REVIEWS OF MODERN PHYSICS VOLUME 25, NUMBER 1 JANUARY, 1953

A Note on Exchange Interactions

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THE purpose of this note is to give a brief account of some theoretical work which was done some time ago and which has a bearing on the resonance phenomena in copper acetate.

The problem considered was that of investigating the exchange interactions between two paramagnetic ions in a crystal field and allowing for the spin-orbit couplings. Two approaches can be used. First it can be assumed that the exchange interactions between the ions are large compared with spin-orbit forces within the ions. This is the method used by Bleaney and Bowers,[1] except that they do not use the Coulomb interaction as the coupling between the ions but replace it by an interaction $J\mathbf{S}_1\cdot\mathbf{S}_2$. This is not strictly correct, but it has the advantage that their theory contains only one unknown, J, apart from the g values. The other approach is to assume that the exchange forces are small compared with the spin-orbit forces and use as unperturbed wave functions the states of the copper ion in its crystal field. We shall give a short account of the results of this in a form suitable for certain other problems as well (e.g., the ceric ion).

Neglecting the interactions the wave functions are

$$A\begin{cases} f^{+}+g^{-} \\ f^{-*}-g^{+*} \end{cases} \qquad B\begin{cases} p^{+}+q^{-} \\ p^{-*}-q^{+*}, \end{cases}$$

where f and g denote orbital wave functions centered on nucleus A, and p and q denote orbital wave functions centered on nucleus B. The above states are the most general possible for a single electron system. The Hamiltonian is written as a 4×4 matrix and expressed in terms of Pauli spin matrices along the lines of the usual spin-Hamiltonian formulation. The result is that the interaction becomes

$$\begin{aligned} u=&\tfrac{1}{2}(A+B)1+\tfrac{1}{2}(A-B)\sigma_z{}^1\sigma_z{}^2+\tfrac{1}{4}(E+\bar{E}+F+\bar{F})\sigma_x{}^1\sigma_x{}^2 \\ &-\tfrac{1}{4}i(F+\bar{F}-E-\bar{E})\sigma_y{}^1\sigma_y{}^2-\tfrac{1}{4}i(E-\bar{E}-F+\bar{F})\sigma_x{}^1\sigma_y{}^2 \\ &-\tfrac{1}{4}i(E-\bar{E}+F-\bar{F})\sigma_x{}^2\sigma_y{}^1+\tfrac{1}{2}(C+\bar{C})\sigma_z{}^1\sigma_x{}^2 \\ &-\tfrac{1}{2}i(C-\bar{C})\sigma_z{}^1\sigma_y{}^2 \\ &+\tfrac{1}{2}(D+\bar{D})\sigma_z{}^2\sigma_x{}^1-\tfrac{1}{2}i(D-\bar{D})\sigma_z{}^2\sigma_y{}^1, \end{aligned}$$

where

$$A=-2\int u_1Vu_2{}^*d\tau, \qquad B=-2\int v_1{}^*Vv_2d\tau,$$

$$C=2\int v_1{}^*Vu_2{}^*d\tau, \qquad D=-2\int u_1Vv_2{}^*d\tau,$$

$$E=2\int v_1{}^*Vv_2d\tau, \qquad F=-2\int u_1Vu_2d\tau,$$

where

$u_1=(f^*p+g^*q)$ for electron 1,
$u_2=(f^*p+g^*q)$ for electron 2,
$v_1=(fq-gp)$ for electron 1,
$v_2=(fq-gp)$ for electron 2,

and V is the Hamiltonian of the combined system.

The wave functions for copper have been given by Polder,[2] so that

$$f=\frac{\phi_2+\phi_{-2}}{\surd 2}-\frac{\lambda}{F_4-F_3}\,\frac{\phi_2-\phi_{-2}}{\surd 2},$$

$$g=\frac{-\lambda}{F_5-F_3}\,\frac{\phi_{-1}}{\surd 2},$$

and p and q are similar but with possibly a different direction for the axis of quantization. It does not seem possible to evaluate the coefficients A, B, etc., without prohibitive labor and the only thing to do is to consider their orders of magnitude. Thus

$$\begin{gathered} A\sim F, \\ C,D\sim(\lambda/\Delta)A, \\ B,E\sim(\lambda/\Delta)^2A, \end{gathered}$$

assuming that the exchange integrals for different orbital states are of the same orders of magnitude. By using these relative magnitudes in the interaction Hamiltonian, one finds that it approximates very closely to that used by Bleaney and Bowers.

It may be noted, in conclusion, that in ions like cerium where there is a strong spin-orbit coupling, similar arguments suggest that exchange interactions may be considerably anisotropic.

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[1] B. Bleaney and K. D. Bowers, Phil. Mag. **43**, 372 (1952).

[2] D. Polder, Physica **9**, 709 (1942).