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Theory of Transition Ion Complexes*

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It is suggested that the observed lowering of the spin-orbit parameters in transition-ion complexes is caused by a screening effect which expands the $3d$ wave functions. Evidence in support of this suggestion is given by neutron diffraction form-factor measurements on Mn^{++} salts. The theory of the transferred hyperfine interaction between the electron spin of Mn^{++} and surrounding F^{19} nuclei is discussed, and the complications introduced into the theory when dealing with other ions are described. The theory is found to be unsatisfactory because it is not possible to treat the interaction via the $1s$ orbitals of F^- with sufficient accuracy.

I. INTRODUCTION

It is generally recognized that the static crystalline field model for a transition ion complex is a good zero-order approximation but that many results are more satisfactorily explained by the more sophisticated treatment known as the ligand field theory.[1] In this paper we discuss several related topics in connection with the latter theory, and in particular we discuss the validity of that special form of ligand field theory which corresponds to the simple Heitler-London state, i.e., no electron transfer from one ion to another. This Heitler-London model is not equivalent to the static crystalline field model because the latter neglects all overlap effects.

Ligand field theory originated with Van Vleck[2] who discussed a transition ion complex consisting of a central ion with an unfilled $3d$ shell surrounded by six ligands (nominally nonmagnetic ions, e.g., F^-, O^{--}, Cn^-) arranged in a regular octahedron. He showed how the mixing between the $3d$ orbitals and the $2p$ orbitals of the ligands could produce a contribution to the crystal field splitting which was to be added to the splitting produced by the static cubic potential. The theory was further developed by Stevens[3] who demonstrated that in suitable circumstances the mixing had the effect of lowering all matrix elements of the orbital current $\mathbf{L}$ by a factor k smaller than unity by an amount which gives a measure of the admixture. Stevens also pointed out that because of this admixture we should expect a large transferred hyperfine interaction between the electron spin and the nuclear spins of the surrounding ligands. Both these effects had been observed experimentally.

Owen[4] later pointed out that a survey of experimental results from paramagnetic resonance and optical spectra shows that the spin orbit parameter λ is smaller in the crystal than in the free ion by about 20% to 30%. Owen interpreted this reduction as another effect of the admixture of ligand wave functions and was thus led to the conclusion that the admixtures were very large: Roughly speaking, if λ is reduced by, say 25%, and if this reduction is due solely to the ligand orbital admixture, then this admixture must be of the order of 25%, i.e., each magnetic electron has roughly a 25% probability of being found on the surrounding ligands and only a 75% probability of being found on the parent ion. In Sec. III we argue that this interpretation of the lowering of λ is incorrect and that in all cases (except possibly for very strongly covalent complexes) the admixture of ligand orbitals leads to an increase in λ, and the experimentally observed decrease is due to an entirely different effect, namely the screening of the $3d$ electrons by the overlapping charge clouds of the surrounding ligands. Experimental evidence in favor of this screening effect is given by measurements of neutron scattering form factors in Mn^{++} salts.

The transferred hyperfine interaction is capable in principle of giving very valuable information on the electronic structure of these complexes. The theory and experimental results have been considered several times,[5–12] but in Sec. IV we show that a careful discussion of the isotropic interaction exposes new terms (involving the $1s$ orbitals of F^-) which are surprisingly large. In Sec. IV we also discuss the anisotropic hyperfine interaction and show that the contribution from π overlaps is not negligible compared to that from σ overlaps.

In Sec. V we discuss the complications introduced into

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the theory when examining ions other than Mn^{++}. These complications arise whenever the transition metal ion does not have a half-filled shell.

In order to illustrate the molecular-orbital and the electron-transfer approaches for interpreting the transferred hyperfine interaction, we discuss in Sec. II a very simple, two-atom, three-electron system. This serves to introduce a notation and also makes it clear that these alternative approaches are different ways of describing the same effects.

II. WAVE FUNCTIONS

In this section we first consider a simple two-atom, three-electron system so as to fix a notation and introduce the calculations later performed in Sec. IV.

For the two-atom system we suppose for simplicity that the only important orbitals are that $3d$ orbital of the magnetic atom which happens to point toward the ligand and that $2p$ orbital of the ligand which points toward the magnetic atom. We may symbolically draw these orbitals as shown in Fig. 1. Now suppose we place three electrons in this system. The Heitler-London state, $\psi_{\mathrm{H-L}}$, will be obtained by placing two electrons in the p orbital, one in p_α and the other in p_β, and the third electron in either d_α or d_β. This state represents a ligand with closed shells of electrons and a magnetic ion with a partly filled $3d$ shell. With proper normalization the wave function is

$$\psi_{\mathrm{H-L}}=\{3![1-(d|p)^2]^{-\frac{1}{2}} \sum_P(\pm)^P P d_\alpha(1)p_\alpha(2)p_\beta(3), \quad (1)$$

where P denotes the permutation operator and $(d|p)$ is the overlap integral between d and p. The only other state it is possible to form for this system is that where the d orbital is doubly occupied and the p orbital is singly occupied. This wave function is

$$\psi_T=\{3![1-(d|p)^2]\}^{-\frac{1}{2}}\sum_P(\pm)^P P d_\alpha(1)p_\alpha(2)d_\beta(3), \quad (2)$$

where the subscript T indicates the state is formed by "transfer" of the β spin electron from p_β to d_β, i.e., from ligand to the magnetic ion. In general, the ground-state eigenfunction ψ_G will be a linear combination of $\psi_{\mathrm{H-L}}$ and ψ_T, i.e.,

$$\psi_G=[1+2B(d|p)+B^2]^{-\frac{1}{2}}[\psi_{\mathrm{H-L}}+B\psi_T]. \quad (3)$$

The usefulness of this approach comes solely from the fact that we can expect the admixture of ψ_T, i.e., B, to be small. On the other hand the one-electron wave functions in (1) and (2), and also $\psi_{\mathrm{H-L}}$ and ψ_T themselves, are not orthogonal and therefore it is very clumsy to work with them.

We may get an alternative description of the system by constructing bonding and antibonding molecular orbitals. The bonding orbitals will consist of mostly a ligand function but with a small admixture of d orbital. Thus

$$\phi_b=M(p+Bd), \quad (4)$$

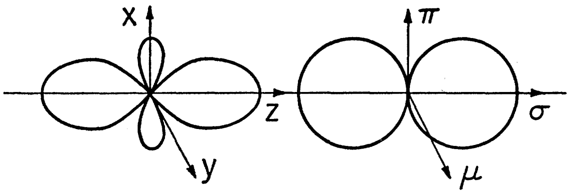

FIG. 1. The two-atom system.

where

$$M=[1+2B(p|d)+B^2]^{-\frac{1}{2}}, \quad (5)$$

and B, which we shall show later is identical to the B in (3), is a small coefficient of the same sign as the overlap integral. Similarly, the antibonding orbital is mostly a d orbital and thus

$$\phi_{ab}=N(d-Ap); \quad (6)$$

$$N=[1-2A(p|d)+A^2]^{-\frac{1}{2}}, \quad (7)$$

and A is another small coefficient. The condition that ϕ_b and ϕ_{ab} be orthogonal gives a relation between B and A of the form

$$B=[A-(p|d)]/[1-A(p|d)]. \quad (8)$$

We can now form the ground eigenstate by placing one electron in the antibonding orbital and two electrons in the bonding orbital to get

$$\psi_G=(3!)^{-\frac{1}{2}}\sum_P(\pm)^P P\phi_{ab}{}^\alpha(1)\phi_b{}^\alpha(2)\phi_b{}^\beta(3). \quad (9)$$

This form is very convenient to use because the wave functions are orthogonal to one another. It is instructive to express (9) in terms of $\psi_{\mathrm{H-L}}$ and ψ_T by substituting from (4) and (6) to get

$$\psi_G=(3!)^{-\frac{1}{2}}NM^2(1+AB) \times\sum_P(\pm)^P P d_\alpha(1)p_\alpha(2)[p_\beta(3)+Bd_\beta(3)], \quad (10)$$

which, using (5), (7), and (8), can be shown to be identical with (3). This demonstrates that the B of (3) is the same as that of (4).

It is now clear that it does not matter which approach we use, but that in practice using molecular orbitals is more elegant. It is important, however, not to misinterpret the results obtained by this approach. For example, when calculating magnetic properties the bonding orbitals always drop out of the calculation because they are doubly occupied and orthogonal to the antibonding orbitals; magnetic properties are therefore concerned only with the antibonding orbitals which represent "the spreading of the magnetic electrons onto the ligands." Within the context of the molecular orbital approach this phrase is quite correct, but it must not be misinterpreted as meaning an actual transfer process of the magnetic electrons outward to the ligands because, as (3) shows, the only transfer process possible is that of β-spin electrons inward from the ligand to the magnetic ion.

Notice that the Heitler-London state is that special form of the molecular orbital description obtained by setting B zero and hence, from (8), A equal to the overlap integral $(p|d)$. Now in calculating transferred hyperfine interactions we are interested in the degree of spin unpairing in the p orbital. In general this is A^2 and in the particular case of the Heitler-London model this becomes $(p|d)^2$. Similarly, the degree of spin unpairing in the s orbital of the ligand is $(s|d)^2$ in the Heitler-London model. The physical origin of these spin unpairings can be seen by reference to (1). The Pauli principle acts in such a way as to reduce the probability of the electron belonging to p_α being found in the region of strong overlap with the other α-spin electron, that belonging to d_α. Hence the probability of the former being found elsewhere, and in particular near the ligand nucleus, is increased. But the probability distribution of the β spin is undisturbed and hence a net α-spin increase is produced near the ligand nucleus. This effect was first pointed out by Mukherji and Das.[9] In general, an additional spin unpairing is to be expected due to deviations from the Heitler-London model, i.e., by transferring β spin from ligand to magnetic ion.

In MnF_2 and other fluorides we are concerned with the spin unpairing produced in the 1s, 2s, and 2p orbitals of F^-. The 1s and 2s orbitals are so low in energy that we may be reasonably confident they can be treated by the Heitler-London model, and hence the spin unpairings should be $(d|1s)^2$ and $(d|2s)^2$, respectively. The 2p orbitals are not so low in energy, so we cannot expect to treat them accurately by the Heitler-London model. We therefore expect the spin unpairing in the 2p orbital to be larger than $(d|2p)^2$, and from the degree by which it is larger we can deduce the departure from the Heitler-London model. We shall find this to be small. In calculating the overlap integrals $(d|1s)$, $(d|2s)$, etc., we must be cautious because we expect the wave functions designated d, 1s, 2s, etc., to be moderately distorted from the free-ion wave functions and we must estimate this distortion before calculating the integrals. This point will be discussed later.

III. THE SPIN-ORBIT PARAMETER

Owen[4] has pointed out that the spin-orbit parameter λ is always smaller in the crystal than in the free ion and has attributed this decrease to the admixture of ligand wave functions into the antibonding orbitals. However, we can estimate that the admixture almost certainly increases λ. The physical origin for this increase is the same as for the spin unpairing discussed in Sec. II; in the Heitler-London state the Pauli principle forces less weight onto regions where d_α and p_α overlap, and hence the electrons of d_α and p_α have a greater chance of being found elsewhere and in particular they have a greater chance of being found near their respective nuclei. This effect on the p_α electron produces an α-spin unpairing near the ligand nucleus in the way discussed in Sec. II; the same effect on the d_α electron increases λ because this parameter is proportional to $\langle 1/r^3\rangle$ where r is the distance of the electron from the parent nucleus. In the molecular-orbitals approach this effect appears through the normalization constant N in (6). Contributions to the spin-orbit parameter come mostly from that part of the wave function near the magnetic ion nucleus (because $\lambda\approx\langle r^{-3}\rangle$), so to a good approximation λ is proportional to the weight given to the d orbitals in antibonding wave functions, i.e., to N^2. For the Heitler-London state A is equal to $(d|p)$ and N^2 becomes $[1-(d|p)^2]^{-1}$. This is larger than unity, so λ is increased from the free-ion value. Only if the bonding were so strong that A were larger than $2(d|p)$ would N^2, and thus λ, be decreased from the free-ion value; this might be the case only in an extremely covalent complex, and therefore for all other cases we may safely conclude that these effects produce an increase in λ of a few percent. For the source of the experimentally observed decrease in λ we must therefore look elsewhere. (The argument we have just given on λ is only approximate because in general λ is proportional to the product of two different normalization constants, say NN', instead of just N^2. But since N and N' are of the same form the qualitative argument is unchanged.)

We have pointed out that for many complexes we might expect the Heitler-London model to be a reasonably good one, but we have not yet discussed the individual atomic wave functions to be used in building up this model. There is certainly no necessity to take them as the free-ion wave functions, and ideally we may imagine them to be determined by the following variational method. Choose individual atomic-like wave functions for the electrons of the magnetic ion and of the ligands and let these wave functions be specified by as many variational parameters as seems necessary. Assuming the crystal to be described by a Heitler-London model, now calculate the total energy of the crystal (working correct to second order, say, in the overlap integrals) and minimize this total energy by varying the parameters. This serves to define the best wave functions to use in constructing the Heitler-London model. Of course such a calculation would be difficult to perform in full, but we can give a plausible estimate of the final result. If there were no interactions between the ions the wave functions obtained would be the Hartree-Fock free-ion wave functions. But the interactions produce a distortion from these free-ion wave functions which is strong in th eregions farthest away from the present nucleus and apparently cannot be reliably estimated. In addition to this strong distortion in the outermost part of the wave functions we can also expect an over-all shift of the wave function outward.[13]

This radial shift outward is essentially a screening

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[13] Since this paper was prepared our attention has been brought to the work of Jorgenson [Discussions Faraday Soc. **26**, 110 (1958)]. The earliest reference to this effect we have been able to trace is a remark by L. Orgel [J. Chem. Phys. **23**, 1824, (1955)].

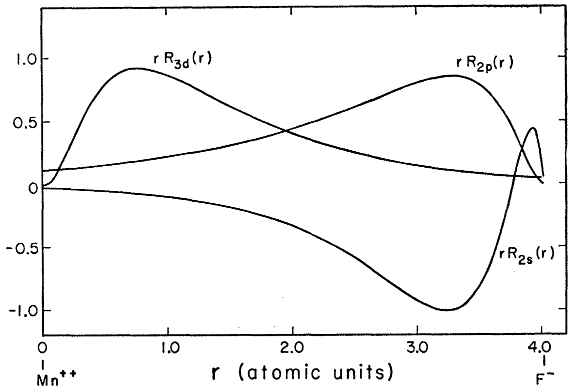

FIG. 2. The radial part of the Hartree-Fock free-ion wave functions of Mn^{++} and F^-. The ions are placed at the interatomic spacing in MnF_2.

effect which we can visualize by considering MnF_2 as an example. In Fig. 2 we show the free-ion wave functions for Mn^{++} and F^- with the two nuclei placed at the proper interaction distance. Notice that the $2p$ electrons of the F^- overlap the Mn^{++} ion very considerably. These $2p$ electrons therefore produce an appreciable charge density in the neighborhood of the Mn^{++} nucleus; hence the $3d$ electrons are screened from their parent nucleus and so move radially outward. An alternative way of visualizing this effect is as follows: When the $3d$ electron is inside the charge cloud of the F^- ion it sees an attractive potential due to the F^- nucleus and therefore gets pulled outward. These two descriptions are exactly equivalent. It follows from this argument that we can expect the radial expansion of the Mn^{++} $3d$ electrons to be the most important effect. The expansion of the F^- $2p$ electrons will be much smaller because the $3d$ electrons do not produce any appreciable charge density near the F^- nucleus; this is essentially because the Mn^{++} ion is so much smaller than the F^- ion.

The electrostatic energy of the $3d$ electrons in the field due to the ligands must surely be positive because the ligands are negatively charged, but it is important to realize that this does not mean the ligands repel the $3d$ electrons inwards. In fact, the electrostatic effect must always expand the $3d$ electrons outwards; to see this we imagine the ligand charge density to be spherically averaged and then we notice that the potential energy of an electron at a distance r from the metal ion is given, apart from a constant, by the total charge enclosed in a sphere of radius r. Since this charge is negative (for $r <$ bond length) the potential energy must fall as r increases, i.e., the $3d$ electrons will move outwards. Physically, we may see what is happening as follows: As r increases the potential energy of interaction with one ligand, the nearest one may increase because the distance from it is decreasing; but the interaction energy with the other ligands decreases because the distance from them is increasing. With a spherical average these effects exactly cancel if the interaction energy is given by a point-charge model and gives a mean energy decrease (as r increases) if the ligand charge density overlaps the magnetic ion.

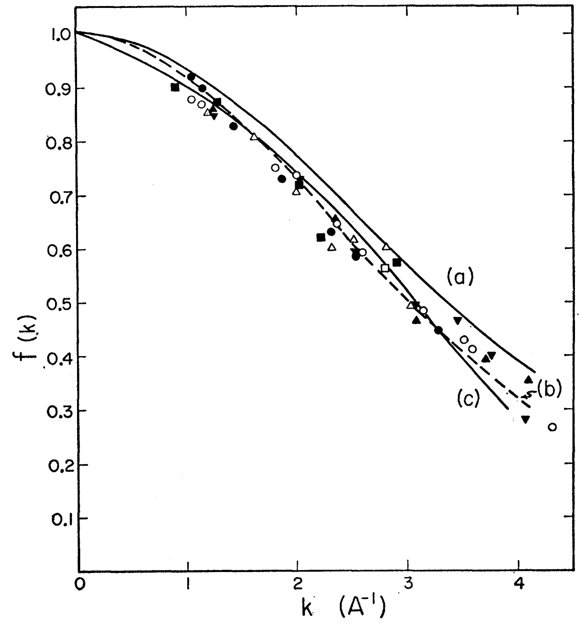

FIG. 3. Neutron form-factor curves. (a) Calculated from free-ion wave functions. (b) Empirical curve obtained by a 10% scaling of curve (a). (c) Erickson's result for MnF_2. The experimental points are those of Hastings, Elliott, and Corliss.

It would be highly desirable to have an explicit calculation of this screening effect, but it is more reliable to appeal to experiment to establish the size of it. We may do this by examining the form factors deduced from neutron diffraction measurements on magnetic salts. This form factor is defined by

$$f(\mathbf{K})=\int d\mathbf{r}\, e^{i\mathbf{K}\cdot\mathbf{r}}\rho(\mathbf{r}), \tag{11}$$

where $\mathbf{K}$ is the wave vector change of the neutron and $\rho(\mathbf{r})$ is the normalized spin density associated with each magnetic ion. Figure 3 shows values of the form factor deduced by Hastings *et al.*[14] for various Mn^{++} salts. Also in Fig. 3 we show the form factor calculated from Hartree-Fock free-ion wave functions, and it is obvious that this calculated curve gives very poor agreement with the experimental points. This discrepancy has been carefully noted by Hastings *et al.*, who observe that the data are fitted reasonably well by an empirical curve obtained from the calculated free-ion curve by simply scaling the form factor inward by 10%. This corresponds to using $3d$ wave functions scaled outward by 10%. Because we are specially interested in MnF_2 we also show in Fig. 3 the form factor measured for MnF_2

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[14] J. M. Hastings, N. Elliott, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).

by Erickson.[15] Within the experimental error this result also follows the Hastings, Elliott, and Corliss empirical curve.

Notice that the discrepancy between the free-ion calculated curve and the experimental results cannot be removed by postulating that the Hartree-Fock calculation fails to give good wave functions for the free ion. This is because if the Hartree-Fock calculation were in appreciable error it would probably be so in the opposite sense to that which is required to explain the experimental results. (The Hartree-Fock scheme omits configurational interaction which, if included, would introduce angular correlation between the electrons and so probably permit the electrons to fall into smaller radii than would be favored otherwise. Hence the Hartree-Fock scheme gives free-ion wave functions which are of slightly greater radial extent than the true wave functions. Correcting the Hartree-Fock free-ion wave functions therefore would slightly increase the discrepancy with experiment.) But this effect is probably very small and in what follows we shall ignore it.

From these results we can deduce that for Mn^{++} salts the expected radial expansion can be represented to a first approximation by a simple scaling of 10% with appropriate renormalization, i.e., the d functions to be used are related to the Hartree-Fock free-ion functions, d_{fi}, by

$$d(\mathbf{r})=w^{\frac{3}{2}}d_{\mathrm{fi}}(w\mathbf{r}), \tag{12}$$

where the scaling parameter, w, is 0.9 in this case. If we assume that roughly the same radial expansion takes place for all transition ion complexes, then we have a simple explanation of the lowering of the spin-orbit parameter, λ. This follows because λ is proportional to $\langle r^{-3}\rangle$ and hence, from (12),

$$\lambda=w^3\lambda_{\mathrm{fi}}, \tag{13}$$

where λ_{fi} is the free-ion value of λ. Equation (13) shows that λ will be lowered by almost 30% and this is certainly a large enough effect to account for the experimentally observed decrease.

Of course we cannot expect the radial expansion of the $3d$ wave functions to be strictly described by a simple scaling factor, nor can we expect this factor to be exactly or always 10%. But we do wish to point out that qualitatively we can always expect this kind of effect and that the experimentally observed lowering of λ is entirely due to this. Covalency effects, we believe, in these almost ionic complexes, tend to increase λ.

It is surprising that a single empirical curve can fit reasonably well all the neutron diffraction data on Mn^{++} salts, because we might have expected the scaling effect to have depended to a considerable extent on the nature of the six ligands surrounding each ion. However, ions do have very well-defined radii, and hence to some extent the crystal chooses a lattice spacing which keeps all overlap effects, and hence screening effects, constant. It must be for this reason that the w values are roughly constant.

Owen[4] has also pointed out that Slater integrals and Racah parameters, which give a measure of electron-electron interaction in the ion, are smaller in the solid than in the free ion. This decrease, we suggest, is also due to the screening effect. The Slater integrals are matrix elements of the electron-electron interaction e^2/r_{12}; they are therefore inversely proportional to the mean radius of the $3d$ orbits and we would thus expect them to be reduced by the factor w, by about 10% from their free-ion values. The observed decreases are not known with any great accuracy and vary somewhat from salt to salt, but they are roughly of this order of magnitude.

Murao[16] has also pointed out that screening effects decrease λ, but he attributes the screening to the additional $3d$ electron density produced by the admixture of $3d$ wave function into the bonding orbitals. In order to fit the theory to experiment, Murao has to postulate, in our notation, a value for the antibonding parameter A equal to 0.4. This we believe is far too large and our estimate of A shows this effect is very small.

Our suggestion that the $3d$ orbitals are always expanded relative to the free-ion wave functions is in direct conflict with estimates made by Phillips[17] indicating that, if anything, a radial contraction should take place. Phillips points out that in addition to the screening effect we have just described there is also an effective repulsion, due to the Pauli effect, from electrons in the closed shells of the ligands. Phillips argues by analogy with other problems that this latter effect will cancel, and indeed slightly exceed, the expansion effect due to screening. It is our opinion that the analogy drawn by Phillips between this problem and that of silicon metal is not close enough for us to accept the quantitative results of his argument.

It would be interesting to obtain neutron form factors for other than Mn^{++} salts in order to see if the expansion is present for them too. Alpern[18] has recently measured the form factor for Ni^{++} in NiO and, in contrast to the experimental results for Mn^{++} salts, he finds a contracted spin density. Blume[19] concludes that some part of this apparent construction can be attributed to scattering from the unquenched part of the orbital moment (which has a different form factor from the spin) but that otherwise there is no ambiguity in the interpretation of the experimental results which, therefore, are in direct contradiction to the expansion we suggest should take place. We have no explanation of this fact but are reluctant to abandon an idea because of a single experiment which involves difficult extinction corrections.

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[15] R. A. Erickson, Phys. Rev. **90**, 779 (1953).

[16] T. Murao, Progr. Theoret. Phys. (Kyoto) **21**, 4 (1959).

[17] J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

[18] H. Alpern, Phys. Rev. Letters **6**, 55 (1961).

[19] M. Blume (private communication).

It is important to recognize that this simple radial expansion is only a first rough approximation to the distortion of the wave functions from their free-ion values. It represents approximately the distortion near the magnetic ion and near the maximum in the $3d$ wave function. At larger distances from the magnetic ion nucleus the perturbation produced by the surrounding ligands is large and we can therefore expect the tail of the d wave function to be seriously perturbed in a way which it is not easy to estimate. However, for some purposes it is not necessary to know exactly the shape of the d-wave function tail; for example, the neutron diffraction form factors are sensitive only to the mean radius of the d orbital. Also we might hope the overlap integrals $(d|2s)$ and $(d|2p)$, because they are reasonably large, would be insensitive to the precise shape of the $3d$ function tail. In contrast to this, the overlap integral $(d|1s)$ is concerned almost exclusively with the tail of the d function and therefore we cannot hope to calculate it with any accuracy. This gives considerable difficulty in interpreting the transferred hyperfine interaction results which we discuss in the next section.

IV. TRANSFERRED HYPERFINE INTERACTION

In this section we discuss the transferred hyperfine interaction between F^{19} and Mn for pure MnF_2, MnF_2 in ZnF_2, and Mn^{++} in other salts. We shall use the independent bonding model, in which we consider each $Mn^{++}F^-$ pair separately and finally add up the effects due to all pairs. This simple procedure is valid only because Mn^{++} has a half-filled $3d$ shell. For other salts a more complex theory is required to interpret the results and so it is convenient to postpone discussion of them until Sec. V, where we indicate briefly the justification of the simple procedure we use here for Mn^{++} salts.

For the simple two-atom system of Fig. 1, construct mutually perpendicular axes σ, π, μ at the F^{19} nucleus and similar axes z, x, y at the Mn nucleus. We take the one-electron atomic orbitals to be $1s$, $2s$, p_σ, p_π, and p_μ on F^-, and on Mn^{++} the $3d$ functions labeled $3z^2-r^2$, x^2-y^2, zx, xy, and yz. Then the only nonzero overlap integrals are $\langle 3z^2-r^2|1s\rangle$, $\langle 3z^2-r^2|2s\rangle$, $\langle 3z^2-r^2|p_\sigma\rangle$, $\langle zx|p_\pi\rangle$, and $\langle zy|p_\mu\rangle$. The three $3d$ functions labeled $3z^2-r^2$, zx, and yz can be used to form several bonding and three antibonding functions. The antibonding functions are

$$\begin{aligned}\phi(3z^2-r^2)&=N_\sigma(|3z^2-r^2\rangle-a_{1s}|1s\rangle-a_{2s}|2s\rangle-a_\sigma|p_\sigma\rangle),\\ \phi(zx)&=N_\pi(|zx\rangle-a_\pi|p_\pi\rangle), \qquad (14)\\ \phi(zy)&=N_\mu(|yz\rangle-a_\mu|p_\mu\rangle),\end{aligned}$$

and the bonding functions could be written down by analogy with (4) but we shall not do this as they will not enter into the calculation. The two $3d$ functions labeled x^2-y^2 and xy do not form bonds with this F^- ion and therefore do not give rise to any transferred hyperfine interaction.

If the hyperfine interaction between the Mn^{++} spin and this F^{19} nucleus is

$$H=\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}, \qquad (15)$$

then we can show that relative to the axes σ, π, μ the tensor $\mathbf{A}$ is diagonal and hence (15) becomes

$$H=S_\sigma I_\sigma A^{\sigma\sigma}+S_\pi I_\pi A^{\pi\pi}+S_\mu I_\mu A^{\mu\mu}. \qquad (16)$$

It is clear that (15) must simplify to the diagonal form of (16) when the crystal has strictly cubic symmetry. However, in crystals of lower symmetry (16) is not correct in general, although in the special case of Mn^{++}, because it has a half-filled shell, (16) is an excellent approximation always.

We must now relate $A^{\sigma\sigma}$, $A^{\pi\pi}$, and $A^{\mu\mu}$ to the parameters a_{1s}, a_σ, etc., appearing in (14). To do this we remember that for Mn^{++} the three antibonding orbitals and also x^2-y^2, xy are occupied with parallel spin electrons so that the spin density associated with any one of these, say $\phi(3z^2-r^2)$, is $\phi^2(3z^2-r^2)\mathbf{S}/2S$ where S is $\frac{5}{2}$ for Mn^{++}. Thus the spin density at the F^{19} nucleus, which arises solely from the amplitude of $(3z^2-r^2)$ at the F^{19} position, gives an isotropic contribution to H which is $A_s\mathbf{S}\cdot\mathbf{I}$, where

$$\begin{aligned}A_s=(16\pi\beta\hbar\gamma/3)(N_\sigma^2/2S)[a_{2s}^2|\phi_{2s}(0)|^2+a_{1s}^2|\phi_{1s}(0)|^2\\ +2a_{1s}a_{2s}\phi_{1s}(0)\phi_{2s}(0)]. \qquad (17)\end{aligned}$$

(We ignore all terms involving the amplitude of $|3z^2-r^2\rangle$ at the F nucleus.) The spin unpairing in the p_σ orbital gives a contribution to H which is

$$(2\beta\hbar\gamma/5S)\langle r^{-3}\rangle_{2p}N_\sigma^2a_\sigma^2\sum_r S_rI_r(3\cos^2\theta_{r\sigma}-1), \qquad (18)$$

where $\theta_{r\sigma}$ is the angle between the axis r and the axis σ. Spin unpairing in p_π and p_μ gives similar terms, with subscript σ replaced by π and μ, respectively. In addition we must include the direct dipole term from the spin density of the Mn^{++} $3d$ orbitals; this is

$$\begin{aligned}(2\beta\hbar\gamma/R^3)\sum_r S_rI_r(3\cos^2\theta_{r\sigma}-1)\\ \times(2+N_\sigma^2+N_\pi^2+N_\mu^2)/5. \qquad (19)\end{aligned}$$

Adding all these contributions, replacing N_σ^2, N_π^2, and N_μ^2 by unity (which is a good approximation), and taking advantage of the relation

$$\cos^2\theta_{r\sigma}+\cos^2\theta_{r\pi}+\cos^2\theta_{r\mu}=1, \qquad (20)$$

we can rearrange the sum to give

$$\begin{aligned}H=A_s\mathbf{S}\cdot\mathbf{I}+(A_\sigma+A_D)\sum_r S_rI_r(3\cos^2\theta_{r\sigma}-1)\\ +A_\pi\sum_r S_rI_r(3\cos^2\theta_{r\pi}-1), \qquad (21)\end{aligned}$$

where

$$A_s=(8\pi\beta\hbar\gamma/3S)a_{2s}^2|\phi_{2s}(0)|^2 \times\{1+[a_{1s}\phi_{1s}(0)/a_{2s}\phi_{2s}(0)]\}^2, \tag{22}$$

$$A_\sigma=(2\beta\hbar\gamma/5S)\langle r^{-3}\rangle_{2p}(a_\sigma^2-a_\mu^2), \tag{23}$$

$$A_D=2\beta\hbar\gamma/R^3, \tag{24}$$

$$A_\pi=(2\beta\hbar\gamma/5S)\langle r^{-3}\rangle_{2p}(a_\pi^2-a_\mu^2). \tag{25}$$

Comparing (16) and (21) gives

$$\begin{aligned} A^{\sigma\sigma}&=A_s+2(A_\sigma+A_D)-A_\pi,\\ A^{\pi\pi}&=A_s-(A_\sigma+A_D)+2A_\pi,\\ A^{\mu\mu}&=A_s-(A_\sigma+A_D)-A_\pi. \end{aligned} \tag{26}$$

Hence we see that the interaction between the Mn spin and the F^{19} nucleus may be expressed in terms of three parameters A_s, $A_\sigma+A_D$, and A_π. For MnF_2 and for MnF_2 in ZnF_2 there are two kinds of bonds which we call I and II and therefore we can determine these three parameters for both kinds of bond and call them A_s^{I}, A_s^{II}, etc. (There are four bonds of type I and two of type II for every Mn^{++} ion.) Ideally, therefore, we would like to determine all six parameters from experiment.

It is not convenient to measure the diagonal components $A^{\sigma\sigma}$, $A^{\pi\pi}$, and $A^{\mu\mu}$ directly; instead the components of the tensor $\mathbf{A}$ are measured relative to the crystal axes x, y, z. The measured components may be expressed in terms of $A^{\sigma\sigma}$, $A^{\pi\pi}$, and $A^{\mu\mu}$ by a simple transformation of coordinates which has been discussed in detail before[11] and which we shall not repeat here.

The complete Hamiltonian describing the interaction of each Mn spin with its six ligands is obtained by summing (15) to give

$$H=\textstyle\sum_N \mathbf{S}\cdot\mathbf{A}_N\cdot\mathbf{I}_N. \tag{27}$$

Clogston *et al.*[11] have emphasized that even if each individual term like (15) can be written in the form of (16) it is not possible to choose axes such that all the tensors $\mathbf{A}_N$ are diagonal simultaneously unless the ligands are arranged in a perfect octahedron. For pure MnF_2 and for MnF_2 in ZnF_2 there is a considerable departure from cubic symmetry and Tinkham's[5] original analysis failed to take this properly into account. Clogston *et al.* have discussed this problem and shown how values of A_s, $(A_\sigma+A_D)$, and A_π may be deduced for the different bonds I and II from their experiments on the paramagnetic resonance of MnF_2 in ZnF_2. Their results are given in Table I.

Before comparing these results to those obtained by Shulman and Jaccarino[6–8] for pure MnF_2, it is necessary to consider what values to use as bond lengths for I and II. Baur[20] gives the bond lengths of I and II as 2.132 A and 2.102 A for MnF_2, and 2.043 A and 2.015 A for ZnF_2. In both crystals bond II is shorter than bond I and therefore the interaction parameters for II should be larger than for I, as is observed. (The lattice parameters of Stout and Reed[21] give bond II longer than bond I and this is quite inconsistent with the interaction parameters given above; we therefore assume the Baur results to be correct.) There is no simple way we can determine the bond lengths for MnF_2 in ZnF_2. We would obviously expect them to be intermediate between those of pure MnF_2 and pure ZnF_2. However, Clogston *et al.* find that parameters measured in pure MnF_2 are essentially identical to those deduced from experiments on MnF_2 in ZnF_2. Hence they conclude that the bond lengths for MnF_2 in ZnF_2 are very close to those in pure MnF_2. We shall assume them to be 2.132 A and 2.102 A, respectively, for both cases. From (24) this gives 2.56 and 2.69 for A_D^{I} and A_D^{II}, respectively; it is these values which have been used to deduce the A_σ values given in the table. The experiments of Shulman and Jaccarino[6,7] on the nuclear magnetic resonance of F^{19} in pure MnF_2 are not capable of yielding all six parameters, and hence when interpreting the results it is necessary to make some further assumptions. Experiments on the paramagnetic phase of MnF_2 give three independent results; in order to interpret these results Shulman and Jaccarino chose to ignore the difference between I and II. With this assumption the number of independent parameters reduces to three—A_s, A_σ, and A_π—which may be determined from the three independent measurements. Their results are also given in Table I. Notice that these experiments give A_σ directly because A_D is most con-

TABLE I. Values of the parameters in 10^{-4} cm^{-1}.

	A_s^{I}	A_s^{II}	A_σ^{I}	A_σ^{II}	A_π^{I}	A_π^{II}
Clogston *et al.*[a]	15.09±0.16	16.54±0.19	0.46±0.3	0.80±0.17	−0.14±0.21	0.18±0.11
Shulman and Jaccarino[b]	15.68±0.3		0.46±0.3		0.11±0.3	
Keffer *et al.*[c]	15.4±0.3	16.2±0.3	0.2±0.3	0.4±0.3	0	0
$w=1.0$, No 1*s*	6.4	7.3	0.27	0.29	0	0
With 1*s*	3.2	3.4	...	...	...	...
$w=0.9$, No 1*s*	12.9	14.5	0.37	0.38	0	0
With 1*s*	5.5	6.1	...	...	...	...

[a] Clogston *et al.*, (see reference 11) do not quote values of A_σ^{I} and A_σ^{II}; the values given in the table have been obtained by subtracting calculated values of A_D^{I} and A_D^{II} from their quoted values of $A_\sigma^{\mathrm{I}}+A_D^{\mathrm{I}}$ and $A_\sigma^{\mathrm{II}}+A_D^{\mathrm{II}}$.
[b] See reference 6.
[c] See reference 10.

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[20] W. H. Baur, Acta Cryst. **11**, 488 (1958).

[21] J. W. Stout and A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

veniently absorbed into the dipole sum giving the field at the F nucleus produced by all the Mn ions. This dipole sum was easily calculated and has already been subtracted from the observed results.

The Jaccarino and Shulman[8] experiment on the antiferromagnetic phase of MnF_2 gives a fourth independent measurement. When interpreting these results Keffer *et al.*[10] chose to assume A_π^{I} and A_π^{II} to be zero. They were then left with four independent parameters which could be fitted to the four independent measurements. Their analysis gives the values shown in Table I.

All these results agree within experimental error, but the results of Clogston *et al.* are complete and have been deduced without any assumptions and should therefore be preferred to the other results.

The calculations of Froese[22] for F^- give

$$|\phi_{2s}(0)|^2=10.726a_0^{-3}, \tag{28}$$

$$\phi_{1s}(0)/\phi_{2s}(0)=4.44, \tag{29}$$

$$\langle r^{-3}\rangle_{2p}=6.405a_0^{-3}. \tag{30}$$

These values of $|\phi_{2s}(0)|^2$ and $\langle r^{-3}\rangle_{2p}$ are slightly different from those given by Moriya.[23] The latter were derived from a Hartree calculation on F^- and from the approximate procedure of Barnes and Smith,[24] whereas the results given here are derived from the recent Hartree-Fock calculation by Froese. Substituting into (22), (23), and (25) gives (in units of 10^{-4} cm^{-1})

$$\begin{aligned}A_s^N&=0.300|a_{2s}^N|^2(1+4.44a_{1s}^N/a_{2s}^N)^2\times10^4,\\A_\sigma^N&=(|a_\sigma^N|^2-|a_\mu^N|^2)0.858\times10^2,\\A_\pi^N&=(|a_\pi^N|^2-|a_\mu^N|^2)0.858\times10^2.\end{aligned}\tag{31}$$

In the independent bonding model, using just the terms we have retained in deriving (31), there is no way of distinguishing the π axis from the μ axis. It follows that a_π and a_μ^N are equal and A_π^N is given as zero. It is not clear whether or not the experimental results should be taken as indicating nonzero values for A_π^{I} and A_π^{II}.

It is worthwhile to list some of the approximations, other than the use of the independent bonding model, made in deriving these results.

(1) In calculating A_s we neglected the amplitude of the $3d$ function $|3z^2-r^2\rangle$ at the F^{19} nucleus. Because $|3z^2-r^2\rangle$ must be severely perturbed near the F^- nucleus we can make no reliable estimate of this term, but it is certainly much smaller than the terms we have retained.

(2) In calculating A_σ and A_π we neglected the dipolar field due to the spin density in the cross terms arising when $\phi(3z^2-r^2)$, $\phi(zx)$, and $\phi(zy)$ are squared. (These are the cross terms linear in the parameters a_{1s}, a_{2s}, a_σ, a_π, and a_μ.) These terms are certainly a good deal smaller than the terms we retain because the "cross" spin density is far from the F nucleus, but it is difficult to estimate them.

(3) The normalization factors N_σ^2, N_π^2, and N_μ^2 were replaced by unity. In calculating the direct dipole term this introduces an error which can be shown to be smaller than, and of opposite sign to, the neglected terms (2). Elsewhere this approximation introduces negligible error.

(4) Inclusion of terms (1), (2), and (3) would not produce a qualitative change in the form of the results. However, there are small terms we have neglected which produce a nonzero value for A_π when the octahedron of F^- ions is not perfect. They arise in the following way. The spin density along an $Mn^{++}-F^-$ bond has an interaction with this particular F^{19} nucleus we have just discussed; in addition this spin density has an interaction with all the other F nuclei. Of course this interaction is small because the other F nuclei are far away. But it can be shown that, provided the octahedron is not perfect, this produces a nonzero value for A_π. It would be desirable to estimate these terms and compare them to the experimental value of A_π, but the labor of doing so is too great.

(5) We have assumed the F^- wave functions are independent of spin and this may be particularly important in deriving a value for A_s. In general we must expect the F orbitals $2s_\alpha$ and $2s_\beta$ (and also $1s_\alpha$ and $1s_\beta$) to be slightly different because the exchange potential seen by the α and β spins is slightly different. Because the α spins get attracted out toward the α spins of the Mn^{++} ion, this effect always gives a diamagnetic contribution to A_s. Shulman[25] has described the same diamagnetic term using a different approach which, however, is fundamentally the same as described here.

As we described in Sec. II, the Heitler-London model gives the coefficients of (14) as the appropriate overlap integrals, i.e., the model gives

$$\begin{aligned}a_{2s}^N&=\langle3z^2-r^2|2s\rangle_N,\\a_{1s}^N&=\langle3z^2-r^2|1s\rangle_N,\\a_\sigma^N&=\langle3z^2-r^2|p_\sigma\rangle_N,\\a_\pi^N&=a_\mu^N=\langle zx|p\pi\rangle_N.\end{aligned}\tag{32}$$

In Table II we give values of these overlap integrals computed for various bond lengths and using two values of the screening parameter w, 1.0 and 0.9. The results are quoted to four figures for ease of interpolation but of course we cannot expect more than one or two figures to be physically significant. Using these computed values for the overlap integrals, we give in Table I the calculated values of the parameters using $w=1.0$ and $w=0.9$ and also including or ignoring the $1s$ orbital of the F^- ion.

Let us consider the value of A_s first. The results using

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[22] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

[23] T. Moriya, Progr. Theoret. Phys. (Kyoto) **16**, 23 (1956).

[24] R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

[25] R. G. Shulman (to be published).

TABLE II. Overlap integrals calculated with free-ion wave functions $w=1.0$ and with expanded wave functions $w=0.9$.

	$\langle d\vert 1s\rangle\times10^3$		$-\langle d\vert 2s\rangle\times10^2$		$\langle d\vert\sigma\rangle\times10^2$		$\langle d\vert\pi\rangle\times10^2$	
R/w	1.0	0.9	1.0	0.9	1.0	0.9	1.0	0.9
2.00	5.145	7.765	6.107	8.378	8.000	9.466	4.938	6.796
2.02	4.898	7.295	5.852	8.075	7.824	9.294	4.757	6.274
2.04	4.556	6.754	5.608	7.784	7.649	9.122	4.582	6.059
2.06	4.198	6.258	5.373	7.500	7.474	8.950	4.413	5.850
2.08	3.865	5.859	5.145	7.221	7.299	8.774	4.251	5.649
2.10	3.546	5.542	4.926	6.948	7.124	8.605	4.094	5.455
2.12	3.192	5.268	4.716	6.684	6.949	8.434	3.944	5.267
2.14	2.778	4.989	4.516	6.427	6.774	8.264	3.798	5.086
2.16	2.358	4.765	4.323	6.175	6.599	8.096	3.658	4.911
2.20	1.620	4.541	3.958	5.689	6.248	7.764	3.393	4.578
2.24	1.103	4.316	3.615	5.235	5.900	7.441	3.148	4.268
2.28	0.772	3.753	3.294	4.819	5.559	7.123	2.920	3.978
2.32	0.589	3.233	0.995	4.430	5.229	6.807	2.708	3.707

$w=1.0$ and ignoring the $1s$ electrons give the approximation of Mukherji and Das[9] and Keffer *et al.*[10] These results are in reasonable agreement with the experimental results given in Table I. The agreement is improved considerably if the screened ($w=0.9$) $3d$ wave functions are used and the $1s$ electrons still ignored. But essentially all agreement disappears with the inclusion of the $1s$ electrons in either calculation because the cross term in (17) involving the product $\phi_{1s}\phi_{2s}$ produces a negative spin density at the F^- nucleus which is much larger than the additional positive term $a_{1s}{}^2|\phi_{1s}(0)|^2$ and almost as large as the original positive term $a_{2s}{}^2|\phi_{2s}(0)|^2$. That this cross term must be negative can be seen as follows: Defining the phase of the wave functions so that $\phi_{1s}(0)$ and $\phi_{2s}(0)$ are both positive, we notice that the overlap integral $\langle 3z^2-r^2|1s\rangle$ must be positive whereas the overlap integral $\langle 3z^2-r^2|2s\rangle$ must be negative because the $2s$ orbital has a radial mode. Hence a_{1s} and a_{2s} must be of opposite signs.

The conclusions to be drawn from these results seem reasonably clear. We are quite confident that it is valid to use the Heitler-London model to treat the $1s$ electrons provided the model is set up in the formal way we described in Section III; but the amplitude of the $1s$ orbitals at the F^- nucleus is so large that we cannot afford to make even a small error in computing the overlap integral $\langle 3z^2-r^2|1s\rangle$, and this unfortunately requires our having a good knowledge of the shape of the $|3z^2-r^2\rangle$ orbital, i.e., the distortion from a simple $3d$ orbital, in the neighborhood of the F^- ion. This good knowledge of $|3z^2-r^2\rangle$ we do not have, and it is clear that in this region near the ligand ion the simple radial scaling we have used is thoroughly inadequate to describe the distortion from the free ion wave functions—although over the bulk of the $|3z^2-r^2\rangle$ orbital the simple radial scaling may be qualitatively reasonable.

These calculations show that no theory of the isotropic transferred hyperfine interaction may be considered as satisfactory until the contribution from the $1s$ electrons of the ligand is properly computed. However, it does seem that using $2s$ electrons alone gives good agreement with experiment, especially when the radially expanded $3d$ wave functions are used, and it is tempting to postulate therefore that the effect of the $1s$ electrons, if properly calculated, would be small. It certainly seems probable that the $1s$ electrons give a negative, i.e., diamagnetic, contribution because no matter what the precise shape of $|3z^2-r^2\rangle$, a_{1s} and a_{2s} are almost certain to have opposite signs and we have already remarked, as approximation (5), that we are neglecting a small diamagnetic contribution from both $1s$ and $2s$ orbitals.

Now let us consider the values of A_σ. The results using $w=1.0$ and ignoring the π overlap integral, a_π, give the approximation of Keffer *et al.* We notice from Table II that the π-overlap integral is reasonably large and that it is a poor approximation to ignore it; Casselman and Keffer[26] have recently reached the same conclusion independently. The results using $w=0.9$ show some improvement in comparing to the experimental results but in this case we do not expect the Heitler-London model to be a very good approximation and therefore we do not expect close agreement with experiment. Indeed, from a comparison between theory and experiment we can get a rough estimate of the degree of departure from a Heitler-London model. Assuming that a_σ and a_π as given by the Heitler-London model are in error by the same factor, and taking the result of Clogston *et al.* for $A_\sigma{}^{\mathrm{II}}$ as the most reliable experimental result, we have

$$a_\sigma=(0.80/0.38)^{\frac{1}{2}}\langle 3z^2-r^2|\sigma\rangle\approx1.4\langle 3z^2-r^2|\sigma\rangle. \qquad (33)$$

Hence from (8) the admixture parameter b_σ in the bonding orbital is

$$b_\sigma\approx a_\sigma-\langle 3z^2-r^2|\sigma\rangle=0.4\langle 3z^2-r^2|\sigma\rangle\approx3\times10^{-2}. \qquad (34)$$

Hence the admixture of ionic state by transfer of electron from ligand to cation is $b_\sigma{}^2\approx10^{-3}$ which is very small. However, this small admixture is somewhat misleading because the "transfer" state and the Heitler-London state are not orthogonal and therefore most properties, including the transferred hyperfine structure, depend linearly on b_σ.

Let us now discuss other experimental results on the transferred hyperfine interaction in Mn^{++} salts. Benedek and Kushida[27] have observed the F^{19} nuclear magnetic resonance in MnF_2 as a function of hydrostatic pressure. They compare their observed variation of the resonance frequency to that calculated using the theory described here and the numerical results of Table II. They found excellent agreement with experiment but at that time we had not noticed the existence of the negative cross term between $2s$ and $1s$ orbitals and it was therefore omitted in their analysis. Their conclusions are therefore meaningful only if we suppose the wave functions used here give $\langle 3z^2-r^2/2s\rangle$ accurately and exaggerate $\langle 3z^2-r^2|1s\rangle$.

Schulman and Knox[12] have observed the F^{19} resonance in KMnF_3 where the environment of each Mn ion is

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[26] R. N. Casselman and F. Keffer, Phys. Rev. Letters **4**, 498 (1960).

[27] G. B. Benedek and T. Kushida, Phys. Rev. **118**, 46 (1960).

cubic; they determine

$$A_s = (16.26\pm0.4)\times10^{-4}\ \mathrm{cm}^{-1},$$
$$A_\sigma = (0.17\pm0.1)\times10^{-4}\ \mathrm{cm}^{-1}.$$

The Mn—F bond length in $KMnF_3$ is approximately the same as that in MnF_2 so it is satisfactory that the value for A_s is approximately the same; but we cannot understand why A_σ is so much smaller for this salt than for MnF_2.

Hayes and Jones[28] have observed the electron paramagnetic resonance of Mn^{++} in NaF and deduced

$$\begin{aligned} A_s &= (14.4\pm0.3)\times10^{-4}\ \mathrm{cm}^{-1}, \\ A_\sigma + A_D &= (2.8\pm0.7)\times10^{-4}\ \mathrm{cm}^{-1}. \end{aligned} \tag{36}$$

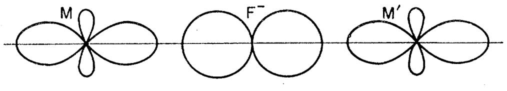
The Na—F bond length in NaF is 2.31 A. When Mn^{++} is substituted for Na we expect the six surrounding F^- ligands to collapse inward so that the Mn—F bond length becomes intermediate between that for NaF and that for MnF in pure MnF_2. We must therefore treat the Mn—F bond length in this crystal as an adjustable parameter and hence these results cannot be used to give an adequate test of the theory. Notice, however, that a bond length of roughly 2.15 would fit both results of (37) provided the expanded wave functions $w=0.9$ were used and $1s$ contributions ignored.

Baker, Bleaney, and Hayes[29] have observed the electron paramagnetic resonance of Mn^{++} in CaF_2 and deduced

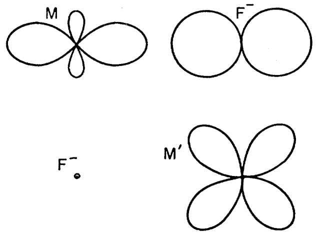
$$\begin{aligned} A_s &= (9.5\pm0.3)\times10^{-4}\ \mathrm{cm}^{-1}, \\ A_\sigma + A_D &= (2.7\pm0.5)\times10^{-4}\ \mathrm{cm}^{-1}. \end{aligned} \tag{37}$$

The Ca—F bond length in CaF_2 is 2.36 A, each Ca being surrounded by a cube of eight F^- ions. On substituting Mn for Ca the eight fluorine ions collapse inward so again we must treat the Mn—F bond length as an adjustable parameter. From Table II we find that, using expanded wave functions ($w=0.9$) and ignoring $1s$ contributions, both results can be obtained within experimental error by a bond length of 2.22 A.

We should note in passing that the large values of the π-overlap integral lead us to suspect the validity of Anderson's 180° rule for superexchange interactions. Anderson[30] argued that superexchange between two magnetic ions would be greatest when they were at 180° from one another as viewed from the nonmagnetic ion, O^{--}, F^-, etc. (i.e., that cation-anion-cation be collinear) because then the p_σ orbital of the anion would overlap strongly with the $3d$ orbitals of both cations simultaneously. This situation is shown in Fig. 4(a). The superexchange integral is proportional to the overlap integral to the fourth power, hence we expect $J_{180}\approx\langle 3z^2-r^2|\sigma\rangle^4$. In contrast to this, coupling between two magnetic ions at 90° to one another as viewed from the nonmagnetic ion must utilize π-bonding as shown in Fig. 4(b) and hence we expect $J_{90}\approx 4\langle 3z^2-r^2|\sigma\rangle^2\langle yz|\pi\rangle^2$, where the factor 4 comes from the fact that in addition to the coupling between the $3z_2-r^2$ orbital of M and the xz orbital of M' (which is shown in the figure) we also have that between xz of M and $3x^2-r^2$ of M' and two similar couplings via the other nonmagnetic ion which completes the square of Fig. 4(b). Taking note of this factor of 4 and that from Table II $\langle yz|\pi\rangle^2$ is roughly 40% of $\langle 3z^2-r^2|\sigma\rangle^2$, we see no reason to suppose that superexchange coupling through 90° is any weaker than that through 180°. A similar conclusion has been arrived at independently by Casselman and Keffer[26] from a consideration of overlap integrals between Mn^{++} and O^{--} wave functions.



(a) 180°



(b) 90°

FIG. 4. Superexchange at (a) 180°, (b) 90°.

V. GENERAL THEORY

In this section we describe briefly the modifications of the theory which are necessary when considering magnetic ions with other than half-filled $3d$ shells. There seem to be four such effects, one of which vanishes in strictly cubic symmetry, and we shall list them one at a time.

(1) When the $3d$ shell is half full the spin density of the magnetic ion has spherical symmetry, and when calculating the dipole-dipole term it is then valid to replace this distributed electron spin density by a point dipole. But when the $3d$ shell is not half full then the electron spin density does not have spherical symmetry and this procedure fails; correction terms, one proportional to $\langle r^2\rangle/R^5$ and one to $\langle r^4\rangle/R^7$, must be added. The correction terms can be of the order 10% of the usual dipole-dipole term.

(2) When the $3d$ shell is not half full then the orbital moment is not completely quenched and the interaction of this moment with the ligand nucleus must be added

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[28] W. Hayes and D. A. Jones, Proc. Phys. Soc. (London) **A71**, 503 (1958).

[29] J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

[30] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

to the dipole-dipole interaction. The bulk of this interaction is taken into account merely by using the proper g value in the dipole-dipole interaction but in general there is a correction term proportional to $\langle r^2\rangle/R^5$.

(3) The spin orbit interaction mixes $3d$ orbitals and gives small corrections to the calculated hyperfine interactions. There are two ways in which this happens: The mixture of $3d$ orbitals gives rise to a slightly changed spin distribution on F^- which, however, is probably too small to be observable; the mixing also gives rise to unquenched orbital moment on the F^- itself and this can produce corrections of 10% to 15%.

(4) When the environment of a magnetic ion is not strictly cubic then, in general, the hyperfine interaction cannot be written in the diagonal form of (16). This point has been carefully emphasized by Clogston *et al.*[11] However, for a simple Heitler-London model, or for a model where it is assumed the admixture parameters a_{1s}, a_σ, etc. are proportional to their corresponding overlap integrals, then it can be shown that (16) is valid for Mn^{++} and this justifies the use of the independent bonding model in Sec. IV.

These may not be all the effects that are important. Indeed, recent results by Shulman and Knox[31] on $KNiF_3$ and K_2NaCrF_6 show such large anisotropic hyperfine interactions that it seems probable some other effect, not yet thought of, is present in these crystals.

VI. CONCLUSIONS

Various aspects of the theory of transition ion complexes have been discussed. It was first pointed out that the Heitler-London model is a special case of the more general ligand field theory and for some purposes we might expect it to be a good approximation. We have emphasized, however, that in constructing this Heitler-London model one should not use free ion wave functions but, in principle, the wave functions must be determined from a variation calculation.

We have suggested that the experimentally observed lowering of the spin orbit parameter is due to a screening effect which causes the $3d$ wave functions to expand from their free ion shape. Neutron diffraction measurements on Mn^{++} salts indicate that to some approximation this expansion can be represented by a simple radial scaling factor of about 10%. We do not think it likely that the expansion is as simple as this but suggest this qualitative effect is always present. It would be very desirable to have neutron form factor measurements on other salts to verify that this expansion takes place in all cases.

In an effort to get further information on the wave functions of the complex we have also discussed the transferred hyperfine interaction between the electron spin of Mn^{++} and the surrounding F^{19} nuclei. The results of this discussion are unsatisfactory. A careful treatment of the isotropic interaction including $1s$ wave functions of F^- in the antibonding orbitals shows that the effect of the $1s$ orbitals alone is relatively small, but that the cross term between the $2s$ and $1s$ orbitals is surprisingly large and negative if its magnitude is assessed using either free ion wave functions or expanded wave functions to calculate the overlap integrals. It is concluded that no theory of the isotropic interaction may be considered as satisfactory until this difficulty is resolved. However, there is some empirical evidence (perhaps fortuitous) that using a Heitler-London model with expanded wave functions and ignoring the $1s$ orbitals of F^- entirely gives reasonable agreement with experiment.

For the anisotropic hyperfine interaction we do not expect, and do not find, good agreement between results predicted from the Heitler-London model and results from experiment. From the disagreement we have made a rough assessment of the degree of departure from the Heitler-London model.

The theory of the transferred hyperfine interaction for ions other than Mn^{++} is more complex because for these other ions the $3d$ shell is not half full. The most important corrections to the theory were briefly described in Sec. V.

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