for halogen ions and

$$X_M = 1+(C_{++}/C_{+-})(Z'/Z)\exp\{a[-\delta-(k-1)r]\} \quad (13b)$$

for metal ions. Hence C_{--} and C_{++} are two more of the Pauling overlap constants, Z' is the number of next-nearest neighbors, δ is given by $\delta = r_- - r_+$, and k is the ratio between next-nearest- and nearest-neighbor distances. These constants and the necessary physical data to calculate $\sigma(P)/\sigma_0$ with the use of Eqs. (10), (11), and (13) are given in Tables V, VI, and VII.

The inclusion of next-nearest neighbor interactions into the Y–M theory presents considerably more difficulties and has not yet been done.

V. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

A. General

As was mentioned before, the changes of σ with pressure are known absolutely, and thus a much more confident comparison of the theory with the data can be made than if the values of σ_0 alone were used. This is primarily because the reference point from which σ is measured is in doubt. The theories of both Y–M and K–Y use the NMR of the bare ion as the reference point from which σ is measured, whereas the experimental values of σ are measured from the NMR of the ion in dilute aqueous solution. There is evidence[6] that the NMR of the ion in dilute solution itself has a rather large chemical shift Σ_0 with respect to the bare ion. Itoh and Yamagata have measured the concentration and temperature dependence of both the chemical shift Σ and the spin-lattice relaxation time for the NMR of iodine nuclei in aqueous solutions of alkali iodides. From this, by means of simple theoretical assumptions, they have estimated that $\Sigma_0 \approx -6\times10^{-4}$ for I^{127}. The NMR of Cs^{133}, Rb^{87}, and Br^{81} ions in aqueous solution also show large changes in Σ with concentration, although not such large changes as does I^{127}, and thus should also have $\Sigma_0 \neq 0$. As will be seen below, the results of this paper tend to confirm that $\Sigma_0 \neq 0$.

TABLE VIII. Ratio of the initial slopes of the chemical shift vs pressure for the metal and the halide nuclei in the same salt. See Sec. VB.

	$(\Delta\sigma_0)_M/(\Delta\sigma_0)_H$				
Nuclei	Y–M 1[a]	K–Y 1[a]	K–Y 2[b]	Sum[c] 1[b]	Exptl.
Rb^{87}, Br^{81}	0.047	1.58	1.46	0.80	0.7 ±0.2
Rb^{87}, I^{127}	0.035	1.19	1.06	0.55	0.3 ±0.1
Cs^{133}, Br^{81}	0.073	2.14	1.88	1.10	1.4 ±0.1
Cs^{133}, I^{127}	0.072	1.60	1.19	0.70	0.78±0.04

[a] Nearest-neighbor interactions only.
[b] Next-nearest-neighbor interactions included with $\delta = \delta_{Cub} + 0.2$.
[c] Suitable sum of K–Y and Y–M, see text.

B. Comparison of Metal with Halide Results

The quantities $\Delta\sigma_0/\sigma_0$, where $\Delta\sigma_0 = \sigma_P - \sigma_0$ with $P = P_T$ for the rubidium halides and $P = 10\,000$ kg/cm² for the cesium halides, can be calculated from the formulas given above. Also, the ratios $(\sigma_0)_M/(\sigma_0)_H$ can be calculated from the theories if certain assumptions are made. In the theory of Y–M, we assume that $|a_p|^2 = \frac{3}{4}$. In the theory of K–Y, we assume that $\langle\Delta E\rangle_H = \langle\Delta E\rangle_M$. We also assume that the ratios $(\lambda_0)_M/(\lambda_0)_H$ and $(\Lambda_0)_M/(\Lambda_0)_H$ are given by the Born–Mayer theory (these ratios will differ from one only if next-nearest-neighbor interactions are included). The ratios

$$\frac{(\Delta\sigma_0)_M}{(\Delta\sigma_0)_H} = \frac{(\Delta\sigma_0/\sigma_0)_M}{(\Delta\sigma_0/\sigma_0)_H}\frac{(\sigma_0)_M}{(\sigma_0)_H},$$

can then be calculated and are given in Table VIII along with their experimental values. The values given by the theory of Y–M are about an order of magnitude too small. The values given by the theory of K–Y, however, give much better agreement as they are all only about a factor of two greater than the experimental values, and they follow the trend of the experimental values from salt to salt. Since the necessity of including the effects of next-nearest-neighbor interactions is indicated in the following section, the effect of these interactions on $(\Delta\sigma_0)_M/(\Delta\sigma_0)_H$ has been calculated. The results of this calculation for the theory of K–Y are given in Table VIII, and do not substantially change the agreement with the experimental data.

If indeed the charge transfer described by Y–M and the overlap described by K–Y are separate, real effects (as they are considered by K–Y) rather than two theoretical aspects of the same physical effect, then σ should really be described by the sum of the chemical shifts predicted by the two theories and is given by

$$\sigma_H = -\tfrac{8}{3}Z\mu_B{}^2\left[\frac{2\Lambda}{\langle\Delta E\rangle_H}\left\langle\frac{1}{r^3}\right\rangle_{H-} + \frac{\lambda}{\Delta E'}\left\langle\frac{1}{r^3}\right\rangle_H\right], \quad (14)$$

for the halide, and by

$$\sigma_M = -\tfrac{8}{3}Z\mu_B{}^2\left[\frac{2\Lambda}{\langle\Delta E\rangle_M}\left\langle\frac{1}{r^3}\right\rangle_{M+} + \frac{\lambda|a_p|^2}{\Delta E'}\left\langle\frac{1}{r^3}\right\rangle_M\right], \quad (15)$$

for the metal. If the additional assumption is made that $A = A'$, then $(\Delta\sigma_0)_M/(\Delta\sigma_0)_H$ can be calculated from Eqs. (14) and (15). These values are also given in Table VIII and, as can be seen, their agreement with the experimental values is quite good in view of the many assumptions about the values of λ, Λ, $\langle\Delta E\rangle_H$, and $|a_p|^2$ which have been made. However, it may be too much of a strain on the present theory to judge from it whether the necessity of adding charge-transfer