A Note on Superexchange Interaction

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In the previous paper\(^1\) we have developed a theory of the superexchange interaction of \(\text{MnO}\) by the method of Heitler, London and Löwdin. The energy difference between the ordered antiparallel spin state and the parallel spin state was found to be

\[
E(\uparrow\downarrow) - E(\uparrow\uparrow) = 6N\left(H_{91} - H_{a1}\right)Q,
\]

where \(N\) is the number of ion pairs in the unit volume, \(H_{91}\) is the energy of the totally ionic state (ground state), \(H_{a1}\) is the energy of the excited state, where one pair of \(\text{Mn}^+ - \text{O}^-\) ions exists, \(H_{9a}\) is the transition matrix element between the ground state and the excited state and \(Q\) is the net energy difference between the two spin arrangements in excited state. We see from eq. (1) that, if \(Q\) is positive, the ordered antiparallel spin state is more stable than the parallel spin state at low temperature.

Thus, in our theory the decision of the sign of \(Q\) is very important. Using Löwdin\'s notation \(Q\) is approximately expressed as

\[
Q = B(2p0|3d0) + C(2p0|3d1),
\]

where \(B\) is the S-energy between a \(2p0\) electron of an \(\text{O}^-\) ion and a \(3d0\) electron of a adjacent \(\text{Mn}^{++}\) ion and \(C\) is the exchange energy between a \(2p0\) electron of an \(\text{O}^-\) ion and \(3d0\) electrons of a adjacent \(\text{Mn}^{++}\) ion. In the previous paper, however, we left quantitative consideration of the quantities \(Q, H_{9a}\) and \((H_{00} - H_{aa})\) untouched. In this note we shall compute them approximately, in order to get the more or less quantitative information about the mechanism of the superexchange interaction developed by Kramers\(^2\) and Anderson.\(^3\).

In fact, the rigorous computation of \(Q\) seems to be a rather complicated problem, because we must have many electron configurations in order to get a good representation of the state of an \(\text{O}^-\) ion within a \(\text{MnO}\) crystal. We, however, want to know only the order of magnitude of \(Q\) at present. Thus for our semi-quantitative purpose it may be allowed to use the Hartree-Fock wave function of \((2p)^5\) state of the \(\text{O}^-\) ion and an approximate \((3d)^5\) wave function of \(\text{Mn}^{++}\) ion, which is determined by the interpolation from the Hartree-Fock wave functions of \(\text{Cu}^+\) and \(\text{Cr}^{++}\).

\[
P_{9a}(r) = \left\{\frac{57.44}{r^{1.43}} - 4.835\right\}r^3.
\]

This function gives the better agreement with the experimental charge distribution\(^4\) than Dancoff\'s exact H-F wave function of free ion. When the wave functions are given, the computation of \(B\) and \(C\) is performed straightforwardly by Löwdin\'s method and the results are as follows (we use the atomic unit) :

\[
S(2p0|3d0) = 0.11, \quad B = 0.021, \quad C = -0.016 \quad \text{and} \quad Q = 0.005.
\]

Next, \(H_{9a}\) is approximately given by

\[
H_{9a} = \frac{1}{2a^2} \int \psi_{p0}(R; \text{O}^-) \left(V_{Mn}(r) + \frac{2aM - 1}{a}\right)
+ V_{o}(r) \psi_{9a}(r; \text{Mn}) dr,
\]

where \(V_{Mn}(r)\) is the potential of a \(\text{Mn}^{++}\) ion, \(aM\) is the Madelung constant and \(2a\) is the lattice constant and the last term gives the correction due to the finite size of the oxygen ion, which is expressed as:

\[
V_{o}(r) = \frac{1}{2a^2} \int \frac{1}{|a-r|} \left(V_{o}(R) - \left(-\frac{2}{R}\right)\right) R dR.
\]

\((V_{o}(R)) = \text{the Hartree field of the oxygen ion.})

Using the above mentioned wave functions we find \(H_{9a} = -0.0075\). Finally \((H_{00} - H_{aa})\) is roughly
estimated by the following expression:

$$\Delta E = (H_{dd} - H_{aa}) = \frac{(4\alpha M - 1)c^2}{a} + E - I + E_p,$$

(6)

where $I$ is the ionization energy of Mn$^{++}$ ion (about 16ev.) and $E$ is the affinity of the O$^{--}$ ion (about -9ev.) and $E_p$ is the polarization energy, which is estimated by Klemm’s$^6$ method (about -5ev).

Using these values we get the value 9ev for $\Delta E$.

In the case of alkali-halide crystals the values of $\Delta E$ estimated from (6) are nearly equal to the observed values (the difference is about one or two ev.). However, in the case of MnO the value of $\Delta E$ is supposed to be two or three ev. Thus we see that eq. (6) fails in giving the right order of $\Delta E$.

Using the value $\Delta E = 3$ev. we find:

$$\frac{E(p) - E(a)}{N} = 6 \times (0.0006) \text{ ev.}$$

Thus we find that our computation gives the right order of magnitude for the superexchange interaction of MnO crystals. Although our computation has only a semi-quantitative nature owing to many approximations, it may be allowed to say that our computation gives some further support to the Kramers-Anderson’s theory. Here we notice that for quantitative consideration our method is much more convenient than the usual spin operator method.

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3) H. A. Kramers, Physica 1 (1934), 182.
5) W. Klemm, Zeits. f. Physik 82 (1933), 529.