Hannay and Smyth Eq. (46)	I.C. Gordy Eq. (49)	I.C. Wilmshurst Eq. (50)	I.C. Batsanov and Durakov	I.C. Lakatos-Bohus
LiH	1.2	0.47	0.79	0.23	0.24	0.6	0.39	0.12	0.128
NaH	1.25	0.46		0.25	0.25	0.63	0.41	0.18	0.096
KH	1.35	0.59		0.28	0.28	0.68	0.46	0.47	0.011
RbH	1.35	0.50		0.28	0.28	0.68	0.46		0.130
CsH	1.40	0.61		0.30	0.29	0.70	0.49		0.132

[a] Electronegativity values from W. Gordy and W. J. O. Thomas, reference 49.
[b] Data for dissociation energies taken from Gaydon, reference 36, and Table I.

Jones,[50] and by Allred.[51] In the following, we have used the values of Gordy and Thomas.[49]

Also, according to Pauling

$$0.208\ \Delta^{1/2} = \lvert x_A - x_B \rvert\ , \qquad (43)$$

where x_A and x_B denote the electronegativities of the two atoms. As Δ is negative, this relationship is inapplicable to the alkali hydrides. Alternatively, in Table XIII, we have compared the values of $0.208\ (\Delta')^{1/2}$ and $\lvert x_A - x_B \rvert$. Here $(x_A - x_B)$ is much larger than $0.208\ (\Delta')^{1/2}$ for all the molecules; thus a relation analogous to Eq. (43) for Δ' does not seem to be possible for these molecules.

A well-known method of estimating the ionic character of a bond is by its dipole moment. The electric moment μ of a diatomic molecule has been interpreted in terms of the amount of ionic character by Fajans[52] and Pauling[28] by the following relationship

$$\text{I.C. (Ionic character)} = \mu / er_e\ . \qquad (44)$$

This definition of ionic character ignores the contribution to the observed dipole moment of the overlap, hybridization, and induced moments. Rittner[22] has shown that polarization effects result in a marked reduction in the dipole moments of the highly ionic alkali halides. The overlap and hybridization moments are often very large (Robinson[53]) and could contribute greatly to the observed dipole moment. Thus, as has been pointed out by earlier workers (Robinson,[53] Hurst[54]), Eq. (44) is not a reliable estimate for the ionic character of a bond.

In this context, we quote a remark due to Dailey and Townes[55]: "Although the observed correlation between μ / er_e and electronegativity differences indicates that dipole moments may be used as some sort of guide in evaluating ionic character, one cannot expect to deduce reliable values of the ionic character from dipole moment data alone."

A value of the dipole moment is available for only one alkali hydride, viz., LiH, which was recently measured by Wharton, Gold and Klemperer.[56] The corresponding value of μ / er_e is shown in Table XIII. We shall discuss this value later on.

The relationship between the amount of ionic character (I.C.) and $\lvert x_A - x_B \rvert$ has also been investigated. Pauling[28] has suggested

$$\text{I.C.} = 1 - \exp\left\{-0.25(x_A - x_B)^2\right\}\ . \qquad (45)$$

However, later work showed that the above relation was not quite satisfactory. Hannay and Smyth[57] have proposed an improved formula

$$\text{I.C.} = 0.16(x_A - x_B) + 0.035(x_A - x_B)^2\ . \qquad (46)$$

Later Pauling[58] also modified Eq. (45) to

$$\text{I.C.} = 1 - \exp\left\{-0.18(x_A - x_B)^2\right\}\ . \qquad (47)$$

Batsanov and Durakov[59,60] find a slightly different value of the constant:

$$\text{I.C.} = 1 - \exp\left\{-0.2(x_A - x_B)^2\right\}\ . \qquad (48)$$

Another relation between the electronegativity difference $\lvert x_A - x_B \rvert$ and the ionic character in the bond is

$$\text{I.C.} = \tfrac{1}{2}\lvert x_A - x_B \rvert\ , \qquad (49)$$

which was obtained by Gordy[61] by plotting the ionic

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[50] E. J. Little and M. M. Jones, J. Chem. Educ. **37**, 231 (1960).

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characters, as determined from nuclear quadrupole coupling constants for some diatomic molecules, against the electronegativity difference of the two atoms in the molecule.

Dailey and Townes[55] have discussed the effects of hybridization, overlap, and polarization on considerations of ionicity and found that it is not possible to obtain a unique curve of ionic character vs electronegativity, since the ionic character apparently depends on such additional variables as bond length. But they found it possible to represent the relationship between the ionic character and $|x_A - x_B|$ by an approximate curve.

Recently Wilmshurst[62] has suggested

$$\text{I.C.} = |x_A - x_B|/(x_A + x_B)\ , \qquad (50)$$

which implies that the ionic character is not a unique function of $|x_A - x_B|$ only. Alternatively we can interpret that Eq. (50) implies that I.C. is a unique function of the ratio x_A/x_B.

Ionic characters as calculated by the above relations have been summarized in Table XIII. There are wide divergences in the ionic characters as calculated by different relations. The values given by the Pauling and Hannay–Smyth equation are very close and also the lowest, while those given by the Gordy equation are the highest.

A different method of calculating the ionic character was given by Wall[63] some 20 years ago. However, it makes use of Pauling's geometric rule. As the geometric rule does not hold for alkali hydrides, we will not discuss Wall's method here.

Quite recently, O-ohata[64] has discussed the relation between the ionicity of the bond and the electronegativity difference by the use of the semilocalized orbital method. He finds that the ionicity of the bond depends not only on the electronegativity difference but also on the overlap integral between the atomic valence orbitals. According to the magnitude of the overlap integral, the diatomic molecules are divided into the two groups that show the different features with respect to the dependence of the ionicity of the bond on the electronegativity difference. The S-shaped curve given by Dailey and Townes seems to be the composite of the above two characteristic groups.

Batsanov and Durakov[59,60] have developed a new method for the determination of the ionic character of bonds; the method involves a comparison between the overlap integral for the real bond and that for a hypothetical covalent bond. Their values for the first three alkali hydrides are also shown in Table XIII. These values show a much greater relative difference between the ionic characters of LiH, NaH, and KH than that predicted by other relations.

Lakatos and his co-workers[65–67] have attempted to calculate the degree of bond polarity by extending the ideas of Fajans. We merely quote here their values (Table XIII). These values are much smaller as compared to the values given by other equations.

The above discussion makes it apparent that the relationship between the ionic character and the electronegativity difference, at least for the alkali hydrides, is not a simple one. Also that there is no simple way to obtain the ionic character by using a classical or semiclassical model.

Quantum-Mechanical Considerations

The concept of "ionic" binding has only a limited significance in quantum-mechanical treatment of molecules. Nevertheless, it is of some interest to examine the available results on the alkali hydrides.

If the covalent state of the molecules is described by the function ψ_c and the ionic state by ψ_i, then the molecule may be described by a linear combination of these two wave functions

$$\psi = \psi_c + \lambda\psi_i\ , \qquad (51)$$

where λ is a constant which is usually determined by the variation method. Its value determines the asymmetry of charge, i.e., the polar character of the bond, sometimes called the degree of ionicity. We may say that the weights of the covalent and ionic parts are in the ratio $1:\lambda^2$.

The "occupation number" (for definition, see Hurley[68]) for the ionic structure is then given by

$$n_i = \lambda^2/(1 + \lambda^2) \qquad (52)$$

and the percentage ionic character by $100\ \lambda^2/(1 + \lambda^2)$.

The LiH molecule is a relatively simple one (four electrons) and since the first investigations of Hutchisson and Muskat,[69] numerous quantum mechanical

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TABLE XIV. Occupation numbers (n_i) for the ionic structure for different wave functions.

Authors	Wave function	a_1	a_2	a_3	a_4	a_5	a_6	b	n_i (ionic)
Fischer[74]	Ψ_1[a]	0.485		−0.07[c]				0.65	0.64
	Ψ_2[b]	.755		−0.01[c]				.345	.17
	Ψ_3[b]	.82		−0.04[c]				.27	.10
Hurst, Miller and Matsen[54]	Ψ_1	0.69158	0.42509	−0.06965	−0.05831	−0.03165		0.22480	.07
Hurley[68]	Ψ_1 (orbital)	−0.0479	−0.0606	+0.6450	−0.0113	+0.3438	−0.0665	+0.2450	.10
	Ψ_2 (orbital)			+0.5729		+0.2968		+0.2805	.16[d]
	Ψ_3 (ICC)	−0.0155	+0.0094	+0.4657	+0.0450	+0.1993	+0.0005	+0.4588	.45
	Ψ_4 (ICC)			+0.4604		+0.2302		+0.4521	.44[d]
Karo and Olson[77]	Ψ_1[e]	0.72	−0.378	+0.055	−0.047	+0.027		−0.23	.073
Robinson, Stuart and Matsen[78]	Ψ_1	0.6123	0.3719					0.2606	.12
	Ψ_2	0.7899	0.5185					−0.0325	.001
	Ψ_3	0.6323	0.4002					0.2200	.08
	Ψ_4	0.6091	0.3797					0.2581	.11
	Ψ_5	0.5627	0.3757					0.2903	.16

[a] Values extrapolated at the energy minimum. Ψ_1 has Li 2*s* orbit with node.
[b] Values interpolated at the energy minimum. Ψ_2 and Ψ_3 have Li 2*s* orbit without node.
[c] Uncertain extrapolation/interpolation.
[d] These values are different from those given by Hurley as we have used a less refined definition of the "occupation numbers."
[e] Values interpolated at the energy minimum from the given values.

treatments[69–79] have been made of this molecule.

As we are interested in the contribution of the ionic binding, we confine ourselves to the treatments based on the valence bond theory with basic wave functions similar to Eq. (51). There exist a number of *ab initio* calculations on this molecule that are more rigorous (Allen and Karo[79]); however, it is difficult to extract information on such questions like "ionicity" from them.

For LiH, the molecular structures of chief importance are:

1. Covalent bonding: Li-H
2. Ionic bonding with the negative charge on the hydrogen atom: Li^+H^-
3. Ionic bonding with the negative charge on the lithium atom: Li^-H^+

We may put the wave function as

$$\Psi = \sum a_n\psi_n + b\phi \tag{53}$$

where the ψ_n's represent structures arising from colent Li-H and ionic Li^-H^+ and ϕ represents the structure Li^+H^-. a_n and b are coefficients.

In analogy with Eq. (52), the "occupation number" for the ionic structure may be defined by.[68]

$$n_i = b^2/(\sum a_n^2 + b^2)\ . \tag{54}$$

In Table XIV are summarized the coefficients a_n and b as determined by a number of workers using different wave functions and different approximations. The last column gives the values of the occupation number for the ionic state n_i as calculated from Eq. (54). These results are not strictly comparable, due to the different approaches and different approximations made by the authors. Nevertheless, they do serve to give a rough orientation to the quantum mechanical results.

The values of n_i as obtained by different treatments fall in a wide interval, from 0.001 to 0.64. However, most of the values are in the neighborhood of 0.15.

Hurley[68] has compared the results due to the "orbital calculations" and those by "intra-atomic correlation correction" (ICC). Table XIV shows that the n_i values for Ψ_3 and Ψ_4 are considerably greater than those by Ψ_1, and Ψ_2, indicating that the principal effect of the intra-atomic correlation cor-

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rection is to increase substantially the ionic character of the bond.

The I.C. as defined by Eq. (44) and n_i as defined by (54) have different significances. We may illustrate it by an example.

Quantum mechanical calculations of the dipole moment of LiH have been carried out on several different types of basic functions by a number of workers[80] and the predicted values are in the range 5.6 to 6.3 Debye. Recently Wharton, Gold, and Klemperer[56] have measured the dipole moment of LiH by the molecular beam electric resonance method and found it to be 5.88 D—in comforting agreement with the theoretical predictions.

As a typical theoretical value we take the result of Hurst, Miller, and Matsen[54] who found a value 6.04 D from a 6-configuration wave function. In terms of Eq. (44), this will mean that the I.C. is 0.79. To interpret it as 79% ionic character is not correct, at least in the quantum mechanical sense, as 90% of the moment comes from hybridization in the covalent structure. The value of n_i for the ionic structure in the wave function of Hurst *et al.* is only 0.07 (Table XIV).

The influence of the overlap integral on the quantity μ/er_e has been examined by Coulson,[81] who using (51), obtains the expression:

$$\frac{\mu}{er_e}=\frac{\lambda^2+2\lambda S_{ab}}{1+\lambda^2+4\lambda S_{ab}/(2+2S_{ab}^2)^{1/2}}, \qquad (55)$$

where S_{ab} is the overlap integral. Only when $S_{ab}=0$ the I.C. as defined by (44) will be equal to n as given by (54).

For LiH, the tables of Fischer[74] and Hurley[68] show that the value of S_{ab} for Li(2s) and H(1s) overlap is $\backsim$0.5. If we assume $S_{ab}=0.5$ and $\lambda=0.5$ (Table XIV), Eq. (52) gives $n=0.2$ while Eq. (55) gives $\mu/er_e=0.4$, which shows that the influence of the overlap is considerable.

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