

Nuclear Magnetic Shielding in Alkali Halide Crystals*

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(Received 5 November 1964)

The overlapping-ion model proposed by Kondo and Yamashita to explain the magnetic shielding of nuclei in alkali halides is extended to derive an expression for the shielding constant σ in terms of all the important one- and two-center integrals in crystals with rocksalt structure. Using the results of Baron's pressure-dependence studies of the magnetic shielding in rubidium bromide in conjunction with our expression for σ , and using available Hartree-Fock wave functions for the ions, we have determined the average energy denominators Δ_+ and Δ_- for the Rb^+ and Br^- ions. These values of Δ_+ and Δ_- are then used to calculate the values of σ_{Rb} and σ_{Br} in the crystal with reference to the free ion. When these latter quantities are combined with the experimental values of the chemical shifts with reference to dilute aqueous solution of RbBr , one obtains

$$\sigma_{\text{Rb}}^{\text{aq}} = 0.63 \times 10^{-4} \quad \text{and} \quad \sigma_{\text{Br}}^{\text{aq}} = 1.94 \times 10^{-4}$$

for the shielding constants in dilute solution relative to the free ions.

INTRODUCTION

CHEMICAL shifts have been studied experimentally in a number of alkali halides¹ and more recently pressure measurements have been performed² in some of the heavier alkali halides. A theoretical interpretation of this data would be expected to provide information on the electronic wave functions and charge distributions in the crystals. Thus, one could use available wave functions to compute the nuclear magnetic shielding in the crystal and use the nature of the agreement with experimental data as a criterion for the accuracy of the wave functions, as has already been done for some simple molecules.³ It would be best if one could use Bloch wave functions for the valence bands of the alkali halides, preferably for a number of internuclear distances. However, detailed band-structure and wave-function calculations have so far been performed^{4,5} in only two of the lighter alkali halides, NaCl and KCl . The chemical shifts in these light crystals are expected to be small for both nuclei and have not been studied experimentally. For the heavier crystals, where experimental data are in greater abundance, one has therefore to take recourse to less sophisticated models for interpreting the magnetic shielding of the nuclei. Two models have been proposed for the origin of the magnetic shielding based on the perturbation-theory approach of Ramsey.⁶ The first is the charge-transfer-covalency model due to Yosida and Moriya⁷ and second the overlapping-ion model by Kondo and Yamashita⁸ (KY). The latter is analogous to the model used by Löwdin⁹ for explaining the co-

hesive energy of the alkali halides. Recent calculations of the quadrupole coupling constants in diatomic-alkali-halide molecules¹⁰ clearly indicate that there is little, if any, covalent binding of the charge-transfer type in these molecules. In the solid state, the internuclear distances are larger than in the free molecules and the covalent binding should be even less significant. It seems therefore that Kondo and Yamashita's model is currently the only plausible one that one could use to explain chemical shift data. In their paper,⁸ Kondo and Yamashita considered the ratio of the shielding constants for the positive- and negative-ion nuclei and since no electronic wave functions were available for the ions at that time they were obliged to make approximations for the overlap and other integrals involved in their expressions. Recently, Watson and Freeman¹¹ have computed Hartree-Fock wave functions for a number of alkali and halogen ions. It is therefore possible now to obtain a more quantitative evaluation of Kondo and Yamashita's theory.

However, in comparing theoretical results with experiments one runs into the difficulty that the experimental shielding data are usually referred to a reference sample in which the shielding constants are not known. The availability of data on the pressure variation of the magnetic shielding enables one to obviate this difficulty because the pressure variation of the shielding is independent of the reference sample. In addition one can evaluate from the pressure data, the average-energy denominators Δ_+ and Δ_- for positive and negative ions that occur in the Ramsey-Kondo-Yamashita theory. These values of Δ_+ and Δ_- can then be used to calculate the absolute values of the shielding constants for the positive- and negative-ion nuclei. On comparing these calculated shielding constants with observed chemical shifts one can obtain the shielding constants for the reference sample, namely, the dilute aqueous solution. For our calculations we have chosen

* Supported by the National Science Foundation.

¹ N. Bloembergen and P. P. Sorokin, *Phys. Rev.* **110**, 865 (1958).

² R. Baron, *J. Chem. Phys.* **38**, 173 (1963).

³ See, e.g., T. P. Das and R. Bersohn, *Phys. Rev.* **115**, 897 (1959); T. Ghose and T. P. Das, *J. Chem. Phys.* **31**, 42 (1959).

⁴ R. C. Casella, *Phys. Rev.* **104**, 1260 (1956).

⁵ L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

⁶ N. F. Ramsey, *Phys. Rev.* **77**, 567 (1950); **78**, 699 (1950).

⁷ K. Yosida and T. Moriya, *J. Phys. Soc. Japan* **11**, 33 (1956).

⁸ J. Kondo and J. Yamashita, *J. Phys. Chem. Solids* **10**, 245 (1959), hereafter referred to as KY.

⁹ P. O. Löwdin, *Advan. Phys.* **5**, 1 (1956).

¹⁰ T. P. Das and M. Karplus, *J. Chem. Phys.* **42**, 2885 (1965).

¹¹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **124**, 1117 (1961).

rubidium bromide because the chemical shift data in this crystal have been obtained by a number of investigators¹, and Baron² has recently studied the variation of the magnetic shielding with pressure for both nuclei.

In Sec. II, we derive an expression for the shielding constant in terms of all the nearest-neighbor overlaps and other two-center integrals. In Sec. III, this equation is used to interpret both the pressure variation of

the magnetic shielding and the chemical shift data for RbBr as outlined in the previous paragraph.

II. DERIVATION OF THE EXPRESSION FOR SHIELDING CONSTANT

Ramsey⁶ was the first to propose an explanation for chemical shifts and obtain an expression for the shielding using standard second-order perturbation theory:

$$\sigma = \sigma^d + \sigma^p = \frac{e^2}{2mc^2} \left[\left\langle \Psi_0 \left| \sum_k \frac{r_k^2 \mathbf{I} - \mathbf{r}_k \mathbf{r}_k}{r_k^3} \right| \Psi_0 \right\rangle + \sum_m (E_0 - E_m)^{-1} \left\{ \left\langle \Psi_0 \left| \sum_k \mathbf{I}_k \right| \Psi_m \right\rangle \left\langle \Psi_m \left| \sum_k \frac{\mathbf{I}_k}{r_k^3} \right| \Psi_0 \right\rangle + \text{c.c.} \right\} \right]. \quad (1)$$

The first term on the right represents the diamagnetic shielding while the second term represents the paramagnetic effect analogous to the Van Vleck second-order paramagnetism.¹² In Eq. (1), Ψ_0 and Ψ_m represent the many-electron ground- and excited-state wave functions, and E_0 and E_m are the ground- and excited-state energies. For the molecules where calculations have been performed,^{3,13} it is found that the diamagnetic shielding constant is always larger than the magnitude of the paramagnetic shielding constant. However, for the alkali halide crystals we are interested in the difference between the shielding constants for the crystal and the free ions. In the appendix we shall show that the contribution to this difference and its pressure dependence from diamagnetic effects is only 10^{-2} – 10^{-3} as effective as from paramagnetic effects. Since the excited-state wave functions and energies are usually not known, Ramsey introduced the average-energy denominator approximation which leads to

We therefore need to calculate the shielding constant along either the x , y , or z axis. Substituting Eq. (3) into Eq. (2) we get the following expression for σ_{xx} :

$$\sigma_{xx} = - \frac{4\alpha^2}{\Delta} \left[\sum_j \left\langle \psi_j \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_j \right\rangle - \sum_{j \neq j'} \left\langle \psi_j \left| \frac{l_{x0}}{r_0^3} \right| \psi_{j'} \right\rangle \left\langle \psi_{j'} \left| l_{x0} \right| \psi_j \right\rangle \right], \quad (5)$$

$$\sigma^p = - \frac{e^2}{\Delta m^2 c^2} \left\langle \Psi_0 \left| \sum_{k,k'} \frac{\mathbf{I}_k \mathbf{I}_{k'}}{r_k^3} \right| \Psi_0 \right\rangle, \quad (2)$$

where Δ is the average excitation energy.

Equation (2) involves only the ground-state wave function Ψ_0 . Since Ψ_0 is a many-electron wave function, for purposes of quantitative calculation, we have to expand it out in terms of one-electron wave functions. Since for the alkali halides, we have a diamagnetic system with doubly occupied states, Ψ_0 can be expressed in the form of a single determinant in the Hartree-Fock approximation

$$\Psi_0 = (2n!)^{-1/2} |\psi_{1\uparrow}(1)\psi_{1\downarrow}(2) \cdots \psi_{n\uparrow}(2n-1)\psi_{n\downarrow}(2n)|, \quad (3)$$

where ψ_n are one-electron wave functions. Also, since we have cubic symmetry, the crystal axes are the principal axes of the magnetic shielding tensor σ and $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$. In a powder, the effective shielding constant is then

$$\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \sigma_{xx} = \sigma_{yy} = \sigma_{zz}. \quad (4)$$

¹² J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

¹³ H. J. Kolker and M. Karplus, *J. Chem. Phys.* **41**, 1259 (1964).

where we have expressed all the quantities on the right-hand side of (5) in atomic units. Thus l_{x0} the x component of the angular momentum about the central nucleus 0, is in units of \hbar , lengths are in units of a_0 , Δ is in Rydbergs ($e^2/2a_0$), and α is the fine-structure constant ($e^2/\hbar c$). The next question we have to decide on is the choice of the one-electron wave functions. One choice is to use calculated Bloch wave functions and integrate in momentum space over the various bands that they refer to. Such a calculation would include both the effects of overlap and charge-transfer covalency. However, as pointed out in the Introduction, detailed band-structure calculations are available only for two of the lighter alkali halides but not for the heavier ones like RbBr. Further, we would like to test the validity of Löwdin's orthogonalized-atomic-orbital model for other properties besides the cohesive energy. We shall therefore use the orthogonalized atomic orbitals (OAO) for the one-electron wave functions in (5) as in KY. There are a number of different choices⁹ that one can make in constructing the OAO. We have chosen for convenience the symmetric orthogonalization procedure employed by Löwdin. Since the inner-core orbitals are very tightly bound and do not extend appreciably to the region between the ions, we can assume that they are completely spherical and cannot contribute to σ_{xx} in Eq. (5). Therefore, the only one-electron wave functions that we have to use in (5) are the outermost s and p orbitals for both the positive and negative ions. In our present calculations we shall consider only the overlaps between orbitals on nearest neighbor ions, and obtain our results correct to second order in these overlap integrals. Also, we shall keep only those matrix elements of $1/r_0^3$

for which at least one of the wave functions in the matrix element is on the central ion 0 since other matrix elements involving $1/r_0^3$ would be expected to be an order of magnitude smaller. Under these conditions, the expression for σ_{xx} is given by Eq. (6), the OAO ψ_{0s} , ψ_{0z} ,

ψ_{0y} , and ψ_{0z} on ion 0 and ψ_{js} , ψ_{jz} , ψ_{jy} , and ψ_{jz} on the six nearest-neighbor ions $j=1, \dots, 6$ being listed in Eqs. (7).

$$\sigma_{xx} = \sigma_{xx}^{\text{direct}} + \sigma_{xx}^{\text{ex I}} + \sigma_{xx}^{\text{ex II}} + \sigma_{xx}^{\text{ex III}},$$

where

$$\begin{aligned} \sigma_{xx}^{\text{direct}} &= -\frac{4\alpha^2}{\Delta} \left[\left\langle \psi_{0y} \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_{0y} \right\rangle + \left\langle \psi_{0z} \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_{0z} \right\rangle + \sum_j \left\{ \left\langle \psi_{js} \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_{js} \right\rangle + \left\langle \psi_{jy} \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_{jy} \right\rangle + \left\langle \psi_{jz} \left| \frac{l_{x0}^2}{r_0^3} \right| \psi_{jz} \right\rangle \right\} \right], \\ \sigma_{xx}^{\text{ex I}} &= -\frac{4\alpha^2}{\Delta} \left[2 \left\langle \psi_{0y} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{0z} \right\rangle \left\langle \psi_{0z} \left| l_{x0} \right| \psi_{0y} \right\rangle \right], \\ \sigma_{xx}^{\text{ex II}} &= -\frac{8\alpha^2}{\Delta} \left[\sum_{j=1, \dots, 6} \left\{ \left\langle \psi_{0y} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{jz} \right\rangle \left\langle \psi_{jz} \left| l_{x0} \right| \psi_{0y} \right\rangle + \left\langle \psi_{0z} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{js} \right\rangle \left\langle \psi_{js} \left| l_{x0} \right| \psi_{0z} \right\rangle \right. \right. \\ &\quad \left. \left. + \left\langle \psi_{0y} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{js} \right\rangle \left\langle \psi_{js} \left| l_{x0} \right| \psi_{0y} \right\rangle + \left\langle \psi_{0z} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{jy} \right\rangle \left\langle \psi_{jy} \left| l_{x0} \right| \psi_{0z} \right\rangle \right\} \right], \\ \sigma_{xx}^{\text{ex III}} &= -\frac{8\alpha^2}{\Delta} \left[\sum_{j=1, \dots, 6} \left\{ \left\langle \psi_{jy} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{jz} \right\rangle \left\langle \psi_{jz} \left| l_{x0} \right| \psi_{jy} \right\rangle + \left\langle \psi_{js} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{jy} \right\rangle \left\langle \psi_{jy} \left| l_{x0} \right| \psi_{js} \right\rangle + \left\langle \psi_{js} \left| \frac{l_{x0}}{r_0^3} \right| \psi_{jz} \right\rangle \left\langle \psi_{jz} \left| l_{x0} \right| \psi_{js} \right\rangle \right\} \right], \\ \psi_{0y} &= \phi_{0y} - \frac{1}{2} \sum_{i=1, \dots, 6} (S_{0i}{}^{ys} \phi_{is} + S_{0i}{}^{yy} \phi_{iy}) + \frac{3}{8} \sum_{i=1, \dots, 6} [(S_{0i}{}^{ys} S_{0i}{}^{ss} + S_{0i}{}^{yy} S_{0i}{}^{ys}) \phi_{0s} \\ &\quad + S_{0i}{}^{ys} S_{0i}{}^{sx} \phi_{0x} + (S_{0i}{}^{ys} S_{0i}{}^{sy} + S_{0i}{}^{yy} S_{0i}{}^{yy}) \phi_{0y} + S_{0i}{}^{ys} S_{0i}{}^{sz} \phi_{0z}], \\ \psi_{jy} &= \phi_{jy} - \frac{1}{2} \sum_{\substack{i=\text{nearest neighbors of} \\ j(n0j)}} (S_{ji}{}^{ys} \phi_{is} + S_{ji}{}^{yy} \phi_{iy}) + \frac{3}{8} \sum_{i=n0j} [(S_{ji}{}^{ys} S_{ij}{}^{ss} + S_{ji}{}^{yy} S_{ij}{}^{ys}) \phi_{js} \\ &\quad + S_{0i}{}^{ys} S_{0i}{}^{sx} \phi_{0x} + (S_{0i}{}^{ys} S_{0i}{}^{sy} + S_{0i}{}^{yy} S_{0i}{}^{yy}) \phi_{0y} + S_{0i}{}^{ys} S_{0i}{}^{sz} \phi_{0z}], \\ \psi_{0s} &= \phi_{0s} - \frac{1}{2} \sum_{i=1, \dots, 6} (S_{0i}{}^{ss} \phi_{is} + S_{0i}{}^{sx} \phi_{ix} + S_{0i}{}^{sy} \phi_{iy} + S_{0i}{}^{sz} \phi_{iz}) + \frac{3}{8} \sum_{i=1, \dots, 6} [(S_{0i}{}^{ss} S_{0i}{}^{ss} + S_{0i}{}^{sx} S_{0i}{}^{sx} + S_{0i}{}^{sy} S_{0i}{}^{sy} \\ &\quad + S_{0i}{}^{sz} S_{0i}{}^{sz}) \phi_{0s} + (S_{0i}{}^{ss} S_{0i}{}^{sx} + S_{0i}{}^{sx} S_{0i}{}^{sx}) \phi_{0x} + (S_{0i}{}^{ss} S_{0i}{}^{sy} + S_{0i}{}^{sy} S_{0i}{}^{yy}) \phi_{0y} + (S_{0i}{}^{ss} S_{0i}{}^{sz} + S_{0i}{}^{sz} S_{0i}{}^{sz}) \phi_{0z}], \\ \psi_{js} &= \phi_{js} - \frac{1}{2} \sum_{n0j} (S_{ji}{}^{ss} \phi_{is} + S_{ji}{}^{sx} \phi_{ix} + S_{ji}{}^{sy} \phi_{iy} + S_{ji}{}^{sz} \phi_{iz}) + \frac{3}{8} \sum_{i=n0j} [(S_{ji}{}^{ss} S_{ij}{}^{ss} + S_{ji}{}^{sx} S_{ij}{}^{sx} + S_{ji}{}^{sy} S_{ij}{}^{yy} \\ &\quad + S_{ji}{}^{sz} S_{ij}{}^{sz}) \phi_{js} + (S_{ji}{}^{ss} S_{ij}{}^{sx} + S_{ji}{}^{sx} S_{ij}{}^{sx}) \phi_{jx} + (S_{ji}{}^{ss} S_{ij}{}^{sy} + S_{ji}{}^{sy} S_{ij}{}^{yy}) \phi_{jy} + (S_{ji}{}^{ss} S_{ij}{}^{sz} + S_{ji}{}^{sz} S_{ij}{}^{sz}) \phi_{jz}]. \end{aligned} \quad (6)$$

In Eqs. (7), $\phi_{0\alpha}$ and $\phi_{j\beta}$ represent the unorthogonalized free-ion wave functions, and the overlap integrals $S_{0i}{}^{\alpha\beta}$ are defined by

$$S_{0i}{}^{\alpha\beta} = \langle \phi_{0\alpha} | \phi_{i\beta} \rangle. \quad (8)$$

We next substitute Eqs. (7) in Eqs. (6) and neglect (a) terms which are of higher order than second in the overlap, (b) terms like $\langle \phi_{i\alpha} | 1/r_0^3 | \phi_{j\alpha} \rangle$, where $i, j \neq 0$, and (c) $\langle \phi_{0\alpha} | 1/r_0^3 | \phi_{j\alpha} \rangle$, $\langle \phi_{i\alpha} | 1/r_0^3 | \phi_{j\alpha} \rangle$, and $\langle \phi_{j\alpha} | 1/r_0^3 | \phi_{j\alpha} \rangle$, where i is a nearest neighbor of ion 0, but j is not. Under these conditions, Eqs. (6) lead to the following expressions, (9), (10), (11), and (12), for $\sigma_{xx}^{\text{direct}}$, $\sigma_{xx}^{\text{ex I}}$, $\sigma_{xx}^{\text{ex II}}$, and $\sigma_{xx}^{\text{ex III}}$ in terms of the free-ion wave functions $\phi_{0\alpha}$ and $\phi_{i\beta}$:

$$\begin{aligned} \sigma_{xx}^{\text{direct}} &= -\frac{8\alpha^2}{\Delta} \left[\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle - \sum_{i=1, \dots, 6} \left\{ S_{0i}{}^{yy} \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{iy} \right\rangle + S_{0i}{}^{ys} \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{is} \right\rangle \right\} \right. \\ &\quad \left. + \sum_{i=1, \dots, 6} \left\{ |S_{0i}{}^{yy}|^2 \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle + |S_{0i}{}^{ys}|^2 \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \right\} \right], \quad (9) \end{aligned}$$

$$\begin{aligned} \sigma_{xx}^{\text{ex I}} &= +\frac{8\alpha^2}{\Delta} \left[\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle - \sum_{i=1, \dots, 6} S_{0i}{}^{yy} \left\langle \phi_{iy} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle + \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \right. \\ &\quad \left. \times \sum_{i=1, \dots, 6} \left\{ \frac{1}{4} |S_{0i}{}^{sz}|^2 + \frac{1}{4} |S_{0i}{}^{yy}|^2 + \frac{1}{4} S_{0i}{}^{sz} S_{0i}{}^{yy} + \frac{1}{4} |S_{0i}{}^{ys}|^2 + \frac{1}{4} |S_{0i}{}^{ss}|^2 \right\} \right], \quad (10) \end{aligned}$$

$$\sigma_{xx}^{\text{ex II}} = +\frac{8\alpha^2}{\Delta} \left[\sum_{i=1, \dots, 6} \left\{ \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{iy} \right\rangle (S_{0i}^{yy} - S_{0i}^{zz}) + \left\langle \phi_{is} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle S_{0i}^{sy} \right\} \right. \\ \left. + \sum_{i=1, \dots, 6} \left\{ \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \left(-\frac{1}{2} S_{0i}^{yy} + \frac{1}{2} S_{0i}^{yy} S_{0i}^{zz} - \frac{1}{2} |S_{0i}^{ys}|^2 \right) \right\} \right], \quad (11)$$

$$\sigma_{xx}^{\text{ex III}} = +\frac{8\alpha^2}{\Delta} \left[\sum_{i=1, \dots, 6} \left\{ -\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{iy} \right\rangle S_{0i}^{zz} + \frac{1}{4} \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle S_{0i}^{yy} S_{0i}^{zz} \right\} \right]. \quad (12)$$

In Eqs. (9)–(12), the summations in i extend over the six nearest neighbors of the central ion O . In deriving these equations, the following relations are very helpful.

$$\begin{aligned} \langle \phi_{0y} | l_{0x} | \phi_{0z} \rangle &= -\hbar/i = \langle \phi_{iy} | l_{0x} | \phi_{iz} \rangle, \\ \langle \phi_{0y} | l_{0x} | \phi_{iz} \rangle &= -(\hbar/i) S_{0i}^{zz}. \end{aligned} \quad (13)$$

From Eqs. (9)–(12), introducing the σ and π notations for p orbitals that are, respectively, symmetric with respect to an internuclear axis and perpendicular to it and performing the summations over i using Fig. 1, we get the following expressions for $\sigma_{xx}^{\text{direct}}$, $\sigma_{xx}^{\text{ex}} = \sigma_{xx}^{\text{ex I}} + \sigma_{xx}^{\text{ex II}} + \sigma_{xx}^{\text{ex III}}$, and total $\sigma_{xx} = \sigma_{xx}^{\text{direct}} + \sigma_{xx}^{\text{ex}}$:

$$\sigma_{xx}^{\text{direct}} = -\frac{8\alpha^2}{\Delta} \left[\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle - \left\{ 4S_{0i}^{\sigma\sigma} \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{i\sigma} \right\rangle + 4S_{0i}^{\sigma s} \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{is} \right\rangle \right. \\ \left. - 8S_{0i}^{\pi\pi} \left\langle \phi_{0\pi} \left| \frac{1}{r_0^3} \right| \phi_{i\pi} \right\rangle \right\} + \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \left\{ 4|S_{0i}^{\pi\pi}|^2 + 2|S_{0i}^{\sigma s}|^2 + 2|S_{0i}^{\sigma\sigma}|^2 \right\} \right], \quad (14)$$

$$\sigma_{xx}^{\text{ex}} = +\frac{8\alpha^2}{\Delta} \left[\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle + \left\{ (-4S_{0i}^{\pi\pi} - 4S_{0i}^{\sigma\sigma}) \left\langle \phi_{i\pi} \left| \frac{1}{r_0^3} \right| \phi_{0\pi} \right\rangle \right. \right. \\ \left. \left. - 4S_{0i}^{\pi\pi} \left\langle \phi_{i\sigma} \left| \frac{1}{r_0^3} \right| \phi_{0\sigma} \right\rangle \right\} + \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \left\{ 2|S_{0i}^{\pi\pi}|^2 + 4S_{0i}^{\sigma\sigma} S_{0i}^{\pi\pi} \right\} \right], \quad (15)$$

$$\sigma_{xx} = -\frac{16\alpha^2}{\Delta} \left[\left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle \left\{ |S_{0i}^{\sigma\sigma}|^2 + |S_{0i}^{\sigma s}|^2 + |S_{0i}^{\pi\pi}|^2 - 2S_{0i}^{\sigma\sigma} S_{0i}^{\pi\pi} \right\} \right. \\ \left. + 2(S_{0i}^{\sigma\sigma} - S_{0i}^{\pi\pi}) \left\{ \left\langle \phi_{0\pi} \left| \frac{1}{r_0^3} \right| \phi_{i\pi} \right\rangle - \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{i\sigma} \right\rangle \right\} - 2S_{0i}^{\sigma s} \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{is} \right\rangle \right]. \quad (16)$$

III. RESULTS AND DISCUSSION

Before considering the application of Eq. (16) to any particular crystal we would like to emphasize that second-order perturbation theory with an average energy denominator cannot be used for a rigorous quantitative test of the wave functions used for the crystal. The reason for this is that the perturbation theoretic expression (16) requires the knowledge of an average energy denominator Δ . Since the latter is not a constant for the system but depends on the property that is being analyzed, we cannot use the value of Δ obtained from some other property—for example, electric polarizability or magnetic susceptibility—and use it to calculate magnetic shielding. Consequently, variational methods have been developed to calculate nuclear magnetic shielding in molecules. It would be very desirable to develop corresponding variational methods for the solid state. There is at present a large body of experimental data^{1,2} available for the nuclear magnetic shield-

ing in alkali halides. In the absence of suitable variational methods, it is imperative to at least obtain a semi-quantitative understanding of these data by perturbation theory. Further, the availability of Baron's pressure data is particularly fortunate because it allows us to

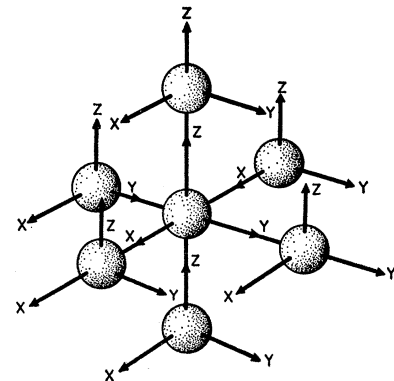


FIG. 1. Orientation of X , Y , and z axes on the central ion and its six nearest neighbors.

obtain Δ from the pressure variation of the magnetic shielding. Experimentally, one measures the chemical shift with respect to a reference system, commonly a dilute aqueous solution of the ion in question. To obtain the absolute value of the shielding coefficient in the crystal, one therefore requires a knowledge of this shielding coefficient for the nucleus in the reference sample. The pressure variation is, however, independent of the reference sample and provides a good estimate of Δ through the use of Eq. (16) for different internuclear distances. One can then use the value of Δ obtained from pressure data to determine the absolute value of the shielding constant from Eq. (16). This calculated absolute value of σ can be compared with the experimentally observed chemical shift for the nucleus to obtain information about the shielding coefficient in the dilute solution.

In Table I we have tabulated for easy reference the

TABLE I. List of values for the necessary one-center and two-center integrals.

| Integral ^a | Internuclear distance R | |
|---|---------------------------|------------|
| | 6.425 a_0 | 6.50 a_0 |
| One-center | | |
| $\langle A\sigma 1 A\sigma \rangle = \langle A\pi 1 A\pi \rangle$ | 0.99859 | |
| $\langle B\sigma 1 B\sigma \rangle = \langle B\pi 1 B\pi \rangle$ | 0.99935 | |
| $\langle As 1 As \rangle$ | 0.99891 | |
| $\langle Bs 1 Bs \rangle$ | 0.99882 | |
| $\langle A\sigma 1/r_A A\sigma \rangle = \langle A\pi 1/r_A A\pi \rangle$ | 0.75447 | |
| $\langle As 1/r_A As \rangle$ | 0.87606 | |
| $\langle B\sigma 1/r_B B\sigma \rangle = \langle B\pi 1/r_B B\pi \rangle$ | 0.57619 | |
| $\langle Bs 1/r_B Bs \rangle$ | 0.73267 | |
| $\langle A\sigma 1/r_A^3 A\sigma \rangle = \langle A\pi 1/r_A^3 A\pi \rangle$ | 20.216 | |
| $\langle B\sigma 1/r_B^3 B\sigma \rangle = \langle B\pi 1/r_B^3 B\pi \rangle$ | 10.245 | |
| Two-center | | |
| $S_{AB}^{\pi\pi} = \langle A\pi B\pi \rangle$ | 0.019582 | 0.018385 |
| $S_{AB}^{\sigma\sigma} = \langle A\sigma B\sigma \rangle$ | -0.086116 | -0.082182 |
| $S_{AB}^{\sigma s} = \langle A\sigma Bs \rangle$ | 0.028881 | 0.026900 |
| $S_{AB}^{\sigma\pi} = \langle A\sigma B\pi \rangle$ | -0.061519 | -0.058275 |
| $S_{AB}^{\pi s} = \langle A\pi Bs \rangle$ | 0.012184 | 0.011243 |
| $\langle A\pi 1/r_A B\pi \rangle$ | 0.007003 | 0.006554 |
| $\langle A\sigma 1/r_A B\sigma \rangle$ | -0.032721 | -0.031089 |
| $\langle A\sigma 1/r_A Bs \rangle$ | 0.009049 | 0.008373 |
| $\langle As 1/r_A B\sigma \rangle$ | -0.03033 | -0.02867 |
| $\langle As 1/r_A Bs \rangle$ | 0.005114 | 0.004704 |
| $\langle B\pi 1/r_B A\pi \rangle$ | 0.004207 | 0.003903 |
| $\langle B\sigma 1/r_B A\sigma \rangle$ | -0.022810 | -0.021463 |
| $\langle B\sigma 1/r_B As \rangle$ | 0.012450 | 0.011636 |
| $\langle Bs 1/r_B A\sigma \rangle$ | -0.009350 | -0.008613 |
| $\langle Bs 1/r_B As \rangle$ | 0.003020 | 0.002750 |
| $\langle A\pi 1/r_A^3 B\pi \rangle$ | 0.001810 | 0.001688 |
| $\langle A\sigma 1/r_A^3 B\sigma \rangle$ | -0.009081 | -0.008582 |
| $\langle A\sigma 1/r_A^3 Bs \rangle$ | 0.001786 | 0.001639 |
| $\langle B\pi 1/r_B^3 A\pi \rangle$ | 0.000337 | 0.000305 |
| $\langle B\sigma 1/r_B^3 A\sigma \rangle$ | -0.002540 | -0.002328 |
| $\langle B\sigma 1/r_B^3 As \rangle$ | 0.000753 | 0.000684 |

^a For brevity, A and B are used to denote the Rb^+ and Br^- ions, respectively. The orbitals $4s$, $4P\sigma$, and $4P\pi$ on the ions are denoted by the symbols s , σ , and π .

calculated values of the various integrals required in Eq. (16) for RbBr as well as some others that are required for the diamagnetic contribution considered in the Appendix. We hope these integrals will be helpful for calculation of other properties of alkali halides. We have considered two nearest-neighbor distances, 6.50 a_0 and 6.425 a_0 , the former being the equilibrium distance at atmospheric pressure and the latter is close to the distance at which RbBr undergoes phase transition from NaCl to CsCl structures. In regard to the electronic wave functions for the two ions, we have used the analytic Hartree-Fock wave functions of Freeman and Watson.¹¹ The two center integrals were all calculated using Löwdin's alpha-function technique.⁹

Substituting the results of Table I into Eq. (16), we can express σ_{xx} for the two distances and the two ions in RbBr in the form

$$\sigma_{xx} = -\frac{16\alpha^2}{\Delta}(A+B+C+D+E),$$

where

$$\begin{aligned} \frac{A}{|S_{0i}^{\sigma\sigma}|^2} &= \frac{B}{|S_{0i}^{\pi\pi}|^2} = \frac{C}{-2S_{0i}^{\sigma\sigma}S_{0i}^{\pi\pi}} \\ &= \frac{D}{|S_{0i}^{\sigma s}|^2} = \left\langle \phi_{0y} \left| \frac{1}{r_0^3} \right| \phi_{0y} \right\rangle, \quad (17) \\ E &= 2(S_{0i}^{\sigma\sigma} - S_{0i}^{\pi\pi}) \left\{ \left\langle \phi_{0\pi} \left| \frac{1}{r_0^3} \right| \phi_{i\pi} \right\rangle \right. \\ &\quad \left. - \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{i\sigma} \right\rangle \right\} - 2S_{0i}^{\sigma\sigma} \left\langle \phi_{0\sigma} \left| \frac{1}{r_0^3} \right| \phi_{is} \right\rangle. \end{aligned}$$

In Eq. (17), E is the contribution from nonlocal terms of the form $\langle \phi_{0\alpha} | 1/r_0^3 | \phi_{i\alpha} \rangle$. The values of A , B , C , D , and E are tabulated in Table II. Kondo and Yamashita in their formulation had neglected the contribution from overlaps between π orbitals. From Table II, however, we notice that the term C , which involves a product of σ and π overlaps, has a magnitude about half as large as the A term which arises from the σ overlaps alone. The term B which involves only π overlaps is an order of magnitude smaller than the A term. Kondo and Yamashita had expected that the overlap between the s orbital on the halogen ion and the p_σ orbital on the metal ion would be important and the overlap integral between the s orbital on the metal ion and the p_σ

TABLE II. Values of the quantities A , B , C , D , and E in Eq. (17).

| Ion \ Term in Eq. (17) | A | B | C | D | E |
|------------------------|----------|----------|----------|----------|----------|
| | Rb^+ | 0.134280 | 0.006830 | 0.061090 | 0.014620 |
| Br^- | 0.068035 | 0.003462 | 0.030957 | 0.034791 | 0.000569 |

orbital on the halogen ion would be small. However, it can be seen from Table I that the reverse is true and the latter overlap is three times the former. The above results give emphasis to the fact that one should be careful about making assumptions as to the relative importance of various contributions to σ_{xx} and that a knowledge of the Hartree-Fock wave functions is really necessary.

From Table II one gets Eqs. (18) and (19) for the change in the shielding constants over the two distances considered for rubidium and bromine nuclei.

$$\Delta\sigma_{\text{Rb}} = \frac{0.20269 - 0.00215}{\Delta_+} \times 10^{-4}, \quad (18)$$

$$\Delta\sigma_{\text{Br}} = \frac{0.12627 - 0.00113}{\Delta_-} \times 10^{-4}. \quad (19)$$

Again it is apparent that the nonlocal term (second term on the right) contributes negligibly to $\Delta\sigma$. The linear dependence of σ_{Rb} and σ_{Br} on R was verified by calculating the local terms at an additional value of $R=6.450$. From the slope of $\Delta\sigma$ versus pressure obtained by Baron, we deduce the values of $\Delta\sigma_{\text{Rb}}$ and $\Delta\sigma_{\text{Br}}$ as 0.32135×10^{-4} and 0.22781×10^{-4} , respectively. Using these values in conjunction with (18) and (19) we obtain¹⁴ $\Delta_+ = 0.8838$ Ry, $\Delta_- = 0.3935$ Ry.

The value of Δ_- is seen to be comparable in magnitude but somewhat smaller than the energy differences¹⁵ from the top of the Br^- valence band to both the lowest exciton levels (0.4771 Ry) and the bottom of the conduction band (0.5872 Ry). If one had used standard second-order perturbation theory, one would have obtained the array of terms on the right-hand side of Eq. (20).

$$a/\Delta = a_1/\Delta_1 + a_2/\Delta_2 + a_3/\Delta_3 + \dots \quad (20)$$

In Eq. (20), $\Delta_1, \Delta_2, \dots$, represent the excitation energies for the excited states and the continuous spectrum of states in the conduction band. The quantities a_1, a_2, \dots , represent products of the matrix elements of the operators, $\sum_j \mathbf{l}_{j0}$ and $\sum_k \mathbf{l}_{k0}/r_{k0}^3$ between ground and excited states. The left-hand side represents the result of the

¹⁴ In obtaining the values of Δ_+ and Δ_- we have ignored the variation of Δ_+ and Δ_- with R in Eqs. (18) and (19). This neglect corresponds to ignoring an additional term in $\delta\sigma$. Thus, from (27), if we write symbolically $\sigma = [f(s)]/[\Delta_0 g(s)]$ where $f(s)$ and $g(s)$ are functions of the overlap integrals, the variation in σ due to change in distance can be expressed as

$$\delta\sigma = \frac{f(s_0)\delta s}{\Delta_0 g(s_0)} - \frac{f(s_0)\delta s}{\Delta_0 [g(s_0)]^2} \left(\frac{\partial g}{\partial s} \right).$$

Unfortunately, we have no way of obtaining $(\partial g/\partial s)$, and hence of estimating how serious its effect is on $\delta\sigma$. We are currently investigating some other alkali halides to study the consistency of the results obtained by neglecting the $\partial g/\partial s$ term in all cases. Further, a variational calculation would not require any knowledge of excitation energies and would hence obviate this particular error in the perturbation treatment.

¹⁵ N. F. Mott and R. Gurney, *Electronic Processes in Ionic Crystals* (Dover Publications, Inc., New York, 1964), p. 96.

average energy approximation. If a_1, a_2, \dots are comparable in magnitude, an examination of Eq. (20) indicates that Δ can be either smaller or larger than Δ_1 .

For the average energy for the positive ion Δ_+ , the choice of excitation energies to compare with is uncertain. A possible reference is the ionization energy of the positive ion which has been estimated¹⁶ to be 2.006 Ry, which is again larger than the calculated Δ_+ .

When we substitute the calculated values of Δ_+ and Δ_- into Eq. (16), we obtain for the equilibrium distance at atmospheric pressure

$$\sigma_{\text{Br}} = 2.99 \times 10^{-4}, \quad \sigma_{\text{Rb}} = 2.14 \times 10^{-4}. \quad (21)$$

The most recent experimental values of the chemical shifts are

$$\begin{aligned} \sigma_{\text{Br}}^{\text{exp}} &= 1.05 \times 10^{-4} = \sigma_{\text{Br}} - \sigma_{\text{Br}}^{\text{aq}} \\ \sigma_{\text{Rb}}^{\text{exp}} &= 1.51 \times 10^{-4} = \sigma_{\text{Rb}} - \sigma_{\text{Rb}}^{\text{aq}}. \end{aligned} \quad (22)$$

A combination of Eqs. (21) and (22) yields

$$\sigma_{\text{Br}}^{\text{aq}} = 1.94 \times 10^{-4}, \quad \sigma_{\text{Rb}}^{\text{aq}} = 0.63 \times 10^{-4}. \quad (23)$$

It is interesting that the $\sigma_{\text{Rb}}^{\text{aq}}$ is smaller than $\sigma_{\text{Br}}^{\text{aq}}$. This result could be used as a check on any model that one assumes for the aqueous solution. We should, however, point out that our result is based on the neglect of the effects of the Lamb diamagnetic term. We estimate in the Appendix that the effects of overlap on the diamagnetic term are only about one-tenth or less than on the paramagnetic term. We do not therefore believe that the neglect of diamagnetic effects is a substantial source of error in the estimation of the variation of σ with pressure or in its absolute magnitude.¹⁷

Itoh and Yamagata¹⁸ have obtained a value for $\sigma_{\text{I}^-}^{\text{aq}} = 6.0 \times 10^{-4}$ for I^- ions in aqueous solution from a combination of relaxation time data and chemical shift data as a function of concentration. They have also reported¹⁸ that a measurement for Rb^+ and Br^- ions led to smaller values for $\sigma_{\text{Br}}^{\text{aq}}$ and $\sigma_{\text{Rb}}^{\text{aq}}$. We hope that our findings for $\sigma_{\text{Rb}}^{\text{aq}}$ and $\sigma_{\text{Br}}^{\text{aq}}$ will stimulate further careful measurements for Rb^+ and Br^- and other ions. Unfortunately, no Hartree-Fock wave functions have yet been published for I^- , so we cannot at present apply our Eq. (16) to obtain $\sigma_{\text{I}^-}^{\text{aq}}$ from Baron's pressure data in RbBr to compare with Itoh's value for $\sigma_{\text{I}^-}^{\text{aq}}$.

IV. CONCLUSION

Our calculations indicate that the overlap mechanism proposed by Kondo and Yamashita⁸ can give a

¹⁶ J. E. Mayer, *J. Chem. Phys.* **7**, 270 (1933).

¹⁷ We should remark that the word "absolute" that we have used is somewhat a misnomer, since our quoted results for σ are really with reference to the free ion. If we wanted to get the total σ , we would have always to add the constant diamagnetic term for the free ion in each case.

¹⁸ J. Itoh and Y. Yamagata, *J. Phys. Soc. Japan* **13**, 1182 (1958).

reasonable explanation of the magnetic shielding in alkali halides and in particular its dependence on pressure. It is significant that the bromine paramagnetic shielding factor for Br^- in aqueous solution comes out larger than the rubidium shielding factor for Rb^+ in solution. This result should be tested using suitable models for the configuration of water molecules around the ions in solution. In order to use magnetic shielding data as a rigorous quantitative criterion for the correctness of wave functions in ionic crystals, one requires variational methods which would obviate the use of an average energy denominator.

APPENDIX

From Ref. 6, the diamagnetic shielding factor σ_{xx}^d is given by

$$\sigma_{xx}^d = -\frac{e^2}{2mc^2} \left\langle \Psi_0 \left| \sum_i \frac{y_i^2 + z_i^2}{r_i^3} \right| \Psi_0 \right\rangle. \quad (\text{A1})$$

Expressing this result in terms of one-electron wave functions and making use of Eq. (4), we get (taking account of a factor of 2 due to spin multiplicity)

$$\sigma^d = -\frac{2}{3}\alpha^2 \sum_j \langle \psi_j | 1/r_0 | \psi_j \rangle, \quad (\text{A2})$$

where r_0 is taken in units of a_0 . Summing over the OAO in Eq. (7) in the same manner as we did in the paramagnetic shielding factor we get for the overlap-

dependent part of σ_d ,

$$\begin{aligned} \sigma^d = & -4\alpha^2 \left[\left\langle \phi_{0y} \left| \frac{1}{r_0} \right| \phi_{0y} \right\rangle (|S_{0i}{}^{\sigma\sigma}|^2 + |S_{0i}{}^{\pi\pi}|^2 + 2|S_{0i}{}^{\pi\sigma}|^2) \right. \\ & + \left\langle \phi_{0s} \left| \frac{1}{r_0} \right| \phi_{0s} \right\rangle (|S_{0i}{}^{\sigma s}|^2 + |S_{0i}{}^{\pi s}|^2) \\ & - 2 \left\langle \phi_{0s} \left| \frac{1}{r_0} \right| \phi_{i\sigma} \right\rangle S_{0i}{}^{\sigma\sigma} - 2 \left\langle \phi_{0\sigma} \left| \frac{1}{r_0} \right| \phi_{is} \right\rangle S_{0i}{}^{\sigma s} \\ & - 4 \left\langle \phi_{0\pi} \left| \frac{1}{r_0} \right| \phi_{i\pi} \right\rangle S_{0i}{}^{\pi\pi} - 2 \left\langle \phi_{0\sigma} \left| \frac{1}{r_0} \right| \phi_{i\sigma} \right\rangle S_{0i}{}^{\sigma\sigma} \\ & \left. - 2 \left\langle \phi_{0s} \left| \frac{1}{r_0} \right| \phi_{is} \right\rangle S_{0i}{}^{\sigma s} \right]. \quad (\text{A3}) \end{aligned}$$

The necessary integrals in (A3) are available in Table I. Substituting the necessary integrals from Table I, we get the values of σ_{Br}^d and σ_{Rb}^d at $r = 6.50a_0$ and $\Delta\sigma_{\text{Br}}^d$ and $\Delta\sigma_{\text{Rb}}^d$ in Eq. (A4).

$$\begin{aligned} \sigma_{\text{Br}}^d(R = 6.50a_0) &= -0.007638 \times 10^{-4}, \\ \sigma_{\text{Rb}}^d(R = 6.50a_0) &= -0.001382 \times 10^{-4}, \\ \Delta\sigma_{\text{Br}}^d &= +0.001049 \times 10^{-4}, \\ \Delta\sigma_{\text{Rb}}^d &= +0.000391 \times 10^{-4}. \end{aligned} \quad (\text{A4})$$

It is seen that these values are more than an order of magnitude smaller than the corresponding paramagnetic terms in Eqs. (18), (19), and (21).