

EXCHANGE IN MAGNETIC INSULATORS

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It's been my experience that giving a talk on material to which my own contribution was mostly completed a number of years ago is a very frustrating thing. In the first place, the advances in the field which have been made recently were by other people and it's always a difficult thing to describe properly other people's work. More serious is the fact that when one has completed a reasonably large job, one is always completely convinced that nothing further can be done and the theory has a beautiful, completed, closed appearance. A couple of years later one finds that this is faded somewhat and one is tempted to start off down the various new avenues of thinking which has opened up since the last time one looked at the subject. So I will admit that the longest part of my talk, which will be about my own work, is really in the nature of a very long introduction and, from my point of view, I am going through it only to reach the more interesting new things which have been opened up by the work of Toru Moriya, Bob Shulman and Conyers Herring. I should mention that practically everything I'm talking about was done in collaboration with Shulman, Sugano, and Moriya.

The contributions I made to this field a while back, were based on a name and the conceptual background to which this name led one. The name, the idea, is the idea of the Magnetic State of an insulating material. The concept which is implied is that there is a specific kind of state of the gas of electrons in a substance which one should call the magnetic state, which is distinguishable from other kinds of states of the electron gas, and which one should understand before one really starts thinking about such properties as exchange. I can best define what I mean by state by giving some examples: The metallic state, the insulating or semi-conducting state, or the super conducting state. Perhaps the most rigorous way of defining this concept of state is in terms of the low lying elementary excitations of the system. For instance, in the metallic state, these low lying elementary excitations are very numerous and have energies which go right down to zero; they are near a surface in momentum space, and they carry charge. In an insulator or semi-conductor or the other hand, the low lying elementary excitations have an energy gap, are near isolated points in momentum space and carry charge. The basic point that I would make about this idea of state is that one can't really hope to make any progress, for example, in understanding the electronic behavior of the metal, the super-conductor, or the semi-conductor unless one has firmly in mind the basic distinguishing characteristics which make it a metal as opposed to a super-conductor, say, and roughly why. For instance, start with a

finite number of individual sodium atoms far apart, and start bringing them closer together. We could know everything we liked about the properties of each of these individual sodium atoms or even about combinations of a few of them but nothing about them is going to tell us anything about the properties of metallic sodium, i.e., of a macroscopic piece of sodium metal in which we have put a macroscopic number of sodium atoms together. Nothing is going to tell us until we actually try it out that the electrons are going to come off the individual atoms and take on free electron properties. I don't mean to imply that the science of magnetism, before the magnetic state came along, was really in such a miserable position as that one would be in if one would try to understand the idea of a metal without the idea of the free electron, but I do mean that there is a distinguishable magnetic state and that the reason for its occurrence is rather uniform in all cases. Using the idea that there is such a state simplifies and clarifies thinking about magnetism. The reason why, for so many years, one could talk reasonably intelligently about magnetism, whereas one couldn't possibly talk about the metallic state without realizing it was a distinguishable state of matter, is that the case in which magnetism is favored is the case in which the individual atoms are reasonably far apart. In a zeroth rough approximation they act like the individual isolated atoms would act. For instance an isolated atom of iron or manganese or gadolinium or sodium itself is magnetic. If we keep the atoms far enough apart, we have examples of magnetic substances. So it's a kind of zeroth approximation to treat magnetism as though the atoms or ions were just individual separated atoms and treat their interactions as perturbations. But it still is important to understand that when we put the atoms together into a solid there is a real problem as to whether the substance will take on the magnetic or metallic or some other state. As I said if we bring sodium atoms together they do not go into the magnetic state, they go into a state in which the free electrons have come off the sodium atoms, paired their spins and the resultant metal may be diamagnetic or paramagnetic but certainly doesn't have the Curie-Weiss behavior that is connected with the magnetic state. We bring the atoms of gadolinium together and we find that they do stay magnetic.

For this audience, actually, I hardly need to go in very great detail into the background of what is really happening in the magnetic state. You all know that the man who first explained what is going on was Mott in 1949. Mott imagined that we had some lattice of ions of the kind which we normally expect to be magnetic, say Ni^{++} ions (see Fig. 1) In order to make the system neutral, of course, we have to make an ionic crystal out of it and we have to put something in between. We can put in oxide ions or we can talk about a really dilute substance like nickel sulfate. Then we can compare the energy of a hypothetical magnetic state with a non-magnetic state. First, suppose that each Ni^{++} ion has the configuration (d^8) and a moment of two Bohr magnetons. You can imagine that each nickel ion has precisely its own 8 d electrons; and then the spins are free and the electrons are localized. Then one can take an electron from one of these Ni^{++} ions making it an Ni^{+++} and put that electron on a very distant Ni^{++} ion, and you will have an Ni^+

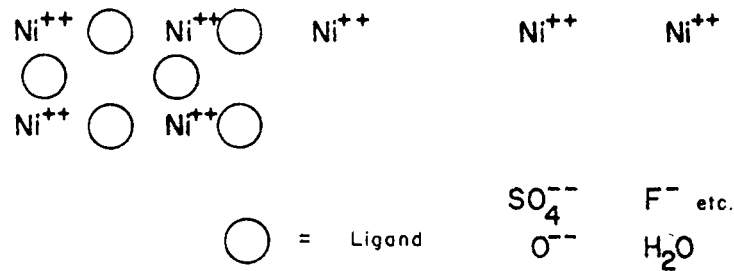


Fig. 1.

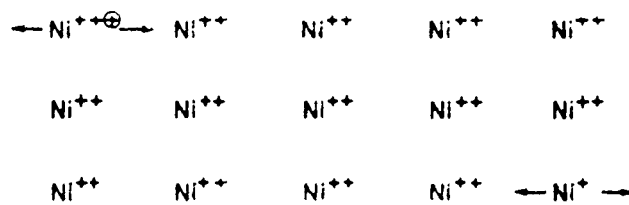


Fig. 2.

ion with 9 d electrons. The Ni^{+++} has only 7. (See Fig. 2.) Two energy changes will have occurred. The first energy change is quite obvious. When we took the electron from one ion and put it on another, we were taking it from an ion where there were only 7 other d electrons and were putting on an ion where there are 8. Thus the extra electron is repelled by the other extra electron on that ion by an amount which to zeroth approximation is given by the Coulomb repulsion integral between two d electrons: we can call it U and estimate it by the integral.

$$U = e^2 \int d^2(r_1) \frac{1}{r_{12}} d^2(r_2) dr_1 dr_2$$

This is the repulsive potential energy between two d electrons in the same orbital d. When one directly evaluates that by integration, one doesn't come out with a very reasonable value; for actually doing the problem, it is sensible to take the difference in energies between an Ni^{+++} and a Ni^+ ion as compared to a pair of Ni^{++} ions from tables. One comes out with numbers of the order of 10 to 15 electron volts. So that's quite a large number and quite a large amount of energy that we've lost. We've regained, however, a certain amount of energy because now the hole on the Ni^{+++} ion and the extra electron on the Ni^+ ion can hop back and forth from one atom to another, and so they are essentially free electrons now instead of localized electrons. If we imagine that there is a d band in the substance,

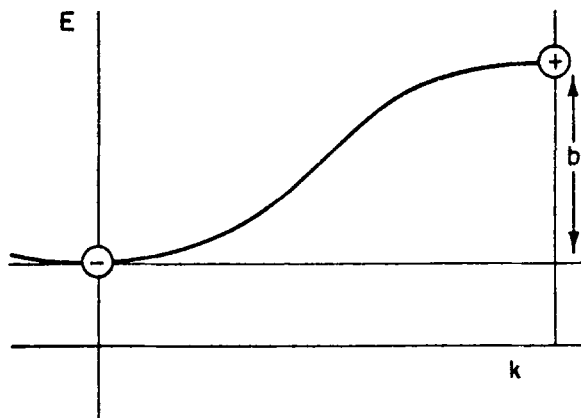


Fig. 3.

(see Fig. 3) the hole can occupy the very highest position in the band and the electron, if it likes, can occupy the very lowest position in the band. Say that the band width is b ; we've gained back an energy of order b because the localized states of course are equal mixtures of all the states in the band. Now, again writing down an integral which does not really represent the most exact way of going at it but is what it would be in this highly oversimplified uncorrelated kind of picture, the band width will be roughly given by the hopping integral between the two local sites:

$$b_{jk} = \int dr d(r - R_j) \left(\frac{p^2}{2m} + v \right) d(r - R_k)$$

R_j and R_k are the positions of neighboring sites.

We find then that if the energy U , the Coulomb repulsive energy, is much greater than b , then we haven't regained enough energy so that the electrons really will continue to separate themselves and become free electrons; therefore they will stay in the localized magnetic state. If U is of order b , (actually it turns out that because of various numerical factors and because of screening the relationship is not symmetrical in U and b) one goes into the metallic state, the electrons separate and free themselves from their sites and one has a metal. It is actually found that in certain oxides of the lower d series, there probably is a thermal transition, between the two possible states, magnetic and metallic.

The great advantage of these ideas in thinking about problems having to do with magnetic materials is that they give one, in the first place, a zeroth order state, from which one can apply perturbation theory. This zeroth order state (or rather the zeroth order states) are then those in which all the electrons stay on their individual sites. The first excitations are those in which the electrons hop from one site to a nearby site, thereby

losing an energy U ; then one can go on from that to a perturbation theory in principle and hope that that perturbation theory converges. If it converges then one has an elementary excitation or quasi-particle way of thinking about magnetic problems. In a metal, it is useful to think of one's elementary excitations as being very like free moving single electrons; in the zeroth approximation the wave function of a single electron is just a plane wave, the first approximation is a Bloch wave in which one has modified the wave function for the effects of the background lattice, but it still is a single electron function and the last approximation is the quasi-particle. And one can think on any one of these three levels depending on how accurately one wants to solve the problem. To this, in the magnetic state one thinks of one's zeroth order of approximation as the electrons in single, isolated atom electronic states, and then one has to take into account in the first approximation the fact that the electron is in a periodic lattice containing ions of Ni^{++} and all kinds of other things, especially the nearby ligands. So from this, one must go to ligand field theory states which have a certain amount of the appropriate ligand functions mixed into the atomic functions, and possibly even the d functions are changed. Finally one comes to a really accurate quasi-particle theory in which one thinks of the electron as completely renormalized for all the possible many kind of electron excitations that should surround it as it sits on its individual site with its given spin. For instance, a certain amount of spin polarization of the background lattice will be carried with it of course. So the lowest energy excitations are the rotations of the spins of the electrons on the localized sites; to this zeroth approximation there is no interaction between the spin directions on the different sites. To a higher approximation, there will be such interactions and it's these interactions that we're interested in finding; but in general the low lying excitations are spin reorientations without real motion of electrons from one site to another, only virtual motions of the electrons between the sites. Then one has real charge carrying excitations, the lowest charge carrying excitations in the zeroth approximation having an energy U . We can correct U then for admixture, for polarization, etc., and then there is presumably some real physical renormalized U which represents the lowest lying energy for excitation of a free electron in the material. So from this point of view we have a certain number of parameters which can be thought of as either integrals over the atomic functions or on a different level as renormalized parameters. The important ones then are basically the quantities b and U ; and a number of others we shall talk about shortly.

Two important points I would like to make before I go any further. One is that the biggest effect, the most interesting effect of the background lattice on this magnetic state problem, is the admixture of the background lattice wave functions into the one electron wave function. Once one has taken that into account it is possible, though of course can't be proved, that the further perturbations due to the background lattice are not really very big. A second point is that it is never correct under the circumstances in which the magnetic state is the correct state, to talk as though one's basic wave functions were

eigenfunctions of the one electron problem because the one electron problem is periodic, and the eigen functions of a periodic hamiltonian are running waves. We see here that the starting wave functions, because of the size of U as opposed to b , must necessarily be localized wave functions, and the only possible zeroth approximation is to make them localized. Thus we must be very careful not to make the standard assumption, that one always makes in all other many body problems, that the one electron hamiltonian is diagonalized by the starting wave functions.

Now starting from this point of view one can identify terms in the interactions of the spins on two neighboring sites. The biggest term is something which I have called kinetic exchange. Let's start from our one-electron orbitals on the two neighboring Ni^{++} ions. The zeroth approximation is the atomic function

$$U_{\text{Ni}}(r - R_j).$$

We have said that we have to admix into these orbitals a certain amount of the p function on the ligand — for instance an F^- function with an admixture parameter λ

$$\phi = U_{\text{Ni}}(r - R_j) - \lambda U_p.$$

Then if we make the same kind of wave function on a second Ni^{++} we do not come out with an orthogonal function, and it is very convenient to work with orthogonal wave functions so we orthogonalize. Then our basic wave function also contains a certain amount of U_{Ni} on the other atom, i.e.

$$\varphi_d(R_j) = U_{\text{Ni}}(r - R_j) - \lambda U_p + \gamma U_{\text{Ni}}(r - R_k)$$

is second order in λ , very small.

Let us study the energy as a function by the relative spin of an electron in $\varphi_d(R_j)$ and $\varphi_d(R_k)$. Now if we start from a zeroth order state in which our two electrons are parallel, that's the full story. We know that the two electrons, because their spins are parallel, must be in orthogonal wave functions because of the exclusion principle. Another way of putting it is that the wave function which contains one parallel spin electron in each of two orthogonal functions cannot be changed by further admixture between the two states. So, the energy of that state is not changed by any possible tendency of the electron to hop from one site to another. That's by no means the case if the two spins are anti-parallel. Then the electron can go from one wave function to the other virtually. The energy of the excited state it goes into is of course U higher because it's an extra electron on this atom. Actually, it's U plus corrections for the proximity of the two atoms, but it's related to our basic parameter U of the problem. The tendency for the electron to hop from R_j to R_k virtually is given by the matrix element b_{jk} , the admixture will be given by b_{jk}/U . So the real wave function will become

$$\varphi_d(R_j) + b_{jk}/U \varphi_d(R_k).$$

The energy improvement that it gets by doing that will be $-bjk^2/U$, but the electron on R_k can do the same thing so we get an energy contribution, if the spins are anti-parallel, $-2bjk^2/U$. This is always anti-ferromagnetic, and I contend it is the largest spin coupling energy in the problem. Therefore in general the spins want to be anti-parallel. That conclusion is true only when bjk does not vanish; if the wave function on R_j , for instance, is a $d\pi$ with a node pointing along the line toward the ligand whereas the wave function on R_k is a $d\sigma$, bjk vanishes by symmetry. In summary, if there is a b_{jk} kinetic exchange is probably the largest contribution.

The second biggest contribution is what I call potential exchange and that comes about because the space wave functions of the two electrons, though orthogonal, do overlap. When the two electrons are anti-parallel as I said that has no particular effect, but when the two electrons are parallel we know that there will be what is called the exchange hole in the overlap region. This occurs because the two electrons really can never be at the same point at the same time. Thus the parallel state is favored because the electrons are not quite as close together when they are parallel as we would think. The correction relative to just taking a straightforward Coulomb interaction integral between the two wave functions is the potential exchange integral, given by

$$\int \varphi_d(r_1 - R_j)\varphi_d(r_1 - R_k) \frac{\varepsilon^2}{(r_1 - r_2)}.$$

We see that this exchange is the self energy of the overlap charge distribution, by

$$\rho_{jk}(r) = \varphi_d(r - R_j)\varphi_d(r - R_k).$$

One of the properties of ρ_{jk} is that because we chose orthogonal wave functions to begin with the integral of ρ over all space is equal to zero. $\int \rho_{jk}(r)dr = 0$. That's just the orthogonality integral. This says that the overlap charge distribution is positive in some places, negative in others, and on the average it vanishes; therefore we should expect that it will not be very large and that the contributions to this integral from different places will tend to cancel. That is basically the reason why the potential exchange integral is usually considerably smaller than the kinetic integral.

That makes two kinds of exchange: the third is everything else, by which I mean all the specifically many body effects which can occur. The magnetic electrons can exchange polarize the electrons in the atom cores and the p band of the fluorine or oxygen. Such effects are probably the largest in the rare earths. They are certainly not the largest in the d band substances which we are interested in here. There are various of these effects and probably none of them are really very big.

Now we come to the question of practically calculating the exchange in a real substance. One of the things this general way of thinking leads to is a set of general rules

as to when exchange will be positive, when negative, when it will be relatively large and when it will be relatively small, in terms of the covalency parameters and the crystal field parameters. These rules tend to work out very nicely in most cases, in fact I don't know of any cases which really contradict them. On the other hand, the really crucial test is to try to calculate something from first principles and really get a value for one exchange integral. There is a particularly fortunate case that one can calculate, the case of KNiF_3 . The most fortunate thing about it is that Shulman and Sugano have already done the ligand field theory. One can think of the ligand field theory as the theory of the isolated elementary excitation of the electron gas, and the exchange theory is a theory of the interacting electrons. We have in this case, a calculation of the isolated electron problem which leads to reasonable values for various parameters and particularly for the crystal field parameter. The second nice thing about KNiF_3 is that it's particularly conveniently set up for the exchange problem. See Fig. 4.

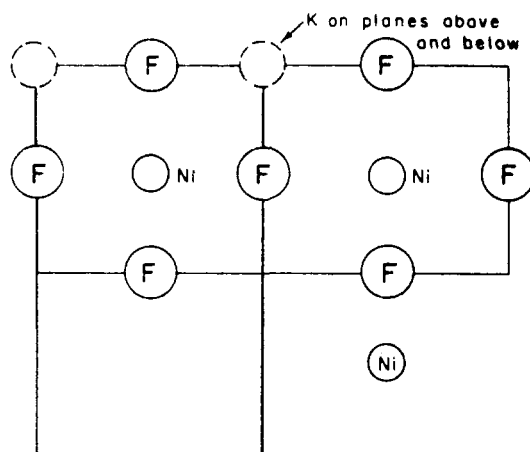


Fig. 4.

One main point is that the next nearest neighbor nickels are practically completely out of touch with each other. One really can treat the classical problem here of two nickel ions on opposite sides of the fluorine ion. It is even true that the only magnetic electrons on the nickel are in d_{z^2} orbitals which point toward the fluorine and so one can have the classical picture of two d_{z^2} orbitals interacting through a $P\sigma$. As I said, Shulman and Sugano have calculated the crystal field splitting $10Dq$. A calculation which leads to $10Dq$ is certain to give a value for b_{jk} because the two processes which lead to the major contributions to these two things are very similar. A major contribution to $10Dq$ comes from the interaction between the d sigma orbital and the p sigma orbital on the fluorine reacting back again, essentially, on the Ni^{++} ion. The major contribution to b_{jk} presumably comes from the

same admixture and interacting with the other nickel. It is really practically the same process.

Thus from Shulman and Sugano's numbers, we calculated a very satisfactory answer for the quantity $2b_{jk}^2/U$. U now is something one gets from atomic tables and corrects with various corrections which seem reasonable and accurate to within any kind of accuracy that we are talking about here, which is not much better than 50%. We came out with a value for J_{jk} . One can calculate the Curie point, knowing this; we came out with a Curie point which was 75%, as I remember, too high. We were very happy about that because we knew that the potential exchange interaction was of the opposite sign to this, and we expected it to be somewhat smaller, and so it looked as though this was about the right answer. Now, however, with Moriya doing most of the work, we have calculated the potential exchange integral. We didn't do it before simply because the potential exchange integral involves a lot of three center integrals which are very hard to do. Using the expression

$$\varphi_d(r - R_j) = U_{Ni}(r - P_j) - \lambda V_p - \gamma U_{Ni}(r - R_k)$$

and putting in an s term also, and pumping that into the potential exchange integral, one can thereby divide it up into integrals involving all the various possible exchange integrals between d on atom j , p or s on the fluorine and d on atom k . There turn out to be something like 18 different 2 and 3 center integrals. Most of them had been done by Shulman and Sugano but a number of the three center ones had to be estimated by Moriya in a way which I think is fairly satisfactory. The way he estimated them was this: for instance, suppose you want to do

$$\int (U_{Ni}(r - R_j))^2 \frac{\epsilon^2}{(r - r')} V_p(r') U_{Ni}(r' - R_k) dr dr' ;$$

that is a three center integral but you can, from looking at values of 2 center integrals, make a fairly good estimate of where the center of charge of the overlap between p and d on atom R_k is. One knows that the center of the charge distribution $(U_{Ni})^2$ is right on atom R_j ; then the integral is obviously pretty close to the overlap between p and d divided by the distance between the centers of charge. One can make a number of estimates like that, I'm sure they're close enough to right for the time being and so one can calculate the potential exchange integral. The result was of the same size as the kinetic exchange integral so we came out with a transition temperature of zero, essentially. Now this was surprising because it represented an unusually large failure of what is called MeWeeny's rule, which is the rule I mentioned before, that exchange integrals are always considerably smaller than direct Coulomb integrals. The biggest Coulomb integral involved is pretty obviously the Coulomb integral on the fluorine, times the admixture of the fluorine orbital

into R_j twice and the admixture twice into R_k . That admixture gives one a term of order λ_p^4 (Coulomb integral of V_p). It turns out that the exchange integral was of the order of $1/3$ of that term; in other words, one has a cancellation only to $1/3$. If one looks at typical potential exchange integrals in other cases, one finds that there is usually a reduction factor of from $1/5$ to $1/35$. So, we're in worse shape here than one usually is with regard to McWeeny's rule, we don't quite understand why it seems to come out that way. This may really not be as bad as all that because these calculations are extremely sensitive to the values of the various parameters one chooses. One really doesn't know U to within better than 20% or maybe even 30 or 40%; on the other hand to make things correct again, one would have had to change U by about 80% and we didn't want to do that, that seemed unlikely to be correct; it's about twice our expected error. Another parameter one could change, is λ_p . This integral is more sensitive to λ_p than b_{jk}/U and the sensitivity of λ_p is such that we would only have to change it by 30 or 40%, to get it back into agreement; but we believe we know λ_p better than that. For one thing, it's an experimental parameter coming from nuclear resonance results; and for another thing the experimental and theoretical values check and all the theoretical values involving λ_p for the properties of the isolated ion check, and why should then this one property convince us that we must use a λ_p 30% smaller. That's somewhat outside, but definitely outside, the error we would like to assign to it.

Now, in view of the fact that there are 20 or 30% effects involved here we went back to our original calculation and found that we had probably not done it much better than 20 or 30% even from a purely theoretical point of view; so Shulman, Sugano and myself are presently involved, with the help of M. Karplus, in redoing the original calculation of b_{jk} . It turns out that b_{jk} does involve at least two rather nasty three center integrals, which we had approximated by assuming Phillips' rule that wave functions which are properly orthogonalized do not see very large contributions from the core potentials. We used this rule to approximate to certain integrals, particularly the integral involving the nickel j , nickel k , and the one electron potential on the fluorine. That may or may not be right so we are going back and recalculating that.

My own personal bias on the other hand is that this and the other possibilities already mentioned are not likely to be the major source of the difficulty. The reason for this is clear from a number of things, perhaps most directly from thinking about the recent work of Conyers Herring on exchange. Herring's approach is quite different from the one here: his approach starts from a more purely theoretical point of view. He starts from the idea that, as I said, the magnetic state is the state of atoms basically at large distances from each other; he says to himself, then, let's start with our atoms infinitely far apart and calculate always the very first term in their interaction energy, which depends on the relative orientations of their spins. He was able to show, for instance, in this limit, that

we'll call the limit r goes to infinity, that the Heisenberg Hamiltonian

$$\sum_{ij} J_{ij} S_i S_j$$

is a complete description of the spin interaction problem. It is correct to order e^{-2R/a_H} where a_H is the radius of the typical orbits on the different atoms. In the limit that r goes to infinity, that goes to zero very rapidly. Thus his approach was to attack the problem from the point of view that he was going to expand in this exponential. From that point of view, one simply has only to consider pairs and consider the interaction of pairs in the order of e^{-2R/a_H} . It all sounds very simple, but the first thing one finds out when one looks at it is that even the simplest of all the exchange problems of this sort, simply an isolated pair of hydrogen atoms, the problem of H_2 , has never been solved. One thinks of H_2 , the hydrogen molecule, as completely solved by numerical methods but numerical methods don't help you much when you get into a mathematical limit because the term you're looking for is exponentially smaller than the terms that the computing machine is giving you. So it's simply impossible to have the computing machine do this "easy" problem. It can't be done.

Herring did in fact solve the problem of H_2 finally, for the first time, in the course of this work but that is not the major result that we're interested in now. What I'd like to talk about is certain very general features of his work. There were three qualitative results on the problem of the exchange between two atoms very far apart. Point No. 1 is that the intermediate region between the two atoms is very much larger than the region in which the electrons are near their separate atoms. Specifically, since the configuration space of this problem is 6 dimensional, (there are 2 electrons and each one of them has 3 coordinates) the amount of space in which both electrons are quite far from both atoms is much larger than the amount of space in which they are close to the atoms. In general almost all the exchange integral of the lowest order comes from the intermediate region, where all the particles in the problem are very far apart from each other, and where the free atom wave functions are not good, so it's not very useful to use an atomic wave function kind of theory. This point No. 1 is not likely to be as important in our kind of problem because we've got an F^- in between the two atoms. It has a core potential which is very deep and quite attractive to the electrons that are involved in the exchange, and therefore it is very likely that the electron, in getting back and forth between the two atoms, will usually go by way of the fluorine atom. We expect to get a fair approximation by confining our considerations to atomic wave functions, although looking at Herring's work without thinking about the presence of the intermediate atom, we might think we would not be correct in doing so.

Point No. 2 — he finds in general that in his problem, in H_2 specifically, the potential and kinetic terms very nearly exactly cancel. One can write out the exchange integral in

various ways in his theory and one of them is to write a rigorous wave function $\chi(r_1, r_2)$ derived from rigorous solutions of the problem. This rigorous 2 particle wave function has electron one centered around atom j and electron two centered around atom k . There is also a wave function one calls $P\chi$ which is the permuted wave function and then one computes the exchange integral by

$$J = \int \chi(r_1, r_2)H(r_1, r_2)P\chi(r_1, r_2).$$

This Hamiltonian H of course contains kinetic energy terms, core potential terms, and e^2/r_{12} . The term in e^2/r_{12} is a kind of a general potential exchange, that in $p^2/2m + v_{\text{core}}$ is a generalized kinetic exchange. He found that these two terms in the hydrogen molecule problem very nearly cancelled. Now at first you would think this cancellation is analogous with our cancellation; again I think that is not a correct conclusion. The point is that in the isolated atom problem so far one is working with neutral atoms and therefore if electron one is near atom j and electron two is somewhere in all the rest of space, the potentials of the core and of the other electron very nearly cancel and so, to a zeroth approximation, the other electron doesn't see the first atom; and that is the basic reason why one gets this cancellation. That is simply not true if they are positive ions instead of atoms. So, the kinetic term should be larger in our problem because we're talking not only not about hydrogen atoms but about atoms which have rather deep core potentials which are very much stronger than the potentials involved in H_2 , and also about atoms which have a charge. Thus we have Conclusion No. 1, exchange comes from all space, not true in our case or not necessarily true although it's yet to be shown. Conclusion No. 2 is that potential and kinetic terms cancel; that can't be true in our case in general, in any case involving ions or in any case involving core potentials because our potentials are just very much larger. Conclusion No. 3 which probably is true is that correlation particularly in the e^2/r_{12} potential exchange term is very important. In fact, the only difference between the Heitler-London exchange answer for the H_2 problem and the true exchange answer is that at really large distance the Heitler-London answer changes sign and the potential exchange term becomes larger than the kinetic exchange term. There is a general theorem that says that can't be true and the only way one can satisfy this general theorem is by concluding that the correlation between the two electrons keeps them farther apart than the straightforward one electron theory would tell you.

Thus the conclusion, which I think is probably true for us also, is that our problem is correlation in the potential exchange term. To see that can have a big effect, one can make a very simple calculation. One of the many integrals of Shulman and Sugano which we used in our calculation of the potential exchange term was the integral involving the Coulomb interaction of two p electrons on the fluorine ion

$$\int V_p^2(r_1)e^2/r_{12}V_p^2(r_2)dr_1dr_2.$$

If you calculate that straightforwardly from just the wave functions, this Coulomb interaction is 23 electron volts. This is just calculated. There's another way to estimate it and that is to go to tables of ionization potentials and ask yourself what is the difference in energy between a fluorine (-) ion and a fluorine (+) ion. That is roughly 4 volts, the electron affinity of fluorine; and the ionization energy of fluorine, $-E$ of F^+ , that is 17 volts roughly. Now if we subtract these two, we get the difference between an F^- and an F^+ relative to a pair of F atoms. Again, we're calculating a U straight from the atomic tables by saying we are going to calculate the process of $F + F$ goes to $F^+ + F^-$ and that difference is if we assume that the wave functions do not change in the interim, that difference is the Coulomb interaction of two electrons. That difference then is 13 eV experimentally, this is actually an overestimate because in this case we are working, on the average, with fluorine wave functions which are considerably more compressed than F^- wave functions presumably are. We really should calculate the problem $F^- + F^-$ going to $F + F^{--}$, but we can't calculate that because it doesn't have the appropriate electrons in it and besides nobody has ever seen F^{--} ; this presumably would have a still smaller Coulomb interaction effect. So, we can conclude that we have seriously overestimated the Coulomb interaction term in the potential exchange interaction, that probably the correct potential exchange interaction can be reduced by a factor something like a half for correlation effect and we are in reasonable agreement. That is the best we can do at this point. So in conclusion we must concede that exchange in d band ionic crystals looks like a more subtle and difficult problem than it looked 2 or 3 years ago. I still believe, personally, that we have calculated the major component and that we are working in the right ballpark. If one wanted actually to do more problems one would get roughly the right value for the exchange integrals. That this is an achievement can be pointed out by the fact that as far as I know, no magnetic curie point has ever been calculated from anything like first principles to within a factor of 10. As far as I know very few second order transition points of any kind, in fact no second order transitions, except possibly the superconducting transition of lead, have ever been calculated to within 100% accuracy. So, even 100% accuracy for a second order transition point is still a remarkably satisfactory result.

Discussion

W. J. Carr Jr., Westinghouse: Isn't it true that also in simpler problems, say in two atom problems, what you call the kinetic exchange, although it's larger, is approximately equal to the potential exchange? I'm not sure of that but I believe it's correct.

Dr. Philip W. Anderson: Yes, in all cases the kinetic exchange is somewhat bigger than the potential exchange, it has to be unless there is actual orthogonality between the two wave functions.

W. J. Carr Jr.: But they are still the same order of magnitude aren't they?

Dr. Philip W. Anderson: Yes, that is what I said in the table. In the only case which

has been really calculated rigorously, H_2 , they are of very much the same order of magnitude. I said however, that I don't think that is a general theorem that we can apply in every other case.

J. Appel, General Atomic: I would like to ask Dr. Anderson whether he can make any comments on how large the correlation correction to the b_{jk} could be, in a particular case, say nickel oxide.

Dr. Philip W. Anderson: It is very hard to say. I have not thought much about it. I have a feeling that the correlation correction to b_{jk} is less than it is to U or to this potential exchange parameter. I don't know how much less but I think considerably so. For one of the important things to realize about b is that although you write it using the whole one electron potential H , there are ways of rewriting it with only the kinetic energy and it is really basically an off-diagonal kinetic energy matrix element. One can approximately take out the dependence on the core potentials and in those circumstances it should be less sensitive to correlation effects.

Dr. Frederic Keffer, University of Pittsburgh: Can you get any estimate out of your theory of the biquadratic exchange which is now believe to be important in manganese oxides?

Dr. Philip W. Anderson: Yes, you can get estimates. It is just a higher term in the kinetic exchange but presumably there are also potential terms. One can get the order of magnitude very easily. It is got to be the order I think b^4/u^3 but there may be a factor 10 in the coefficient because there are many more terms possible here than there are otherwise.

R. F. Wood, Oak Ridge: In your wave function you mix in F^- orbitals in a molecular orbital type of calculation. You're trying to get the description of the electron in the vicinity of the fluorine. Do you feel that this approach really allows enough flexibility into the wave function or should you perhaps mix in higher excited states on the fluorine atom also. You say that you can measure the covalency parameter through NMR experiments. But if you did allow higher excited fluorine functions into the calculation, what then would you be comparing your experimental results on covalency to theoretically?

Dr. Philip W. Anderson: Well the second part is not mine to answer. I think that's really directed to Bob Shulman and the resonance experimentalists. The first part I would say yes if one makes a correlation correction to the part of the potential exchange that comes from the F^- , a considerable part of that is coming from excitations to higher states on the F^- . You can describe an expansion or a contraction of one of

- the F^- orbitals such as one would have if another electron goes in as an excitation to a lot of higher states. I think it will be there and I don't know, something like 10% is certainly kind of a minimum order of magnitude for what it would be.
- R. F. Wood: I really wonder if this covalency parameter is very well defined except, perhaps, on this somewhat simplified model. There's only one parameter entering into the wave function that you are using now, as I understand.
- Dr. Philip W. Anderson: Yes.
- R. G. Shulman, Bell Labs: I'll try to answer the second part of the question. Certainly if you could mix in excited states of fluorine — or any number of other excited states of the isolated atoms in the crystal, one should be able to get a better wave function and a better solution. There is no disagreement about it. But the question is how far can you go by mixing in the first most obvious excited state which is the state starting with the fluorine electron in the 2s 2p orbitals. So you go that far. You do your experiments and you interpret your experiments in terms of a certain amount of that mixture of 2p 2s. You calculate also, assuming that this is the only degree of departure from the free ion of the nickel plus 2. And you get pretty good agreement with whatever parameters of the d electrons that you are able to calculate which are fairly extensive. In fact, at that first go around, the agreement was good enough in the calculation that we didn't feel justified in increasing the flexibility of the wave function. I mean you could always make it a better wave function but what would the criterion be. The criterion should be that it would give better agreement with experimental results. Well we had pretty good agreement with experimental results considering the accuracy of the measurements, and the accuracy of the calculation so that we felt that there was no justification in invoking some new physical mechanism, which say would be an excited state of one of the two atoms involved, so that what you say is certainly true in the ideal case. Now the consequences of that upon this second case, the more complicated case of how things interact through the fluorine has been answered.
- Dr. Philip W. Anderson: Perhaps I did not make it clear enough when I was talking about 10 to 20 percent accuracy, I don't think from a one electron point of view you would want to put in that much of some higher state. I think the calculations in terms of just the states we're using are probably very accurate from a one electron point of view. They are probably the best you can do, and you will get relatively minor corrections by including higher states. What I meant when I said there are probably a lot of higher states around is that in the correlation effects there will be a lot of excitations and a lot of polarization effects involving higher excited states, probably.
- R. F. Wood: This says that you think you have a fairly good approximation to the Hartree-Fock one electron state.
- Dr. Philip W. Anderson: Yes.
- R. G. Shulman: There too I would like to point out that the approximation is quite good to

the antibonding state because we are concerned with an electron which is primarily a d electron. So the d electron involves a small amount of fluorine mixture and you minimize the energy of the mixture. But the properties that we were concerned with were the properties of a magnetic electron, primarily a d electron, and we set up the Hamiltonian with a nickel surrounded by six fluorines in order to calculate the properties of an electron which was centered there and detached it from the crystal. I don't think we would want to make claims about knowing very much about the p electrons on the fluorines because they are out toward the edge of our problem and did not have the magnetic properties that we were generally concerned with. The problems we were concerned with were the electrons in an orbital which was predominately d in character with just a small admixture of the p.

John B. Goodenough: Lincoln Lab, M.I.T.: In your estimate of the b_{ji} that entered the kinetic energy term, you did not make clear how much of the splitting $10Dq$ was assumed to be due to the admixture of wave functions from the fluorine ions. There is also a large electrostatic portion to $10Dq$. What do you feel are the relative magnitudes of the electrostatic and the covalent contributions to this splitting.

Dr. Philip W. Anderson: Well that again is a question for Bob but I know the answer. The answer is there are lots and lots of contributions. I said that's the largest one and it is perhaps the largest one but there are many contributions. For instance, when one is thinking about these things qualitatively one does not think exchange contributions are going to be very large — they are, they're quite large. The Shulman-Sugano calculation of the crystal field theory has all of the various kinds of terms in and they all turn out to be roughly of the same order of magnitude. You can regroup them in certain ways and perhaps after regrouping, a large fraction comes from the covalency, but not by any means all. There's an electrostatic contribution, an s contribution, a p contribution, etc., it's a mess. Incidentally, they add up in an entirely different way in b_{jk} so that agreement between the two is strictly coincidental.

R. G. Shulman: In answer to your question about the point charge contributions to the crystal field splitting, we did publish it but it is a very long thing to read and it goes like this. It depends upon what you mean by point charge contribution but let us take the semiclassical model of the point charge and calculate it in a quantum-mechanical way not in a semiclassical way. You see the semiclassical way of calculating the point charge model is to assume that you have D electrons in the metal in quantum-mechanical orbitals and then you have point charges out here although they are really atoms and they are not really quantum-mechanical, they are point charges. Now of course this point charge calculation gives a certain contribution to $10Dq$ of the correct sign, and in the case of potassium nickel fluoride it gives a contribution of about 1200 wave numbers whereas the major part of the calculated value of 6,000 wave numbers or so came from the off diagonal matrix element which Anderson mentioned.