The Zeeman Effect of the Absorption Lines of Crystalline KCr(SO4)2–12H2O

F. H. Spedding and G. C. Nutting

Articles you may be interested in

Phase transition temperature and paramagnetic effect in Al1 − x Cr x K(SO4)2·12H2O (x= 0, 0.07, and 0.2) crystals studied by 27Al nuclear magnetic resonance relaxation time
J. Appl. Phys. **113**, 17E105 (2013); 10.1063/1.4793603

Sound absorption in aqueous mixtures of MgSO 4 HCl and MgSO 4 H 2 SO 4
J. Acoust. Soc. Am. **73**, S49 (1983); 10.1121/1.2020418

Temperature and Zeeman Measurements on the 1.64mm H2O Absorption Line
J. Chem. Phys. **43**, 2919 (1965); 10.1063/1.1697242

The Absorption Spectrum of Eu+++ in Crystalline Eu2(SO4)3–8H2O
J. Chem. Phys. **3**, 621 (1935); 10.1063/1.1749564

The Line Absorption Spectrum of Crystalline KCr(SO4)2–12H2O
J. Chem. Phys. **2**, 421 (1934); 10.1063/1.1749501

The Zeeman Effect of the Absorption Lines of Crystalline $KCr(SO_4)_2 \cdot 12H_2O$

F. H. SPEDDING AND G. C. NUTTING, *Department of Chemistry, University of California, Berkeley*

(Received April 22, 1935)

The Zeeman effect of the absorption lines of chrome alum crystals cooled to 20°K has been photographed for field strengths of from 12,000 to 25,000 gauss. Each of the three strong lines splits into three elliptically polarized components, whose separation of very close to 2ω suggests "spin only" orientation in the field. At 50°K, but not at 20°, the pattern depends upon the orientation of the crystal lattice with respect to the magnetic field. Interaction between closely spaced levels seems to be small and is evidenced only by slight intensity dissymmetries. No shift of the central components from the positions of the field-free lines is observed, and the magnitude of a possible second-order Zeeman effect is estimated as less than 10 percent that of the first-order effect. The selection rule for the magnetic quantum number, $\Delta m = \pm 1, 0$, seems to be obeyed, making it impossible for the present to decide whether the upper levels belong to the quartet or doublet system. Various possible coupling schemes are considered in the light of the experimental evidence and it is concluded that the actual one existing in chrome alum is either the strong field case in which L and S do not interact appreciably and L is almost completely quenched, or the very strong field case in which the coupling of the individual l's is broken down and the individual orbital moments are quenched.

R ECENTLY there has developed considerable interest in the nature of the energy levels of solids. Already a number of experimental and theoretical papers in this field have appeared and many more will appear in the near future. This subject is of the utmost importance, for the majority of the physical and chemical properties of a substance are intimately connected with the energy states of the outermost electrons of its atoms.

The application of group theory to the wave mechanics has made it possible to treat the problem from the theoretical standpoint. The theoretical papers that have appeared so far can be divided into two groups. The first group deals with solids in which the lowest state is an ionized or metallic one,[1] and the second considers those in which the basic state of at least one of the elements is atomic. Because the treatment is simpler, the former class has received by far the more attention, but discussion of it will not be pursued here since chrome alum is not a solid of this type. Among the papers in the second group is one by Bethe[2] in which he shows that the splitting of an energy level in the electric field of a crystal is determined primarily by the symmetry of the atomic pattern. Van Vleck,[3]

utilizing the work of Bethe, and making certain simple and reasonable assumptions as to the behavior of atoms in solids, has been able to explain the experimentally determined magnetic susceptibilities of salts of the iron group and the manner in which the susceptibilities depend upon the crystal structure. Schlapp and Penney[4] have applied Van Vleck's theory to the specific case of chrome alum and have been able to account for the observed magnetic susceptibility very satisfactorily. At the same time their theory necessarily predicts the nature and position of the energy levels in the solid. Thus far the theoretical physicists have been greatly handicapped in their treatment of this problem by the meager amount of good experimental data upon which to base the model from which they start their calculations, and, naturally, this same lack of data has also prevented them from adequately checking their conclusions.

For some years we have been interested in the nature of energy states in solids from the experimental standpoint. In a recent paper[5] we pointed out that the experimentally determined energy levels of $KCr(SO_4)_2 \cdot 12H_2O$ do not seem to be in agreement with the theories and calculations of Van Vleck, Schlapp and Penney. This paper is a continuation of the previous research presenting further evidence as to the real nature of the energy states in chrome alum and indicating

---

[1] By an ionized state we mean one in which an electron is not quantized with respect to any specific atom, yet remains in the crystal lattice.

[2] Bethe, Ann. d. Physik **3**, 133 (1929).

[3] Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932.

[4] Schlapp and Penney, Phys. Rev. **42**, 666 (1932).

[5] Spedding and Nutting, J. Chem. Phys. **2**, 421 (1934).

where changes in Schlapp and Penney's model will have to be made before their theories can be brought into accord with experiment.

Experimental Methods and Observations

The experimental methods have been described previously.[5] Our earlier difficulty in cooling the chrome alum crystals to 20° when they were contained in a narrow Dewar flask has been overcome, partly by using thinner crystals (1.8 mm thick) and partly by mounting them in a holder of improved design. The spectrograph had this time seven instead of five prisms and the dispersion was 3.8A per mm at 6700A. A Nicol prism was used in two positions, the one allowing passage of light polarized in a direction perpendicular to the direction of the magnetic field, the other light polarized parallel to the magnetic field. Various field strengths from 12,000 to 25,000 gauss were used.

The three absorption lines of chrome alum at 14,932, 14,925 and 14,858 cm^{-1} have absorption coefficients many times larger than those of the surrounding lines of the 6700A multiplet. With thick crystals the intensities of the absorption lines differ little from one another since all or nearly all of the incident light of the corresponding frequencies is absorbed. With thin crystals, however, while ν14,932, 14,925 and 14,858 attain complete absorption, the weaker ones do not and appear much fainter. Thus, by taking crystals of the proper thickness, the three strongly absorbing lines can be made to appear intense and at the same time the weaker neighbors at 14,935, 14,928.5 and 14,854 cm^{-1} be made so faint that they can scarcely be seen. The latter then completely disappear into the background when a magnetic field is applied and the original intensity is spread over three or four components. One therefore observes Zeeman patterns of only the three intense lines, but it is not to be overlooked that the levels giving rise to the faint lines are still present and are still close to the levels giving rise to the strong lines. If these levels exert any influence upon one another it must be reflected in the Zeeman patterns observed. When a magnetic field is applied to the crystal cooled to 20°K, the strong lines split into triplets of approximately equal

separation, the separation being twice the normal Larmor splitting.

Photographs were made with the light ray and the magnetic field mutually perpendicular and passing along fourfold axes of the chrome alum octahedron; and with the light and field perpendicular, the light passing along a fourfold axis and the field directed perpendicular to a natural crystal edge. Schnetzler[6] has investigated at liquid air temperature the Zeeman effect of the corresponding lines of potassium chromium selenate and he reports that there is dependence of the Zeeman pattern on the position of the lattice in the field. We have not observed such an effect in the lines of potassium chromium sulfate at 20°K.[7] However, in a group of photographs of thicker crystals, whose temperature we estimate to be about 50°, the patterns observed are more complicated and more varied. One expects this, for in the absence of a magnetic field the lines are still diffuse because of thermal agitation. In addition, the "high temperature" line[5] ν14,928.5 falling between the two lines under observation, while absent at 20°, is at 50° almost as intense as these other two, and the Zeeman patterns of the three are to some extent superposed. One accordingly observes a pattern which is the resultant of all three lines. This with the temperature broadening almost certainly prevents true resolution of the components, so that the pattern observed is in reality the sum of the envelopes of the three Zeeman patterns. This summed intensity itself gives rise to components which should show peculiar (nonlinear) behavior in fields of different strength. They should also show different behavior with rotation of the crystal axes in the field, since the relative intensity of the "high-" and "low temperature" lines even at zero field strength varies for different crystal directions due to different polarization caused by the electric field of the crystal. It has actually been observed that, with the crystal at 50° and with

[6] Schnetzler, Ann. d. Physik 10 (3), 373 (1931).
[7] The low frequency component of the line ν14,925 appears in slightly different positions in the photographs taken in the two directions of the magnetic field. Since this is the only difference greater than our probable error of either the intensities or positions of the components, and since this difference is only about twice the probable error, we have not attached much weight to it.

the field and light ray directed along four-fold axes, the composite pattern of ν14,932, 14,928.5 and 14,925 consists of four lines, and on changing the orientation of the light and the field with respect to the crystal the four become six lines.

At 20°K as the magnetic field is applied the lines broaden, and, with the instrument used, first resolve at about 18,000 gauss. With $H=24,800$ the components are well separated from one another. At this latter field strength, even though the outer components of the strong lines must have crossed the outer components of the weak lines lying close to them, the Paschen-Back effect is extremely small. Since these lines are absorption lines of a solid at a very low temperature, the levels from which they arise lie equally close, yet the interaction between them must be very small. That there is some interaction can be seen from the fact that there is unsymmetrical distribution of intensity about the central components. This dissymmetry in intensity is appreciable for the line ν14,858 but for the other two lines is small. There appears also to be slight dissymmetry in the position of the components, amounting to about 10 percent of the distance between them. This dissymmetry too is greatest in the line 14,858, but since its components are very weak, the errors in measurement are also largest here. In any case the amount of the dissymmetry cannot be stated surely because it is of the same order of magnitude as the possible error of measurement.

No certain differences in the separation of the components of lines photographed with their light polarized parallel to the field and those with light perpendicular to the field have been detected. The intensities, however, are different. With the light polarized perpendicular to the field the unshifted components, corresponding to $\Delta m=0$, are more intense than the outer components, for which $\Delta m=\pm1$; and of these latter the low frequency ones of ν14,858 and 14,935 and the high frequency one of 14,932 are the weaker. The low frequency component of ν14,858 is so faint that it was measured only with difficulty. With the light polarized parallel to the field the components are of about the same intensity, with the high frequency components being perhaps the strongest.
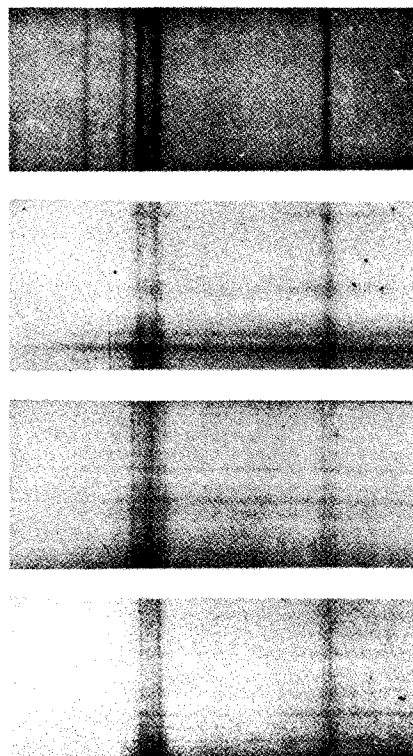

FIG. 1. Enlarged reproductions of the 6700A multiplet of chrome alum. All temperatures are 20°K. 1. $H=0$; thickness of crystal, 4.2 mm. 2. $H=18,700$ gauss; thickness, 1.8 mm; s components. 3. $H=24,850$; thickness, 1.8 mm; p components. 4. $H=24,850$; thickness 1.8 mm; s components.

No shift of the central components with respect to the field-free lines has been noted[8] and therefore any second-order Zeeman effect must be less than 10 percent of the first-order splitting and any relative shift less than 5 percent. The fact that the components arising from transitions in which $\Delta m=0$ are more intense when the light is polarized perpendicular to the field is surprising and must be attributed to the predominating influence of the electric field of the crystal. Since all the components can be seen with both directions of the Nicol prism, the

[8] Our earlier report (see reference 5) of the positions of the absorption lines of chrome alum at 20° in the absence of a magnetic field was incorrect. The values given for the 6700A multiplet were too high by 1 cm^{-1}.

lines are elliptically polarized, as one might expect when electric and magnetic fields are crossed.

Table I summarizes the observations on the

Plate 1 ⊥	2 ‖	3 ⊥	4 ‖	1	2	3	4
						Δν	
14855.4f	14855.2f	14855.2f	14855.1f				
				2.4	2.8	2.6	2.4
57.8	58.0f	57.8	57.5f				
				2.5	2.9	2.3	2.9
60.3vf	60.9f	60.1vf	60.4f				
14922.8f	14922.7	14922.4f	14922.5				
				2.4	2.3	2.6	2.6
25.2	25.0	25.0	24.9				
				2.2	2.5	2.4	2.6
27.4	27.5	27.4	27.5				
14929.8	14929.8	14929.7	14929.7				
				2.3	2.3	2.3	2.3
32.1	32.1	32.0	32.1				
				2.7	2.7	2.7	2.7
34.8f	34.9	34.7f	34.8				

spectra. In making plates 1 and 2 the magnetic field was directed down a fourfold axis, in plates 3 and 4 perpendicular to a crystal edge. The letters f and vf indicate components which are faint and very faint, while ⊥ and ‖ denote that the plane of polarization of the light ray is perpendicular and parallel, respectively, to the direction of the magnetic field. The probable errors in ν and $\Delta\nu$ for the components of $\nu14,858$ are estimated at ±0.2 cm^{-1}, and for 14,925 and 14,932 at ±0.1 cm^{-1}. In a field of 24,800 gauss twice normal splitting is 2.3 cm^{-1}.

DISCUSSION OF RESULTS

We shall discuss theoretically the Zeeman patterns which would arise from the various coupling which one might imagine to occur in a solid. We shall discuss these in light of the experimental evidence and point out wherein such types of coupling are supported by that evidence, and wherein they are unlikely or are completely ruled out.

In our previous paper we have examined the various theories as to the nature of the sharp absorption lines of chrome alum. We concluded that they very probably arise from transitions between states originating from a $3d^3$ electron configuration. From magnetic considerations it was evident that the basic state must arise from

a level belonging to the quartet system, and that the other low lying levels which were shown at that time to be present in chrome alum must also belong to this system. The experimental evidence, however, was not sufficient to determine whether or not the electric fields are strong enough to break down the $\Sigma l = L$ coupling, and thus whether the lines are transitions from the ^4F to the ^4P, ^2H, ^2G, ^2F, ^2D and ^2P terms or whether they are from a strong field $^4\Gamma$ term to another $^4\Gamma$ or $^2\Gamma$ term. It was shown that the weak field case in which J is still a good quantum number is excluded.

Various possible methods of coupling are:

Case I

The coupling is similar to that which takes place in a gaseous ion and the effect of the electric fields on the levels is either negligible or very small. This suggestion was put forward by Deutschbein[9] and is of course ruled out by the magnetic considerations. Bose and Datta[10] have suggested, however, that while most of the ions have their orbits bound so that only the spins can orient, a very few may be situated in pockets or holes in the solid in which they are free to orient like gaseous ions, and that it is these that give rise to the sharp absorption lines of chrome alum. Apart from the difficulty in conceiving of such "holes" in solids at the temperature of liquid hydrogen, the possibility is set aside for the following reason. If we grant that intercombination jumps may be made freely and that the ΔJ selection rule is invalid, the lines at 20°K could arise from transitions from a $^4F_{3/2}$ term to a term such as $^4P_{5/2}$, $^2G_{7/2}$, $^2D_{5/2}$ and others. The g factors of all these terms are different, being 2/5 for $^4F_{3/2}$, 8/5 for $^4P_{5/2}$, 8/9 for $^2G_{7/2}$, and so on. The Zeeman patterns of the absorption lines would then be very complicated and very different from the ones observed, even though the levels are considerably altered by the electric fields of the lattice.

Case II

The electric fields of the crystal are sufficient to split the levels considerably, but the amount of the splitting is still small compared to the

⁹ Deutschbein, Zeits. f. Physik 77, 489 (1932).
¹⁰ Bose and Datta, Zeits. f. Physik 80, 376 (1933).

multiplet separations, so that J remains a good quantum number. Each original state is split into $J+\frac{1}{2}$ doubly degenerate levels.[11] As soon as a magnetic field is applied there is a fixed reference direction in space, and each of these levels splits into two new levels. For the new levels there is a variety of g values and consequently the separation between pairs of them is different.[12]

This case is ruled out for the same reasons as Case I.

Case III

The electric fields of the crystal are strong enough to break down the coupling between L and S so that J no longer has meaning. We may distinguish three variants of this case.

(a) J is not a good quantum number, and while L and S orient separately, there is nevertheless marked interaction between the two. The original level is split apart through the action of the electric field on the orbital moment. The magnetic levels are of course not split by the electric field directly, but rather by the magnetic field set up by the orbital moment precessing about the electric axis. In this case, except for a few specially degenerate levels, all levels are completely nondegenerate and hence cannot split further in a magnetic field, but can merely change their positions.[13]

It is unlikely that this case is the correct one because of the magnetic behavior of the chrome alum crystal, and because all the absorption lines observed split in a magnetic field,[14] yet do not

show any shift of the center of the Zeeman pattern from the field-free line.

(b) The theory of Van Vleck and Schlapp and Penney. The basic ^4F term is split by a cubic crystal field into three levels, two triply degenerate and one, the lowest, a single level. The separation of the highest and lowest levels is about nine volts. A much weaker rhombic field causes the two triply degenerate levels to become nondegenerate. In a magnetic field all the levels split further into four components. Since the lowest level is far removed from the others, its interaction with them is small, and since it is already nondegenerate with respect to the orbital moment, only the spin moment orients in a magnetic field, thus giving a g factor of 2. The excited levels, on the other hand, interact with one another strongly and therefore do not have g factors of 2. They also show an appreciable second-order Zeeman effect. Thus the magnetic susceptibility of chrome alum, whose Curie constant corresponds to a g factor of 2 arises from a very special case of the energy levels of solids.

This theory seems highly improbable for the following reasons. Firstly, there are actually several low-lying levels belonging to the quartet system, and the theory permits only one. And secondly, the g factor of the excited levels as well as the low levels must be very close to 2. In the theory a g factor of 2 can arise only in the special case in which there is no strong interaction with a neighboring level, and it seems very unlikely that all the levels observed should be of this unusual type. Furthermore, although the levels occur close together, in some cases being so close that when split by a magnetic field their components actually cross, there is no interaction. Any second-order Zeeman effect or interaction that exists must certainly be less than 10 percent of the first-order Zeeman splitting.

(c) There is slight or no interaction between L and S. Here the electric field of the crystal in splitting the levels apart has so completely

[11] Kramers (Proc. Amst. Acad. **33**, 959 (1930)) has shown that for atoms containing an odd number of equivalent electrons there is in crystal fields no distinction between states with the same absolute value of m. Stated loosely this means that there is no distinction between electrons revolving clockwise and anticlockwise in their orbits. In fields of high symmetry two or more of these $J+\frac{1}{2}$ levels may combine to give a level of still higher degeneracy.

[12] Penney and Schlapp have treated such a case in their theory of the magnetic susceptibilities of rare earth salts.

[13] Mulliken, Rev. Mod. Phys. **2**, 60 (1930).

[14] If the g factors of the high excited states were zero, triplets would also be observed on account of the multiple character of the basic state. In this instance all the dissymmetries in the patterns would have to be due to the lowest state, and since all the lines originate at the lowest state the dissymmetries would perforce be the same for all the patterns. It is observed that this is not the case. While the separation dissymmetries may be attributed to experimental error, the intensity dissymmetries cannot. Further,

if these upper levels had g factors of zero because of nondegeneracy they should show a second-order Zeeman effect. None is observed. Finally it seems unreasonable to suppose that the excited states should be nondegenerate and the basic states not, particularly when one considers that in the ions of the iron group there is a variety of lowest levels, and in almost every case they are known to split.

quenched the orbital moment that it does not orient in attainable magnetic fields. Besides, the electric field has so tightly bound the electron in its orbital potential trough that magnetic fields are not able to shift the positions of the levels appreciably. In other words, there is either a very small second-order Zeeman effect or none at all. This case or Case IVb seems most probable in view of the experimental evidence.

Case IV

The very strong field case. The crystal electric fields are strong enough to produce splitting which is large compared to the distance between multiplets, and they thus break down the coupling between the individual electrons, $\Sigma l = L$. (a) Strong interaction between l and s. This case is ruled out for the same reasons given in IIIa. (b) Little or no interaction. Except for different positions of the levels this case cannot be distinguished from IIIc.

We feel that in the present state of our knowledge the experimental data are insufficient to distinguish between the strong field Case IIIc and the very strong field Case IVb. We feel also that we cannot yet determine whether the excited states belong to the doublet or to the quartet system. However, we might point out that in the cubic crystal of chrome alum the magnetic selection rule $\Delta m = 0, \pm 1$ is obeyed, and that if transitions of the type for which $\Delta m = \pm 2$, ± 3 occur they must be very rare. In the absorption spectrum of gadolinium (Gd^{+++}) ion in a monoclinic crystal the selection rule $\Delta m = \pm 4$ is known to hold, and such transitions are very frequent. Therefore, when the selection rules for cubic fields are known (and we have work under way at present in which we hope to determine them) this distinction may perhaps be made; for if jumps for which $\Delta m = \pm 3$ are permitted, the upper states must be doublets to account for their absence.

In the unit cell of chrome alum there are four Cr^{+++} ions, each surrounded by six molecules of water. After the water molecules the nearest neighbors of a chromium ion are two $SO_4^=$ ions, placed symmetrically about it, which produce an electric field directed along the line joining the ions. The three ions lie on a trigonal axis of the cell, and the trigonal axes for the four chromium

ions point in four different directions. In zero field or so long as spin-orbit interaction is so small that the spin can orient freely, the absorption lines arising from these four types of chromium ions are superposed. On the other hand, if the orbital moments orient in a magnetic field or if they influence the orientation of the spin moments, the positions of the lines in the presence of a magnetic field are different, for these positions are determined by the resultant of the magnetic and electric fields. The resultant will be different for each of the four types of chromium ions, and four Zeeman patterns which do not perfectly superpose but instead yield a very complex and difficultly resolvable spectrum will be produced. Thus the fact that we obtain fairly simple and sharp Zeeman patterns is in itself evidence that only the spin orients and that interaction terms must be small.

Lehmann[15] has investigated the Zeeman effect of the absorption lines of ruby at liquid air temperature and he reports that the Zeeman pattern both as to the separation and intensity of its components is dependent upon the orientation of the lattice in the magnetic field. If this effect is not due to the presence of another level, which might or might not fade out when the temperature is further lowered, the orbital moment must contribute to some extent in ruby. It is interesting to note that the magnetic behavior of Cr_2O_3, which is the coloring matter in ruby, is decidedly anomalous and that the susceptibility at low temperatures shows departures from Curie's law in the same direction as for the free Cr^{+++} ion, in which the orbit does contribute largely to the magnetic moment. One might think from the two cases of chromic oxide and chrome alum that the basic state of an ion in a crystal is not intrinsically different from the excited states; it is not a special case. Accordingly, if the magnetic susceptibility shows that the orbit is contributing to the magnetic moment, the Zeeman pattern of the absorption lines will show the same, and if the magnetic susceptibility shows that the orbital moment is completely frozen out, the Zeeman pattern will indicate spin only orientation.

---

[15] Lehmann, Ann. d. Physik **19**, 99 (1934).

In concluding, we feel that the experimental evidence is not in agreement with the theories of Van Vleck and Schlapp and Penney and that their basic model will have to be changed to conform with the following experimental evidence from chrome alum. The energy levels appear in groups of closely spaced levels, the lowest *group* belonging to the quartet system.

These levels split in a magnetic field and possess a *g* factor very close to 2. Any interaction between the levels, if it exists, must be very small, of the order of magnitude of 10 percent or less of the splitting. In addition, these levels cannot show a second-order Zeeman effect of more than 5 percent of the normal Zeeman splitting in fields of 25,000 gauss.

Electronic Structures of Polyatomic Molecules and Valence

VI. On the Method of Molecular Orbitals

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*
(Received April 18, 1935)

The use of the method of nonlocalized molecular orbitals in building up a *conceptual scheme* or qualitative theoretical framework into which empirical data (chemical and spectroscopic) can be fitted, is emphasized. This should be distinguished from the use of the method, often with rough "LCAO" approximations (linear combinations of atomic orbitals), in semiquantitative calculations.

IN earlier papers of the present series and elsewhere[1] an attempt is made to describe and interpret electronic structures of molecules in terms of electron configurations composed, so far as reasonably possible, of molecular orbitals. Since the object of this work seems not to have been made entirely clear, it seems desirable to restate it briefly.

The whole matter turns about the meaning and use of the idea of electron configurations. Ever since Bohr succeeded in explaining the main features of atomic structures and spectra and of the periodic system, electron configurations have been in constant use for describing atomic structures approximately. Each electron is assigned to a definite orbit (or orbital, in the quantum mechanics), having a fairly definite energy or term value, at least for an atom in a

definite state of ionization. It must be agreed, to be sure, that this term value varies somewhat depending on the state of the atom-as-a-whole, e.g., $3p$ has somewhat different term values in $\cdots 3s3p$, ^3P and $\cdots 3s3p$, ^1P.

The quantum mechanics, of course, shows that the concept of an electron configuration is in final analysis incompatible with an exact correct description of the electronic structure of an atom. Nevertheless it shows, particularly when Hartree's idea of the self-consistent field is introduced, that one can still in ordinary cases use a unique electron configuration as a basis for a simple and relatively good approximation. (Wave function of atom = antisymmetrical linear combination of permutations of a definite electron configuration assignment.)

With molecules, matters become more complicated. Because of the less simple force field, the possibility of specifying a unique electron configuration tends more easily to be lost. In other words, the inexactness of the electron configuration idea is sufficiently great here to admit the possibility of two or more alternative electron configurations each of which may form the basis for a fairly good approximation to the complete wave function. In such a situation, as

[1] This series: R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751 (1932); **43**, 279 (1933): I, II, III, IV; J. Chem. Phys. **1**, 492 (1933); V. Also R. S. Mulliken, Chem. Rev. **9**, 347 (1931); Phys. Rev. **43**, 765 (1933); **47**, 413 (1935). Also J. E. Lennard-Jones, Trans. Faraday Soc. **30**, 70 (1934); in Table III and the text of this paper, the designations T_1 and T_2 have been interchanged as compared with IV of this series, evidently due to a misunderstanding caused by excess of brevity in the writer's discussion of electric moment components in IV. Also papers of Hund, Herzberg, Hückel and others.