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Valence Bond Theory in Coordination Chemistry

In an article entitled "A Comparison of Theories: Molecular Orbital, Valence Bond, and Ligand Field," Andrew D. Liehr (1) has recently suggested to the readers of the JOURNAL OF CHEMICAL EDUCATION that, of the various theories of valency, the valence bond theory has suffered a rapid fall from favor, and that there has been a consequent rise in esteem of the molecular orbital and crystal field theories.

I do not agree with this opinion.

I have been pleased that it has been possible for theoretical chemists interested in consideration of symmetry of complexes and in numerical calculations to make significant progress by use of the methods described as those of molecular orbital theory, crystal field theory, and ligand field theory. I have also been pleased that some refinements and improvements of the valence bond theory of the electronic structure of molecules have been made during the past 30 years (2). I have not observed a decrease in the value of valence bond theory, especially as applied by the organic or inorganic chemist who is not a specialist in theoretical chemistry, and it is my opinion that the best way of discussing the ground states and even some of the excited states of most molecules and complex ions is still that described as the valence bond theory.

In the article mentioned above there occur the following sentences:

Thus in all fields of chemistry *except* inorganic, valence bond ideas concerning the nature of excited molecular states made their exit in the years 1945–55. But with the accelerated interest in inorganic spectroscopy by inorganic chemists commencing around 1955, even this last stronghold of valence bond concepts has begun to fall. Indeed, in the particular area of inorganic chemistry called coordination chemistry, valence bond theory has suffered its most grievous blows; even its descriptions of the ground electronic charge distributions have proved false in many important cases, especially with regard to the much vaunted, but completely specious magnetic criterion.

I am unable to understand why the author makes the statement that valence bond descriptions of the ground electronic charge distributions have proved false in many important cases. I am not aware of any case in which such proof has been presented.

In particular, I do not know any case in which the magnetic criterion of bond type, which I described (3) in 1931 and which is discussed in detail in the three editions of my book "The Nature of the Chemical Bond" (2), has been shown to be in serious error. This criterion remains of great value; I see no justification to call it "completely specious."

The author makes no attempt to substantiate his statement, aside from making brief mention of one compound of copper, described below, which should not be included under application of the magnetic criterion.

Let me refresh the memories of the readers by presenting an example of the application of the valence bond method and the magnetic criterion. Complexes of bipositive nickel may be discussed by first discussing the assignment of electrons to the doubly charged nickel cation. This cation has eight electrons outside of the argon shell. These electrons would be expected to occupy the 3d subshell, which consists of five orbitals. The other low-lying energy levels for electrons are the 4s orbital and the three 4p orbitals. If all five of the 3d orbitals are available for occupancy by the eight electrons, then, in accordance with Hund's first rule, three of the orbitals would be occupied by electron pairs and the other two by odd electrons with parallel spin. A complex of this sort, in which bonds to ligands would be ionic or could have covalent character involving the 4s, 4p, and perhaps 4d orbitals, would be paramagnetic. If, however, one of the 3d orbitals was involved in bond formation the eight atomic electrons outside of the argon shell would occupy the other four 3d orbitals as four electron pairs, and the complex would accordingly be diamagnetic. It was pointed out in the paper in which the hybridization of bond orbitals and the magnetic criterion were first described (3) that the best set of bond orbitals formed by use of one 3d orbital and the 4s and 4p orbitals are four dsp^2 orbitals lying in one plane and directed toward the corners of a square. It was predicted as a consequence of these arguments that the complexes of bipositive nickel that had been found by experiment to be diamagnetic would have a square planar configuration, and this configuration was later verified by experiment for many of these complexes.

No mention of complexes of bipositive copper was made in this paper, because the magnetic criterion is not applicable to these complexes.

It was pointed out in my book some years later that the ninth atomic electron of bipositive copper might occupy some orbital other than the fifth 3d orbital, which could thus be available for the formation of square dsp^2 bonds, as observed for a number of complexes of bipositive copper. It was suggested that the odd electron in a complex of this sort might occupy the third 4p orbital.

Following his statement about the specious magnetic criterion, the author of the article criticizing the valence bond theory makes the following statement:

A most recent example of such a blow is the demonstration by McGarvey[4] that the odd electron in square planar Cu^{+2} complexes is in a 3d-like orbital and not a 4p-like orbital.

This statement is not quite true, because McGarvey in fact did *not* show that the odd electron is in a 3d-like orbital.

Moreover, no matter what results McGarvey obtained about the substance that he investigated, a single crystal of copper (II) acetylacetonate, his work

would not constitute an argument about the speciousness of the magnetic criterion, because the magnetic criterion does not include compounds of bipositive copper in its area of application.

In discussing his electron-spin magnetic resonance experiments on a single crystal of this substance, McGarvey mentioned that calculations made for the case of a square complex in which the odd electron occupies a $3d$ orbital lead to the values 2.4 and 2.1 for the parallel and perpendicular g-factor, whereas calculations for an odd electron in a $4p$ orbital lead to the values 2.0 and 2.1, respectively. The somewhat uncertain experimental values obtained by McGarvey are 2.254 and 2.075, respectively. McGarvey comments on his result in the following words:

> Although the uncertainty in the symmetry leads to some uncertainty concerning the g-values, the results do show that that both Pauling's theory and the crystalline field theory are incorrect for this compound.

The statement that I made, about the odd electron occupying a $4p$ orbital, applies to an isolated square planar complex of bipositive copper. For an isolated complex with the nuclei occupying the same plane, symmetry requires that the odd electron be either in an orbital symmetric with respect to the plane or in an orbital antisymmetric with respect to the plane. In the crystal there is no such rigorous requirement, and the electronic structure may be an intermediate one, as indicated by McGarvey's results.

Continuing his comparison of theories of valency, Liehr says:

> The valence bond theory, although it is by far and away the superior outlook for *ground* electronic states, becomes hopelessly complex as a description of *excited* electronic states. . . . Therefore as long as ground electronic state properties were the vogue, valence bond theory shone, but when the properties of electronically excited states became the style its gleam was dulled. With this historical perspective behind us, let us now see how to extend the ligand field technique to encompass all inorganic compounds.

He then mentions that two mathematical papers, by Kimball (5) and Eisenstein (6), have led to the tabulation of symmetry classifications for most geometries of interest, and he discusses the structure of the molecule $CuCl_2$ with use of the results obtained in these papers and of several accessory assumptions about relative energy values of different molecular orbitals. He reaches the conclusion that the normal state of the molecule should be a $^2\Sigma_g^+$ state and the first two excited states should be $^2\Pi_g$ and $^2\Delta_g$, as observed.

The valence bond theory permits us to reach conclusions about the normal state and the first excited state in a far simpler way, without having to draw upon the rather complex group-theory considerations given in the papers of Kimball and Eisenstein. Moreover, it permits us to make a prediction about the configuration of the molecule, rather than requiring us to assume, as in the ligand-field consideration given by the author, that it is linear.

Let us first consider the molecule as consisting of a bipositive copper ion and two chlorine anions. The anions have the argon structure, with the outer electron pairs in $3s$ and $3p$ orbitals. If one of these pairs for each chloride atom is used in bond formation, the bond orbital is expected (reference 2, 3rd edition, pages 120–

128) to have largely p character, with about 7 per cent s character and a smaller amount of d and f character.

The ion Cu^{+2} would have the nine outer electrons occupying the five $3d$ orbitals, with the ninth as an unpaired electron in the fifth $3d$ orbital. However, as in the case of the square planar complexes of bipositive copper, we expect that the odd electron would be promoted in energy, liberating part of the $3d$ orbital for bond formation, because the gain in bond energy accompanying use of hybrid bond orbitals with considerable d character would lead to this promotion. The electroneutrality principle indicates that the copper atom will form an electron-pair bond with each of the chlorine atoms. A simple calculation of the best hybrid bond orbitals for two bonds when only one d orbital is available shows that these orbitals have $^5/_{12}$ d character, $^1/_{12}$ s character, and $^1/_2$ p character, and are oppositely directed (7). We accordingly reach the conclusion that the molecule is linear.

Aside from the odd electron, the electronic structure of the molecule can be described by saying that each chlorine atom has achieved the argon structure, with one electron pair used in bonds to the copper atom. The bond orbitals are those described above. In addition, there are four $3d$ orbitals of the copper atom occupied by unshared electron pairs.

The electronegativity of chlorine is 3.0 and that of copper is 1.9. The difference, 1.1, corresponds to 76 per cent covalent character and 26 per cent ionic character. Accordingly 0.63 of the fifth $3d$ orbital is used in bond formation, and 0.13 of the s orbital (two times 76 per cent of $^5/_{12}$ and $^1/_{12}$, respectively). The amount of 0.37 of the d orbital and the amount 0.87 of the s orbital are available for occupancy by the odd electron.

With the linear symmetrical configuration, the $CuCl_2$ molecule must have the odd electron occupying an orbital that is either symmetric or antisymmetric about the copper nucleus. Both the d orbital and the s orbital are symmetric, whereas the p orbitals are antisymmetric.

The $3d$ orbital and the $4s$ orbital correspond to greater stability than the $4p$ orbital. They are available for occupancy, and we conclude that in the normal state of the molecule the odd electron occupies an orbital that is a hybrid of these two orbitals, with approximately 37 per cent $3d$ character and the remainder $4s$ character.

This straightforward argument leads to the conclusion that the normal state of the $CuCl_2$ molecule is that represented by the linear symmetrical configuration, with symbol $^2\Sigma_g^+$.

Moreover, it is evident that the first excited state would be similar, but with the odd electron occupying one of the p orbitals not involved in bond formation. Since the p orbital extending along the molecular axis is involved in bond formation, the odd electron would occupy one of the other p orbitals, corresponding to a unit of angular momentum parallel to the nuclear axis of the molecule. We thus conclude that the first excited state of the molecule has a linear configuration and is represented by the symbol $^2\Pi_g$.

The second excited state of the molecule can also be discussed on the basis of the valence bond theory, but the arguments are less straightforward than the fore-

going. I think, however, that further attack on the problem of excited states by use of the valence bond theory could permit it to become of even greater value and to compete successfully with the molecular orbital theory and ligand field theory in this region of application as well as in the region of application to the ground states. The best way of discussing excited states of molecules and complexes may, of course, turn out to be a combination of valence bond theory and the other theories.

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