

Theory of the Electronic Energy Levels of Simple Hydrides

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Theory of the Electronic Energy Levels of Simple Hydrides

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The conventional extremely simplified form of the Heitler-London theory is applied to the energy levels of the molecules BH, CH, NH, OH, FH. The exchange integrals, determined empirically to make the theory fit the known levels, are found to vary slowly and regularly from one molecule to the next. The energies of states as yet unobserved are predicted.

INTRODUCTION

VAN VLECK and Sherman¹ have discussed the many reasons why the molecular theory of Heitler, London, Slater and Pauling, should not be accurate, especially in the simplified form in which it is commonly applied. Yet, as they also point out, it is just that simplified form which has enjoyed the most success. The present work constitutes further evidence of its effectiveness, in a group of molecules as yet untried, *viz.* in hydrides of the type XH, where X represents an element of the first row of the periodic table: B, C, N, O or F. The work is also of use in calculations on certain more complicated molecules, such as CH₄ and H₂O.² The simplified HLSP theory calculates the energy of a polyatomic molecule in terms of the energy parameters characteristic of pairs of atoms in the molecule, and the energy parameters for the pairs XH are of course found here.

By proper choice of atomic orbitals, one should be able to calculate the values of these parameters. But a less laborious (and, for our purposes, more accurate) method of evaluation is the empirical one. The parameters are so chosen as to make the theoretical energy expressions most nearly represent the known energy levels of the molecules XH.

THEORETICAL ENERGY EXPRESSIONS

We consider XH as being formed from atom X in its normal configuration $1s^2 2s^2 2p^n$ plus atom H

in the configuration $1s$. The $2p$ orbits of X for $\lambda=0, 1$, and -1 , and the $1s$ orbit of H are denoted, respectively, by σ , π_+ , π_- , and h . The $1s$ and $2s$ orbits of X are given no special symbols, for in our approximation the energy contributions of these orbits are identical for the various states of a given molecule and can therefore be combined with the "Coulomb" terms. A typical molecular configuration is then $\sigma^2 \pi_+ h$, which happens to represent a Π state of NH.

We assume that:

(1) All configurations other than those of the type just described can be neglected.³ Thus we do not consider the perturbing effects of ionic configurations, such as $1s^2 2s^2 2p^{n+1}$, in which all the electrons are effectively attached to the X nucleus. Nor do we consider configurations in which one of the electrons of X is excited, e.g., $1s^2 2s^2 2p^{n+1} h$. In addition, we neglect interactions among those configurations which are considered (e.g., in NH, $\sigma^2 \pi_+ h$ and $\pi_+^2 \pi_- h$).

(2) All orbitals are orthogonal to one another.⁴

(3) The magnitude of an "exchange integral" (defined below) is roughly proportional to the amount of "overlapping" of the orbits concerned in the exchange. Therefore $|J_{\sigma h}| \gg |J_{\pi h}|$.

(4) Coulomb terms are nondirectional; that is, $K_{\sigma h} = K_{\pi h}$.

(5) The states of a given molecule have the same equilibrium separation, r_e , so that the parameters (Coulomb and exchange integrals)

¹ J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.* **7**, 167 (1935). This admirable summary article should be consulted on questions concerning the terminology and underlying philosophy of the work.

² H₂O—J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.* **1**, 357 (1933). H₂O₂, N₂H₄—W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* **2**, 492 (1934). CH₄—J. H. Van Vleck, *J. Chem. Phys.* **2**, 20 (1934). CH₂, CH₃, CH₄—H. H. Voge, *J. Chem. Phys.* **4**, 581 (1936).

³ This assumption is based mainly on energy considerations. It appears to be invalid for FH, where, in agreement with standard chemical ideas, ionic configurations are probably important.

⁴ Values of their S integrals by C. E. Ireland, *Phys. Rev.* **43**, 329 (1933), and by W. H. Furry and J. H. Bartlett, Jr., *Phys. Rev.* **39**, 210 (1932), show how invalid this assumption really is. A far-reaching discussion of the effects of nonorthogonality is given by A. S. Coolidge and H. M. James, *J. Chem. Phys.* **2**, 811 (1934).

have identical values for all the states of a given molecule. Calculations for repulsive states refer only to this same separation, of course—similarly with applications of the parameters to polyatomic molecules. Fortunately, the molecules considered here conform fairly well to this assumption. Note that r_e values for different molecules need not be equal.

These assumptions are roughly analogous to those made by Eyring and his colleagues in their extensive activation energy calculations.⁵ Here, however, we take into account the directional properties of the orbitals, as well as the internal energy of the X atom, and we thus ought to obtain more accurate results.

The Dirac vector model, as used by Van Vleck⁶ and Serber,⁷ offers perhaps the most elegant method of deriving the energy expressions. On the basis of assumptions (1) and (2) above, we need merely the fundamental formula for the Hamiltonian matrix:⁸

$$\mathcal{H} = \sum_{\text{all pairs}} K_{ij} - \sum_{i, \mu} J_{i\mu} - 2 \sum_{\mu > \nu} J_{\mu\nu} - \sum_{i > j} \frac{1}{2} (1 + 4\mathbf{s}_i \cdot \mathbf{s}_j) J_{ij}$$

K_{ij} and J_{ij} are, respectively, the Coulomb and exchange integrals between orbits i and j :

$$K_{ij} \equiv \iint \psi_i^*(1) \psi_j^*(2) \mathcal{H} \psi_i(1) \psi_j(2) d\tau_1 d\tau_2,$$

$$J_{ij} \equiv \iint \psi_i^*(1) \psi_i^*(2) \mathcal{H} \psi_i(1) \psi_j(2) d\tau_1 d\tau_2.$$

The Roman and Greek subscripts on the J 's refer, respectively, to "free" and to "filled" orbits, i.e., to those which appear once and to those which appear twice in the configuration. The \mathbf{s}_i are vector spin matrices.

To determine the characteristic values of \mathcal{H} , we need those of $\sum [-\frac{1}{2}(1 + 4\mathbf{s}_i \cdot \mathbf{s}_j) J_{ij}]$. These are, for the cases in which we are interested, and for various values of the total spin, S :

2 free electrons:

$$S=1: -J_{12} \\ S=0: +J_{12}$$

⁵ See, for example, A. Sherman and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

⁶ J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

⁷ R. Serber, Phys. Rev. **45**, 461 (1934) and J. Chem. Phys. **2**, 697 (1934).

⁸ Reference 6, Eq. (7). The use of J and K there is the opposite of that here.

3 free electrons:

$$S = \frac{3}{2}: -J_{12} - J_{13} - J_{23} \\ S = \frac{1}{2}: \pm 2^{-1} [(J_{12} - J_{13})^2 + (J_{12} - J_{23})^2 + (J_{13} - J_{23})^2]^{\frac{1}{2}}$$

4 free electrons, with $J_{13} = J_{23}$, $J_{14} = J_{24}$:

$$S=2, S_{12}=1: -J_{12} - J_{34} - 2J_{13} - 2J_{14} \\ S=1, S_{12}=1: -J_{12} - \frac{1}{2}J_{13} - \frac{1}{2}J_{14} \\ \quad \pm [(J_{34} - \frac{1}{2}J_{13} - \frac{1}{2}J_{14})^2 + 2(J_{13} - J_{14})^2]^{\frac{1}{2}} \\ S=1, S_{12}=0: +J_{12} - J_{34} - J_{13} - J_{14} \\ S=0, S_{12}=1: -J_{12} - J_{34} + J_{13} + J_{14} \\ S=0, S_{12}=0: +J_{12} + J_{34} - J_{13} - J_{14}$$

The formulas for the cases of 2 and 3 free electrons are well known.¹ Those for the 4 electron case, on the assumption made above that two pairs of J 's are equal, can be readily worked out by a variant of Goudsmit's inspection method,⁹ since this assumption reduces the problem to that of three vectors, \mathbf{s}_3 , \mathbf{s}_4 and \mathbf{S}_{12} ($\equiv \mathbf{s}_1 + \mathbf{s}_2$). It is also possible to obtain these results from the work of Johnson,¹⁰ Schlapp,¹¹ or especially of Merrill¹² on more general 4 vector problems. The explicit permutation matrices given by Serber¹³ offer still another way of deriving these formulas.

The only 4-free-electron problem we consider is that of the $\pi_+ \pi_- \sigma H$ configuration of NH. From obvious symmetry considerations, $J_{\sigma\pi_+} = J_{\sigma\pi_-}$, and $J_{H\pi_+} = J_{H\pi_-}$; that is why the characteristic

TABLE I. BH. ($K = -1.36$, $J_\pi = +0.62$, $J_\sigma = -2.23$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma H {}^3\Sigma^+$	${}^2P + K_\sigma - J_\sigma$	${}^2P + 0.87 = +0.87$	
$\pi H {}^1\Pi$	${}^2P + K_\pi + J_\pi$	${}^2P - 0.74 = -0.74^*$	-0.74
$\pi H {}^3\Pi$	${}^2P + K_\pi - J_\pi$	${}^2P - 1.98 = -1.98$	
$\sigma H {}^1\Sigma^+$	${}^2P + K_\sigma + J_\sigma$	${}^2P - 3.59 = -3.59^*$	-3.59

⁹ S. Goudsmit, Phys. Rev. **35**, 1325 (1930). The method is also illustrated on p. 226 of reference 1.

¹⁰ M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).

¹¹ R. Schlapp, Proc. Roy. Soc. Edinburgh **54**, 109 (1934).

¹² R. A. Merrill, Phys. Rev. **46**, 487 (1934). Merrill's vectors \mathbf{L} , \mathbf{S}_d , \mathbf{J}_d , \mathbf{s}_m , \mathbf{s}_n , \mathbf{S} , \mathbf{J} , correspond to our \mathbf{s}_1 , \mathbf{s}_2 , \mathbf{S}_{12} , \mathbf{s}_3 , \mathbf{s}_4 , \mathbf{S}_{34} , \mathbf{S} . His matrices do not give the $\mathbf{s}_1 \cdot \mathbf{s}_3$ and $\mathbf{s}_1 \cdot \mathbf{s}_4$ interactions; but these can be found in our case, where $\mathbf{s}_1 = \mathbf{s}_2 = \frac{1}{2}$, by observing that $\mathbf{s}_1 \cdot \mathbf{s}_3 = \mathbf{s}_2 \cdot \mathbf{s}_3$ if \mathbf{s}_1 and \mathbf{s}_2 are parallel ($S_{12}=1$) and that $\mathbf{s}_1 \cdot \mathbf{s}_3 = -\mathbf{s}_2 \cdot \mathbf{s}_3$ if \mathbf{s}_1 and \mathbf{s}_2 are antiparallel ($S_{12}=0$). Formulas are also given for the 3 vector problem which we would have if we let $J_{34}=0$; these should allow a check in one limiting case. However, there is a slight error in Merrill's 3 vector formulas (2) on p. 488; the quantity $\frac{1}{2}B_d S_d$ should be added to each of the first three expressions for W , while $-\frac{1}{2}B_d(S_d+1)$ should be added to the last expression for W . This error in no way affects the remaining results of Merrill's paper, as it merely introduces an additive constant which cancels out in all his applications.

¹³ R. Serber, J. Chem. Phys. **2**, 697 (1934).

TABLE II. CH. ($K = -1.79$, $J_\pi = +0.80$, $J_\sigma = -2.27$, $3F_2 = +0.55$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2 H^2\Sigma^+$	$^1S - 6F_2 + 2K_\sigma - J_\sigma$	$^1S - 0.62 = +2.04$	
$\pi\sigma H^2\Pi$	$^1D - \frac{3}{2}F_2 + K_\pi + K_\sigma + \frac{1}{2}J_\pi - J_\sigma$	$^1D + 0.60 = +1.85$	
$\pi_+\pi_- H^2\Sigma^+$	$^1D + 6F_2 + 2K_\pi - J_\pi$	$^1D - 1.49 = -0.24$	-0.25
$\pi\sigma H^4\Pi$	$^3P + K_\pi + K_\sigma - J_\pi - J_\sigma$	$^3P - 0.32 = -0.32$	
$\pi_+\pi_- H^2\Sigma^-$	$^3P + 2K_\pi + J_\pi$	$^3P - 0.99 = -0.99^*$	-0.99
$\pi_+^2 H^2\Delta$	$^1D + 2K_\pi - J_\pi$	$^1D - 2.59 = -1.34^*$	-1.33
$\pi_+\pi_- H^4\Sigma^-$	$^3P + 2K_\pi - 2J_\pi$	$^3P - 3.39 = -3.39$	
$\pi\sigma H^2\Pi$	$^3P + \frac{3}{2}F_2 + K_\pi + K_\sigma - \frac{1}{2}J_\pi + J_\sigma$	$^3P - 4.18 = -4.18^*$	-4.18

TABLE III. NH. ($K = -2.01$, $J_\pi = +0.90$, $J_\sigma = -2.20$, $3F_2 = +0.69$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2\pi_+ H^1\Pi$	$^2P - 3F_2 + K_\pi + 2K_\sigma + J_\pi - J_\sigma$	$^2P + 0.40 = +3.95$	
$\pi_+\pi_-\sigma H^1\Sigma^-$	$^2D + 2K_\pi + K_\sigma + J_\pi - J_\sigma$	$^2D + 1.09 = +3.46$	
$\pi_+\pi_-\sigma H^3\Sigma^+$	$^2P + 2K_\pi + K_\sigma - J_\pi - J_\sigma$	$^2P - 0.71 = +2.84$	
$\sigma^2\pi_+ H^3\Pi$	$^2P - 3F_2 + K_\pi + 2K_\sigma - J_\pi - J_\sigma$	$^2P - 1.40 = +2.15$	
$\pi_+\pi_-\sigma H^3\Sigma^-$	$^2D - 3F_2 + 2K_\pi + K_\sigma - J_\sigma$	$^2D - 0.50 = +1.87$	
$\pi_+^2\sigma H^3\Delta$	$^2D + 2K_\pi + K_\sigma - J_\pi - J_\sigma$	$^2D - 0.71 = +1.66$	
$\pi_+^2\pi_- H^1\Pi$	$^2D + 3F_2 + 3K_\pi$	$^2D - 1.32 = +1.05^*$	+1.07
$\pi_+^2\pi_- H^3\Pi$	$^2D + 3F_2 + 3K_\pi - 2J_\pi$	$^2D - 3.12 = -0.75^*$	-0.73
$\pi_+\pi_-\sigma H^1\Sigma^+$	$^2P + 2K_\pi + K_\sigma - J_\pi + J_\sigma$	$^2P - 5.11 = -1.56$	-1.66
$\pi_+\pi_-\sigma H^3\Sigma^-$	$^4S + 2K_\pi + K_\sigma - 2J_\pi - J_\sigma$	$^4S - 1.61 = -1.61$	
$\pi_+^2\sigma H^1\Delta$	$^2D + 2K_\pi + K_\sigma - J_\pi + J_\sigma$	$^2D - 5.11 = -2.74^*$	-2.72
$\pi_+\pi_-\sigma H^3\Sigma^-$	$^4S + 3F_2 + 2K_\pi + K_\sigma - J_\pi + J_\sigma$	$^4S - 4.42 = -4.42^*$	-4.40

values were tabulated above only for the restricted 4 electron problem. Furthermore in this problem, as in any other involving a $\pi_+\pi_-$ pair of free electrons, the states are Σ^+ or Σ^- according as $S_{\pi_+\pi_-}$ is 0 or 1.

The atomic J 's and K 's can be evaluated in terms of the Slater-Condon-Shortley parameters F_0 and F_2 :¹⁴

$$\begin{aligned} K_{\sigma\sigma} &= F_0 + 4F_2 \\ J_{\pi\sigma} &= 3F_2, \\ K_{\pi\sigma} &= F_0 - 2F_2, \\ J_{\pi_+\pi_-} &= 6F_2, \\ K_{\pi_+\pi_-} &= F_0 + F_2. \end{aligned}$$

It is convenient to include in the energies of the molecular states the energies of the atomic states into which they dissociate; thus the F_0 terms are eliminated. This is done by means of Slater's formulas¹⁴ for the energies of p^n configurations. For example, the states of the N atom have energies: $^2P = 3F_0$, $^2D = 3F_0 - 6F_2$, $^4S = 3F_0 - 15F_2$.

The molecular J 's and K 's will be abbreviated by omission of the subscript H ; thus $J_\sigma \equiv J_{\sigma H}$, etc. In Tables I-V, we have used the fact that $|J_\sigma|$ is larger than the other J 's (assumption 3)

¹⁴ J. C. Slater, Phys. Rev. **34**, 1293 (1929); E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

to expand all the square roots into expressions linear in the J 's. This is effectively the approximation of electron pairing. That it is quite a good one here (the maximum resulting error being 0.05 volt) is in large part due to the approximate equality of $J_{\pi H}$ and $J_{\pi\sigma}$.

DETERMINATION OF PARAMETERS

Although there are explicitly five parameters in the energy expressions, atomic spectra fix the value of one of them, F_2 .¹⁵ The remaining four are more than can be determined from the observed molecular energy levels. To simplify matters, and to follow the precedent of many another work on molecular theory, we have arbitrarily chosen K_π equal to K_σ (assumption 4). This makes the Coulomb terms equal for all states of a given molecule. In the case of CH and NH the three parameters remaining, J_π , J_σ , and K (the sum of the Coulomb and inner shell contributions), were determined so as to fit best the four or five observed energy levels. In the case of BH

¹⁵ Actually, as Slater, reference 14, has shown, two values of F_2 can be found, depending on which pair of atomic levels (in C, N, and O) is assumed to be given correctly by his theory. We have here used the average of these two values.

and OH, which possess but two observed levels apiece, the three parameters could not be completely specified. Here, then, values of the parameters were chosen which simultaneously fitted the observed pairs of levels and ran smoothly from one hydride to the next. In the case of FH, both J_π and J_σ were extrapolated, while K was chosen to fit the single observed level.

TABLES

All values are in electron volts. Predicted energy values denoted by an asterisk are effectively the ones which were adjusted (by proper choice of parameters) to fit the experimental values. Experimental energy values have been corrected for the zero-point vibrational energy before being tabulated here. They come from the following sources:

BH and CH: from Mulliken.¹⁶

NH: from the recent compilation of Lunt, Pearse, and Smith.¹⁷ The singlet-triplet separation ($\alpha, \equiv {}^1\Delta - {}^3\Sigma^-$) has been arbitrarily chosen here to fit the theoretical separation. The heat of dissociation of the ${}^3\Sigma^-$ level is Mulliken's estimate.¹⁶

OH: from Mulliken.¹⁶ Recent work¹⁸ would seem to favor

¹⁶ R. S. Mulliken, Rev. Mod. Phys. 4, 1 (1932), Table XVIII.

¹⁷ R. W. Lunt, R. W. B. Pearse, and E. C. W. Smith, Proc. Roy. Soc. A155, 173 (1936).

¹⁸ H. Sponer, *Molekülspektren*, Vol. I (1935), p. 27, quotes 4.4 volts as the heat of dissociation of OH. 4.3 volts is the value which would have been obtained (rather than 5.1) by O. Riechmeier, H. Senftleben, and H.

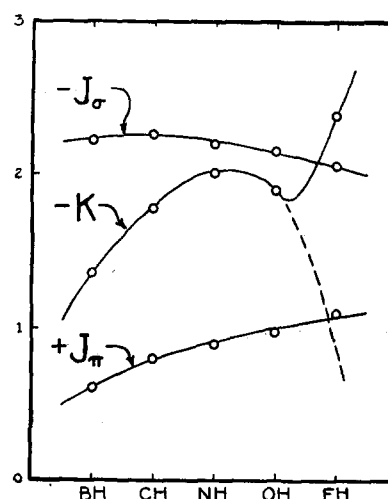


FIG. 1. Values in electron volts of the exchange integrals, J_π and J_σ , and of the total Coulomb terms K , as a function of atomic number. $-J_\pi$ and $-J_\sigma$ are, respectively, Van Vleck's $N_{\pi\pi}$ and $N_{\sigma\sigma}$, reference 2. The dashed curve represents the course the $-K$ curve would presumably take if there were no ionic effect in FH.

raising the levels about 0.5 volt, but see later discussion of Results (2).

FH: quoted by Pauling.¹⁹

Pastorff, Ann. d. Physik 19, 202 (1934), if they had used in their calculations a reasonably recent value of the heat of dissociation of O_2 . This value is found indirectly from their measurements on the energy of dissociation of H_2O into $H+OH$.

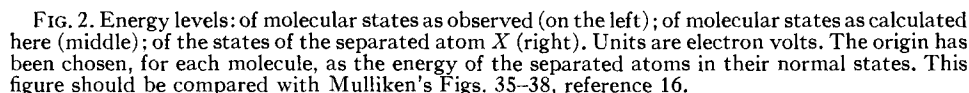
¹⁹ L. Pauling, J. Am. Chem. Soc. 54, 3570 (1932). This chemical value agrees even better with the band-spectroscopic estimate of D. E. Kirkpatrick and E. O. Salant, Phys. Rev. 48, 945 (1935), than does the older chemical value they quote.

TABLE IV. OH. ($K = -1.90$, $J_\pi = +0.98$, $J_\sigma = -2.16$, $3F_2 = +0.85$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2\pi_+\pi_- H {}^2\Sigma^+$	${}^1S - 3F_2 + 2K_\pi + 2K_\sigma - J_\pi - J_\sigma$	${}^1S - 1.57 = +2.58$	
$\pi_+^2\pi_- \sigma H {}^2\Pi$	${}^1D - \frac{3}{2}F_2 + 3K_\pi + K_\sigma - \frac{1}{2}J_\pi - J_\sigma$	${}^1D - 0.65 = +1.29$	
$\sigma^2\pi_+\pi_- H {}^2\Sigma^-$	${}^3P + 2K_\pi + 2K_\sigma + J_\pi - J_\sigma$	${}^3P + 1.24 = +1.24$	
$\sigma^2\pi_+^2 H {}^2\Delta$	${}^1D + 2K_\pi + 2K_\sigma - J_\pi - J_\sigma$	${}^1D - 0.72 = +1.22$	
$\pi_+^2\pi_-^2 H {}^2\Sigma^+$	${}^1D + 3F_2 + 4K_\pi - 2J_\pi$	${}^1D - 3.01 = -1.07^*$	-1.07
$\sigma^2\pi_+\pi_- H {}^4\Sigma^-$	${}^3P + 2K_\pi + 2K_\sigma - 2J_\pi - J_\sigma$	${}^3P - 1.70 = -1.70$	
$\pi_+^2\pi_- \sigma H {}^4\Pi$	${}^3P + 3K_\pi + K_\sigma - 2J_\pi - J_\sigma$	${}^3P - 1.70 = -1.70$	
$\pi_+^2\pi_- \sigma H {}^2\Pi$	${}^3P + \frac{3}{2}F_2 + 3K_\pi + K_\sigma - \frac{3}{2}J_\pi + J_\sigma$	${}^3P - 5.10 = -5.10^*$	-5.10

TABLE V. FH. ($K = -2.44$, $J_\pi = +1.10$, $J_\sigma = -2.06$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\pi_+^2\sigma^2\pi_- H {}^1\Pi$	${}^2P + 3K_\pi + 2K_\sigma - J_\sigma$	${}^2P - 0.33 = -0.33$	
$\pi_+^2\sigma^2\pi_- H {}^3\Pi$	${}^2P + 3K_\pi + 2K_\sigma - 2J_\pi - J_\sigma$	${}^2P - 2.53 = -2.53$	
$\pi_+^2\pi_-^2\sigma H {}^3\Sigma^+$	${}^2P + 4K_\pi + K_\sigma - 2J_\pi - J_\sigma$	${}^2P - 2.53 = -2.53$	
$\pi_+^2\pi_-^2\sigma H {}^1\Sigma^+$	${}^2P + 4K_\pi + K_\sigma - 2J_\pi + J_\sigma$	${}^2P - 6.65 = -6.65^*$	-6.65



by a comparison of Fig. 2 with Mulliken's Figs. 35-38. The unobserved levels which should be stable according to both methods of prediction are the $^3\Pi$ of BH and the $^4\Sigma^-$ of CH. It is very likely that these levels would be observed as stable states if intersystem combinations were not necessary thereto. It is very interesting that this theory confirms Mulliken's predictions for these cases, because the two approaches are basically very different.

(4) For levels involving a large amount of promotion, the predictions made here are much lower than Mulliken's and are probably quite inaccurate. The most striking examples of this are those levels which are quite stable according to this theory but are repulsive by Mulliken's prediction: $^5\Sigma^-$ of NH, $^4\Sigma^-$ and $^4\Pi$ of OH, $^3\Pi$ and $^3\Sigma^-$ of FH. Although these levels, being of higher multiplicity than the observed levels of these molecules, would in any case be difficult to observe, the concept of promotion which is the

basis of Mulliken's predictions is too well founded for one to attach much significance to the predictions here. Furthermore, there is considerable evidence that the $^3\Pi$ state of HI is repulsive—further reason for believing that state to be likewise in HF.

Thus it appears that, however lacking in rigor the simplified HLSP theory may be, it does give reasonably accurate predictions of certain levels of the molecules studied here—of the levels, that is, which involve no electron promotion. It is by no means clear why this theory should be even so accurate as it is.²¹

In conclusion, I wish to express my deep gratitude to Professor Van Vleck, whose suggestions were essential to this work, and to thank Professor Mulliken for helpful discussions.

²¹ The discussion of Coolidge and James, reference 4, throws much light on the subject, but they admit failure to explain completely the success of "semi-empirical" processes such as the one used here.

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Energy States of Solids with Particular Reference to the Energy States of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

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The absorption spectrum of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ crystals has been photographed at 20°, 78°, 169° and 298°K. The absorption lines occur in multiplets and originate in transitions from two low excited states as well as from the normal state. The excited levels of the basic multiplet are situated 77 and 260 cm^{-1} above the lowest state and undoubtedly arise through splitting of the normal state of the free Nd^{+++} ion in the electric field set up by its immediate neighbors in the crystal lattice. The positions of the observed levels are not in accord with conclusions of Penney and Schlapp from their study of the influence of

crystal fields on the temperature variation of the paramagnetic susceptibility of Nd ion in neodymium sulfate octahydrate. Based in part upon the susceptibility measurements of Gorter and de Haas, Penney and Schlapp's work requires that the levels be at 0, 243 and 834 cm^{-1} . If the data of Gorter and de Haas may be considered in error as regards absolute values the positions of the levels we have found are in excellent agreement with predictions of the theories of Van Vleck and Penney and Schlapp, and with the experimental results of Meyer and of Zernicke and James.

VAN VLECK² and his associates, using the methods of group theory and wave mechanics, have developed a very attractive theory of the behavior of such energy levels of the

¹ The major portion of this investigation was carried out under the George Fisher Baker Research Fellowship at Cornell University.

² J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932).

common paramagnetic ions as normally contribute to their paramagnetic properties, when the ions are brought into the electric field of their neighboring atoms in a solid. Penney and Schlapp³ have applied the theory to the specific case of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Making the assump-

³ W. G. Penney and R. Schlapp, *Phys. Rev.* **41**, 194 (1932).