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A Quantum Mechanical Theory of Complex Ion Formation

The electrostatic nature of binding

his paper will concern itself with the present state of the theory of chemical binding of coordination compounds in general and of the complexes formed by the transition metals in particular.

Before quantum mechanics was developed, most of the discussion of coordination compounds was in terms of rather simple electrostatic models, developed particularly by Sidgwick and Fajans. The complex was considered as composed of a central positive ion, which attracted the ligands to itself by electrostatic forces. If the ligands were themselves negative ions, the attraction was simply the attraction of the opposite charges. If the ligands were such neutral molecules as H_2O or NH_3 , the attraction was ascribed to the dipole moments of such molecules. The various ions and molecules were usually thought of as spheres of definite radius. The water molecule, for example, was a sphere with a dipole at its center. Polarization effects were thought of as producing dipole moments, and these dipole moments were treated as if there were ideal dipoles at the centers of the polarized molecules.

These very simple concepts suffice to explain a great many experimental facts amazingly well. In many cases, however, the predictions of these theories are at variance with the facts not only quantitatively but even qualitatively. It is sometimes supposed, quite erroneously, that the fault lies in the fundamental, classical picture with its assumption of electrostatic forces only and that quantum mechanics remedies this by the introduction of new forces, which have no classical counterpart, such as "valence forces," "exchange forces," or "resonance." This is not the case. It cannot be too strongly emphasized that the only forces of sufficient importance to be considered are still electrostatic forces only.

The real reason for the failure of the simple model in many cases lies in the neglect of the nonspherical form of many molecules and of the easy deformability of many of those that are spherical. Furthermore, the forces between aggregates of electric charge can be successfully approximated by those between ideal dipoles only when the distance between the aggregates is large. In the close packed arrangement of a complex ion the approximation does not even converge. Because of these two difficulties the simple model could not be expected to do well.

Much of the progress which has been credited to quantum mechanics has in fact been due to the overcoming of these difficulties. The description of the electron cloud of the central ion in terms of s, p, d orbitals can be looked upon as a device for getting away from spherical symmetry. The formation of molecular orbitals is a way of expressing the problem of packing the ligands around the central ion, and such few energy calculations as have been made have treated the interactions of the electron clouds without the resort to idealized dipoles.

Wave Functions and What They Mean

The application of quantum mechanics to the elucidation of the structure of coordination compounds starts with the same general principle as its application to any other problem.

We can take as our starting point the Schrödinger equation for stationary state, $H\Psi = E \Psi(1)$, where *H* is the Hamiltonian operator,¹ *E* the total energy of the system, and Ψ ("the wave function") a function of all the coordinates of all the electrons whose square indicates the probability of finding the electrons in various space elements. Another, and very useful, interpretation of Ψ is this: If we give up the idea of the electrons being point charges and imagine their charges to be "smeared out" over space, then Ψ^2 is a measure of the local density of this charge distribution.

Mathematically, the Schrödinger equation is a differential equation whose solutions are the wave functions Ψ . Owing to the physical meaning of Ψ most solutions are unacceptable. Acceptable (i.e., physically meaningful) solutions exist only for certain values of the parameter E, i.e., certain values of the total energy of the system (2).

In principle, the solution of a problem then proceeds as follows: The Schrödinger equation is set up (this is, even for complicated problems, a relatively simple and straightforward matter) and the set of acceptable solutions found. The values of E so found

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¹ To see that quantum mechanics does not involve the introduction of new, nonclassical energies, we consider that the Hamiltonian operator is derived from the classical Hamiltonian function for the same problem by the substitution of certain linear operators for the coordinate and momentum variables. only potential energy term of any importance which the classical Hamiltonian contains in the cases under discussion is coulombic (electrostatic) energy and therefore only electrostatic potential energy appears in the quantum-mechanical Hamiltonian. Since, according to the virial theorem (EYRING, WALTER, KIMBALL, p. 355; SCHIFF, p. 140), valid in quantum mechanics as well as in classical theory, the average kinetic energy at equilibrium is $-\frac{1}{2} \vec{V}$ where \vec{V} is the average potential energy, it follows that the total energy of the system is completely determined by this electrostatic potential energy. This statement neglects the quantum-mechanical phenomenon of spin which has no classical counterpart; however, it can be shown that the direct influence of spin on the energy is so small as to be negligible in a qualitative or semiquantitative discussion.

give the different energies the system may have, and the corresponding Ψ 's, indicating the corresponding electron distributions, give a complete description of the system including all the information that is experimentally obtainable.

The difficulty is that although we are convinced of the existence of solutions to the Schrödinger equation, it is prohibitively difficult to find them. Very drastic simplifications have therefore to be resorted to to find approximations to these solutions. A major difficulty is due to the fact that Ψ is a function of many variables whose number depends on the number of electrons. The magnitude of this difficulty can be gathered from the fact that no complete solution for a system containing more than one electron has yet been found. The way one tries to circumvent this difficulty is by expressing Ψ as a product of functions, each one of which is a function of the coordinates of one electron only, i.e., setting

$$\Psi(1,2,\ldots,n) = \psi_1(1) \quad \psi_2(2) \quad \psi_3(3),\ldots,\psi_n(n)$$

where 1,2, etc. stand for the coordinates (including the spin coordinate) of the first, second, etc. electrons, respectively. Such a simple product wave function can, however, never be an acceptable approximation for a very fundamental reason: Its use violates the indistinguishability of the electrons and the Pauli exclusion principle (3). To avoid this, we have to choose as our approximation a particular sum of such product wave functions as the above.

For instance, if ψ_1 and ψ_2 are different functions, then $\Psi(1,2) = \psi_1(1)\psi_2(2)$ or $\psi_1(2)\psi_2(1)$ are not acceptable functions since their squares change their values when the labels of electrons one and two are interchanged and hence the electrons appear distinguishable. However, the linear combinations (sums) $\psi_1(1)\psi_2(2)$ + $\psi_1(2)\psi_2(1)$ and $\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)$ conserve the indistinguishability since the values of their squares are unchanged when the labels are interchanged. The Pauli principle can be expressed as an assertion that only those wave functions which change sign (are antisymmetric) when any two electrons are interchanged describe existing states. Hence, in the example above only the second sum is acceptable. It can be shown that such an antisymmetric linear combination can be formed from any product of one-electron wave functions in a fashion analogous to the one just described. This process is called "antisymmetrization" (4) and the particular linear combination is called an antisymmetrized product or determinantal wave function.

However, the simplification involved in using product wave functions is not enough to enable us to tackle the problem. We cannot in general find the best one-electron wave functions and in our choice of them we have to resort to further approximations. Two such methods have been in general use, both based on extensive use of physical intuition; the Heitler-London or valence bond method, and the molecular orbital method. Although these two approaches appear to be very different, the differences are not really profound, and they disappear completely if one proceeds with an actual calculation beyond the first few steps. In both methods it is customary (although not necessary) to use the so-called atomic orbitals as elementary building blocks for the construction of the one-electron wave functions.

These are very closely related to the wave functions describing the possible states of the hydrogen atom (5). One reason for their use is the fact that they form an orthonormal set (6), i.e., they have the property that any arbitrary function can be expressed in terms of them to any desired degree of approximation. Atomic orbitals are not unique in this; there are many other sets of functions having this property. It is really immaterial which set of orthonormal functions we choose to approximate our one-electron wave functions, if only we take a sufficient number of them (which is generally very large). However, if we take only very few in order to make explicit calculations practicable, the choice of a set becomes important: A set whose very first members already give a relatively good approximation is clearly preferable. There is serious doubt whether from this point of view the set of atomic orbitals is really as advantageous as its almost universal use might suggest; indeed more recently, other "building blocks" (7) have been tried.

Very often we are primarily interested in calculating the lowest possible energy values of the system (ground state) and comparing these with the experimental values. We can then proceed as follows: We guess a wave function Ψ which is of the acceptable type and then evaluate the expression:

$$W = \frac{\int \dots \int \Psi^* H \Psi d\tau_1 d\tau_2 \dots d\tau_n}{\int \dots \int \Psi^* \Psi d\tau_1 d\tau_2 \dots d\tau_n}$$

where $d\tau_1, d\tau_2, \ldots, d\tau_n$ are volume elements in the coordinate space of electron $1, 2, \ldots, n$. This is relatively easy to do. The remarkable fact is that the value of W so obtained is always higher than the true ground state energy of the system (8), and approaches it more closely the more the assumed wave function Ψ resembles the true wave function of the ground state in describing the actual charge distribution in the system. If we have a series of wave functions to try out, the one that gives the lowest value of W is therefore the best approximation.

The value of W obtained is actually quite insensitive to the form of Ψ and that means that even with very poor assumed wave functions one can get rather good energy values. The reverse side of the coin is of course that a "good" (i.e., close to experimental) value of Wdoes not indicate that the wave function is close to the true one. Indeed, a quantitative calculation shows that the error in the approximate wave function is proportional to the square root of the error in the energy (9).

Exchange Forces: Mathematical Fictions

If we look at the expression for W more closely we find that we recognize a number of terms as simple coulombic energy terms corresponding to the attraction and repulsion of electrons and nuclei. However, usually terms constituting a large, or even major part of the total energy cannot be given such a simple interpretation. These are the terms which are often called "exchange energy" (10). It must be emphasized again that this does not in any way indicate the existence of new forces; they are only mathematical fictions which appear because of our poor choice of approximation wave functions and, in a sense, undo the damage to the energy caused by this choice.

That the division of the energy into separate terms is

artificial can be seen most easily by the following argument: One privilege we always have is to take the set of one-electron wave functions we have used and to form new linear combinations from these in any way we please. This leaves the form of the final wave functions and the value of the final energy completely unchanged. Mathematically, the whole process is trivial, but it does redistribute the energy, puts different amounts in the "exchange" terms and in the "coulombic" terms. This, of course, shows that the division of energy into "coulombic" and "exchange" terms depends only on the way the wave function happens to be written and is hence clearly devoid of any physical significance.

Minimizing Exchange Energy. A Physical Picture for Li_2

We might ask ourselves whether it is not possible to rearrange our starting approximation in such a way that almost all the energy appear as coulombic energy and the exchange energy be minimal. This indeed can usually be done. This is because the exchange energy is a measure of the overlap of the basic wave functions; hence if a set can be chosen which consists of functions which are essentially separate in space, our goal will be achieved. If this is done it has the great advantage that one can now look at the terms that are left and understand these in quite simple language, and one can begin to see in what way electrostatic forces only are holding the molecule together. A more technical and elaborate discussion of this point is to be found elsewhere (11).

In order to illustrate these ideas and procedures it is best to start out with a very simple case, not a coordination compound at all but a typical covalent bond. Most people in talking about the typical covalent bond start out with a hydrogen molecule. Unfortunately, the hydrogen molecule is far from being typical and for that reason it should be avoided. Let us take instead the lithium molecule, Li₂, which is still a reasonably simple system and yet has in it most of the essential features of chemical bond formation, and let us see how by the molecular orbital method one goes about the process of demonstrating its properties.

As we already mentioned, in almost all the work of this kind that has been done the starting points have been the atomic orbitals. The reason for this is the flexibility possessed by this set of functions; they are not actually present in lithium or any other molecule. As we shall see by the time we get through, practically all traces of these original functions have disappeared. One begins the process of molecular orbitals by putting together a number of these hydrogen-like orbitals to try to make orbitals suitable for the problem at hand. It turns out, for example, that it is desirable to put an orbital of the s type near each of the two lithium nuclei. It is then customary for reasons connected with symmetry to take these two functions, one around each nucleus and replace these two by their sum and their difference. In addition to these, one provides some further orbitals by the combination of other atomic wave functions. The variety of shapes and forms obtainable in this way is amazing. In other words, we begin our whole process by constructing from these building blocks some new pieces which are called molecular orbitals.

Electrons are now assigned to these orbitals in much the same way that we fill up the orbitals in an atom when we are considering the structure of the periodic table; that is to say, we put two electrons in each orbital, one electron of each of the two spins, beginning with the orbital of lowest energy until all the electrons have been assigned. In the present case of the lithium molecule there are six electrons in all, two each going into clouds concentrated around each nucleus and the last two going into a mixture of the 2s and 2p orbitals.

A good many of the popular descriptions stop at this point, indicating that this is how the electrons are distributed in the molecule. This unfortunately is mis-When we have made our electron assignleading. ments we have essentially built a wave function for the entire molecule by multiplying together these various functions for the six electrons. And the product wave function obtained in this way cannot be used to describe the actual molecule because of the fact that it violates the Pauli exclusion principle, as explained above. It is now necessary to go through the process of antisymmetrizing the wave function, which is a process of some algebraic complexity and which completely destroys the identity of the electrons and also the shapes of the molecular orbitals with which we started.

After this antisymmetrizing process we have a function satisfying the Pauli exclusion principle but bearing very little resemblance to the original "building blocks." It is very difficult, if not impossible, to recognize the original atomic orbitals or even the secondary molecular orbitals which have been used in its construction, since very large and drastic changes occur during this antisymmetrization.

A symptom of these large changes is the exchange



Figure 1. Li₂ molecule.

energy mentioned above. That is, if the energy is calculated, certain terms appear which can be interpreted as describing the coulombic interactions of the electrons in the original molecular orbitals. But other, very large, terms appear which cannot be interpreted physically (the exchange energy, referred to previously). If one now rearranges the starting molecular orbitals so as to minimize this exchange energy in the manner outlined before, one comes out with a picture which in schematic form is presented in Figure 1. Our set of functions consists now basically of just three parts. Two are the functions which are essentially the 1s function around the two lithium atoms; what is left is essentially a cloud located in between the two 1s orbitals with only minor fringes in other parts of space. There are two electrons in each one of the regions. Curiously enough, we began with two 1s functions. In the usual routine involving group theory these two are combined with each other. The process of eliminating exchange terms then undoes this process again and returns us right to where we started as far as those two orbitals are concerned.

The energy now consists simply of the following parts: First of all there is a certain kinetic energy for these electrons, which, because of the Heisenberg uncertainty principle, is related to the size of the clouds (the smaller the cloud, the larger the energy). And then the rest of the energy is simply the electrostatic interaction of the two +3 nuclei and the three clouds with a charge of -2 each. It is evident that this is equivalent to just two lithium ions with a pair of electrons in between; the whole thing is held together by the negative charge sandwiched between two positive charges, very similar to the arrangement one has in a sodium fluoride crystal. There are no mysterious forces acting at all. Of course, one has to consider not only what holds it together but also what opposes further shrinkage. The thing that prevents that is simply the kinetic energy. If the arrangement is compressed any further the increase in the kinetic energy of the electrons outweighs the lowering of the potential energy. The equilibrium separation is clearly the one at which the total energy has a minimum. The total energy is the sum of the kinetic energy, which is always positive (repulsive) and decreases with increasing internuclear distance, and the potential energy, which is always negative (attractive) and becomes less so with increasing internuclear separation. At the equilibrium point the total energy is negative (i.e., there is binding) and equal in magnitude and opposite in sign to the kinetic energy and equal to one half the potential energy. This follows from the virial theorem mentioned before.

This is all there is to the chemical bond in Li_2 , and all other chemical bonds are extremely similar if the situation is analyzed to its logical conclusion.

The Picture for "Ion-Dipole" Complexes

One can apply exactly the same ideas to coordination compounds and see in what way a complex is held together. To take a common, typical example, we will take an iron(III) ion and examine its complexes with ammonia and with cyanide. The iron(III) ion itself consists basically of two parts. There is the center core, bearing a charge of +8, which is an argon-like structure with 18 electrons and the iron nucleus. Around this are five valence electrons which occupy a region with perfect spherical symmetry and with no signs of any



 $Fe^{+3} + 6NH_3 = Fe(NH_3)e^{+3}$

Figure 2. The formation of $Fe(NH_3)_6^{+3}$ ion from Fe⁺³ and NH₃. Only four of the NH₃ molecules are shown for reasons of clarity.

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difference between directions at all. In this respect the ion is very much like an alkali ion but it differs from the latter in one very important respect: although we do have a spherical shell of valence electrons, it is incomplete since it is only half full. Therefore, more electrons can be inserted in it and that is basically what accounts for the difference between an alkali ion and one of a transition metal.

Let us suppose now that we bring up to this ion an ammonia molecule. The ammonia molecule again is nearly spherical; however, its electric charges have a lopsided distribution mainly because of the fact that we have the three hydrogen nuclei off center in the electron cloud. The ammonia molecule will then orient itself in such a way that the region nearest to the iron-(III) ion is a region of negative charge whereas the other side has the positive charge to compensate it. In other words, we have here essentially a dipole arrangement, but the distances are so small that if one attempts to calculate energies by using the dipole moment one is making a very bad error. However, because of the fact that the ammonia molecule is turned with its negative side toward the positive ion there certainly is an attraction, a simple electrostatic attraction, between the two molecules and this causes the ammonia to move inward until it gets to the point where it touches the outer shell of valence electrons in the ion.

Now, however, comes a very basic question. Will it go any further? It is possible for the ammonia to push right in until its electron clouds are in contact with the central core of the iron(III) ion. There is a strong electrical force tending to pull the ammonia molecule in. The reason that this does not happen is the fact that we are not dealing with just one ammonia, but with as many as can crowd around the central ion, and that number is six. The inward forces on these ammonias are acting on all six of them; they are all being driven in toward the center. However, in order to accommodate them closer to the inner core, the five electrons that were already occupying the space have to go somewhere In other words, these electrons have to be moved else. from an energetically favorable position right next to a +8 charge out to some distance from that. And apparently in the case of the iron(III)-ammonia complex the energy required to move out the electrons is more than that which can be gained by pulling the ammonias in. As a result, the ammonias do not approach more closely than the fringes of the central ion electron shell and form what is commonly called the ion-dipole type of bond. This is represented schematically in Figure 2 on which, however, only four of the six ammonia molecules surrounding the central ion are shown. The other two are to be thought of as situated vertically above and below the central ion.

The Picture for "Covalent" Complexes

Let us now contrast the situation in the ammonia case with what happens if we bring in cyanide ions instead. The cyanide group has two atoms, a carbon and a nitrogen. These two are held together by a triple bond, which means simply that there are three pairs of electrons shared between the two atoms (which are still held together by electrostatic forces only). We can again bring up six of these cyanides until they have just reached the surface of the valence electron shell of the Fe^{+3} . Again, there is the same force as there was with the ammonia pulling them in toward the center. It is somewhat greater in fact because the cyanide ion has a negative charge. However, this difference is not at all important: for example, the fluoride ion, which has a negative charge, does not get pulled in. But now there is one rather important difference which arises primarily from the fact that the carbon has a triple bond connecting it to the nitrogen. This means that six of the electrons around the carbon are pulled off toward the nitrogen atom leaving, as it were, the central +4 core of the carbon atom somewhat exposed. Let us now consider an electron displaced out of the valence shell of the Fe⁺³ ion as the cvanides come in. Such an electron can get into a region in which it is, although farther away from the iron nucleus, now quite close to the carbon nucleus. In other words, it can get back some of the energy it loses in being forced away from the iron by attraction to the carbon nucleus. This difference is apparently large enough in the cyanide case so that these cyanides are driven all the way in until they to all intents and purposes touch the central core. This is represented schematically in Figure 3 on which, however, only four of the six cyanide groups surrounding the central ion are shown. The other two are to be thought of as situated vertically above and below the central ion.

This type of bonding is usually referred to as covalent and often described not in direct electrostatic terms, as we have done here, but in terms of resonance; in this case resonance with states in which there are double bonds between the iron and carbon and between the carbon and nitrogen. Conversely, an ionic bond can also be described in covalent terms; for instance, in the case of the ferric ion-ammonia complex we can construct molecular orbitals using the 4s, 4p, and 4d orbitals of the iron and put into these the unshared electron pairs of the ammonia, combine them into octahedral hybrids and come out with a perfectly satisfactory picture of the compound.

These are simply different ways of saying the same thing, not different explanations. As was pointed out before, all binding is basically and exclusively electrostatic in nature; the difference between those bonds that are commonly called "ionic" and those that are commonly called "covalent" is simply that in the former case the binding can be expressed in terms of the elec-



Figure 3. The formation of $Fe(CN)_6^{-3}$ ion from Fe⁺³ and CN⁻. Only four of six cyanide groups are shown for reasons of clarity.

trostatic interactions of the constituent ions or atom groups, considered as essentially undeformed charged spheres or dipoles, while in the latter case the charge distributions holding the compound together are very different from those in the constituent parts.

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