JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Recent Theoretical Work on Magnetism at Harwell

W. MARSHALL

Atomic Energy Research Establishment, Harwell
Berks, England

Some of the recent theoretical research on magnetism at the Atomic Energy Research Establishment, Harwell, is briefly reviewed. Topics discussed are, (1) the validity of the unrestricted Hartree-Fock method; (2) the polarization of the conduction electrons in ferromagnets; (3) the neutron form factor for Ni^{++} salts, (4) correction terms for the transferred hyperfine interaction in magnetic complexes.

In this paper I shall briefly review some of the recent theoretical research on magnetism at the Atomic Energy Research Establishment, Harwell. I shall not be able to mention everything and therefore will concentrate on the work with which I am most familiar.

Recently, great interest has been aroused in hyperfine interactions and one of the main contributions to this interaction, the core polarization, is usually calculated using the Unrestricted Hartree-Fock (U.H.F.) method[1]. Because of this, Mr. M. Powell and the author have examined the validity of the U.H.F. method and we illustrate the problem with the Li atom as example. In the conventional Hartree-Fock (H.F.) calculation, the configuration is taken as $(1s)^2(2s)^1$ and the spin density and hyperfine interaction arise solely from the $2s$ orbital which has an unpaired spin. In the U.H.F. method, the $1s_\alpha$ and $1s_\beta$ orbitals are allowed to differ so the configuration is taken as $1s_\beta 1s_\alpha 2s_\alpha$ and a spin density is produced both by the unpaired $2s$ electrons and the difference between the $1s$ orbitals. Unfortunately, the U.H.F. method does not give an eigenfunction of the total spin and is therefore an admixture of doublet and quartet states. We define two normalised orthogonal functions, P and R, and a small parameter x by

$$1'=(1+x^2)^{-\frac{1}{2}}(P-xR)$$
$$1''=(1+x^2)^{-\frac{1}{2}}(P+xR) \qquad (1)$$
$$2x^2/(1+x^2)=1-(1'\,|\,1'')$$

and then the U.H.F. wavefunction can be written as

$$\Psi_{\text{U.H.F.}}=(1+x^2)^{-1}[(P_\beta P_\alpha 2_\alpha)$$
$$+x\{(P_\beta R_\alpha 2_\alpha)+(P_\alpha R_\beta 2_\alpha)\}-x^2 R_\beta R_\alpha 2_\alpha] \qquad (2)$$

whereas a pure doublet constructed from the same functions would be

$$\Psi_{\text{T}}=(1+6\,y^2+z^2)^{-\frac{1}{2}}[(P_\beta P_\alpha 2_\alpha)$$
$$+y\{(P_\beta R_\alpha 2_\alpha)+(P_\alpha R_\beta 2_\alpha)-2\,(P_\alpha R_\alpha 2_\beta)\}$$
$$+z(R_\beta R_\alpha 2_\alpha)] \qquad (3)$$

Correct to first order, (2) and (3) give the same spin density if x and y are equal; but the energy evaluated with (1) or (2) involves x and y quite differently and therefore we would not expect that a minimisation process relative to x or y would give the same value and hence the same spin density. Nevertheless it has been shown[2] that x and y would be equal if certain exchange integrals could be neglected. Explicit calculation is needed to examine this point further; evaluating the unpaired spin density at the nucleus we find

$$2\langle S^z(0)\rangle_{\text{H.F.}}=2.06 \qquad 2\langle S^z(0)\rangle_{\text{T}}=2.72$$
$$2\langle S^z(0)\rangle_{\text{U.H.F.}}=2.82 \qquad 2\langle S^z(0)\rangle_{\text{Exp}}=2.91$$

The difference between the H.F. value of 2.06 and the experimental 2.91 shows that core polarization is important. The value of 2.72 obtained in this calculation shows that this bulk of the discrepancy is due to this kind of configuration interaction but it is disappointing that a sizeable error, 0.19, remains and this we attribute to higher correlation effects, i.e., to configuration interaction involving the substitution of more than one orbital in $1s_\beta 1s_\alpha 2s_\alpha$. The U.H.F. value of 2.82 is closer to experiment than our value but we believe this to be fortuitous.

Our calculation is essentially similar to an earlier one by Nesbet who obtained a result of 2.87—very close to the experimental result—and who therefore concluded "that these specific configuration interaction effects can account for the hyperfine splitting of lithium to within one percent of the experimental value". Unfortunately Nesbet used a poor wavefunction for the 2*s* electron so that his starting H.F. value was 2.29 (in place of the accurate H.F. value of 2.06) and this "error" is almost exactly what is required to compensate for the deficiency we found and therefore we can easily understand the agreement with experiment he obtained. It is of course true that if configuration interaction is taken to high enough order the starting point is irrelevant and therefore we cannot, strictly speaking, talk about the "error" in a starting point. But in practice configuration interaction is taken to only first order and then the starting point is significant. The real value of Nesbet's calculation is that it demonstrated in principle how core polarization could be taken into account using configuration interaction methods.

We recognise that the core polarization term is 0.85 experimentally, 0.76 according to the U.H.F. method and 0.66 according to this calculation. We conclude that the U.H.F. method is in error both because S^2 is not a good quantum number and because of correlation effects and therefore any discrepancy between the U.H.F. result and experiment cannot be interpreted. The calculation described here is more satisfying in the sense that the remaining discrepancies can be unambiguously assigned to correlation effects, but on the other hand we can hold no hope that these discrepancies will be smaller than those given by the U.H.F. method.

In metals another contribution to the hyperfine interaction comes from the polarization of the conduction band electrons. Anderson[3] has recently drawn attention to the effects of *s*-*d* admixtures in the transition metals and shows that under very special conditions this admixture produces no change in the hyperfine interaction (contrary to an earlier and incorrect calculation by the author which predicted a positive term). Recently J. Hubbard and D. Goodings have examined the Anderson effect under conditions more appropriate for a transition metal. They do, of course, have to assume an explicit model for the band structure and for simplicity they assume a parabolic form for both 4*s* and 3*d* bands; the adjustable parameters of the model are the width of the *d* band, the splitting of the d_α and d_β half bands, the height of the bottom of the *d* band above the bottom of the *s* band, and the Fermi energy and the matrix element (assumed constant) coupling *s* and *d* states of the same wavevector. The calculation shows that for a given *s*-*d* matrix element it is possible to place eight electrons in the model to give a moment of 2.2 μ_B only for a very narrow range of parameters and that over this narrow range the spin polarization of *s*-like character is roughly constant. Thus it is found that for a matrix element of 2 e.v. the *s* polarization is negative and varies from 4% to 6% of an electron, whereas for 1 e.v. the *s* polarization is negative and varies from 0.1% to 0.4% of an electron. It is concluded therefore that for iron the 4*s* electrons give a small negative term sensitive to the *s*-*d* coupling and this added to the large negative term coming from the core polarization seems sufficient to account for the fields observed experimentally.

Recently Alperin has measured the magnetic form factor for Ni^{++} in antiferromagnetic NiO. He finds quite strong departures from spherical symmetry which are of the order of magnitude expected and he also finds that the form factor appears to be expanded relative to that calculated for the free ion. This last effect is the exact opposite to that observed for MnO and other Mn^{++} salts and seems to indicate that in MnO they expand. In an attempt to understand this Dr. M. Blume has therefore considered the contribution to the Ni^{++} form factor which should come from the unquenched part of the orbital moment. Typically $g \approx 2.2$ in Ni^{++} salts so that about 10% of the magnetic moment is due to orbital motion. Because the orbital current density appears closer to the nucleus than the spin density, the orbital form factor is more extended than the spin form factor; but the calculation shows that the 10% of the moment due to orbit is only able to give 4% expansion of the total form factor, whereas the experiment indicated a 17% expansion. We are therefore forced to the conclusion that Ni and Mn salts behave quite differently in this respect.

Recent experiments by Shulman and Knox[5] on the transferred hyperfine interaction between the unpaired electron spin of Ni^{++} and the F^{19} nucleus in $KNiF_3$ have proved extremely useful in an interpretation of the electronic structure of these transition ion salts. Using their notation the author has recently calculated a corrected expression for the anisotropic interaction which is

$$A_\sigma/\beta\hbar\gamma = 0.4\, a_\sigma^2 \langle r^{-3}\rangle + g/R^3 + 5\langle r^4\rangle/R^7 - 5(g-2)\langle r^2\rangle/28R^5 + (g-2)\, a_\pi a_\sigma \langle r^{-3}\rangle/4\sqrt{3} + \{7(g-2)^2/384\}\, A_s/\beta\hbar\gamma$$

The first term is the dominant one, $\langle r^{-3}\rangle$ is evaluated for the F^- $2p$ orbital and a_σ^2 represents the degree of admixture of the $2p_\sigma$ orbital in the antibonding orbital. The second term is just the magnetic dipole interaction at distance R and the third and fourth terms are the corrections to this due to the nonspherical distribution of spin density and orbital current respectively; in these terms $\langle r^4\rangle$ and $\langle r^2\rangle$ are evaluated for the $3d$ orbital. The fifth term represents the interaction with the unquenched portion of the orbital current on the F^- ion. The sixth term is the asymmetrical portion of the contact interaction produced through the action of the spin-orbit coupling. To illustrate roughly the origin of this last term we recall that the Ni^{++} ion has two holes, one in the orbital d_0 and the other in $(d_2+d_{-2})/\sqrt{2}$. We then notice that a perturbation $\lambda L^z S^z$ does not affect the admixture of d_0 state [because $L^z d_0=0$] but it does affect the admixture of $(d_2+d_{-2})/\sqrt{2}$ state, because $L^z(d_2+d_{-2})=2(d_2-d_{-2})$. But a perturbation $\lambda L^x S^x$ or $\lambda L^y S^y$ does affect the admixture of d_0 state. Hence to second order in λ the admixture of d_0, and hence the contact interaction with the ligands on the positive and negative z axes, depends on the effective potential, i.e., on the spin orientation. This gives a small asymmetrical contribution to the contact interaction.

All the correction terms given above are small and do not appreciably alter the conclusions of Shulman and Knox.

References

1 A. Freeman and R. Watson: Phys. Rev. **120** (1960) 1125.
2 W. Marshall: Proc. Phys. Soc. **78** (1961) 113.
3 P. W. Anderson and A. M. Clogston: Bulletin of American Physical Society **6** (1961) 124.
4 N. Alperin: Phys. Rev. Letters **6** (1961) 55.
5 Shulman and Knox: Phys. Rev. Letters **4** (1960) 603.

DISCUSSION

A. J. FREEMAN: I should like to make two comments:

(1) Dr. Marshall did not have time to discuss the point that the more correct way to calculate the hyperfine field in a case like Li with an eigenfunction which is also an eigenfunction of S^2 is to determine the orbitals from a variational principle after symmetrization—not before. This however is a very difficult calculation to carry out and to date no one has done it.

(2) The Ni^{++} form factor calculated with the inclusion of exchange polarization and crude crystal field effects is expanded by about 4% compared with the free atom value. The 4% expansion due to orbital scattering, found by Blume, brings the theoretical value to about 1/2 the difference between the free atom and experimental values. This is not enough. Covalency effects, of the type now being considered at Harwell may provide the answer to the remaining difference, but I wonder as to the exact role played by domain structure in NiO on the measured form factor.

W. MARSHALL: I agree with Freeman that our calculation is only a first order perturbation-type theory but I think it is adequate. With regard to the Ni^{++} form factor, it seems to us that the great difference between it and that for Mn^{++} is difficult to explain.