

Electronic Structure of the First Row Hydrides

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the ions, one cannot be certain, but it does seem probable that the transition in Cs is from a body centered to a more close packed structure, which is probably face centered.

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Electronic Structure of the First Row Hydrides

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Stehn's formulae for the energies of the first row hydrides, BH to FH, in terms of Heitler-London exchange integrals have been applied to more recent data. The empirically derived values for the integrals are now smooth functions of the atomic number, Z . They are also considered as functions of the internuclear distance, r_e , and taken in conjunction with data on BeH, and with the facts that r_e and the force-constant, k , are smooth functions of Z , but invariant to electronic excitation, the results show that it is $2s^2-1s$ exchange that predominates in fixing the internuclear distance and force-constant. On the contrary, the dissociation energies cannot be expected to be smoothly dependent on Z , r_e or k . The heat of dissociation of NH is calculated by Stehn's formulae, after interpolating one exchange integral.

INTRODUCTION

PRESENT theories of heats of dissociation of molecules with more than four electrons are quite crude, and any correlation between theory and experiment, even for the simplest molecules would have value in giving theoretical thermochemistry a better quantitative basis. Stehn¹ made a considerable contribution in deriving formulae for the energies of the first row hydrides, BH, CH, NH, OH, FH, in terms of exchange and Coulomb integrals which can be determined empirically and tested for self-consistency. Since his publication new data have appeared, and in this paper the integrals are recalculated. The three classes of integrals are now smooth functions of the atomic number, and combined with facts known about the internuclear distances and force-constants give a more detailed picture of the orbitals in these molecules.

REDETERMINATION OF THE INTEGRALS

Stehn applied the usual Heitler-London theory, building the molecules from a hydrogen $1s$ electron and various configurations of the heavy atom, to obtain expressions for the electronic

energy

$$W = A + a_1 B + a_2 K + a_3 J_\pi + a_4 J_\sigma, \quad (1)$$

where A is the atomic level of the heavy atom into which the molecule adiabatically decomposes, B is an atomic exchange integral, K the exchange of the hydrogen $1s$ electron with s electrons plus Coulomb terms, J_π and J_σ the exchange with π or σp electrons. The a 's are numerical coefficients of the matrix elements. Stehn noticed that the internuclear distance remains practically the same in all excited states of any one molecule, so that the J 's and K remain the same, permitting simultaneous equations in them to be set up and solved. In this application then the principal defect of the Heitler-London method, that of nonorthogonality, cancels out; but other corrections, such as higher order terms destroy the linearity of Eq. (1).

DISCUSSION OF THE DATA

The excitation energies ν_{mol} and ν_{atom} are usually known quite accurately, and sometimes the J integrals can be calculated from them alone. But a complete solution also depends on one dissociation energy, which is invariably the weakest datum. However, for any one molecule only one

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¹ J. R. Stehn, J. Chem. Phys. 5, 186 (1937).

such energy need be known, by virtue of the well-known cycle connecting upper and lower level dissociation energies, D_e' and D_e'' ,

$$\nu_{\text{mol}} + D_e' = \nu_{\text{atom}} + D_e''. \quad (2)$$

The literature on the dissociation energies of this series of hydrides has been investigated thoroughly. In our calculations we have not used any approximate D 's, e.g., from the formula $\omega_e^2/4x_e\omega_e$, or from extrapolation to the limiting vibrational quantum numbers, but only those obtained from dissociation through rotation, which gives an upper and a lower limit to D_e , (BH, CH), or from thermal data, (OH, FH).

Further details

An error in D for CH or NH will not change the values of their J_π or J_σ , which are obtained from the ν 's. The CH datum is reliable, so K of CH is a good point, Fig. 1. There is not enough data for the evaluation of all three integrals in the case of BH. However, if J_σ of BH is taken to fit in with J_σ of C, N, OH, then J_π automatically will fit in with J_π of C, N, OH, and K will fit with the K 's of CH and OH. Since J_σ and J_π of NH fall smoothly on their respective curves, we can expect to interpolate K of NH.

There is no value for the heat of dissociation of NH; but in the appendix we show this interpolated value of K is probably very good.

The heat of dissociation of FH can only be obtained with the help of thermochemical data. Three investigators report² a heat of formation of +63.0 kcal. To get the dissociation energy of FH, the dissociation energy of F_2 is also needed. This has been evaluated as -62.6 kcal. by Franck's method from the onset of continuous absorption in the spectrum.³ This value can be verified from spectroscopic constants⁴ as follows:

The upper state of F_2 , $^1\Pi$, has an $\omega_e = 837 \text{ cm}^{-1}$ and anharmonicity $x_e\omega_e = 140$. The formula $\omega_e^2/4x_e\omega_e$ gives a value of D_e that is usually too high, but the absolute error in this case is very small, of the order of magnitude of D_e' itself, 0.155 ev. Mulliken⁵ has shown that the upper state dissociates into normal atoms. Hence the dissociation energy of the lower state, D_e'' , (which cannot be reliably determined by $\omega_e''^2/4x_e''\omega_e''$), is $D_e' + \nu_{\text{mol}} = 0.155 + 2.575 = 2.73 \text{ ev}$ or 63 kcal, as above. The D_e for HF then is 6.35 ev.

Kirkpatrick and Salant⁶ obtained bands with high

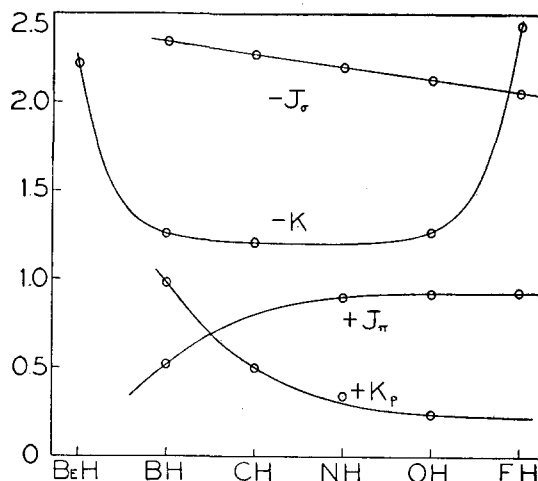


FIG. 1. Values in electron volts of the exchange integrals J_π and J_σ , the total Coulomb terms plus $2s^2-1s$ exchange K , and the $2p-1s$ Coulomb term K_p , as functions of the atomic number.

vibrational quantum numbers in the infra-red, and extrapolated to get $D_e'' = 6.1 \text{ ev}$.⁷

DISCUSSION OF THE INTEGRALS

The solutions obtained for J_σ , J_π , and K are plotted against the atomic number Z in Fig. 1, and against the internuclear distance in Fig. 2. The principal remark is that the integrals are fairly constant for the series and that the curves are quite smooth. The values for K especially have become less erratic than in Stehn's figure, and show less variation. The fact that fairly constant values are obtained, even though the internuclear distance has changed markedly (from a constriction of the wave functions with increasing Z) shows that overlapping occurs to nearly the same extent and in the same relative positions.

The integral J_σ is large, as to be expected. As will be shown below the equilibrium distance is fixed by $2s^2-1s$ interchange. The minimum of J_σ is beyond this point, because the radius, and also the maximum value, of a $2p$ electron in a "dumbbell" orbital is larger than that of the $2s$ electron. The relative positions of the minima of $1s-2s$ and $1s-2p$ exchange can also be

² Bichowski and Rossini, *Thermochemistry of Chemical Substances* (1937).

³ von Wartenburg, Sprenger and Taylor, *Zeits. f. physik. Chemie, Bodenstein Festschrift*, 61 (1931).

⁴ Sporer, *Molekulspektren I*, p. 18.

⁵ R. S. Mulliken, *Phys. Rev.* **36**, 701 (1930).

⁶ D. E. Kirkpatrick and E. O. Salant, *Phys. Rev.* **48**, 945 (1935).

⁷ Landolt-Börnstein, *Tabellen*, Vol. 3, p. 2873, state thermochemical data gives $D_e'' = 120 \text{ kcal.}$ or 5.2 ev, but this probably was old thermal data, *ibid.* Vol. 2, p. 1489, uncorrected for polymerization, *ibid.*, Vol. 3, p. 2746 and also Bichowski and Rossini, reference 2.

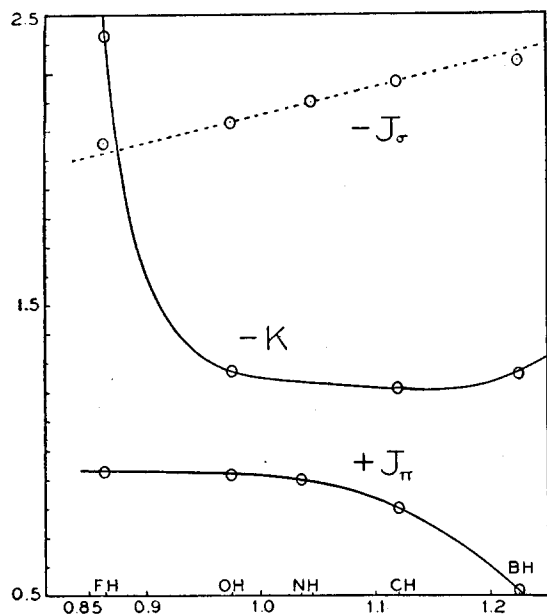


FIG. 2. Values of the integrals J_π , J_σ and K as functions of the internuclear distance. The dotted curve represents J_σ as calculated from Rosen's expression for this integral.

estimated from the integrals derived by Rosen.⁸ The J_σ integral is quite flat, so that the points on Figs. 1 and 2 are very close to the maxima of this integral.

The second-order effect, the slight increase of J_σ with increasing r_e can also be accounted for by simple exchange integral theory. Rosen evaluated the integral between a $2p$ and a $1s$ electron, which is, except for $1/r_{12}$ terms,

$$J_\sigma = NZ_1^2 r_e (Z_1 r_e + 1) e^{-Z_1 r_e}, \quad (3)$$

N being unity minus a nonorthogonality function, fairly independent of Z_1 . In this derivation both nuclei are supposed to have the same charge Z_1 . Since the heavy nucleus is heavily shielded in these molecules, (3) should not be a bad formula for comparisons. It can in fact be fitted to the straight line of J_σ versus r_e of Fig. 2 by two parameters, the "constant" N and a shielding constant of 0.63 for each p electron on the p electron that is exchanging. Usual values of shielding of $1s^2 2s^2$ were taken,⁹ but the calculations are insensitive to them. Shielding constants are discussed again later. The same value is obtained assuming Z_1 to be the average of the effective charge of the heavy nucleus and proton, indicating (3) may be fairly good even when there is asymmetry.

The integral J_π decreases with increasing r_e , and quite suddenly farther out, as would be expected of overlapping of the hydrogen $1s$ with

⁸ N. Rosen, Phys. Rev. **38**, 2009 (1931).

⁹ Slater and Frank, *Introduction to Theoretical Physics*, p. 432.

π electrons. As r_e decreases to form the united atom, J_π becomes an atomic exchange integral between a $2p_\pi$ and a $2p_\sigma$ electron, equal to $3F_2$ (Shortley-Condon notation). An extrapolated value of $3F_2$ through C, N, O, F, is just about the value of 0.94 ev to which J_π of Fig. 2 converges.

The quantity K is actually a sum of several terms; the exchange and Coulomb integrals of $2s^2-1s$ binding, say K_s , and Coulomb integrals of the hydrogen $1s$ with the p_π and p_σ electrons, K_π and K_σ in Stehn's notation. To solve the equations Stehn made the reasonable assumption that $K_\sigma = K_\pi = K_p$. Thus

$$\begin{aligned} K &= K_s + a_5 K_\pi + a_6 K_\sigma \\ &= K_s + Z_p K_p, \end{aligned} \quad (4)$$

where Z_p is the number of p electrons.

In view of the constancy of J_σ , the $2s^2-1s$ exchange K_s should also remain reasonably constant (as contrasted with the variation in K), and should be equal to the dissociation energy of BeH, which has no p electrons. The difference $K_p = (K - K_s)/Z_p$ is calculated and plotted on Fig. 1. This, then, is the Coulomb energy (other than the attraction $-e^2/r_e$ of each electron to the other nucleus, which is canceled by the nuclear repulsion term in the energy expression) of the hydrogen $1s$ and a $2p$ electron. As the series approaches more to a united atom K_p falls off to a small value of 0.2 ev, of the right order of magnitude for an atomic electrostatic repulsion of two $2p$ electrons.

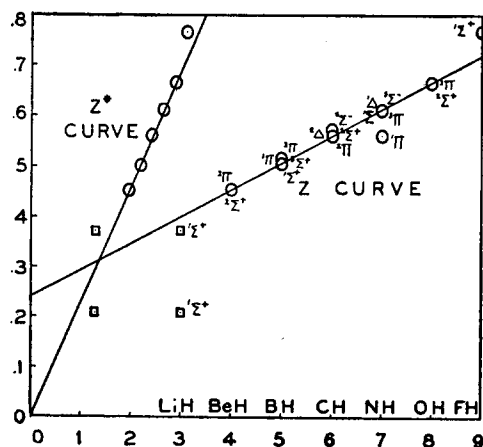
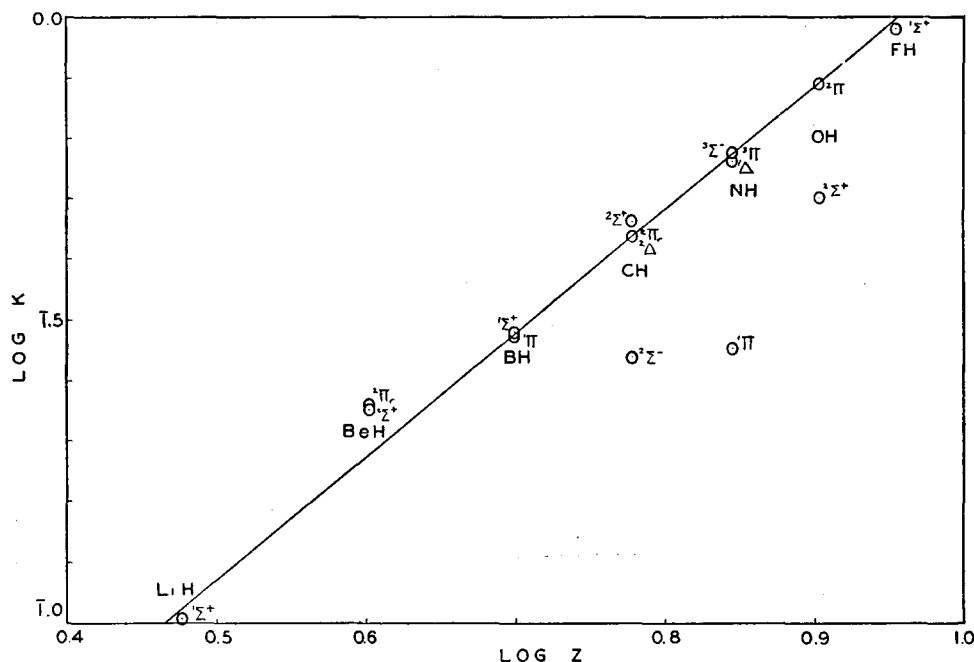


FIG. 3. The linear dependence of $1/(r_e - 0.34)$ on the atomic number Z , and the effective nuclear charge Z^* . For most excited states the internuclear distance is the same as in the ground state.



with a minimum relatively far out, as our J 's, will not affect appreciably the r_e of the whole molecule.

The force-constant of the molecule is given by the second differential of (1), viz.,

$$k = a_2 K'' + a_3 J_{\pi}'' + a_4 J_{\sigma}''. \quad (7)$$

Spectroscopic data show k is independent of a_3 and a_4 , so the quantities J_{π}'' and J_{σ}'' must be small relative to K'' ; that is, the energy curves for exchange with p electrons are relatively flat.

RELATIONS BETWEEN INTERNUCLEAR DISTANCE, FORCE-CONSTANT AND NUCLEAR CHARGE

With this picture of strong $1s-2s^2$ bonding it is possible to derive laws relating r_e , k and Z by a

simple theory of the dependence of the dimensions of the $2s^2$ orbits on Z . These relations are smooth functions, which fit the data (including the excited states) very well for the series F, O, N, C, B, BeH. The values for LiH show a discontinuity, as is to be expected at the transition from the configuration $2s^2$ to $2s$. But there is no discontinuity apparent on the change of number of p electrons, either π or σ . These electrons have an effect only through shielding.

If then, the potential curve has a component in the form of $2s^2-1s$ exchange which predominates because of a sharp minimum at the short-

TABLE I.

MOL	Z	STATE	CONFIG.	ENERGY	D_e	r_{mol}	r_{atom}	$r_e A$	$\omega_e \text{ cm}^{-1}$	REFS.
LiH	3	$X^1\Sigma^+$ $1\Sigma^+$	— —	— —	2.47	0	0	1.593 2.600	1405.65 234.41	19
BeH	4	$2\Sigma^+$ 2Π	— —	$1S + K_e$ —	2.22	0	0	1.340 1.330	2058.5 2087.6	8
BH	5	$A^1\Sigma^+$	σ	$2P + K_{\sigma} + J_{\sigma}$	3.60	0	0	1.225	2366	2, 3
		$D^3\Pi$	π	$2P + K_{\pi} - J_{\pi}$	0.73	2.847	0	1.198	2344	3, 4
		$C^1\Pi$	π	$2P + K_{\pi} + J_{\pi}$			0	1.219		2, 3
		$B^3\Sigma^+$	σ	$2P + K_{\sigma} - J_{\sigma}$			0	1.220		3, 4
CH	6	$X^2\Pi_r$	$\pi\sigma$	$3P + \frac{3}{2}F_2 + K_{\pi} + K_{\sigma} - \frac{1}{2}J_{\pi} + J_{\sigma}$	3.602	0	0	1.12	2824	5, 6
		$A^2\Delta$	π_+^2	$1D + 2K_{\pi} - J_{\pi}$	0.39	2.860	1.25	1.11	2800	8
		$B^2\Sigma^-$	$\pi_+\pi_-$	$3P + 2K_{\pi} + J_{\pi}$		3.175	0	1.094	2242	5, 6
		$C^2\Sigma^+$	$\pi_+\pi_-$	$1D + 6F_2 + 2K_{\pi} - J_{\pi}$		3.928	1.25	1.12	2906	8
NH	7	$X^3\Sigma^-$	$\pi_+\pi_-\sigma$	$4S + 3F_2 + 2K_{\pi} + K_{\sigma} - J_{\pi} + J_{\sigma}$	—	0	0	1.035 1.045	~ 3300	9, 10, 11 13
		$a^1\Delta$	$\pi_+^2\sigma$	$2D + 2K_{\pi} + K_{\sigma} - J_{\pi} + J_{\sigma}$	—	a	2.37	1.041 1.12	3060 3183	13, 14 12
		$b^1\Sigma^+$	$\pi_+\pi_-\sigma$	$2P + 2K_{\pi} + K_{\sigma} - J_{\pi} + J_{\sigma}$	—	$1.058 + a$	0	1.043		13
		$A^3\Pi$	$\pi_+^2\pi_-$	$2D + 3F_2 + 3K_{\pi} - 2J_{\pi}$	—	3.670	2.37	1.034 1.046	~ 3300	9, 10, 11 13
		$C^1\Pi$	$\pi_+^2\pi_-$	$2D + 3F_2 + 3K_{\pi}$		$3.79 + a$	2.37	1.123 1.122	2270	13, 14 13, 14
OH	8	$A^2\Pi_i$	$\pi_+^2\pi_-\sigma$	$3P + \frac{3}{2}F_2 + 3K_{\pi} + K_{\sigma} - \frac{3}{2}J_{\pi} + J_{\sigma}$	4.35	0	0	.964 .974	3735	15, 16 17, 18
		$B^2\Sigma^+$	$\pi_+^2\pi_-^2$	$1D + 3F_2 + 4K_{\pi}$	2.26	4.03	1.94	1.009 1.015	3184	8 17, 18
FH	9	$1\Sigma^+$	$\pi_+^2\pi_-\sigma$	$2P + 4K_{\pi} + K_{\sigma} - 2J_{\pi} + J_{\sigma}$	6.35	0	0	.864	4037 4141	8 20

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est r_e , the whole series Be to FH should have r_e and k of the same potential curve, variation being due solely to contraction with increasing Z .

Internuclear distance

It is well established from measurements of the interatomic distances and from the simple idea of maximum overlapping that the internuclear distance is roughly the sum of the atomic radii. For $2s^2-1s$ binding

$$r_e = (n^2/Z - S) + a. \quad (8)$$

Here S is the shielding constant for the heavy atom, and n^2 is a little more than 2^2 in the case of s electron binding.¹² The distance a can be taken either as the hydrogen radius, of 1 atomic unit, or as the position of the *maximum* of the $1s$ hydrogen wave function from the hydrogen nucleus, 0.34 atomic units.

Curve I of Fig. 3 is a plot of $1/(r_e - 0.34)$ versus Z , showing linearity in agreement with (8).

Since the $2s$ interchange fixes r_e , S refers to the shielding of a $2s$ electron. It is equal to $A - BZ_p$,

where A is the $1s^2 2s$ shielding, B the shielding constant for a $2p$ on a $2s$ electron, and Z_p is the number of $2p$ electrons. Thus

$$\frac{1}{r_e - a} = \frac{Z^*}{n^2}, \quad (9)$$

$$Z^* = Z(1 - BZ_p) - A. \quad (10)$$

For A the usual⁹ 0.85 for each $1s$ electron, 0.35 for the other $2s$ electron were used. The constant B then plays the role of a parameter which is adjusted to make the graph of $1/(r_e - 0.34)$ versus Z^* pass through the origin in accordance with (9). It turns out that the points still lie on a straight line, Fig. 3, with a slope of 4.28, which is a good value for n^2 .

The required value of 0.77 for the shielding of p electrons (along the internuclear axis) is larger than the values found in the central fields of atoms. This is to be expected as p_σ electrons in cylindrical fields of molecules are well intermingled with the bonding electrons, and even p_π electrons have orbits located along the internuclear axis, not "dumbbells" at the end of the

¹² Reference 9, p. 445.

TABLE II.

MOL	Z^*	$-J_\sigma$	$+J_\pi$	$-K$	$+K_p$	STATE	k MEGADYNES/CM	k_{calc} /CM	$Z^* \times$ ($r_e - .34$)	kr_e^2/Z^{*2} ev	$k \times$ ($r_e - .63$) ²
LiH	1.30	—	—	—	—	$X^1\Sigma^+$ $^1\Sigma^+$	0.102 0.0311	0.037	4.284 4.247	4.80 3.88	0.203 .359
BeH	1.95	—	—	—	—	$^2\Sigma^+$ $^2\Pi_r$	0.225 0.231	0.211	3.349 5.957	3.33 3.37	.228 .228
BH	2.18	2.34	0.52	1.26	0.98	$A^1\Sigma^+$ $D^3\Pi$ $C^1\Pi$ $B^3\Sigma^+$	0.302 0.297	0.303	4.314 4.203 4.290 4.292	2.99 2.91	.213 .207
CH	2.41	2.27	0.80	1.21	0.50	$X^2\Pi_r$ $A^2\Delta$ $B^2\Sigma^-$ $C^2\Sigma^+$	0.434 0.426 0.273 0.459	0.438	4.290 4.244 4.172 4.290	2.94 2.84 1.77 3.12	.210 .198 .119 .222
NH	2.64	2.20	0.90	(1.20)	0.34	$X^3\Sigma^+$ $a^1\Delta$ $b^1\Sigma^+$ $A^3\Pi$ $C^1\Pi$	0.599 0.515 0.599 0.283	0.615	4.274 4.324 4.306 4.313 4.269 4.710	2.89 2.94 2.51 2.85 1.61	.205 .222 .181 .205 .138
OH	2.87	2.13	0.92	1.27	0.24	$A^2\Pi_i$ $B^2\Sigma^+$	0.774 0.5622	0.838	4.261 4.506	2.75 2.19	.292 .172
FH	3.10	2.06	0.93	2.43	~0	$^1\Sigma^+$	0.9601	1.10	4.018	2.34	.142

molecule. There is some indication that π electrons have a smaller shielding effect than the σ type.

This value of 0.77 for $2s-2p$ shielding is in agreement with the $2p-2p$ shielding of 0.63 obtained from our discussion of the exchange integral J_σ , and further, is the only one that fits the following equations for the force-constants.

Force-constants

From the theoretical calculations of the potential energy curves for H_2 , H_2^+ , HeH^+ and other studies of interatomic forces, it is seen that the attractive forces fall off as $-\exp(-ar)$, or as $-a'/r^6$, while repulsive forces have a range about the square of this, $\exp(-2ar)$ or b/r^{12} . Following Slater and Frank¹² we can estimate the constant a as Z^*/r_e , where Z^* is the effective nuclear charge for the principal binding electrons (10), giving a potential curve of the Morse type,

$$De^{-2Z^*(r-r_e)/r_e} - 2De^{-Z^*(r-r_e)/r_e}. \quad (11)$$

The force-constant for this function is

$$k = (2Z^{*2}/r_e^2)D. \quad (12)$$

If it is true that $2s^2-1s$ exchange fixes k in the series BeH to FH, the D in (11) and (12) will be practically constant, and equal to K_s ; therefore the quantity $kr_e^2/2Z^{*2}$ should be roughly constant, equal to K_s . Column (11) in Table II shows that the data are in fair agreement with this simple theory. The trend in K_s is almost the same as for J_σ ; the average value is 2.94 ev, whereas the dissociation energy of BeH, also approximately equal to K_s is 2.22 ev.

Equations (9) and (12) can be combined to express the force-constant k as a function of Z^* alone,

$$k = \frac{2K_s Z^{*4}}{(n^2)^2 + 0.68(n^2)Z^* + 0.12Z^{*2}}. \quad (13)$$

The best fit, column (9) of Table II, is with values of $K_s = 2.94$ ev and $(n^2) = 4.29$, values in excellent agreement with those obtained with the simpler formulae. At first sight this might be expected, but had there been a real trend from (9) and (12), the constants from (13) would not have been the same.

As a comparison, Badger's constant¹³ is calculated in column (12), to show the agreement with the theoretical is as good as with the empirical formulae.

SUMMARY

By the aid of Stehn's energy expressions we have made some analysis of the potential curves of the molecules BeH, BH, CH, NH, OH, FH. The force-constant and the internuclear distance are determined by $2s^2-1s$ exchange, and are not influenced by the p electrons. This accounts for their regular variation with Z , and invariance to electronic excitation. On the other hand this regularity is entirely dispersed in the case of the dissociation energies. That is, we cannot expect graphs of D versus Z , r_e or k to be simple curves, because in the formulae for D the p electrons contribute largely, in a fashion quite irregular with respect to Z , r_e or k , as displayed explicitly by Stehn's formulae.

The author takes pleasure in acknowledging the help of Professor J. H. Van Vleck and of Dr. J. R. Stehn in preparing this paper, and also the hospitality of the physics, chemistry and mathematics departments of Princeton University.

APPENDIX

Heat of dissociation of NH

There is no known value of the dissociation energy of NH. [The value of 102.2 kcal. quoted by Bichowski and Rossini² from Bates¹⁴ is an upper limit.]

If we can rely on the smooth curves of Fig. 1 we can calculate, by means of Stehn's formulae, this dissociation energy as $D_e = 3.61$ ev, or 83 cal. The thermal dissociation energy, D_0 will be $D_e - \frac{1}{2}\omega_e = 79$ kcal.

¹³ R. M. Badger, J. Chem. Phys. 2, 128 (1934).

¹⁴ Bates, Zeits. f. physik. Chemie, Bodenstein Festschrift, 329 (1931).

TABLE III. Bond energies of simple and saturated hydrides.

CH	78.9 kcal.	$\frac{1}{4}$	CH ₄	87.6 kcal.
NH	79 kcal.	$\frac{1}{3}$	NH ₃	83.9 kcal.
OH	100.2 kcal.	$\frac{1}{2}$	OH ₂	110.4 kcal.

This seems to be a good value in comparison with $\frac{1}{3}$ of the heat of formation of NH₃ from atoms, namely 84 kcal., a calculation suggested by the theory of directed valency. Table III is a summary of such a computation for CH, NH, and OH.