THE HOLE-EQUIVALENCE PRINCIPLE, THE VAN VLECK RELATION AND THE APPLICATION TO THE THEORY OF d-IONS IN LIGAND FIELDS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
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HANS WILLEM CAPEL
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DRUKKERIJ PASMANS — 'S-GRAVENHAGE

Promotor: Prof. Dr. S. R. de Groot

Aan mijn ouders

Aan mijn vrouw

Promotor: Prof. Dr. S. R. de Groot

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgen hier enkele gegevens over mijn studie.

In 1954 legde ik het eindexamen gymnasium β af aan het Huygens Lyceum te Voorburg. In het zelfde jaar begon ik mijn studie aan de Rijksuniversiteit te Leiden en legde in mei 1958 het candidaatsexamen wis- en natuurkunde (A) af. In januari 1962 legde ik het doctoraal examen af met als hoofdvak theoretische natuurkunde en als bijvakken wiskunde, mechanica en experimentele natuurkunde. De hiervoor benodigde tentamina werden afgelegd bij Prof. Dr. S. R. de Groot, Prof. Dr. P. Mazur, Dr. J. A. M. Cox en Prof. Dr. A. Visser. Van januari 1960 tot juni 1960 was ik werkzaam op het Kamerlingh Onnes Laboratorium en verrichtte daar in de groep van Dr. L. C. van der Marel en Dr. J. van den Broek, onderzoek over de spin-rooster-relaxatie. In augustus 1961 woonde ik bij de Scottish Universities' Summer School in Physics te Newbattle Abbey over Fluctuation, Relaxation and Resonance in Magnetic Systems. Hierbij werd ik financieel gesteund door een beurs van de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek Z.W.O.

Vanaf februari 1961 tot september 1963 was ik werkzaam op het Instituut-Lorentz voor theoretische natuurkunde, waar ik onder leiding van Prof. Dr. S. R. de Groot onderzoek verrichtte op het gebied van overgangsmetaal-ionen in kristalvelden, meer in het bijzonder over de in dit proefschrift behandelde onderwerpen, The Hole Equivalence Principle en de van Vleck relatie.

Gedurende het jaar september 1963 tot september 1964 werkte ik bij de Service de Physique du Solide et de Résonance Magnétique van het Centre d'Etudes Nucléaires de Saclay. In deze tijd bestudeerde ik het probleem van de magnetische dipoolkoppelingen in de Aluminium en Gallium garnets onder leiding van Prof. Dr. A. Herpin en in nauwe samenwerking met Dr. D. Saint James en Dr. B. Vivet. Tevens onderzocht ik de mogelijkheid om matrixelementen van de magnetische moment operator tussen toestanden behorend bij verschillende energieniveaux te beschrijven met behulp van g factoren. Hierbij had ik enige nuttige discussies met Prof. Dr. A. Abragam. Het jaar in Saclay werd mij financieel mogelijk gemaakt door een NAVO-beurs, mij toegekend door bemiddeling van de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek Z.W.O.

Vanaf september 1964 ben ik werkzaam op het Instituut-Lorentz voor theoretische natuurkunde, waar ik onderzoek verricht onder leiding van Prof. Dr. P. W. Kasteleyn.

Publicaties

The Hole Equivalence Principle, Proc. Kon. Ned. Akad. van Wetensch. B **67** (1964) 80.

The van Vleck Relation, Proc. Kon. Ned. Akad. van Wetensch. B **67** (1964) 98.

On the Theory of d-ions in Ligand Fields I, Proc. Kon. Ned. Akad. van Wetensch. B **67** (1964) 441.

On the Theory of d-ions in Ligand Fields II. Proc. Kon. Ned. Akad. van Wetensch. B **67** (1964) 454.

Propriétés Magnétiques des ions de Kramers des Terres Rares dans les Grenats de Terres Rares et d'Aluminium et de Terres Rares et de Gallium, Physics Letters **11** (1964) 7.

Propriétés Magnétiques des ions de Kramers des Terres Rares dans les Grenats de Terres Rares et d'Aluminium et de Terres Rares et de Gallium, Rapport Commissariat à l'Energie Atomique, in publicatie.

Magnetic properties of rare earth ions in Aluminium and Gallium Garnets, aangeboden voor publikatie in Physica.

On the representation of matrix elements of the magnetic moment operator between states belonging to different energy levels by means of generalized g factors, aangeboden voor publikatie in de Proc. Kon. Ned. Akad. van Wetensch.

CONTENTS

The Chapters I, II and III have been published in the Proceedings Kon. Ned. Akad. van Wetensch. (B **67** (1964) 80, 98, 441, 454).

INTRODUCTION AND SUMMARY

In this thesis we shall deal with the Hole Equivalence Principle, the van Vleck relation and the application to the theory of d-ions in crystal (Ligand) fields. The lowest configuration of a given ion will consist of a number of closed shells and a partly filled shell. The shells are defined by means of a self consistent one-electron hamiltonian h. The hole equivalence principle and the van Vleck relation apply to partly filled shells and we shall discuss in an introductory Chapter whether the influence of closed shells can be neglected. The one-electron states determining the partly filled shell can be taken to be $u_i(\mathbf{r})\uparrow$, $u_i(\mathbf{r})\downarrow$, $i = 1, 2, \ldots, p$, where the u_i form an orthonormal set and span the linear manifold of eigenstates of h for one or more eigenvalues. They span also a number of irreducible representations of the symmetry group G which leaves h invariant. $\uparrow$ and $\downarrow$ are the spin states $s_z = \frac{1}{2}$ and $s_z = -\frac{1}{2}$.

The hole equivalence principle can now be formulated as follows. If we have an arbitrary basis in the configuration L with n electrons, then we can choose a basis in the configuration R with $2p$-n electrons in the partly filled shell such that
i) Both bases have the same transformation properties relative to the group O_p of orthogonal transformations in the space of and hence in particular relative to the group G.
ii) There are simple relations between the matrix elements of one and two electron operators relative to both bases.

The van Vleck relation can be formulated as follows:
Starting from a basis $\varphi^{(n)}$ of maximal S_z states in the configuration with n electrons we can obtain by coupling with the minimal S_z state of the half closed shell and antisymmetrization a basis $\varphi^{(n+p)}$ of minimal S_z states in the configuration with $n + p$ electrons.

Both bases have the same transformation properties relative to the group SU_p of unitary transformations with determinant 1 in the space of $u_1, u_2, \ldots, u_p$ and in particular the transformation properties of $\varphi^{(n+p)}$ and $\varphi^{(n)}o$ relative to the group G are the same. o is the high spin state of the half-closed shell and belongs to a one-dimensional representation of G. In addition there are simple relations for the matrix elements of one- and two-electron operators not acting on spin relative to both bases.

A general proof for both relations independent of the group G and the choice of one-electron states will be given in Chapters I and II. In Chapter III we shall apply the hole equivalence principle and the van Vleck relation to the theory of d-ions in Ligand fields. As is well known an octahedral Ligand will split the states of a d^1 ion in a t_2 level and an e level, e and t_2 being certain representations of the octahedral group. We can choose as a basis of maximal S_z states in the configuration d^1 a basis consisting of a basis of the t_2 level and a basis of the e level.

For the maximal S_z states of a d^2 ion there are various possibilities in particular:
i) The weak field representation, in which the Coulomb interaction is diagonal.
ii) The strong field representation, in which the octahedral component of the Ligand field is diagonal.
iii) The intermediate representation, in which the Hamiltonian consisting of the Coulomb interaction and the octahedral component of the Ligand field is diagonal.

In the configurations d^4, d^6, d^9 and d^3, d^7, d^8 we can find bases corresponding to the bases in d^1 and d^2 according to the hole equivalence principle and the van Vleck relation.

The matrix elements of one-electron operators relative to these basis can be calculated easily from the matrix elements for d^1 and d^2. Although in principle everything may be calculated exactly by means of computors, there is some need for closed formulae which form reasonable approximations. Various approximations are closely connected to the choice of basis in d^2: the weak field approximation, the strong field approximation and the intermediate approximation in which the Hamiltonian $\mathcal{H}_o$ consisting of the Coulomb interaction and the octahedral component of the Ligand field is treated in an exact way and the other terms of the Hamiltonian by means of perturbation calcalution. In spite of the frequent use of the first two approximations, the intermediate approximation will be much better in many cases and we shall present some results based on this approximation. From the results the influence of the weak field and strong field approximation can be investigated.

We are in particular interested in:
1) The splitting pattern due to the tetragonal or trigonal component of the Ligand field and the spin orbit coupling.
2) Some quantities appearing in the spin hamiltonian such as for instance the g factors $g_{\parallel}$ and $g_{\perp}$ and the hyper fine structure constants A and B. Simple approximations for the so-called second order contributions to the g factors and the dipolar parts of the hyper fine structure constants have been obtained by neglecting the admixture of excited states in the wave functions of the ground level of $\mathcal{H}_o$ due to the tetragonal or trigonal field.

In general the weak and strong field approximation can give bad results for the quantities 1) and 2). This is also the case for the constants describing the tetragonal and trigonal distortions in the static Jahn Teller effect.

In Chapter I we shall deal with the hole equivalence principle, in Chapter II with the van Vleck relation and in Chapter III with the application to the theory of d-ions in Ligand fields. The physical background is discussed more into detail in an introductory Chapter.

DISCUSSION OF THE PHYSICAL BACKGROUND

In this thesis we shall deal with the Hole Equivalence Principle, the van Vleck relation and their application to the theory of d-ions in Ligand fields. A Ligand field is an operator which represents generally the electrostatic interaction of a transition metal ion and the surrounding ions, including in particular covalent bondings. We shall speak of Ligand fields rather than crystal fields since according to many authors crystal field expansions imply the assumption that the surrounding ions can be considered to be point charges. This assumption can not explain the experimental data in a satisfying way and it is better to introduce a number of parameters in agreement with the symmetry in order to fit the experimental data.

In order to describe properly the content of the Hole Equivalence Principle and the van Vleck relation we shall briefly review the building up of electron shells. The main terms of the Hamiltonian acting on an ion or neutral atom are the electrostatic interaction between nucleus and electrons, the electrostatic Coulomb interaction between electrons and eventually also a Ligand field. (The spin orbit coupling is assumed to be small compared with the Coulomb interaction between the electrons). These terms of the Hamiltonian can be replaced by a self consistent one-electron hamiltonian h, *cf.* for instance the Hartree Fock approximation in the case of free ions or atoms [1]. The eigenvalue problem arising from h may be solved at least in principle. The eigenvalues ε_i of h will have certain degeneracies n_i (n_i will be an even number due to the two fold spin degeneracy).

In this approximation the lowest energy state of an ion can be obtained by constructing a Slater determinant of one-electron states such that the eigenstates of h for the lowest eigenvalues occur in the Slater determinant. Here the Pauli principle must be taken into account. The Slater determinant will vanish, if the one-electron states are not linearly independent. If we have an ion with n electrons and $n_0 + n_1 < n < n_0 + n_1 + n_2$, then the lowest energy state can be obtained by constructing a Slater determinant from the n_0 linearly independent states of energy ε_0, the n_1 linearly independent states of energy ε_1 and $n - n_0 - n_1$ linearly independent states of energy ε_2. So we arrive at the situation in which all the states of the lowest energies are occupied, *i.e.* occur in the Slater determinant. If all the states up to a certain energy are occupied, then we can speak of a closed shell. In addition there may be a number of states which form a partly filled shell. In the example this are the $n - n_0 - n_1$ linearly independent states of energy ε_2. Partly filled shells give always rise to a degeneracy (within this approximation). In the example there are $n_2! \{(n - n_0 - n_1)! \, (n_2 - n + n_0 + n_1)!\}^{-1}$ ways in order to select $n - n_0 - n_1$ states from a set of n_2 linearly independent states and this number is equal to the degeneracy of the lowest level.

The degeneracy will be lifted (completely or partly) by the other terms of the Hamiltonian, which are not contained in the self consistent one-electron hamiltonian *h*, for instance the Ligand field as far as not contained in *h*, the Coulomb interaction between the electrons of a partly filled shell, the spin orbit coupling, the coupling with an applied magnetic field and so on. In some cases if the other operators in the Hamiltonian are not very small relative to the operators occurring in *h*, or if two different energy levels of *h* are close to each other, it can be of interest to consider excited configurations in which more than one partly filled shell occurs. This for instance is the case in the neutral transtion atoms of the iron group, where the 3d shell and the 4s shell can be partly filled at the same time. It is also of interest in problems of configuration interaction. The remaining terms in the Hamiltonian not contained in *h* may give an important admixture of states belonging to excited configurations in the configuration corresponding to the lowest energy of *h*. This picture does not change the situation in an essential way. We can consider all the electrons in partly filled shells to belong to one same partly filled shell, if we admit the possibility that the one-electron states of the partly filled shell span the linear manifold of eigenstates of *h* for more than one eigenvalue.

Now the Hole Equivalence Principle as well as the van Vleck relation deal with partly filled shells and it will be assumed that the influence of closed shells can be neglected. This assumption is correct for one-electron operators. In the matrix elements between Slater determinants which differ in one one-electron state of the partly filled shell, the states of the closed shells do not appear. In addition the states of closed shells give a constant contribution to the diagonal elements, independent of the basis states. For two-electron operators the situation is more involved. In the matrix elements between Slater determinants which differ in two one-electron states of the partly filled shell, the states of the closed shells do not appear. Moreover the states of the closed shells give a constant contribution to the diagonal elements. However the closed shells can give an essential contribution to the matrix elements of Slater determinants which differ in one one-electron state of the partly filled shell. This contribution can be represented in terms of a fictitious one-electron operator as has been observed by GRIFFITH [2].

The most important two electron operator is the Coulomb interaction which is invariant for all rotations and in particular for all transformations of the point group G which leaves the one-electron hamiltonian determining the electron shells invariant. (In the case of free ions G will be the full rotation-reflection group. However in the case that also a Ligand field is to be contained in *h*, G will be the point group consisting of all proper (pure) rotations and improper rotations (rotations combined with an inversion), which leave the Ligand field invariant). The fictitious one-electron operator corresponding to the Coulomb interaction is also invariant for all transformations of G and has the same transformation properties as the one-electron hamiltonian. This is more exactly the reason why the Coulomb interaction can be contained in the self-consistent one-electron hamiltonian *h*.

The Hole Equivalence Principle is an important relation between two ions with the same closed shells and one partly filled shell. If the configuration *L* contains *n* electrons in the partly filled shell and there are *q* linear independent states in the shell, then the related configuration *R* will have *q-n* electrons in the partly filled shell *i.e.* *R* is the closed shell in which *n* electrons are missing. (The symbols *L* and *R* indicate left and right and refer to the positions of both the configurations in a periodical system). The Hole Equivalence Principle is not only a relation between the classifications of energy levels in both configurations. There is also a relation between the matrix elements of one- and two-electron operators within both configurations *L* and *R*.

The following simple argument is sometimes used in order to establish such a relation for one-electron operators: choose the basis of one-electron states in the configuration with one electron such that a given one-electron operator *A* is diagonal. In the configurations *L* and *R* bases consisting of Slater determinants of these one-electron states are chosen. Then it can be easily shown that the matrix elements of *A* in *R* are equal to minus the matrix elements of *A* in *L* apart from a constant diagonal contribution.

This simple argument is not exactly the content of the Hole Equivalence Principle. More precisely: If we have an arbitrary basis in the configuration *L*, then we can indicate a basis in the configuration *R* such that:

i) Both bases have the same transformation properties relative to the group G which leaves the self consistent one-electron hamiltonian *h* invariant. In particular, if we apply a transformation of G to the linear manifolds of states corresponding to the configurations *L* and *R*, then the linear manifolds will be mapped on itself. Hence if we choose bases in the linear manifolds, then the transformation can be represented by means of transformation matrices. Both bases have the same transformation properties, if and only if the transformation matrices are the same for all transformations of the group G.

ii) There also simple relations between the matrix elements of arbitrary one- and two-electron operators relative to both bases. These relations are independent of the transformation properties of the one- and two-electron operators. The relations hold simultaneously for all one- and two-electron operators, whether they are commuting or not. It must be noted that the simple argument for one-electron operators cannot be used, for, if we apply an unitary transformation in the space of one-electron states in order to diagonalize a given one-electron operator, then the unitary transformations within the configurations L and R induced by the unitary transformation in the space of one-electron states are not necessarily the same.

We shall now give a short historical review of the development of the Hole Equivalence Principle. PAULI was the first to observe that for the case of free ions in the configurations L and R the same LS terms occurred and each LS term the same number of times, *i.e.* we can choose the bases such that they have the same transformation properties relative to the rotation group. In 1942 RACAH [3] proved the Hole Equivalence Principle for the case of free ions. The basis states in the configuration L were taken to be $| \alpha S L M_S M_L >$, where α is an additional parameter in order to distinguish between different LS terms with the same L and S value. RACAH indicated the corresponding basis states in the configuration R by means of an expansion for the closed shell state. The equivalence for matrix elements for one-electron operators was formulated in terms of reduced matrix elements of tensor operators.

In 1961 GRIFFITH [2] gave a proof for the case of d-ions in octahedral Ligand fields. This proof is necessary since because of covalent bonds [4] the wave functions cannot be taken to be of the form $| \alpha S L M_S M_L >$. GRIFFITH observed that for the calculation of the lowest energy levels it will be correct to assume that the one electron orbitals of the partly filled shell span the same representations of the octahedral group, as they would do in the free ion case, *i.e.* the representations e (two dimensional) and t_2 (three dimensional). The basis states of the configuration $L(d^n)$ were taken to be $| t_2^{n_1} (S_1 \Gamma_1) e^{n_2} (S_2 \Gamma_2) S \Gamma M_S M_\Gamma >$ where $n_1 + n_2 = n$, S_1 and S_2 are the spin quantum numbers of the configurations with n_1 electrons in the t_2 shell and n_2 electrons in the e shell, Γ_1 and Γ_2 are representations of the octahedral group. The basis functions of the configuration d^n are obtained by coupling the representations Γ_1 and Γ_2 to the representation Γ and the spins S_1 and S_2 to the total spin S. $M_S = S, S - 1, \ldots, - S$ and M_Γ indicates tho rows of the representation Γ. It may be noted that for the case of d-ions these symbols give an unique description of all possible states, so that there is no need for additional parameters α. For this choice of basis GRIFFITH indicated the corresponding states in the configuration R by means of the closed shell expansion. The Hole Equivalence Principle was proved first for t_2 shells and e shells separately and then by coupling and antisymmetrization for configurations d^n.

GRIFFITH showed clearly that the relation between the matrix elements of one-electron operators relative to the corresponding bases in L and R is independent of the transformation properties of the operators. The crucial point is here the behaviour of the operators with respect to the time reversal operator K [5]. Real operators which commute with K such as for instance all electrostatic interactions and the spin orbit coupling have a relation of the type minus, *i.e.* the matrix elements in R are equal to minus the matrix elements in L apart from a constant diagonal term. Imaginary operators which anticommute with K such as for instance all angular momenta and hence the coupling with an applied magnetic field have an equivalence of the type plus, *i.e.* the matrix elements in R are equal to the matrix elements in L.

This fact suggested strongly that the Hole Equivalence Principle is independent of the transformation properties of the one-electron states of the partly filled shell. In Chapter I we shall give a formulation and a derivation of the principle for an arbitrary electron shell. As basis states in the configuration c^1 with one electron in the partly filled shell we can choose $u_i(\mathrm{r})\uparrow$, $u_i(\mathrm{r})\downarrow$, $i = 1, 2, \ldots, p$, where the u_i form an orthonormal set and span one or more irreducible representations of the group G, which leaves h invariant. $\uparrow$ and $\downarrow$ are the spin states $s_z = \frac{1}{2}$ and $s_z = -\frac{1}{2}$. As basis states in the configuration L (c^n) with n electrons in the partly filled shell we can take Slater determinants constructed from n of the $2p$ one-electron states, but also an arbitrary basis which can be obtained from the basis of Slater determinants by means of an unitary transformation. The crucial point is that we can find a basis in the configuration R, which has the same transformation properties as a given basis in the configuration L relative to the group O_p of orthogonal transformations in the space of $u_1, u_2, \ldots, u_p$.

An essential assumption is that h is a real operator, *i.e.* commutes with the time reversal operator K [5]. This assumption is correct since h does not contain magnetic fields. Then the space of $u_1, u_2, \ldots, u_p$ will be invariant for the action of the time reversal operator and the basis functions $u_1, u_2, \ldots, u_p$ can be chosen to be real. Hence each transformation of the point group G, which leaves the self consistent one-electron hamiltonian h invariant, can be represented by means of an orthogonal $p \times p$ matrix. Hence the basis in the configuration R will have the same transformation properties as the basis in the configuration L relative to the group G. In this way the Hole Equivalence Principle can be derived independent of the transformation properties of the one-electron states.

The advantage of this treatment can be summarized as follows:

i) The background of the Hole Equivalence Principle has been demonstrated more clearly.

ii) A justification for arbitrary electron shells has been given. This can be useful if there are large Ligand fields with lower symmetry than octahedral symmetry and also in problems where configuration interaction is important.

iii) If we have an arbitrary basis in the configuration L expressed in terms of linear combinations of Slater determinants of n one-electron states, then we can express immediately the corresponding basis in the configuration R in terms of Slater determinants of $2p$-n one-electron states. If we change the basis states u_i

in the configuration with one electron, then the bases in R corresponding to a given basis in L with respect to both sets of one-electron states are equal apart from a common phase factor $e^{i\varphi}$. In this way we do not have to bother about phase conventions.

iv) The formulations of RACAH and GRIFFITH suggest strongly to use a special choice of basis. In the case of free ions it is always good to choose a basis of the form $| \alpha\, S\, L\, M_S\, M_L >$. The choice of basis by GRIFFITH is appropriate in the case of very strong octahedral Ligand fields, *i.e.* if the Ligand fields are much stronger than the Coulomb interaction. In other cases where the Ligand field and the Coulomb interaction are of the same order of magnitude it may be useful to choose the basis such that the Hamiltonian of Ligand field and Coulomb interaction together is diagonal. The treatment given in Chapter I leaves the choice of basis completely free.

In Chapter II we shall deal with the van Vleck relation. It is well known that that the maximal spin levels of a d-ion in an octahedral Ligand field can be expressed in terms of a splitting parameter, in particular the splitting Δ which the same Ligand field would give between the e level and the t_2 level of a d^1 ion. In 1932 VAN VLECK [6] observed that the maximal spin levels expressed in terms of Δ have the same relative positions in the configurations d^n and d^{n+5} and also in the configurations d^{5-n} and d^{10-n}, if the order of the levels is inverted. The relations $d^n \rightarrow d^{10-n}$ and $d^{5-n} \rightarrow d^{5+n}$ are due to the Hole Equivalence Principle. In addition there is a relation $d^n \rightarrow d^{n+5}$ which we might call a van Vleck relation according to JØRGENSON [7] who observed possibilities for application of such a relation.

This relation holds also for arbitrary electron shells and is independent of the transformation properties of the one-electron states. Starting from an arbitrary basis $\varphi^{(n)}$ of maximal S_z states in the configuration c^n with n electrons in the partly filled shell we can obtain by coupling with the minimal S_z state of the half closed shell (c^p) and antisymmetrization a basis $\varphi^{(n+p)}$ of minimal S_z states in the configuration c^{n+p}. Both bases have the same transformation properties with respect to the unimodular group SU_p of unitary transformations with determinant 1 in the space of one-electron orbitals $u_1, u_2, \ldots, u_p$. This implies in particular that the basis states $\varphi^{(n+p)}$ in c^{n+p} transform in the same way as the states $\varphi^{(n)}o$ with respect to the symmetry group G of the one-electron hamiltonian h. o is the minimal S_z state of the half closed shell, o is symmetric in the spin dependent part and completely antisymmetric in the orbital part, o belongs to a one dimensional representation of the group G which is not necessarily the identical representation. For instance is the case of t_2 shells (d-ions in octahedral fields), the high spin state of the half closed shell t_2^3 is a $^4A_2$ state.

There are also simple relations between the matrix elements of one- and two-electron operators not acting on spin relative to both bases $\varphi^{(n)}$ and $\varphi^{(n+p)}$. These relations are somewhat analogous to the corresponding hole equivalence relations, but now there is no difference between real and imaginary operators. In both cases we have a relation of type plus, *i.e.* the matrix elements are the same apart from a constant term in the diagonal.

Contrarily to the Hole Equivalence Principle, the van Vleck relation applies only to the maximal spin states of the configurations c^n and c^{n+p} and only to operators not acting on spin. The latter restriction is not serious, the matrix elements between maximal S states in the configuration c^{n+p} of an operator which can be written as a linear combination of products of spin angular momentum operators and operators not acting on spin can be easily calculated. It must be noted that the spin quantum numbers of the maximal S states in the configurations c^n and c^{n+p} are different in general. The maximal S value in c^n for $n \leqslant p$ is equal to $\frac{1}{2}\, n$, whereas the maximal S value in c^{n+p} is equal to $\frac{1}{2}(p\text{-}n)$.

A more serious limitation of the van Vleck relation is the restriction to the maximal S states. The van Vleck relation will be useful if we are only interested in the lowest energy levels and if Hund's rule is well obeyed, *i.e.* the maximal S states have the lowest energy. This will be correct in the case of free ions if the spin orbit coupling is small relative to the Coulomb interaction and we can use the Russell Saunders coupling scheme rather than *jj* coupling. Hund's rule will also hold in the case of Ligand fields, if the Ligand fields are not very large. The Ligand fields cannot give a mixing between different S states. However in the configurations d^4, d^5, d^6, d^7 it can occur that the ground state has a lower spin value than the maximal value. Let us for instance consider an octahedral Ligand field with 6-coordination. Then the energy of the t_2 level of a d^1 ion will be lower than the energy of the e level. If the splitting Δ between the t_2 level and the e level is very large, then the lowest energy level in the configuration d^6 can be obtained by putting all the six electrons in a t_2 orbital. The ground state is a $^1A_1$ state corresponding to the closed t_2 shell. It the splitting Δ is not very large, then the ground level in the configuration d^6 will be a $^5T_2$ level which can be obtained by putting in an appropriate way 4 electrons in a t_2 orbital and 2 electrons in an e orbital.

In Chapter III we shall apply the Hole Equivalence Principle and the van Vleck relation to the high spin states of d-ions. We can choose bases of maximal S_z states in the configurations d^1 and d^2 and corresponding bases of maximal S_z states in the configurations d^9 and d^8 according to the Hole Equivalence Principle and also bases of minimal S_z states in the configurations d^6, d^7 and d^4 and d^3 according to the van Vleck relation. The matrix elements of one-electron operators for d^4, d^6, d^9 and d^3, d^7, d^8, follow from the matrix elements for d^1 and d^2 using the Hole Equivalence Principle and the van Vleck relation.

We consider in particular the following one-electron operators: A large Ligand field of octahedral symmetry, a much smaller component of tetragonal or trigonal symmetry, the spin orbit coupling, the Zeeman term, *i.e.* the coupling with an applied magnetic field, and hyper fine structure and quadrupole coupling. In order to take into account the effect of covalent bondings between the d-ion and the surrounding Ligands we have introduced two orbital reduction factors k and k' for the matrix elements of the orbital angular momentum appearing in the Zeeman term and in the same way two spin orbit interaction constants ζ and ζ' for the spin orbit coupling. For the evaluation of the hyper fine structure we also need the matrix elements of a tensor operator of degree two which describes the dipolar part of the hyper fine structure. Although for an exact parametrization in the octahedral case four parameters are needed we shall assume that the matrix elements can be found from the corresponding matrix elements for the free ion case by multiplying them with one reduction factor p.

The most important two-electron operator is the Coulomb interaction. It has been assumed that the Coulomb interaction can be described effectively in terms of Racah parameters which can be different from the free ion case. Then the Coulomb interaction does not give a splitting of the high spin states of d^1, d^4, d^6 and d^9. The Coulomb interaction for the high spin states of d^2, d^3, d^7 and d^8 can be described in terms of a splitting parameter E_p, *i.e.* the difference in energy between a 7-fold degenerated "F level" and a 3-fold degenerated "P level". In an exact approach if we are restricted to the high spin states four parameters are needed *cf.* [2]. Up till now no progress has been made in order to arrive at an unique determination of these parameters.

For the configuration d^1 we can choose a basis of maximal S_z states consisting of a basis of the t_2 level and a basis of the e level. We shall be in particular interested in octahedral complexes with 6-coordination, so that the t_2 level is the lowest level and the splitting parameter Δ is positive. In the configuration d^2 we can choose a basis of maximal S_z states consisting of the 10 Slater determinants which we can construct from the five one-electron states with $s_z = \frac{1}{2}$. An arbitrary basis can be introduced by application of an unitary transformation. We consider in particular the following possibilities:

i) The weak field representation in which the Coulomb interaction is diagonal.

ii) The strong field representation in which the octahedral component of the Ligand field is diagonal.

iii) The intermediate representation in which the Hamiltonian $\mathcal{H}_o$ consisting of the Coulomb interaction and the octahedral component of the Ligand field is diagonal. The basis states can be expressed in terms of the parameter $x = \Delta/E_p$.

It must be noted that it is possible to calculate matrix elements of arbitrary operators relative to any reasonable choice of basis. In this picture the choice of basis is not important. The physical quantities of interest can be solved exactly by diagonalizing large matrices by means of computors. Although this procedure will be necessary in order to obtain exact results, the procedure in general will be very laborious since the parameters are not known a priori but must be chosen in order to fit the experimental data as good as possible. This is the reason why there is some need for closed formulae which form reasonable approximations.

The various approximations are closely connected to the choices of basis:
i) The weak field approximation, in which the octahedral component of the Ligand field is treated as a small perturbation relative to the Coulomb interaction.
ii) The strong field approximation in which the Coulomb interaction is treated as a small perturbation relative to the octahedral component of the Ligand field.
iii) The intermediate approximation in which all the one-electron operators apart from the octahedral component are treated as a small perturbation relative to the Hamiltonian $\mathcal{H}_0$ consisting of the Coulomb interaction and the octahedral component of the Ligand field.

In spite of the frequent use of the first two approximations we want to present in Chapter III the results of some calculations according to the intermediate approximation. This approximation will be in many cases much better than the weak and strong field approximation since the octahedral component of the Ligand field and the Coulomb interaction are of the same order of magnitude and the tetragonal or trigonal component are often much smaller. The physical quantities according to the intermediate approximation are expressed in terms of $x = \Delta/E_p$ and from the formulae obtained in this way we can investigate the influence of the weak field and strong field approximation by taking the limits $x \to 0$ and $x \to \infty$.

In particular we shall be interested in the lowest energy level by the action of the Hamiltonian $\mathcal{H}_0$. For d^1 and d^6 this level will be a T_2 level, for d^2 and d^7 a T_1 level, for d^3 and d^8 an A_2 level and for d^4 and d^9 an E level. We shall not deal extensively with d^4 and d^9 since the formulae for the physical quantities are simple and well known from many text books *cf.* [2], [4] and also from the original publication of Abragam and Pryce [8]. The cases of d^2, d^3, d^7 and d^8 are more interesting because of the various approximations. The case of d^6 has not been treated extensively up till now and in the case of d^1 we shall complete the Abragam and Pryce formulae for hyper fine structure and quadrupole coupling which apply only to the case of tetragonal fields [8].

In the case of a T_1 or T_2 level the orbital angular momentum acting on the states arising originally from the T_1 or T_2 level but somewhat modified by the action of the tetragonal or trigonal field can be associated with the action of an orbital angular momentum operator on the states of a p electron [8], [9]. The relation between the two angular momenta involves two constants α and α'. An analogous relation holds for the spin orbit coupling and involves two constants γ and γ'. The constants γ and γ' follow from α and α' by replacing the orbital reduction factors k and k' by the spin orbit interaction constants ζ and ζ'. In addition the T_1 or T_2 level is split in a doublet and a singlet with separation δ. We shall give formulae for the quantities $\alpha, \alpha', \gamma, \gamma'$ and δ. The expressions for the configurations d^1, d^4, d^6 and d^9 are exact. The expressions for d^2, d^3, d^7 and d^8 have been obtained by means of a second order perturbation calculation in the intermediate approximation.

Now due to the spin orbit coupling and the axial field, the T_1 or T_2 level will be split into a number of energy levels. We consider in particular the group of the lowest energy levels such that the separation between the levels of the group is small (of order of some tens of cm^{-1}).

Then using the theory of Abragam and Pryce [8] we can establish a spin hamiltonian for this group of states. The remaining terms in the Hamiltonian are replaced by fictitious spin angular momentum operators. The Zeemanterm of the Hamiltonian involves two g factors $g_{\parallel}$ and $g_{\perp}$ and the hyper fine structure constants A and B.

The g values $g_{\parallel}$ and $g_{\perp}$ can be considered to consist of two contributions: The first order contribution which can be calculated neglecting the matrix elements of the spin orbit coupling between different energy levels of the Hamiltonian $\mathcal{H}_0$ consisting of the Coulomb interaction and the octahedral component of the Ligand field and the second order contribution which arises from the admixture of excited levels in the ground level of $\mathcal{H}_0$ by means of the spin orbit coupling. The calculation of the first order contribution is well known from many detailed analyses and we shall review the results. The exact calculation of the second order contribution which in general is small but not negligible is very laborious. Abragam and Pryce [9] have obtained numerical values for the case of Co^{++} (d^7). A reasonable approximation can be obtained by neglecting the admixture in the wave functions due to the trigonal or tetragonal field. In this way we can derive simple formulae for the second order contributions which depend on $x = \Delta/E_p$ for d^2 and d^7.

The hyper fine structure constants consist also of two contributions [9], the contribution of the orbital angular momentum and the contact (Fermi) term which can be easily expressed in terms of g factors and the contribution of the dipolar part of the hyper fine structure. The latter contribution in general is rather small. A good approximation can be obtained by neglecting the admixture in the wave functions due to the trigonal or tetragonal field. The formulae for these contributions *Asd* and *Bsd* to the hyper fine structure constants *A* and *B* in the configurations d^2 and d^7 are extremely dependent on a correct choice of $x = \Delta/E_p$.

A correct choice of *x* will also be important for the constants describing the tetragonal and trigonal distortions in the static Jahn Teller effect [10], [11]. For instant in the case of d^2 we can expect that in the weak field approximation the trigonal distortions are stable. whereas in the strong field approximation and probably also in actual cases the tetragonal distortions will be stable.

We see that some quantities such as the constants relative to the Jahn Teller effect and the dipolar part of the hyper fine structure are extremely dependent on a correct choice of *x*. Such a choice will also be important for the second order contributions to the *g* factors, and the quantities α, α', γ, γ' and δ. In these cases neither the weak field approximation nor the strong field approximation will lead to good results. We have also calculated the *g* factors for the case of d^3 and d^8, where an A_2 level is the lowest level. The results are not very dependent on a correct choice of *x* and both the weak field approximation and strong field approximation will be good.

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CHAPTER I

THE HOLE-EQUIVALENCE PRINCIPLE

§ 1. *Introduction*

We might call "hole theories" all theories which establish simple relations between an electron configuration L with n electrons in a shell and the corresponding hole configuration R (closed shell with n electrons missing).

From a good hole theory we can expect that, given a basis in the configuration L, a basis in R is indicated such that

i) the matrices of one and two-electron operators with respect to both bases are simply related to each other;

ii) corresponding states in L and R have the same transformation properties with respect to the symmetry group G of the problem, *i.e.* the one-electron states which determine the shell can be considered as eigenstates of a one-electron Hamiltonian h for one or eventually more eigenvalues. G is the group of transformations which leave h invariant.

For the case of full rotational symmetry (free ions or atoms, l shells) the problem was solved by Racah [1, 2]. As a basis in the configuration L $|\alpha SLM_SM_L\rangle$ was taken where α is a parameter classifying the repeated SL terms. In fact, α can be taken to be the seniority v, but in the case of f shells an additional classification is necessary [2, 3]. The corresponding functions in R were defined by the expansion of the antisymmetric wave function of the closed shell as a sum of products of states of L with states of R. An equivalence for the matrix elements of one-electron operators was formulated in terms of reduced matrix elements of tensor operators by application of the Wigner–Eckart theorem [4, 5].

In the case of d ions in octahedral Ligand fields it is not allowed to identify the one-electron states with pure d states. For the lowest levels it is reasonable to assume that the partly filled shells of the complex span the same representations e_g+t_{2g} of O_h (eventually $e+t_2$ in the case of tetrahedral symmetry T_d), just as those of a d electron would do [6]. For this case a hole theory was established by Griffith, first for t_2 shells and e shells separately then for configurations $t_2^m e^n$ by coupling and antisymmetrization [7]. The equivalence for matrix elements of one-electron operators was formulated with the help of KRAMERS' star operator [8], apart from a change in sign of the time scale identical with WIGNER's time reversal operator [9, 10].

Here a hole theory will be established which is independent of the transformation properties of the one-electron states. Starting with an arbitrary basis in the configuration L expressed as linear combinations of determinantal functions, a basis in the configuration R is indicated satisfying i) and ii).

§ 2. *Basic concepts*

Consider an electron which can be described by the functions

$$u_i(\boldsymbol{r})\uparrow,\ u_i(\boldsymbol{r})\downarrow \qquad i = 1, \ldots, p$$

the u_i form an orthonormal set

$\uparrow$ and $\downarrow$ are the spin states $s_z = \frac{1}{2}$ and $s_z = -\frac{1}{2}$.

The u_i can be considered as basis functions of the space of eigenfunctions of a one-particle Hamiltonian h for one or more eigenvalues.

Assumption: h is a real operator, *i.e.* h commutes with Kramers' star operator K.

This assumption is satisfied in physically important cases.

The operator K can be defined in different ways by some of its properties, see for instance [9, 10, 11, 12], but all the definitions lead to the same operator, specified uniquely apart from a phase factor.

We shall define K by

$$K = D_{y_1} D_{y_2} \ldots D_{y_n} C, \tag{1}$$

where C takes the complex conjugate of all coefficients and orbital parts of wave functions and D_{y_k} is an operator working on the spin of the kth electron in the same way as $-\mathrm{i}\sigma_{y_k}$, σ_y being the Pauli operator.

For instance for one electron

$$K|m_s\rangle = (-1)^{s-m_s}|-m_s\rangle, \quad m_s = \pm\tfrac{1}{2}. \tag{2}$$

The phase convention for orbital wave functions is such that

$$K|l, m_l\rangle = |l, m_l\rangle^* = (-1)^{l-m_l}\,|l, -m_l\rangle. \tag{3}$$

($|l, m_l\rangle$ corresponds with $\mathrm{i}^l Y_{lm}$).

When we have two angular momenta j_1 and j_2 satisfying

$$K|j_i, m_i\rangle = (-1)^{j_i-m_i}|j_i, -m_i\rangle \text{ for } i = 1, 2 \tag{4}$$

and couple these to an angular momentum J in the standard way with Clebsch–Gordan coefficients:

$$K|J, M\rangle = (-1)^{J-M}|J, -M\rangle. \tag{5}$$

This can be derived with a symmetry property of Clebsch–Gordan coefficients

$$\langle j_1 j_2 - m_1 - m_2|J - M\rangle = (-1)^{j_1+j_2-J}\langle j_1 j_2 m_1 m_2|JM\rangle. \tag{6}$$

The functions $|v_i\rangle_L$ $(i=1, 2, \ldots, 2p;\ 2p=q)$ obtained by an unitary transformation from $u_i\uparrow$ and $u_i\downarrow$ form an arbitrary orthonormal basis of the *configuration* c^1.

An orthonormal basis of the configuration c^n is formed by

$$|g_i^{(n)}\rangle_L = |v_{i_1}, v_{i_2}, \ldots, v_{i_n}\rangle;\ i_1 < i_2 < \ldots < i_n \leqslant q \tag{7}$$

with the notation

$$|\phi_1, \phi_2, \ldots, \phi_m\rangle \equiv \frac{1}{\sqrt{m!}}\begin{vmatrix} \phi_1(1) & \phi_1(m) \\ & \\ \phi_m(1) & \phi_m(m) \end{vmatrix} = \frac{1}{\sqrt{m!}}\sum_\sigma \varepsilon(\sigma)\, \phi_{\sigma(1)}(1) \ldots \phi_{\sigma(m)}(m) \tag{8}$$

where the summation is over the permutations of $1, 2, \ldots, m$; $\varepsilon(\sigma)$ being the sign of the permutation.

The subscript L is added in order to distinguish the functions from the corresponding functions $|\rangle_R$ in the hole configuration R to be defined in a moment.

The index i characterizes in an unique way the $\binom{q}{n}$ possibilities $i_1 < i_2 < \ldots < i_n \leqslant q$.

An arbitrary orthonormal basis in the configuration c^n is given by

$$|f_i^{(n)}\rangle_L = \sum_j U_{ji}|g_j^{(n)}\rangle_L, \tag{9}$$

the matrix U being unitary.

The closed shell state (configuration c^q) is described by

$$|O\rangle = |v_1, v_2, \ldots, v_q\rangle. \tag{10}$$

Apart from G, we want to consider the following groups:

i) U_p of unitary transformations in the space of $u_1, u_2, \ldots, u_p$.

ii) O_p of orthogonal transformations in the space of $u_1, u_2, \ldots, u_p$.

All transformations of O_p commute with K. This together with the fact that the space of $v_1, v_2, \ldots, v_q$ is invariant for K which follows from the assumption that h is a real operator plays an essential role.

§ 3. *The equivalence of representations*

For each value of $n \leqslant q$ the functions $|g_i^{(n)}\rangle_L$ span a representation $\Gamma^{(n)}$ of $\mathrm{U_p}$.

Let us apply a transformation of $\mathrm{U_p}$

(11) $$T|v_i\rangle_L = \sum_k t_{ki}|v_k\rangle_L.$$

The functions $|g_i^{(n)}\rangle_L$ transform like

(12) $$T|g_i^{(n)}\rangle_L = \sum_{k_1<k_2<\ldots<k_n} \begin{vmatrix} t_{k_1 i_1} & t_{k_1 i_n} \\ t_{k_n i_1} & t_{k_n i_n} \end{vmatrix} |g_k^{(n)}\rangle_L.$$

The character of $\Gamma^{(n)}$ is given by

(13) $$\chi^{(n)}(T) = \sum_{k_1<k_2<\ldots<k_n} \begin{vmatrix} t_{k_1 k_1} & t_{k_1 k_n} \\ t_{k_n k_1} & t_{k_n k_n} \end{vmatrix} = \sum_{k_1<k_2<\ldots<k_n} \lambda_{k_1}\lambda_{k_2}\ldots\lambda_{k_n} = (-1)^n\,\tau_{q-n}.$$

Here

$$\sum_{k_1<k_2<\ldots<k_n} \begin{vmatrix} t_{k_1 k_1} & t_{k_1 k_n} \\ t_{k_n k_1} & t_{k_n k_n} \end{vmatrix}$$

is one of the so-called invariants of the matrix t_{ki} (in fact, the invariance follows from its definition as a group character).

Also

(14) $$\chi^{(q-n)}(T) = (-1)^{q-n}\,\tau_n.$$

If λ^{-1} satisfies the secular equation of T, then λ satisfies the secular equation of $T^{-1} = T^{\dagger}$, where $T^{\dagger} = \widetilde{T^*}$ is the hermitian adjoint matrix of T, and also of T^*.

Thus

$$\sum_n \tau^*_{q-n}\lambda^{q-n} = 0 \text{ and } \sum_n \frac{\tau_n}{\tau_0}\,\lambda^{q-n} = \sum_n (-1)^q\,\frac{\tau_n}{|T|}\,\lambda^{q-n} = 0$$

have the same roots and the coefficient of λ^q equal to 1.

Hence

(15) $$\tau^*_{q-n} = \frac{(-1)^q\tau_n}{|T|}.$$

If we restrict ourselves to O_p then all τ_n are real and $|T|=1$. (Choose as a basis in c^1 $u_i\uparrow, u_i\downarrow$, where the u_i are real functions. This is possible as h is a real operator. Then each operation of O_p generates an orthogonal matrix T_0 among the states $u_1, u_2, \ldots, u_p$.

$$|T_0| = \pm 1 \quad (T) = \begin{pmatrix} T_0 & O \\ O & T_0 \end{pmatrix}, \text{ so } |T| = |T_0|^2 = 1.)$$

Then

$$\tau_{q-n} = (-1)^q \tau_n .$$

and

$$\chi^{(q-n)}(T) = \chi^{(n)}(T). \tag{16}$$

$|g_i^{(n)}\rangle_L$ and $|g_i^{(q-n)}\rangle_L$ span equivalent representations $\Gamma^{(n)}$ and $\Gamma^{(q-n)}$ of O_p. It is possible to find a basis in the configuration c^{q-n}, which transforms in the same way as $|g_i^{(n)}\rangle_L$ under all operations of O_p. The functions $|g_i^{(n)}\rangle_L$ and $|g_i^{(q-n)}\rangle_L$ however span different representations of U_p, so the group U_p is useless for our purpose.

It is of interest that, in the case of l shells, use has been made of the irreducible representations of O_{2l+1} to give a classification, *i.e.* the seniority classification, for different SL terms [1, 2, 3].

§ 4. *Expansion of the closed shell state*

We define as the corresponding functions in the hole configuration R

$$|g_i^{(q-n)}\rangle_R \equiv (-1)^{i_1+\ldots+i_n+n(n-1)/2} K|O-(v_{i_1}, v_{i_2}, \ldots, v_{i_n})\rangle \tag{17} \qquad \text{(i)}$$

where

$$|O-(v_{i_1}, v_{i_2}, \ldots, v_{i_n})\rangle = |v_{j_1}, v_{j_2}, \ldots, v_{j_{q-n}}\rangle \tag{18}$$

and $j_1<j_2<\ldots<j_{q-n}\leqslant q$ together with $i_1<i_2<\ldots<i_n\leqslant q$ form the set of subscripts $1, 2, \ldots, q$.

$$|f_i^{(q-n)}\rangle_R = \sum_j U_{ji}|g_j^{(q-n)}\rangle_R, \tag{19} \qquad \text{(ii)}$$

where U has been given in (9).

In fact the functions $|f_i^{(q-n)}\rangle_R$ form an orthonormal basis of c^{q-n}, which can be easily derived using the antiunitarity of K.

From this definition a simple expansion of the closed shell state can be derived.

$$|O\rangle = \frac{1}{\sqrt{q!}} \sum \varepsilon(\sigma)\, v_{\sigma(1)}(1) \ldots v_{\sigma(q)}(q). \tag{20}$$

Given a permutation σ, we can denote the set $\sigma(1), \ldots, \sigma(n)$ by $i_1, i_2, \ldots, i_n$, such that $i_1 < i_2 < \ldots < i_n$, and the set $\sigma(n+1), \ldots, \sigma(q)$ by $j_1, j_2, \ldots, j_{q-n}$, such that $j_1 < j_2 < \ldots < j_{q-n}$.

Now the inverse permutation σ^{-1} can be performed in the following way:

(i) Bring $\sigma(1), \ldots, \sigma(n)$ in the order $i_1, i_2, \ldots, i_n$ by τ_1 interchanges of two numbers.

Define σ_1 by $\sigma_1(i_k) \equiv \sigma(k)$, so that $\varepsilon(\sigma_1) = (-1)^{\tau_1}$.

(ii) Bring $\sigma(n+1), \ldots, \sigma(q)$ in the order $j_1, j_2, \ldots, j_{q-n}$ by τ_2 interchanges of two numbers.

Define σ_2 by $\sigma_2(j_k) \equiv \sigma(n+k)$, so that $\varepsilon(\sigma_2) = (-1)^{\tau_2}$.

(iii) Bring $i_1, \ldots, i_n, j_1, \ldots, j_{q-n}$ in the order $1, 2, \ldots, q$.

This can be carried out by

$$\sum_{k=1}^{n} (i_k - k) = i_1 + \ldots + i_n - \frac{n}{2}(n+1)$$

interchanges.

Then both σ^{-1} and σ may be performed by

$$\tau = \tau_1 + \tau_2 + i_1 + \ldots + i_n - \frac{n(n+1)}{2}$$

interchanges.

Hence

$$\varepsilon(\sigma) = (-1)^{n(n+1)/2}\,(-1)^{i_1 + \ldots + i_n}\,\varepsilon(\sigma_1)\,\varepsilon(\sigma_2). \tag{21}$$

Thus

$$\left\{\begin{aligned} |O\rangle &= \frac{(-1)^{n(n+1)/2}}{\sqrt{q!}} \sum_{i_1 < i_2 < \ldots < i_n} (-1)^{i_1 + \ldots + i_n} \sum_{\sigma_1} \varepsilon(\sigma_1) v_{\sigma_1(i_1)}(1) \ldots v_{\sigma_1(i_n)}(n) \\ &\qquad \sum_{\sigma_2} \varepsilon(\sigma_2) v_{\sigma_2(j_1)}(n+1) \ldots v_{\sigma_2(j_{q-n})}(q) \\ &= (-1)^n \binom{q}{n}^{-\frac{1}{2}} \sum_i |g_i^{(n)}\rangle_L \cdot |h_i^{(q-n)}\rangle, \end{aligned}\right. \tag{22}$$

where

$$|h_i^{(q-n)}\rangle = (-1)^{n(n-1)/2 + i_1 + \ldots + i_n}\,|O - (v_{i_1}, \ldots, v_{i_n})\rangle. \tag{23}$$

Now

$$|g_i^{(q-n)}\rangle_R = K|h_i^{(q-n)}\rangle \qquad (cf.\ 17). \tag{24}$$

Making use of

$$(25) \qquad K^2\psi = (-1)^m\psi$$

for an arbitrary m-electronstate

$$(26) \qquad (-1)^n|h_i^{(q-n)}\rangle = K|g_i^{(q-n)}\rangle_R.$$

Hence

$$(27) \qquad |O\rangle = \binom{q}{n}^{-\frac{1}{2}} \sum_i |g_i^{(n)}\rangle_L \cdot K|g_i^{(q-n)}\rangle_R.$$

When we take an arbitrary orthonormal basis (9) of c^n, it follows the antilinearity of K and the orthogonality relations of U, that

$$(28) \qquad |O\rangle = \binom{q}{n}^{-\frac{1}{2}} \sum_i |f_i^{(n)}\rangle_L \cdot K|f_i^{(q-n)}\rangle_R.$$

Remarks: Alternatively we can consider (27) as the definition of the corresponding hole states $|f_i^{(q-n)}\rangle_R$. When we start from another basis v_i' in c^1, we can also define a basis $|f_i^{(q-n)}\rangle_R$ by (17) and (19) corresponding to $|f_i^{(n)}\rangle_L$. The basis $|f_i^{(q-n)}\rangle_R$ obtained from v_i' is not necessarily equal to the basis $|f_i^{(q-n)}\rangle_R$ obtained from v_i, but (27) ensures that both bases are equal apart from multiplication by the complex conjugate of the phase factor by which the closed shell state is multiplied, *i.e.* the determinant of the inverse transformation $v_i' \rightarrow v_i$.

The definitions (15a) of RACAH [3] and (9.41) of GRIFFITH [7] for the corresponding hole states can be considered as special cases of (27). In the case of l shells, (RACAH [3])

$$|O\rangle = \binom{4l+2}{n}^{-\frac{1}{2}} \sum_{\alpha,S,L,M_S,M_L} (-1)^{S-M_S+L-M_L}\,|\alpha SLM_SM_L\rangle_L\,|\alpha SL-M_S-M_L\rangle_R.$$

In the case of d ions in octahedral Ligand fields (GRIFFITH [7])

$$|O\rangle = \binom{10}{m+n}^{-\frac{1}{2}} \sum (-1)^{S-M_S}\,|t_2^m(S_1\Gamma_1)\,e^n(S_2\Gamma_2)\,S\Gamma M_SM_\Gamma\rangle_L \cdot$$
$$\cdot\,|t_2^{6-m}(S_1\Gamma_1)\,e^{4-n}(S_2\Gamma_2).S\Gamma-M_SM_\Gamma\rangle_R.$$

(The representations Γ, M_Γ are supposed to have been brought into a real form).

§ 5. *Transformation properties of the corresponding functions in the hole configuration*

The functions $|f_i^{(q-n)}\rangle_R$ have the same transformation properties as the $|f_i^{(n)}\rangle_L$ for all operations of $\mathrm{O_p}$.

Proof I: Let us apply a transformation of $\mathrm{O_p}$.

The transformation properties of the functions $|g_i^{(n)}\rangle_L$ are given by (12). The functions $|h_i^{(q-n)}\rangle$, (*cf.* 23)), transform like

$$T|h_i^{(q-n)}\rangle = \sum_k (-1)^{i_1+\dots+i_n+k_1+\dots+k_n} \begin{vmatrix} t_{l_1 j_1} & t_{l_1 j_{q-n}} \\ & \\ t_{l_{q-n} j_1} & t_{l_{q-n} j_{q-n}} \end{vmatrix} |h_k^{(q-n)}\rangle, \tag{28}$$

where $l_1<l_2<\dots<l_{q-n}<q$ together with $k_1<k_2<\dots<k_n<q$ form the set $1, 2, \dots, q$ of subscripts and $j_1<j_2<\dots<j_{q-n}$ and $i_1<i_2<\dots<i_n$ form a similar set.

(29) Now $$(-1)^{i_1+\dots+i_n+k_1+\dots+k_n} \begin{vmatrix} t_{l_1 j_1} & t_{l_1 j_{q-n}} \\ & \\ t_{l_{q-n} j_1} & t_{l_{q-n} j_{q-n}} \end{vmatrix} = T'_{k_1\dots k_n, i_1\dots i_n},$$

where $T'_{k_1\dots k_n, i_1\dots i_n}$ is the determinant of the matrix T' obtained from T by putting (for $\alpha=1, \dots, n$) all elements of the k_αth row and the i_αth column equal to zero, except the $k_\alpha i_\alpha$th element which is set equal to one. $T'_{k_1\dots k_n, i_1\dots i_n}$ can be considered as a n-fold underdeterminant.

Making use of the fact that each operation of $\mathrm{O_p}$ commutes with K and also of the antilinearity of K

$$T|g_i^{(q-n)}\rangle_R = \sum_k T'^{*}_{k_1,\dots,k_n, i_1,\dots,i_n} |g_k^{(q-n)}\rangle_R. \tag{30}$$

From the explicit formula

$$T'_{k_1\dots k_n, j_1\dots j_n} = \sum_\sigma \varepsilon(\sigma)\, t'_{1,\sigma(1)} \dots t'_{q,\sigma(q)}, \tag{31}$$

where

$$t'_{r,\sigma(r)} = \begin{cases} \delta_{\sigma(k_\alpha), j_\alpha}, & \text{if } r \text{ is one of the numbers } k_\alpha \\ t_{r,\sigma(r)}, & \text{if } r \neq k_\alpha \text{ for } \alpha = 1, \dots, n \end{cases} \tag{32}$$

it can be shown that

$$\left\{ \begin{aligned} \sum_{j_1,\dots,j_n=1}^{q} t_{k'_1 j_1}\dots t_{k'_n j_n} T'_{k_1\dots k_n, j_1\dots j_n} = |T''| = \varepsilon\begin{pmatrix} k_1' \dots k_n' \\ k_1 \dots k_n \end{pmatrix} |T| = \\ = \varepsilon\begin{pmatrix} k_1' \dots k_n' \\ k_1 \dots k_n \end{pmatrix}, \end{aligned} \right. \tag{33}$$

where T'' is the matrix obtained from T by replacing the k_αth row by the $k_{\alpha'}$th row and

$\varepsilon\begin{pmatrix} k_1' \dots k_n' \\ k_1 \dots k_n \end{pmatrix}$ is the sign of the permutation $\begin{pmatrix} k_1' \dots k_n' \\ k_1 \dots k_n \end{pmatrix}$ and is zero when the sets k_α and k_α' are not identical.

(33) can be considered as a straight-forward generalization of a well-known determinant property.

Now taking the complex conjugate of (33), multiplying by $t_{k_1' i_1} \dots t_{k_n' i_n}$, summing over $k_1', \dots, k_n'$ and making use of the orthogonality relations of T

$$(34) \qquad T'^{*}_{k_1 \dots k_n, i_1 \dots i_n} = \sum_\sigma \varepsilon(\sigma)\, t_{\sigma(k_1) i_1} \dots t_{\sigma(k_n) i_n} = \begin{vmatrix} t_{k_1 i_1} & t_{k_1 i_n} \\ & \\ t_{k_n i_1} & t_{k_n i_n} \end{vmatrix}.$$

From (12), (30) and (34) it follows that $|g_i^{(n)}\rangle_L$ and $|g_i^{(q-n)}\rangle_R$ have the same transformation-properties. In addition it is now easy to show (*cf.* (9) and (19)) that $|f_i^{(n)}\rangle_L$ and $|f_i^{(q-n)}\rangle_R$ have the same transformation properties.

This derivation has certain features in common with a derivation of Condon and Shortley of a relation between transformations connecting two systems of zero order states for L and the corresponding hole configuration R [13].

Proof II: Suppose the functions $|f_i^{(n)}\rangle_L$ and $|f_i^{(q-n)}\rangle_R$ transform like

$$(35) \qquad \begin{cases} T|f_i^{(n)}\rangle_L = \sum\limits_k T^{(n)}{}_{ki} |f_k^{(n)}\rangle_L \\ T|f_i^{(q-n)}\rangle_R = \sum\limits_k T^{(n)\prime}{}_{ki} |f_k^{(q-n)}\rangle_R. \end{cases}$$

We have to prove then:

$$(36) \qquad T^{(n)} = T^{(n)\prime} \text{ for all } T \in \mathrm{O_p}.$$

Clearly $|O\rangle$ is invariant, *i.e.*

$$(37) \qquad T|O\rangle = |O\rangle, \text{ since } |T| = 1.$$

From (28) it follows that

$$(38) \qquad K|f_i^{(q-n)}\rangle_R = \binom{q}{n}^{\frac{1}{2}} \langle f_i^{(n)}{}_L|O\rangle.$$

Since K commutes with all operations of $\mathrm{O_p}$

$$(39) \qquad \begin{cases} TK|f_i^{(q-n)}\rangle_R = KT|f_i^{(q-n)}\rangle_R = K\sum\limits_k T^{(n)\prime}{}_{ki}|f_k^{(q-n)}\rangle_R = \\ \qquad = \sum\limits_k T^{(n)\prime *}{}_{ki}\, K|f_k^{(q-n)}\rangle_R. \end{cases}$$

In addition, from (37) and (38)

$$(40)\quad \begin{cases} TK|f_i{}^{(q-n)}\rangle_R = \binom{q}{n}^{\frac{1}{2}} \langle T\, f_i{}^{(n)}{}_L|TO\rangle = \binom{q}{n}^{\frac{1}{2}} \langle \sum_k T^{(n)}{}_{ki}\, f_k{}^{(n)}{}_L|O\rangle = \\ \qquad\qquad\qquad\qquad\qquad\qquad = \sum_k T^{(n)*}{}_{ki}\, K|f_k{}^{(q-n)}\rangle_R. \end{cases}$$

Now (36) follows directly from (39) and (40).

§ 6. *One-electron operators*

If $\sum_k A_k$ is an arbitrary hermitian one-electron operator

$$(41)\quad \begin{cases} P^{(n)}_{L\,ij} = \langle f_i{}^{(n)}| \sum_{k=1}^{n} A_k|f_j{}^{(n)}\rangle_L \\ P^{(q-n)}_{R\,ij} = \langle f_i{}^{(q-n)}| \sum_{k=1}^{q-n} A_k|f_j{}^{(q-n)}\rangle_R, \end{cases}$$

then

$$(42)\qquad P_{R^{(q-n)}} = -\,\eta P_{L^{(n)}} + \mathbb{1}\, Tr\, A,$$

where

$\eta = 1$, if A is a real operator, *i.e.* commutes with K,

$\eta = -1$, if A is an imaginary operator, *i.e.* anticommutes with K,

$\mathbb{1}$ is the unit matrix and $Tr\, A$ is taken over a basis in the configuration c^1.

Proof I: With the rules for matrix elements of one-electron operators between determinantal functions [14].

We can restrict ourselves to the basis $|g_i{}^{(n)}\rangle_L$. The transformation to $|f_i{}^{(n)}\rangle_L$ is achieved by a similarity transformation with the unitary matrix U (*cf.* (9) and (19)), leaving the relation (42) invariant.

Now

(i) If at least two indices i_j' of $|g_i{}'^{(n)}\rangle_L$ are different from all i_j of $|g_i{}^{(n)}\rangle_L$, then

$$(43)\qquad \langle h_i{}'^{(q-n)}| \sum_{k=1}^{q-n} A_k|h_i{}^{(q-n)}\rangle = \langle g_i{}^{(n)}| \sum_{k=1}^{n} A_k|g_i{}'^{(n)}\rangle_L = 0.$$

(ii) If i_k of $i_1, \dots, i_n$ differs from i_k' of $i_1', \dots i_n'$, the indices i_α and i_α' being furthermore the same, then

$$(44)\quad \left\{\begin{aligned} \langle h_i'^{(q-n)}|\sum_{k=1}^{q-n} A_k|h_i^{(q-n)}\rangle &= (-1)^{\sum\limits_{k=1}^{n} i_k+\sum\limits_{k=1}^{n} i_k'+n_i(i_k,i_k')+n_j(i_k,i_k')} \langle g_i^{(n)}|\sum_{k=1}^{n} A_k|g_i'^{(n)}\rangle_L \\ &= -\langle g_i^{(n)}|\sum_{k=1}^{n} A_k|g_i'^{(n)}\rangle_L. \end{aligned}\right.$$

(The indices $j_1<j_2<\ldots<j_{q-n}$ together with $i_1<i_2 \ \ldots <i_n$ form the set $1, 2, \ldots, q$ of subscripts. $n_i(i_k, i_k')$ and $n_j(i_k, i_k')$ are the number of indices $i_\alpha=i_\alpha'$ and $j_\alpha=j_\alpha'$ in the open interval (i_k, i_k').

Clearly $n_i(i_k, i_k')+n_j(i_k, i_k')=|i_k-i_k'|-1$.

Hence $\sum\limits_{k=1}^{n} i_k+\sum\limits_{k=1}^{n} i_k'+n_i(i_k, i_k')+n_j(i_k, i_k')$ = odd integer.)

(iii) If the indices i_α and i_α' are identical, then

$$(45)\qquad \langle h_i^{(q-n)}|\sum_{k=1}^{q-n} A_k|h_i^{(q-n)}\rangle = -\langle g_i^{(n)}|\sum_{k=1}^{n} A_k|g_i^{(n)}\rangle_L + Tr\,A.$$

Now we consider separately the two possibilities $\eta=1$ and $\eta=-1$, remembering that $Tr\,A$ vanishes, if $\eta=-1$.

Making use of the facts that K is antiunitary and $\sum A_k$ is hermitian (42) can be established from (24), (43), (44) and (45).

Proof II: (This proof is essentially the same as the proof of GRIFFITH [7], but in an appropriate formulation.)

From (28) it can be shown that

$$(46)\qquad |f_i^{(n)}\rangle_L\, K|f_j^{(q-n)}\rangle_R = \binom{q}{n}^{-\frac{1}{2}} |O\rangle\, \delta_{ij} + \sum \psi,$$

where the ψ belong to other representations than the antisymmetric representation of the permutation group S_q.

As $\sum\limits_{k} A_k$ belongs to the identical representation of S_q, it follows from the orthogonality relations for inner products (see for instance Ch. 12 of reference [10]) that

$$(47)\qquad \langle\psi|\sum_{k=1}^{q} A_k|O\rangle = 0.$$

Hence

$$(48)\quad \left\{\begin{aligned} \langle\langle f_i^{(n)}|_L\, K\langle f_j^{(q-n)}|_R\,|\sum_{k=1}^{q} A_k|O\rangle &= \delta_{ij}\binom{q}{n}^{-\frac{1}{2}} \langle O|\sum_{k=1}^{q} A_k|O\rangle = \\ &= \delta_{ij}\binom{q}{n}^{-\frac{1}{2}} Tr\,A. \end{aligned}\right.$$

Furthermore, splitting up

$$\sum_{k=1}^{q} A_k = \sum_{k=1}^{n} A_k + \sum_{k=n+1}^{q} A_k,$$

and making use of the expansion (28) of the closed shell state and again of the facts that K is antiunitary and $\sum A_k$ is hermitian, the left hand side of (48) reduces to

$$\left. \begin{aligned} &\binom{q}{n}^{-\frac{1}{2}} \left\{ \langle f_i^{(n)} | \sum_{k=1}^{n} A_k | f_j^{(n)} \rangle_L + \langle K f_j^{(q-n)} | \sum_{k=1}^{q-n} A_k | K f_i^{(q-n)} \rangle_R \right\} = \\ &\qquad\qquad = \binom{q}{n}^{-\frac{1}{2}} \{ P_L{}^{(n)}{}_{ij} + P_R{}^{(q-n)}{}_{ij} \}. \end{aligned} \right\} \tag{49}$$

From (48) and (49), (42) follows directly.

§ 7. *Two-electron operators*

If $\sum_{k<l} A(k, l)$ is an arbitrary hermitian two-electron operator

$$\left\{ \begin{aligned} Q_L{}^{(n)}{}_{ij} &= \langle g_i^{(n)} | \sum_{k<l}^{n} A(k, l) \, | g_j^{(n)} \rangle_L \\ Q_R{}^{(q-n)}{}_{ij} &= \langle g_i^{(q-n)} | \sum_{k<l}^{q-n} A(k, l) \, | g_j^{(q-n)} \rangle_R, \end{aligned} \right. \tag{50}$$

then

$$Q_R{}^{(q-n)} = Q_L{}^{(n)} - (n-1) \, \langle O | \sum_{k<l}^{q} A(k, l) | O \rangle \, \mathbb{1} + C^{(q-1,n)}, \tag{51}$$

where the matrix elements of $C^{(q-1,n)}$ are formed as follows:

(i) If at least two of the two-electron states of $|g_i^{(n)}\rangle_L$ are different from all one-electron states of $|g_i{}'^{(n)}\rangle_L$, then

$$C_{ii'}^{(q-1,n)} = 0. \tag{52a}$$

(ii) If only one one-electron state v_{i_k} of $|g_i^{(n)}\rangle_L$ differs from one one-electron state $|v_{i_k}{}'\rangle$ of $|g_i{}'^{(n)}\rangle_L$, the one-electron states being furthermore the same, then writing $|v_{i_k}{}^{(q-1)}\rangle_R$ and $|v_{i_k}{}'^{(q-1)})\rangle_R$ for the functions corresponding (*cf.* (17)) with $|v_{i_k}\rangle_L$ and $|v_{i_k}{}'\rangle_L$, it follows that

$$C_{ii'}^{(q-1,n)} = (-1)^{n_i(i_k, i_k')} \, \langle v_{i_k}{}^{(q-1)} | \sum_{k<l}^{q-1} A(k, l) | v_{i_k}{}'^{(q-1)} \rangle_R. \tag{52b}$$

$n_i(i_k, i_k')$ is the number of indices $i_\alpha = i_\alpha'$ in the open interval (i_k, i_k').

(iii) When all the one-electron states are the same the (diagonal) elements are given by

$$C_{ii}^{(q-1,n)} = \sum_{k=1}^{n} \langle v_{i_k}{}^{(q-1)} | \sum_{k<l}^{q-1} A(k, l) | v_{i_k}{}^{(q-1)} \rangle_R. \tag{52c}$$

Proof: The proof can be established with common rules for matrix elements of two-electron operators [14].

For instance, if one one-electron state v_{i_k} of $|g_i^{(n)}\rangle_L$ differs from one one-electron state v_{i_k}' of $|g_i'^{(n)}\rangle_L$, then

$$(53)\quad \left\{\begin{aligned} &\langle h_i'^{(q-n)}|\sum_{k<l}^{q-n} A(k,l)|h_i^{(q-n)}\rangle = \langle g_i^{(n)}|\sum_{k<l}^{n} A(k,l)|g_i'^{(n)}\rangle_L + \\ &\qquad + (-1)^{n_i(i_k,i_k')-1}\sum_{j\neq i_k,i_k'}\{\langle v_{i_k}v_j|A|v_{i_k}'v_j\rangle - \langle v_{i_k}v_j|A|v_jv_{i_k}'\rangle\}, \end{aligned}\right.$$

with the notation

$$(54)\qquad \langle ab|A|cd\rangle \equiv \langle a(1)\,b(2)|A(1,2)|c(1)\,d(2)\rangle.$$

Writing

$$(55)\qquad |v_{i_k}^{(q-1)}\rangle_R = (-1)^{i_k} K|O-(v_{i_k})\rangle,$$

then

$$(56)\quad \left\{\begin{aligned} &\langle v_{i_k}^{(q-1)}|\sum_{k<l}^{q-1} A(k,l)|v_{i_k}'^{(q-1)}\rangle_R = \\ &\qquad = -\eta\sum_{j\neq i_k,i_k'}\{\langle v_{i_k}\,v_j|A|v_{i_k}'\,v_j\rangle - \langle v_{i_k}\,v_j|A|v_j\,v_{i_k}'\rangle\}. \end{aligned}\right.$$

If the one-electron states of $|g_i^{(n)}\rangle_L$ and $|g_i'^{(n)}\rangle_L$ are identical

$$(57)\quad \left\{\begin{aligned} &\langle h_i^{(q-n)}|\sum_{k<l}^{q-n} A(k,l)|h_i^{(q-n)}\rangle = \\ &\qquad = \langle g_i^{(n)}|\sum_{k<l}^{n} A(k,l)|g_i^{(n)}\rangle + \sum_{i<j} f(i,j) - \sum_{i_k,j} f(i_k,j), \end{aligned}\right.$$

where

$$(58)\quad \left\{\begin{aligned} &f(i,j) = J(i,j) - K(i,j) \\ &J(i,j) = \langle v_iv_j|A|v_iv_j\rangle \text{ like a Coulomb integral} \\ &K(i,j) = \langle v_iv_j|A|v_jv_i\rangle \text{ like an exchange integral.} \end{aligned}\right.$$

$$(59)\qquad \langle O|\sum_{k<l}^{q} A(k,l)|O\rangle = \sum_{i<j}^{q} f(i,j) \qquad (=0, \text{ if } \eta=-1).$$

$$(60)\quad \sum_{k=1}^{n}\langle v_{i_k}^{(q-1)}|\sum_{k<l}^{q-1} A(k,l)|v_{i_k}^{(q-1)}\rangle_R = \eta n\sum_{i<j}^{q} f(i,j) - \eta\sum_{i_k,j} f(i_k,j).$$

Remark: Formula (51) holds also in the trivial cases $n=0$ and $n=1$. The matrix $C^{(q-1,n)}$ does not vanish because no simple correspondence exists for arbitrary two-electron operators between the configurations c^1 and c^{q-1}. Hence the relation (51) is as simple as it can be.

§ 8. *Transformation and coupling properties*

I) Transformation properties.

(i) $|f_t^{(n)}\rangle_L$ and $|f_t^{(q-n)}\rangle_R$ have the same transformation properties for all operations of O_p. In particular they have the same transformation properties with respect to G, as each transformation of G generates an operation of O_p. If $|f^{(n)}\rangle_L$ belongs to the row M_Γ of an irreducible representation of Γ of G, then $|f^{(q-n)}\rangle_R$ does too.

(ii) From the general relation (42) it follows that the matrix elements of $\sum s_{t_x}$, $\sum s_{t_y}$, $\sum s_{t_z}$ with respect to the bases $|f_t^{(n)}\rangle_L$ and $|f_t^{(q-n)}\rangle_R$ are identical. (All angular momenta are imaginary operators).

Now $\sum s_{t_x}$, $\sum s_{t_y}$, $\sum s_{t_z}$ do not have non-vanishing matrix elements between states of c^n and other (orthogonal) n-electron states.

The matrices of $(\sum s_{t_x})^2$, $(\sum s_{t_y})^2$, $(\sum s_{t_z})^2$ can be found by matrix multiplication and also are identical. In particular: if $|f^{(n)}\rangle_L$ is an eigenstate of $\mathbf{S}^2 = (\sum \mathbf{s}_t)^2$ for the eigenvalue $S(S+1)$ and of $S_z = \sum s_{t_z}$ for the eigenvalue M_S then the same holds for $|f^{(q-n)}\rangle_R$.

II) Coupling properties.

The functions u_t span a representation γ of G.

The decomposition of γ in irreducible representations is given by

$$\gamma = \sum_{k=1}^{r} \gamma_k. \tag{61}$$

We choose $u_t\uparrow$, $u_t\downarrow$ as a basis in the configuration c^1, where the u_t belong to the rows of the representations γ_k.

Then each function $|g_t^{(n)}\rangle_L$ (*cf.* 7) belongs to a subconfiguration $c_1^{n_1}\, c_2^{n_2} \ldots c_r^{n_r}$, if n_k of the functions v_{t_k} belong to γ_k.

If we assume that each representation γ_k is a representation of type a, *i.e.* γ_k can be brought into a real form by an appropriate choice of basis [15], then if $|f^{(n)}\rangle_L$ belongs to $c_1^{n_1}\, c_2^{n_2} \ldots c_r^{n_r}$, it follows that $|f^{(q-n)}\rangle_R$ belongs to $c_1^{2l_1-n_1}\, c_2^{2l_2-n_2} \ldots c_r^{2l_r-n_r}$, where l_k is the dimension of γ_k.

We now choose the numbering of the v_t such that

$$\begin{array}{ll} u_k\uparrow = v_{2k-1} & u_1, \ldots, u_{l_1} \text{ span } \gamma_1 \\ u_k\downarrow = v_{2k} & u_{l_1+1}, \ldots, u_{l_1+l_2} \text{ span } \gamma_2 \\ & u_{p-l_r+1}, \ldots, u_p \text{ span } \gamma_r. \end{array}$$

Then, if $|g_t^{(n)}\rangle_L$ belongs to the subconfiguration $c_1^{n_1} \ldots c_r^{n_r}$, we can write

$$|g_t^{(n)}\rangle_L = A^{(n)}\left[|g_{t\,(1)}^{(n_1)}(1, 2, \ldots, n_1)\rangle_L \ldots |g_{t\,(r)}^{(n_r)}(n-n_r+1, \ldots, n)\rangle_L\right] \tag{62}$$

where

$$|g_{i\,(1)}^{(n_1)}\rangle_L = |\overbrace{v, v, \ldots, v}^{n_1 \text{ functions}}\rangle, \tag{63}$$

and v moves through the functions v_{i_k} (i_k increasing), belonging to γ_1.

$$A^{(n)} = \frac{1}{\sqrt{n!}} \sum_P \varepsilon(P)\, P, \tag{64}$$

summed over the permutations of 1, 2, …, n, implies antisymmetrization and normalization.

From (17) it follows that

$$\left\{\begin{aligned} g_i{}^{(q-n)}\rangle_R &= (-1)^{i_1+\ldots+i_n+n(n-1)/2}\, K|O-(g_i{}^{(n)})_L\rangle \\ &= (-1)^{i_1+\ldots+i_n+n(n-1)/2}\, K\, A^{(q-n)}\,[|O_1-(g_{i\,(1)}^{(n_1)})_L\rangle \ldots |O_r-(g_{i\,(r)}^{(n_r)})_L\rangle] \\ &= (-1)^{n(n-1)/2} A^{(q-n)}\,[|(-1)^{\Sigma i^{(1)}} K|O_1-(g_{i\,(1)}^{(n_1)})_L\rangle\rangle \ldots |(-1)^{\Sigma i^{(r)}} K|O_r-g_{i\,(r)}^{(n_r)})_L\rangle\rangle] \end{aligned}\right. \tag{65}$$

where

$$|O_1\rangle = |u_1\uparrow, u_1\downarrow, \ldots, u_{l_1}\uparrow, u_{l_1}\downarrow\rangle. \tag{66}$$

is a notation for the closed γ_1 shell.

$\sum i^{(1)}$ is the sum of the indices i_k such that v_{i_k} belongs to γ_1. Then

$$|g_i{}^{(q-n)}\rangle_R = (-1)^{\sum\limits_{i<j}^{r} n_i n_j} A^{(q-n)}[|g_{i\,(1)}^{(2l_1-n_1)}\rangle_R \ldots |g_{i\,(r)}^{(2l_r-n_r)}\rangle_R]. \tag{67}$$

Alternatively we can take linear combinations $|f_{i\,(1)}^{(n_1)}\rangle_L$ of the basis functions $|g_{i\,(1)}^{(n_1)}\rangle_L$.

Since the antisymmetrizing operator does not act on the coefficients, the corresponding function of

$$|f^{(n)}\rangle_L = A^{(n)}\,[|f_{i\,(1)}^{(n_1)}\rangle_L \ldots |f_{i\,(r)}^{(n_r)}\rangle_L] \tag{68}$$

is given by

$$|f^{(q-n)}\rangle_R = (-1)^{\sum\limits_{i<j}^{r} n_i n_j} A^{(q-n)}\,[|f_{i\,(1)}^{(2l_1-n_1)}\rangle_R \ldots |f_{i\,(r)}^{(2l_r-n_r)}\rangle_R]. \tag{69}$$

So if $|f^{(n)}\rangle_L$ can be obtained by coupling from states of $c_1{}^{n_1}, c_2{}^{n_2}, \ldots, c_r{}^{n_r}$ with given transformation properties with respect to G and rotations in spin space (for instance $S_1\Gamma_1, S_2\Gamma_2, \ldots, S_r\Gamma_r$), then $|f^{(q-n)}\rangle_R$ can be obtained by coupling from states of

$$c_1{}^{2l_1-n_1},\ c_2{}^{2l_2-n_2},\ \ldots,\ c_r{}^{2l_r-n_r}$$

with the same transformation properties with respect to G and rotations in spin space.

(for instance $S_1\Gamma_1, S_2\Gamma_2, \ldots, S_r\Gamma_r$).

The factor $(-1)^{mn}$ appearing in formula (9, 42) of reference [7] can be considered as a special case of the factor $(-1)^{\sum\limits_{i<j} n_i n_j}$.

§ 9. *Coulomb interaction*

For the sake of convenience we choose the basis functions $v_1, v_2, \ldots, v_q$ as in § 8 II.

Assumption: Each irreducible representation of G occurs at most once in the reduction (61) of γ.

This assumption is justified in most physically important cases.

Then, if $i \neq i'$, $|v_i^{(q-1)}\rangle_R$ and $|v_{i'}^{(q-1)}\rangle_R$ are either eigenstates of S_z for different eigenvalues, or belong to different representations or different rows of the same representation of G. As the Coulomb interaction belongs to the identical representation of G, all off-diagonal elements of $C^{(q-1,n)}$ (*cf.* (52)) vanish.

If

$$v_{i_1}, \ldots, v_{i_{l_k}} \text{ span } \gamma_k, \text{ being eigenstates of } S_z = \tfrac{1}{2}$$
$$v'_{i_1}, \ldots, v'_{i_{l_k}} \text{ span } \gamma_k, \text{ being eigenstates of } S_z = -\tfrac{1}{2},$$

then

$$\left\{\begin{array}{l} \langle v_{i_j}{}^{(q-1)} | V_{\text{Coul.}} | v_{i_j}{}^{(q-1)}\rangle_R = \langle v'_{i_j}{}^{(q-1)} | V_{\text{Coul.}} | v'_{i_j}{}^{(q-1)}\rangle_R \text{ (which} \\ \text{is independent of } j) \quad = E_{\gamma_k}{}^{(q-1)}, \end{array}\right. \tag{70}$$

where $E_{\gamma_k}{}^{(q-1)}$ is the Coulomb energy of the closed shell in which a γ_k electron is missing.

If $|g_i{}^{(n)}\rangle_L$ belongs to the subconfiguration $c_1{}^{n_1} \ldots c_r{}^{n_r}$, then

$$C_{ii}^{(q-1,n)} = D(n_1, n_2, \ldots, n_r) = n_1 E_{\gamma_1}{}^{(q-1)} + \ldots + n_r E_{\gamma_r}{}^{(q-1)} \tag{71}$$

and

$$Q_R{}^{(q-n)} = Q_L{}^{(n)} - (n-1) E_0 \mathbb{1} + D(n_1, n_2, \ldots, n_r), \tag{72}$$

where

$D(n_1, n_2, \ldots, n_r)$ is a diagonal matrix with elements $D(n_1, n_2, \ldots, n_r)$ and E_0 is the Coulomb energy of the closed shell.

The same relation (72) holds if we choose a basis in c^n composed from arbitrary bases in spaces corresponding to subconfigurations $c_1^{n_1} \dots c_r^{n_r}$.

Application of (72) for the maximal S states in the configuration c^p gives the relation

$$(p-1)\, E_0 = D(l_1, l_2, \dots, l_r) = l_1\, E_{\gamma_1}{}^{(q-1)} + \dots + l_r\, E_{\gamma_r}{}^{(q-1)}. \tag{73}$$

When the representation is irreducible, which is the case in shells, the matrices $Q_R{}^{(q-n)}$ and $Q_L{}^{(n)}$ are equal for any choice of basis in c^n apart from a constant diagonal energy.

That is, *i.e.*

$$Q_R{}^{(q-n)} = Q_L{}^{(n)} + (E_0 - na)\, \mathbb{1}, \tag{74}$$

where a is the difference between the Coulomb energy of the closed shell and of the shell from which one electron is missing.

In particular

$$E_0 = p\, a, \tag{75}$$

which relation is well-known for l shells.

The conclusions of this section also hold for any real two-particle operator, not acting on spin and invariant for transformations of G.

§ 10. *Applications for a half-closed shell*

Let us choose a basis $|f_i{}^{(p)}\rangle_L$ of the configuration c^p.

By (17) and (19) we can define another orthonormal basis $|f_i{}^{(p)}\rangle_R$ of c^p.

If now for certain i

$$|f_i{}^{(p)}\rangle_L = \alpha\, |f_i{}^{(p)}\rangle_R, \tag{76}$$

then we call $|f_i{}^{(p)}\rangle_L$ self conjugated.

We now assume that the phase of the closed shell state is such that

$$K|O\rangle = |O\rangle. \tag{77}$$

This condition is satisfied for instance if we choose as a basis in the configuration c^1

$$v_1, \dots, v_p, v_{p+1}, \dots v_q \leftrightarrow u_1\!\uparrow, \dots, u_p\!\uparrow, u_1\!\downarrow, \dots, u_p\!\downarrow, \quad \text{or} \quad u_k\!\uparrow = v_{2k-1};\ u_k\!\downarrow = v_{2k},$$

where the u_i are such that the determinant of the transformation $u_i \to u_i{}^*$ is equal to 1. The latter condition is satisfied in a trivial way, if the u_i are chosen real, but also if the u_i are functions $|l, m\rangle$. (l is an integer, the transformation to $|l, m\rangle^*$ being described by the matrix

$$\langle l, m' | (l, m)^* \rangle = (-1)^{l-m}\, \delta_{m', -m}. \tag{78}$$

If $K|O\rangle = |O\rangle$, then each self conjugated state has a definite parity, *i.e.* $\alpha = \pm 1$.

Proof: From (28)

$$\left\{ \begin{aligned} |O\rangle &= \sum_i |f_i^{(p)}(1, 2, \ldots, p)\rangle_L\, K|f_i^{(p)}(p+1, \ldots, q)\rangle_R \\ K|O\rangle = |O\rangle &= \sum_i K|f_i^{(p)}(1, 2, \ldots, p)\rangle_L\, K^2|f_i^{(p)}(p+1, \ldots, q)\rangle_R = \\ &= (-1)^p \sum_i |f_i^{(p)}(p+1, \ldots, q)\rangle_R\, K|f_i^{(p)}(1, 2, \ldots, p)\rangle_L. \end{aligned} \right. \tag{79}$$

In addition

$$|v_{p+1}, \ldots, v_q, v_1, \ldots, v_p\rangle = (-1)^{p^2}\, |v_1, \ldots, v_p, v_{p+1}, \ldots, v_q\rangle = (-1)^p |O\rangle. \tag{80}$$

Hence

$$|O\rangle = \sum_i |f_i^{(p)}(1, 2, \ldots, p)\rangle_R\, K|f_i^{(p)}(p+1, \ldots, q)\rangle_L. \tag{81}$$

Alternatively we can take $|f_i^{(p)}\rangle_R$ as a basis $|\phi_i^{(p)}\rangle_L$ of c^p.

The conjugated basis of $|\phi_i^{(p)}\rangle_L$ is defined by

$$|O\rangle = \sum_i |\phi_i^{(p)}\rangle_L\, K|\phi_i^{(p)}\rangle_R. \tag{82}$$

Thus

$$|\phi_i^{(p)}\rangle_R = |f_i^{(p)}\rangle_L. \tag{83}$$

If

$$|f_i^{(p)}\rangle_R = \alpha |f_i^{(p)}\rangle_L, \text{ then } |\phi_i^{(p)}\rangle_R = \alpha |f_i^{(p)}\rangle_R = \alpha^2 |f_i^{(p)}\rangle_L. \tag{84}$$

So $\alpha = \pm 1$, and $|f_i^{(p)}\rangle_L$ has a definite parity.

Remark: A generalization of the considerations above is possible. We can define the double conjugated state $|f^{(n)}\rangle_{RR}$ of $|f^{(n)}\rangle_L$ by

$$|f^{(n)}\rangle_{RR} = |\phi^{(n)}\rangle_R, \text{ if } |\phi^{(q-n)}\rangle_L = |f^{(q-n)}\rangle_R. \tag{85}$$

Then, if $K|O\rangle = |O\rangle$, for arbitrary $|f^{(n)}\rangle_L$:

$$|f^{(n)}\rangle_{RR} = |f^{(n)}\rangle_L. \tag{86}$$

For states with a definite parity we have the following selection rules (*cf.* [1]):

(i) All matrix elements of real traceless hermitian operators between states of the same parity vanish;

(ii) All matrix elements of imaginary hermitian operators between states of different parity vanish.

We can now take as a basis states of the form $|\alpha S\Gamma M_S M_\Gamma\rangle_L$, where α is a set of parameters in order to distinguish the different possibilities $S\Gamma$, Γ is a representation of G and M_Γ indicates the rows of Γ.

(i) If we choose a basis composed from bases of subconfigurations $c_1^{n_1} \dots c_r^{n_r}$, only the states of $c_1^{l_1} \dots c_r^{l_r}$ have a definite parity.

(ii) Each $|\alpha S\Gamma\rangle_R$ can be written as a linear combination of functions $|\alpha S\Gamma\rangle_L$, the coefficients being independent of M_S and M_Γ.

By choosing appropriate linear combinations to be the new $|\alpha S\Gamma\rangle_L$, we can diagonalize the unitary matrix $\langle\alpha' S\Gamma_R|\alpha S\Gamma_L\rangle$.

Then, if $K|O\rangle=|O\rangle$, each $|\alpha S\Gamma\rangle_L$ has a definite parity (*cf.* [1]). Such a situation is realized, if we take the basis functions such that they belong to irreducible representations of O_p. Since corresponding functions $|\rangle_L$ and $|\rangle_R$ have the same transformation properties with respect to O_p, the parity of the basis functions can depend only on the representations of O_p.

In the case of l shells, RACAH has expressed the parity in terms of the seniority v making use of fractional parentage coefficients [2, 3]. For particular cases another approach is very simple.

The parity of the maximal $S=p/2$ states in the configuration c^p can be evaluated in an elementary way by (17). Furthermore for all states of the form $|\dots u_i\uparrow, u_i\downarrow, \dots\rangle$ the diagonal element of the parity operator vanishes, if the u_i are chosen real. Hence we can say that the sum of parities of all states with fixed S_z value is equal to the parity of the maximal S states. Furthermore we can reduce the space of functions with fixed S_z value according to irreducible representations of O_p. Then by application of the diagonal sum rule it may be possible to determine the parities, taking into account that the parity has to be ± 1. A general justification of this procedure may be a difficult problem concerning the irreducible representations of O_p.

We now assume that the high-symmetry (G) components of the Hamiltonian, not acting on spin, give a well defined splitting, and that the low-symmetry (real) one-electron operators and also the spin-orbit coupling are "small". Then, if a certain energy level has a definite parity, (this is certainly the case if $S\Gamma$ occurs once in the decomposition of the space of c^p states), we can conclude that the real low-symmetry one-electron operators and the spin-orbit coupling do not give a first order perturbation on the level *SΓ*. This for instance was pointed out by Sugano and Tanabe for the configuration t_2^3, where all levels *SΓ* occur once [16].

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CHAPTER II

THE VAN VLECK RELATION

§ 1. *Introduction*

The high spin levels of d ions in octahedral symmetric Ligand fields can be expressed in terms of a splitting parameter, for instance the splitting Δ, which the same Ligand field would give in the configuration d^1. In 1932 Van Vleck remarked that in this case the high spin levels have the same relative positions in the configurations d^n and d^{n+5} and also in the configurations d^{5-n} and d^{10-n}, apart from the fact that the order of the levels is inverted [1].

More generally, if we assume that the Coulomb interaction, as for the case of free ions, can be described by Racah parameters [2], we can characterize the Coulomb interaction for the high spin states of d^2, d^3, d^7 and d^8 by $E_p = 15B$, where E_p is the splitting between the "F" and "P" levels in the limit $\Delta \rightarrow 0$.

In actual complexes E_p is always smaller than for the free ion. If now the high spin levels in the configuration d^2 are given by $f_i(\Delta, E_p)$, the relative positions of the high spin levels in the configuration d^7 are the same, but the relative positions in the configurations d^3 and d^8 are given by $f_i(-\Delta, E_p)$.

This can be explained by the hole-equivalence principle [3, 4] together with an additional relation between the high spin states of d^n and d^{n+5} which we might call a Van Vleck relation, in agreement with Jørgenson [5]. (If it is taken into account that the one-electron states cannot be identified with pure d states in an exact way, nine parameters are needed to describe the relative positions of the Coulomb levels [3] and four if we restrict ourselves to high spin states. The relations now are less simple.)

However, a Van Vleck relation holds very generally for arbitrary electron shells and the proof of it is very simple.

Starting from an arbitrary basis of maximal S_z states in the configuration c^n (*cf.* § 2 of [4]) we can obtain by coupling with the minimal S_z state of the half-closed shell and antisymmetrization a basis of minimal S_z states in the configuration c^{n+p}. Both bases have the same transformation properties with respect to the unimodular group SU_p of unitary transformations with determinant 1 in the Hilbert space of $u_1, u_2, \ldots, u_p$.

The basis of minimal S_z states in the configuration c^{n+p} is determined uniquely, apart from a common phase factor, by its transformation properties with respect to SU_p.

Simple relations hold for the matrix elements of one- and two-electron operators not acting on spin.

§ 2. *Basic concepts*

Working with the same formalism as § 2 of [4] we take $|v_i\rangle = |u_i\uparrow\rangle$ $i = 1, 2, \ldots, p$ as basis of maximal $S_z = \frac{1}{2}$ states in the configuration c^1. Furthermore $v_{p+1}, \ldots, v_q = u_1\downarrow, \ldots, u_p\downarrow$.

An orthonormal basis of maximal S_z states in the configuration c^n $(n \leqslant p)$ is given by

$$\psi_i^{(n)} = |v_{i_1}, v_{i_2}, \ldots, v_{i_n}\rangle;\ i_1 < i_2 < \ldots < i_n \leqslant p \tag{1}$$

where i characterizes in an unique way the $\binom{p}{n}$ possibilities

$$i_1 < i_2 < \ldots < i_n \leqslant p.$$

An arbitrary orthonormal basis of maximal S_z states in the configuration c^n is given by

$$\phi_i^{(n)} = \sum_j V_{ji}\, \psi_j^{(n)}, \tag{2}$$

the matrix V being unitary.

As basis states with minimal S_z in the configuration c^{n+p} we can take

$$\psi_i^{(n+p)} = |v_{i_1}, v_{i_2}, \ldots, v_{i_n}, v_{p+1}, \ldots, v_q\rangle \tag{3}$$

and

$$\phi_i^{(n+p)} = \sum_j V_{ji}\, \psi_j^{(n+p)}. \tag{4}$$

Each transformation of SU_p generates an unitary transformation among the $v_1, v_2, \ldots, v_q$

$$U|v_i\rangle = \sum_k U_{ki}\, v_k, \text{ where } \langle v_k|U|v_i\rangle = U_{ki},\ i, k = 1, 2, \ldots, q. \tag{5}$$

Introducing the notation

$$\langle u_k|U|u_i\rangle = u_{ki},\ i, k = 1, 2, \ldots, p, \tag{6}$$

it is obvious that

$$(7)\qquad U_{ki} = \begin{cases} u_{ki} & \text{if } i, k < p \\ u_{k-p,\, i-p} & \text{if } i, k > p \\ 0 & \text{if } i < p\ k > p;\ i > p\ k < p \end{cases}$$

$$|u| = 1$$

since the transformation of SU_p do not act on spin states.

§ 3. *Transformation properties of corresponding functions*

The functions $\phi_i^{(n+p)}$ have the same transformation properties as the functions $\phi_i^{(n)}$ with respect to SU_p.

Proof: We can restrict ourselves to the basis ψ_i and the transformation to the basis ϕ_i in both cases is realized by a similarity transformation with the unitary matrix V.

The functions $\psi_i^{(n+p)}$ transform like

$$U\psi_i^{(n+p)} = \sum_{k_1 < k_2 < \ldots < k_n < k_{p+1} < \ldots < k_q \leqslant q} U_{k_1, \ldots, k_n, k_{p+1}, \ldots, k_q; i_1, \ldots, i_n, p+1, \ldots, q} \times \\ \times |v_{k_1}, \ldots, v_{k_n}, v_{k_{p+1}}, \ldots, v_{k_q}\rangle$$

where

$$(8)\qquad U_{k_1, \ldots, k_q; i_1, \ldots, q} = \left| \begin{array}{cc:cc} U_{k_1 i_1} & U_{k_1 i_n} & U_{k_1\, p+1} & U_{k_1 q} \\ & \mathrm{I} & & \mathrm{II} \\ U_{k_n i_1} & U_{k_n i_n} & U_{k_n\, p+1} & U_{k_n q} \\ \hdashline U_{k_{p+1} i_1} & U_{k_{p+1} i_n} & U_{k_{p+1}\, p+1} & U_{k_{p+1} q} \\ & \mathrm{III} & & \mathrm{IV} \\ U_{k_q i_1} & U_{k_q i_n} & U_{k_q\, p+1} & U_{k_q q} \end{array} \right| .$$

All $k_1, \ldots, k_n$ in the right hand side of (8) must satisfy

$$(9)\qquad k_1 < k_2 < \ldots < k_n \leqslant p.$$

Then from (7)

$$(10)\qquad \begin{cases} \mathrm{II} = 0 \\ |\mathrm{IV}| = \delta_{k_{p+1}, p+1} \ldots \delta_{k_q, q}. \end{cases}$$

$$(11)\qquad \left| \begin{array}{c:c} \mathrm{I} & \mathrm{II} \\ \hdashline \mathrm{III} & \mathrm{IV} \end{array} \right| = |\mathrm{I}|\,|\mathrm{IV}| = U_{k_1 \ldots k_n, i_1 \ldots i_n}\, \delta_{k_{p+1}, p+1} \ldots \delta_{k_q, q}.$$

Substituting this in (8)

$$U\psi_i^{(n+p)} = \sum_{k_1<\ldots<k_n\leqslant p} U_{k_1\ldots k_n,\, i_1\ldots i_n}\, \psi_k^{(n+p)}. \tag{12}$$

Clearly also

$$U\psi_i^{(n)} = \sum_{k_1<\ldots<k_n\leqslant p} U_{k_1\ldots k_n,\, i_1\ldots i_n}\, \psi_k^{(n)}. \tag{13}$$

Remark: Corresponding functions $\phi^{(n)}$ and $\phi^{(n+p)}$ have the same transformation properties with respect to SU_p. In particular $\phi^{(n+p)}$ has the same transformation properties as $\phi^{(n)}o$ with respect to the symmetry group G, which leaves the one-particle Hamiltonian h invariant (*cf.* § 2 of [4]). o is the high spin state of the half-closed shell; it is symmetric in the spin-dependent part and anti-symmetric in the orbital part. It belongs to a one dimensional representation of the symmetry group G which is not necessarily the identical representation. For instance, in the case of t_2 shells, d ions in octahedral fields [3], the high spin state of the half-closed shell is $^4A_2$. Then $^3T_1$ of $t_2{}^4$ corresponds to $^2T_2$ of $t_2{}^1$ and $^2T_2$ of $t_2{}^5$ corresponds to $^3T_1$ of $t_2{}^2$. In the case of l shells o belongs to the identical representation $D^{(0)}$ of the rotation group and $\phi^{(n)}$ and $\phi^{(n+p)}$ have the same transformation properties with respect to G.

The basis $\phi_i^{(n+p)}$ is determined uniquely apart from a common phase factor by its transformation properties with respect to SU_p. This follows directly from Schur's lemma [6] and the fact that the matrices

$$U_{k_1\ldots k_n,\, i_1\ldots i_n} = \begin{vmatrix} u_{k_1 i_1} & u_{k_1 i_n} \\ u_{k_n i_1} & u_{k_n i_n} \end{vmatrix} \quad \begin{matrix} k_1<\ldots<k_n\leqslant p \\ i_1<\ldots<i_n\leqslant p \end{matrix} \tag{14}$$

span an irreducible representation of SU_p.

Although the latter fact is well-known from more general group theoretical considerations [7], a simple proof is possible along the lines of Wigner's proof [8] of the irreducibility of representations $D^{(L)}$ of the rotation group, making use of Schur's lemma.

Suppose $V_{k_1\ldots k_n,\, i_1\ldots i_n}$ commutes with $U_{k_1\ldots k_n,\, i_1\ldots i_n}$ for all $U \in SU_p$ then

$$\left\{ \begin{aligned} &\sum_{j_1<j_2<\ldots<j_n\leqslant p} U_{k_1\ldots k_n,\, j_1\ldots j_n}\, V_{j_1\ldots j_n,\, i_1\ldots i_n} = \\ &= \sum_{j_1<j_2<\ldots<j_n\leqslant p} V_{k_1\ldots k_n,\, j_1\ldots j_n}\, U_{j_1\ldots j_n,\, i_1\ldots i_n}. \end{aligned} \right. \tag{15}$$

When the sets $k_1 \dots k_n$ and $i_1 \dots i_n$ are not identical

$k_1 \dots k_n$ contains an index a, not occurring in $i_1 \dots i_n$

$i_1 \dots i_n$ contains an index b, not occurring in $k_1 \dots k_n$.

Define: u diagonal

$$\begin{cases} u_{aa} = e^{i\alpha} & \alpha \neq k\pi \\ u_{bb} = e^{-i\alpha} & \\ u_{ii} = 1 & \text{for } i \neq (a, b) \end{cases} \tag{16}$$

then

$$U \in \mathrm{SU_p} \text{ and } V_{k_1, \dots, k_n, i_1, \dots, i_n} = 0. \tag{17}$$

So V is a diagonal matrix.

Hence for all $U \in \mathrm{SU_p}$

$$U_{k_1 \dots k_n, i_1 \dots i_n} V_{i_1 \dots i_n, i_1 \dots i_n} = V_{k_1 \dots k_n, k_1 \dots k_n} U_{k_1 \dots k_n, i_1 \dots i_n}. \tag{18}$$

Suppose $l_1 < l_2 < \dots < l_{p-n}$ form together with $k_1 < k_2 < \dots < k_n$ the set of subscripts $1, 2, \dots p$ and $j_1 < j_2 < \dots < j_{p-n}$ form together with $i_1 < i_2 < \dots < i_n$ a similar set.

Define

$$\begin{cases} u_{k_\alpha m} = \delta_{m i_\alpha} \text{ for } \alpha = 1, \dots, n \\ u_{l_\beta m} = \delta_{m j_\beta} \text{ for } \beta = 1, 2, \dots, (p-n-1) \\ u_{l_{p-n} m} = \varepsilon \delta_{m j_{p-n}}, \text{ where } \varepsilon \text{ is such that } |u| = 1, \end{cases} \tag{19}$$

then

$$U \in \mathrm{SU_p} \text{ and } U_{k_1 \dots k_n, i_1 \dots i_n} = 1 \neq 0. \tag{20}$$

So V is a multiple of the unit matrix and the matrices $U_{k_1 \dots k_n, i_1 \dots i_n}$ span an irreducible representation of $\mathrm{SU_p}$.

It is interesting to remark that the functions $\phi^{(n)}$ also span an irreducible representation of $\mathrm{O_p}$. If the one-particle hamiltonian h is a real operator (*cf.* [4]), we can choose the basis functions u_i real and then the orthogonal transformations among $u_1, u_2, \dots, u_p$ are represented by the group of orthogonal matrices with p rows and columns.

When the sets $k_1 \dots k_n$ and $i_1 \dots i_n$ are not identical, we can define (*cf.* 16)

$$\begin{cases} t_{aa} = -1 & \\ t_{ii} = 1 & \text{for } i \neq a, \end{cases} \tag{21}$$

so that V is a diagonal matrix. Furthermore, each matrix $V_{k_1 \dots k_n, i_1 \dots i_n}$ commuting with all $T_{k_1 \dots k_n, i_1 \dots i_n}$ for $T \in \mathrm{O_p}$ is a multiple of the unit matrix.

§ 4. *One- and two-electron operators*

If $\sum_k A_k$ is an arbitrary (linear) one-electron operator not acting on spin

$$(22)\qquad \begin{cases} P^{(n+p)}{}_{ij} = \langle \phi_i{}^{(n+p)} | \sum_{k=1}^{n+p} A_k | \phi_j{}^{(n+p)} \rangle \\ P^{(n)}{}_{ij} \quad = \langle \phi_i{}^{(n)} | \sum_{k=1}^{n} A_k | \phi_j{}^{(n)} \rangle, \end{cases}$$

then

$$(23)\qquad P^{(n+p)} = P^{(n)} + \mathbb{1}\, Tr^0 A,$$

where

$$(24)\qquad \mathbb{1} \text{ is the unit matrix and } Tr^0 A = \sum_{k=1}^{p} \langle u_k | A | u_k \rangle.$$

If $\sum_{k<l} A(k,l)$ is an arbitrary (linear) two-electron operator not acting on spin

$$(25)\qquad \begin{cases} Q^{(n+p)}{}_{ij} = \langle \psi_i{}^{(n+p)} | \sum_{k<l}^{n+p} A(k,l) | \psi_j{}^{(n+p)} \rangle \\ Q^{(n)}{}_{ij} \quad = \langle \psi_i{}^{(n)} | \sum_{k<l}^{n} A(k,l) | \psi_j{}^{(n)} \rangle, \end{cases}$$

then

$$(26)\qquad Q^{(n+p)} = Q^{(n)} - (n-1) \langle o | \sum_{k<l}^{p} A(k,l) | o \rangle\, \mathbb{1} + C^{(p+1,n)},$$

where o is the high spin state of the half-closed shell.

The matrix elements of $C^{(p+1,n)}$ are formed as follows:

(i) If at least two of the one-electron states of $\psi_i{}^{(n)}$ are different from all one-electron states of $\psi_i{}'^{(n)}$, then

$$(27a)\qquad C_{ii'}^{(p+1,n)} = 0.$$

(ii) If only one one-electron state v_{i_k} of $\psi_i{}^{(n)}$ differs from one one-electron state v_{i_k}' of $\psi_i{}'^{(n)}$, the one-electron states being furthermore the same and in addition in the configuration c^{p+1} the functions $v_{i_k}{}^{(p+1)}$ and $v_{i_k}{}'^{(p+1)}$ (with minimal S_z) correspond with v_{i_k} and v_{i_k}', then

$$(27b)\qquad C_{ii'}^{(p+1,n)} = (-1)^{n_i(i_k, i_k')} \langle v_{i_k}{}^{(p+1)} | \sum_{k<l}^{p+1} A(k,l) | v_{i_k}{}'^{(p+1)} \rangle,$$

where $n_i(i_k, i_k')$ is the number of indices $i_\alpha = i_\alpha'$ in the open interval (i_k, i_k').

(iii) If the sets of the one-electron states are identical, then

$$C_{ii'}^{(p+1,n)} = \sum_{k=1}^{n} \langle v_{i_k}{}^{(p+1)}| \sum_{k<l}^{p+1} A(k,l)|v_{i_k}{}^{(p+1)}\rangle. \tag{27c}$$

The proof of these relations is simple, making use of the rules for matrix elements of one- and two-electron operators between determinantal functions [9]. In addition we can use the following relations, (*cf.* [4])

$$\langle v_{i_k}{}^{(p+1)}| \sum_{k<l}^{p+1} A(k,l)|v_{i_k}{}'^{(p+1)}\rangle = \sum_{j=1}^{p} \langle u_{i_k} u_j|A|u_{i_k}{}' u_j\rangle \tag{28a}$$

$$\langle v_{i_k}{}^{(p+1)}| \sum_{k<l}^{p+1} A(k,l)|v_{i_k}{}^{(p+1)}\rangle = \sum_{j=1}^{p} \langle u_{i_k} u_j|A|u_{i_k} u_j\rangle + \langle o| \sum_{k<l}^{p} A(k,l)|o\rangle \tag{28b}$$

$$\langle o| \sum_{k<l}^{p} A(k,l)|o\rangle = \sum_{i<j}^{p} f(i,j) = \sum_{i<j}^{p} \{\langle u_i u_j|A|u_i u_j\rangle - \langle u_i u_j|A|u_j u_i\rangle\}. \tag{28c}$$

Formula (26) holds also in the trivial cases $n=0$ and $n=1$. The matrix $C^{(p+1,n)}$ does not vanish because no simple correspondence exists for two-electron operators between the high spin states of c^1 and c^{p+1}. The analogy of (26) and (27) with the corresponding hole-equivalence relations (51) and (52) of reference [4] is remarkable.

§ 5. *Coulomb interaction*

We choose the functions u_i such that they belong to different rows of the representations γ_k into which the representation $\gamma = \sum_{k=1}^{r} \gamma_k$ can be decomposed (*cf.* § 8, § 9 of [4]).

Assumption: Each irreducible representation of G occurs at most once in the reduction of γ.

Then all off-diagonal elements of $C^{(p+1,n)}$ vanish.

If $u_{i_1}, \ldots, u_{i_{l_k}}$ span γ_k, then

$$\langle v_{i_j}{}^{(p+1)}|V_{\text{Coul.}}|v_{i_j}{}^{(p+1)}\rangle = (\text{which is independent of } j) = E_{\gamma_k}{}^{(p+1)}, \tag{29}$$

where $E_{\gamma_k}{}^{(p+1)}$ is the Coulomb energy of the high spin state o of the half-closed shell, to which a γ_k electron is added.

Each function $\psi_i{}^{(n)}$ belongs to a subconfiguration $c_1{}^{n_1} \ldots c_r{}^{n_r}$ with $n_1 + \ldots + n_r = n$, if n_j of the functions $v_{i_1}, \ldots, v_{i_n}$ belong to γ_j. (Only those combinations $n_1 + \ldots + n_r = n$ appear which can give maximal S_z states in the configuration c^n.)

Then

$$Q^{(n+p)} = Q^{(n)} - (n-1)\, E_{ho}\; \mathbb{1} + D_1\,(n_1, n_2, \ldots, n_r), \tag{30}$$

where E_{ho} is the Coulomb energy of the high-spin state of the half-closed shell.

$$D_1(n_1, n_2, \ldots, n_r) = n_1\, E_{\gamma_1}{}^{(p+1)} + \ldots + n_r\, E_{\gamma_r}{}^{(p+1)}. \tag{31}$$

The same relation holds if we choose a basis of maximal S_z states in c^n composed from arbitrary bases in spaces corresponding to the subconfigurations $c_1{}^{n_1} \ldots c_r{}^{n_r}$.

In particular for $n = p$

$$D_1(l_1, l_2, \ldots, l_r) = l_1\, E_{\gamma_1}{}^{(p+1)} + \ldots + l_r\, E_{\gamma_r}{}^{(p+1)} = E_o + (p-2)\, E_{ho}, \tag{32}$$

where E_o is the Coulomb energy of the closed shell.

When the representation γ is irreducible, which is the case in l shells, the matrices $Q^{(n)}$ and $Q^{(n+p)}$ are equal for any choice of basis of maximal S_z states in c^n, apart from a constant diagonal energy.

That is,

$$Q^{(n+p)} = Q^{(n)} + \{E_{ho} + nb\}\, \mathbb{1}, \tag{33}$$

where b is the increase in Coulomb energy if we add an electron to the high spin state of the half-closed shell.

Here in particular

$$pb = E_o - 2\, E_{ho}. \tag{34}$$

The conclusions of this section hold also for any real two-particle operator not acting on spin and invariant for G.

(In the case of the Coulomb interaction in l shells, b reduces to $(2l+1)\, F_o$, where F_o is the Slater–Condon parameter, which can be derived using the addition theorem for spherical harmonics.)

§ 6. *Remarks*

(i) From the Van Vleck relation and the hole-equivalence principle, we get a simplified calculation scheme for the high spin states for matrix elements of one- and two-electron operators, not acting on spin. We only have to calculate the matrix elements for the high spin states in the configurations c^n with $n < p/2$ if p is even and $n < \frac{1}{2}(p-1)$ if p is odd. The corresponding basis functions are given by (§ 3 and § 4 of [4]).

(35)

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\begin{array}{l}\text{Maximal } S_z \text{ states in } c^n\\ \psi_i^{(n)}=|u_{i_1},\dots,u_{i_n}\rangle\uparrow(1)\dots\uparrow(n)\\ \qquad\qquad i_1<i_2<\dots<i_n\leqslant p\\ \phi_i^{(n)}=\sum\limits_k V_{ki}\psi_k^{(n)},\ V \text{ unitary}\end{array} \arrow[r, "\begin{array}{l}\text{Hole-}\\ \text{equivalence}\\ \text{principle}\end{array}"] \arrow[d, "\begin{array}{l}\text{Van}\\ \text{Vleck}\\ \text{relation}\end{array}"', "\begin{array}{l}\text{Same transformation}\\ \text{properties for } \mathrm{SU}_p\\ \phi_i^{(n+p)} \text{ transforms like}\\ \phi_i^{(n)}\, o \text{ with respect to G}\end{array}"] & \begin{array}{l}\text{Maximal } S_z \text{ states in } c^{q-n}\\ \psi_i^{(q-n)}=(-1)^{i_1+\dots+i_n+n(n-1)/2+p}\times\\ \times|u_{j_1}^*\downarrow,\dots,u_{j_{p-n}}^*\downarrow,u_1^*\uparrow,\dots,u_p^*\uparrow\rangle\\ \phi_i^{(q-n)}=\sum\limits_k V_{ki}\psi_k^{(q-n)}\end{array} \arrow[d, "\begin{array}{l}\text{Same}\\ \text{transformation}\\ \text{properties for}\\ \mathrm{O}_p \text{ in particular}\\ \text{for G}\end{array}"', "\begin{array}{l}(j_1<j_2<\dots<j_{p-n} \text{ from together with}\\ \qquad i_1<i_2<\dots<i_n\\ \text{the set of subscripts } 1,2,\dots,p)\end{array}"] \\
\begin{array}{l}\text{Minimal } S_z \text{ states in } c^{n+p}\\ \psi_i^{(n+p)}=|u_{i_1}\uparrow,\dots,u_{i_n}\uparrow,u_1\downarrow,\dots,u_p\downarrow\rangle\\ \phi_i^{(n+p)}=\sum\limits_k V_{ki}\psi_k^{(n+p)}\end{array} \arrow[r, "\begin{array}{l}\text{Hole-}\\ \text{equivalence}\\ \text{principle}\end{array}"'] & \begin{array}{l}\text{Minimal } S_z \text{ states in } c^{p-n}\\ \psi_i^{(p-n)}=(-1)^{i_1+\dots+i_n+n(n-1)/2+pn}\times\\ \qquad\times|u_{j_1}^*\downarrow,\dots,u_{j_{p-n}}^*\downarrow\rangle\\ \phi_i^{(p-n)}=\sum\limits_k V_{ki}\psi_k^{(p-n)}\end{array}
\end{tikzcd}$$

All the bases in this scheme are defined uniquely (apart from a common phase factor) by their transformation properties with respect to O_p and SU_p (see § 3). The matrix elements P and Q of one- and two-electron operators not acting on spin can be obtained from those in the configuration c^n by applying the hole-equivalence relations (§ 6, § 7 and § 9 of reference [4]) and the Van Vleck relations (§ 4 and § 5).

(ii) In the foregoing it has been assumed that all one-electron wave functions have the same radial part in all configurations c^n.

If n increases this assumption is not allowed because of the increasing effective nuclear charge. However, most relevant one-electron operators are separable, *i.e.* $A(r, \theta, \phi)=A_r(r)\, A_\omega(\theta, \phi)$.

If we introduce a set of parameters $\langle\alpha|A_r(r)|\alpha'\rangle$, where α and α' can be substituted for the different possibilities of the radial part, the equivalences still hold, if one expresses the matrix elements in terms of the parameters. Also if one introduces an appropriate parametrization for the Coulomb interaction (for instance Slater–Condon parameters or RACAH parameters [2, 9, 10] in the case of l shells or ten parameters

$a, b, \ldots, j$ for d ions in octahedral complexes [3]), the hole-equivalence relation and the Van Vleck relation will be satisfied in terms of the parameters.

(iii) The treatment of the hole-equivalence principle (see [4]) can be generalized for nuclear shells by a generalization of WIGNER's time reversal operator K [11] in the sense of a conjugation operator $K=K_o U$ [12]. However, some difficulties appear. For instance, if we consider configurations j^k where j is a half odd integer together with the isotopic spin $\boldsymbol{T}$ [13], the group of unitary transformations commuting with K is not the orthogonal group O_{2j+1}, but the symplectic group Sp_{2j+1}, which leaves the bilinear form $\sum_m (-1)^{j-m}\,\phi_1(m)\,\phi_2(-m)$ invariant. The matrices in the configuration c^1 form a representation of type c, which in spite of the real group characters cannot be brought into a real form [14]. In this case it is not true that the maximal T_z states of a configuration j^k span an irreducible representation of Sp_{2j+1}, (for an example see e.g. [7]).

In nuclear shell theory, however, the deviations of spherical symmetry are less important and the hole-equivalence relations can be expressed in terms of reduced matrix elements of tensor operators.

§ 7. *Spin-orbit coupling*

In general we can write the spin-orbit coupling in the form

$$\mathfrak{H}_{so}=\zeta \sum_{k=1}^{n} \mathbf{t}_k\cdot \mathbf{s}_k, \tag{36}$$

where $\mathbf{t}_k$ is an imaginary operator transforming with respect to G as an axial vector. By the group replacement theorem (see e.g. [3]) each operator $\boldsymbol{S}_i$ can be replaced by $\alpha_n(S)\boldsymbol{S}$ if we are restricted to the states with fixed value of S in any configuration c^n. $\alpha_n(S)$ is independent of i, as the spin-orbit coupling is symmetric for interchanging particles.

Thus for the high spin states of c^n:

$$\mathfrak{H}_{so}=\zeta\alpha_n(S_{\max})\,\boldsymbol{T}\cdot\boldsymbol{S}, \tag{37}$$

where

(38) $\boldsymbol{T}$ is a formal expression for $\boldsymbol{T}=\sum_i \mathbf{t}_i$.

For $n<p$ the high spin states are symmetric in the spin-dependent part. Thus

$$\alpha_n(S_{\max})=\frac{1}{n}=\frac{1}{2\,S_{\max}}. \tag{39}$$

From the hole-equivalence relation (42) of reference [4]

$$P^{(q-n)} = -P^{(n)}. \tag{40}$$

for the spin orbit coupling.

Hence for the high spin states

$$\mathfrak{H}_{so} = \pm \frac{\zeta}{2\,S_{\max}}\, \boldsymbol{T} \cdot \boldsymbol{S}, \tag{41}$$

where + holds if the shell is less than half filled and − holds if the shell is more than half filled.

The matrix elements of $\boldsymbol{T} = \sum_i \mathbf{t}_i$ in the configuration c^n can be evaluated with the rules for matrix elements of one-electron operators between determinantal functions. The matrices of $\boldsymbol{T}$ with respect to the four bases in the scheme (35) are identical (*cf.* (23) and also (42) of reference [4]).

Analogous evalations are possible for the hyper fine structure. Here we get a term of the form $\boldsymbol{I} \cdot \mathrm{T} \cdot \boldsymbol{S}$, where T is a real one-electron operator, transforming under operations of G as a tensor of rank two.

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CHAPTER III

ON THE THEORY OF d-IONS IN LIGAND FIELDS

§ 1) *Introduction*

There are two relations which can be useful in order to establish a scheme of properties of an arbitrary electron shell.

i) The hole equivalence relation between the configuration with n electrons in the shell and the configuration with $2p-n$ electrons *i.e.* the closed shell ($2p$ electrons) with n electrons missing.

ii) The van Vleck relation between the high spin states of the configuration with n electrons and the high spin states of the configuration with $n+p$ electrons. The latter states can be obtained by coupling to the high spin states of the configuration with n electrons the high spin state of the half closed shell and antisymmetrizing.

These relations can be formulated as follows. Starting from an arbitrary basis of n electron states, we can indicate a basis in the equivalent configurations, which is closely connected in transformation properties with respect to the symmetry group of the Hamiltonian (*i.e.* in the case of the hole equivalence principle exactly the same transformation properties and in the case of the van Vleck relation the same transformation properties apart from the factor by which the orbital part of the high spin state of the half closed shell, – completely antisymmetric in interchanging electrons –, is multiplied) and such there is a very simple correspondence between the matrix elements of one electron operators relative to the bases.

As distinct from the hole equivalence relation which applies generally to all the states of equivalent configurations, the van Vleck relation is restricted to the maximal S states of the configurations and the correspondence for the matrix elements of one electron operators is restricted to operators not acting on spin.

The hole equivalence principle was proved for the case of spherical symmetry by Racah [1] and for the case of d ions in octrahedral Ligand fields by Griffith [2]. However a proof is possible independent of the transformation properties of the one electron states, which determine the shell [3]. This is also the case for the van Vleck relation [4], originally established for a simple case by van Vleck [5]. The name van Vleck relation is due to Jørgenson [6]. Using these relations a simple survey of some properties of electron shells can be established. In particular we shall treat the problem of d ions in octahedral Ligand fields, with in addition a small tetragonal or trigonal component.

Since we are restricted to the high spin states, the following considerations are useful for paramagnetic resonance quantities, if no spin pairing occurs, *i.e.* the Ligand field is not so strong as to give the spin in the ground state of the configurations d^4, d^5, d^6, d^7 a lower value than the maximal S value.

§ 2) *d ions in octahedral Ligand fields*

Let us consider a d ion in an octahedral Ligand field. Due to the covalent bonds the one electron states can not be identified with pure d states. We may choose linear combinations of atomic orbitals [7–10]. However, since we are restricted to the lowest energy levels, it is reasonable to assume, that the partly filled shells of the complex span the same representations of the octahedral group O_h as pure d states [11].

As a basis of one electron orbitals we choose the functions u, v, ξ, η, ζ, where u and v span the representation e of O_h and transform as $(2z^2-x^2-y^2)$ and $(x^2-y^2)\sqrt{3}$, and ξ, η, ζ, span the representation t_2 of O_h and transform as yz, xz, xy.

(The parity subscripts g and u of the representations have been omitted in order to make the considerations of this section applicable to the case of the tetrahedral symmetry T_d. In the case of d ions all the representations have even parity and hence are representations g.)

The octahedral Ligand field acting on a d ion gives a splitting in two levels e and t_2, separated by a distance Δ.

$$E_e - E_{t_2} = \Delta,\ E_e = {}^3/_5\,\Delta,\ E_{t_2} = -\,{}^2/_5\,\Delta.$$

Δ is positive in octahedral complexes with 6 co-ordination as can be shown easily from electrostatic as well from molecular orbital considerations.

However, in tetrahedral complexes and also in octahedral complexes with 8 and 12 co-ordination, Δ is negative [12].

The high spin states of the configuration d^2 are antisymmetrical in the orbital part and symmetrical in the spin dependant part ($S=1$). Omitting for the moment the spin dependant part, we can take as a basis the 10 orbitals

$$|u, v\rangle, \ldots, |\eta, \zeta\rangle,$$

where

$$|u, v\rangle \equiv \frac{1}{\sqrt{2}} \{u(1)\, v(2) - v(1)\, u(2)\}.$$

On the other hand we can take a basis of the form

1)

Subconfiguration of d^2	representation of O_h	energy	basis states	transformation properties relative to O_h
e^2	A_2	$\frac{6}{5}\Delta$	$\|e^2A_2\rangle$	a_2
t_2e	T_1	$\frac{1}{5}\Delta$	$\|X_{t_2eT_1}\rangle, \|Y_{t_2eT_1}\rangle, \|Z_{t_2eT_1}\rangle$	I_x, I_y, I_z
	T_2		$\|X_{t_2eT_2}\rangle, \|Y_{t_2eT_2}\rangle, \|Z_{t_2eT_2}\rangle$	ξ, η, ζ
t_2^2	T_1	$-\frac{4}{5}\Delta$	$\|X_{t_2^2T_1}\rangle, \|Y_{t_2^2T_1}\rangle, \|Z_{t_2^2T_1}\rangle$	I_x, I_y, I_z.

I_x, I_y, I_z, are the x, y, z components of an angular momentum operator. This basis is called the *strong field representation*, the basis states are eigenstates of the Hamiltonian in the limit $\Delta \to \infty$, *i.e.* if the Coulomb interaction can be neglected with respect to the Ligand field.

Another choice of basis is the *Russell Saunders representation*, the basis states are eigenstates of the Hamiltonian in the limit $\Delta \to 0$, *i.e.* if the Ligand field can be neglected compared with the Coulomb interaction.

Due to the Coulomb interaction the two T_1 levels in (1) will be mixed up. If we take into account the Ligand field as well as the Coulomb interaction, then the states of the lowest T_1 level will be given by

$$a|\ \ldots\ t_2{}^2T_1\rangle + b|\ \ldots\ t_2eT_1\rangle,$$

whereas the states of the highest T_1 level will be given by

$$-b|\ \ldots\ t_2{}^2T_1\rangle + a|\ \ldots\ t_2eT_1\rangle, \ \ldots \text{ signifies } X, Y, \text{ or } Z.$$

If we assume the other terms in the Hamiltonian, in particular, the low symmetry components of the Ligand field and the spin orbit coupling small with respect to the Coulomb interaction and the octahedral component of the Ligand field, then we can apply a perturbation calculation. In this way physical quantities such as for instance g factors and hyper fine structure constants can be expressed in terms of a and b. This can be useful, since in most cases the Coulomb interaction and the Ligand field are of the same order of magnitude, so that neither the strong field approximation in which the states of the strong field representation are assumed to be the eigenstates of the Hamiltonian, nor the Russell Saunders approximation will give correct results. In addition, from the formulae obtained in this way, the correctness of both approximations can be investigated directly.

Using the van Vleck relation and the hole equivalence principle we can construct a basis of high spin orbitals of d^4, d^6, d^9 with the same transformation properties as u, v, ξ, η, ζ (the high spin state of d^5 is invariant for rotations). In addition we can choose a basis of high spin orbitals of d^3, d^7, d^8 with the same transformation properties as the basis for d^2.

For an arbitrary, hermitian and traceless, one electron operator, not acting on spin, we have the following relations for the matrix elements relative to the bases in the equivalent configurations:

i) If the operator is real, (*i.e.* commutes with WIGNER's time reversal operator K [13]), then the matrix elements in d^1 and d^6 resp. d^2 and d^7 are the same, whereas the matrices for d^4 and d^9 resp. d^3 and d^8 follow from the matrices for d^1 and d^2 by multiplication with -1.

ii) If the operator is imaginary, (*i.e.* anticommutes with K, such as is the case for all angular momenta), then the matrices with respect to d^1, d^4, d^6, d^9 resp. d^2, d^3, d^7, d^8 are the same.

The most important two electron operator is the Coulomb interaction. Although in the general case of octahedral symmetry an exact description of the Coulomb interaction involves 10 parameters *cf.* [2] or 5, if we are restricted to the high spin states, we shall assume, that the Coulomb interaction as in the case of free ions can be described by RAČAH parameters [14]. This can be justified in a sense since in most cases it is not possible to determine all the parameters uniquely.

In particular:

The Coulomb interaction in the absence of a Ligand field splits the high spin states of d^2 in two levels:

i) a "F level" with 7-fold degeneracy, the eigenstates being obtained from the one electron states by coupling with the same coupling coefficients as the ^3F states of the pure configuration d^2 from pure d states.

ii) a "P level" with 3-fold degeneracy, the eigenstates being obtained from the one electron states by coupling with the same coupling coefficients as the ^3P states of the pure configuration d^2 from pure d states.

Then the Coulomb interaction for the high spin states can be described by one parameter E_p, *i.e.* the splitting between the "F level" and the "P level". Due to covalent bonds E_p is always smaller than in the case of free ions. If we choose an arbitrary basis of high spin orbitals of d^2 and construct the corresponding bases of d^3, d^7, d^8, then the matrices of the Coulomb interaction with respect to the four bases are the same.

Now the problem of calculating matrix elements of operators has been reduced to the problem of calculating them for d^1 and d^2. The work involved in these calculations can be reduced greatly by application of well-known methods such as for instance methods of tensor operators, for the case of d ions in octahedral Ligand fields developed by TANABE and KAMIMURA [15].

§ 3) *d ions in octahedral Ligand fields* (*continued*)

We consider the problem of a d^2 ion. The Ligand field together with the Coulomb interaction does not have non vanishing matrix elements between the Z states of both T_1 levels and other states. Denoting those states by $|Z_{t_2^2 T_1}\rangle$ and $|Z_{t_2 e T_1}\rangle$ we get the following matrix

$$(2) \qquad \left\{ \begin{array}{lcc} \mathscr{H}_{\text{lig.}} + \mathscr{H}_{\text{coul.}} & |Z_{t_2^2 T_1}\rangle & |Z_{t_2 e T_1}\rangle \\ \langle Z_{t_2^2 T_1}| & -{}^{4}/_{5}\Delta + {}^{1}/_{5}E_p & {}^{2}/_{5}E_p \\ \langle Z_{t_2 e T_1}| & {}^{2}/_{5}E_p & {}^{1}/_{5}\Delta + {}^{4}/_{5}E_p. \end{array} \right.$$

Now from (1) and (2) we find the following energy levels

$$(3) \qquad \left\{ \begin{array}{l} E_{T_1'} = {}^{1}/_{2}(E_p - {}^{3}/_{5}\Delta) + {}^{1}/_{2}(\Delta^2 + E_p^2 + {}^{6}/_{5}\Delta E_p)^{1/2} \\ E_{A_2} = {}^{6}/_{5}\Delta \\ E_{T_2} = {}^{1}/_{5}\Delta \\ E_{T_1} = {}^{1}/_{2}(E_p - {}^{3}/_{5}\Delta) - {}^{1}/_{2}(\Delta^2 + E_p^2 + {}^{6}/_{5}\Delta E_p)^{1/2}. \end{array} \right.$$

The constants a and b are given by

$$(4) \qquad \left\{ \begin{array}{l} a = [{}^{25}/_{8}(1 + x^2 + {}^{6}/_{5}x) - ({}^{15}/_{8} + {}^{25}/_{8}x)(1 + x^2 + {}^{6}/_{5}x)^{1/2}]^{-1/2} \\ b = [{}^{3}/_{4} + {}^{5}/_{4}x - {}^{5}/_{4}(1 + x^2 + {}^{6}/_{5}x)^{1/2}]\, a, \end{array} \right.$$

where

$$x = \frac{\Delta}{E_p}.$$

In the limit case $x \to 0$ one gets $a = \sqrt{{}^{4}/_{5}}$, $b = -\sqrt{{}^{1}/_{5}}$.

For these values the basis corresponds with the Russell Saunders representation.

If $x \to \infty$, then $a = 1$, $b = 0$.

For these values the basis corresponds with the strong field representation.

If x goes from 0 to ∞, then a goes monotonously from $\sqrt{4/5}$ to 1
b goes monotonously from $-\sqrt{1/5}$ to 0.

The constants a and b are not very sensitive to $x = \Delta/E_p$. A rather crude estimation of x may lead to accurate values of a and b.

The energy levels and constants a and b for d^7 are the same.

For d^3 and d^8 the energy levels and a and b can be found from (3) and (4) by substituting $E_p \rightarrow E_p$, $\Delta \rightarrow -\Delta$, $x \rightarrow -x$.

If x goes from 0 to ∞, then a goes monotonously from $\sqrt{4/5}$ to 0
b goes monotonously from $-\sqrt{1/5}$ to -1.

§ 4) *Matrix elements of the orbital angular momentum and the spin orbit coupling*

From general group theoretical considerations it can be shown, that the matrix elements of the components $\sum_i l_{i_x}$, $\sum_i l_{i_y}$, $\sum_i l_{i_z}$ of the orbital angular momentum between two E, A_1 and A_2 states vanish.

If we have an arbitrary T_1 or T_2 level, then we can choose as basis functions

$$|X\rangle, |Y\rangle, |Z\rangle$$

where

$|X\rangle, |Y\rangle, |Z\rangle$ transform like l_x, l_y, l_z in the case of a T_1 level
ξ, η, ζ in the case of a T_2 level.

Abragam and Pryce [16] have observed that the effect on a T level can be represented by

$$\sum_i \boldsymbol{l}_i = -\alpha \boldsymbol{l}_p, \tag{5}$$

where $\boldsymbol{l}_p$ is a fictitious angular momentum operator acting on the states $|X\rangle, |Y\rangle, |Z\rangle$ in the same way as the angular momentum on the states x, y, z of a p electron.

It may be stressed upon, that formula (5) applies for any imaginary tensor operator which belongs to the representation T_{1g} of O_h or T_2 of T_d.

Since the one electron states are not pure d states the matrix elements of the orbital angular momentum in the configuration d^1 must be described with two so called orbital reduction factors: k for the matrix elements between t_2 states, k' for the matrix elements connecting a t_2 state with an e state.

The matrix elements can be obtained by calculating them for a *pure* d^1 ion and multiplying the matrix elements $\langle t_2|\boldsymbol{l}|t_2\rangle$ with k and the matrix elements $\langle t_2|\boldsymbol{l}|e\rangle$ with k'.

For pure d states $k=k'=1$, but due to covalent bonds k and k' are always smaller than 1.

Now α is given by

$$(6)\quad \begin{cases} \alpha = k & \text{for the } T_2 \text{ levels of } d^1,\ d^4,\ d^6, \text{ and } d^9 \\ \alpha = -{}^1/_2 k & \text{for the } T_2 \text{ levels of } d^2,\ d^3,\ d^7 \text{ and } d^8 \\ \alpha = (a^2-{}^1/_2 b^2)k - 2abk' & \text{for the lowest } T_1 \text{ levels of } d^2,\ d^3,\ d^7,\ d^8 \\ \alpha = (b^2-{}^1/_2 a^2)k + 2abk' & \text{for the highest } T_1 \text{ levels of } d^2,\ d^3,\ d^7,\ d^8. \end{cases}$$

The spin orbit coupling can be written with two spin orbit interaction constants:

ζ for the matrix elements between t_2 states

ζ' for the matrix elements connecting t_2 and e states.

In the free ion $\zeta=\zeta'=\zeta_0$

In an actual complex ζ and ζ' are always smaller than ζ_0.

The effect of the spin orbit coupling on a T_1 or T_2 level can be represented by

$$(7)\qquad \mathscr{H}_{so} = \mp \frac{\gamma}{2S}\, \boldsymbol{l}_p \cdot \boldsymbol{S},$$

where + holds if the shell is less than half filled
− holds if the shell is more than half filled.

γ is given by (6) with ζ and ζ' in stead of k and k'.

The T level is split into levels $j'=|l_p'-S|, \ldots, l_p+S;\ l_p=1$, with

$$(8)\qquad E_{j'} = E_T \mp \frac{\gamma}{2S}\{{}^1/_2(j'(j'+1) - S(S+1)) - 1)\}.$$

§ 5) *Influence of a tetragonal field*

We now suppose that in addition to the octahedral component the Ligand field has a small tetragonal component with D_{4h} symmetry around the z axis.

The action of a tetragonal field on a T_1 or T_2 level can be represented by

(9)

energy	eigenstates	transformation relative to D_{4h}	properties relative to O_h, if the tetragonal field → 0
$\varepsilon_{T_{xy}}$	$\vert X\rangle, \vert Y\rangle$	$I_x, I_y; \xi, \eta$	I_x, I_y, I_z in the case of a T_1 level
ε_{T_z}	$\vert Z\rangle$	$I_z; \zeta$	ξ, η, ζ in the case of a T_2 level.

If the eigenstates are defined in this way, then the effect of the orbital angular momentum on the T level can be represented by, *cf.* [16],

$$(10)\qquad \sum_i \boldsymbol{l}_i = -\boldsymbol{\alpha}\cdot\boldsymbol{l}_p,$$

where $\boldsymbol{\alpha}$ is diagonal with $\alpha_{xx}=\alpha_{yy}=\alpha'$, $\alpha_{zz}=\alpha$.

In addition an e level is split by the tetragonal field in an u level and v level

$$(11)\quad \left\{\begin{array}{lcccc} & \text{energy} & \text{eigenstates} & \begin{array}{c}\text{transformation}\\ \text{relative to } \mathrm{D_{4h}}\end{array} & \begin{array}{c}\text{properties}\\ \text{relative to } \mathrm{O_h}\text{, if the}\\ \text{tetragonal field} \to 0\end{array} \\ \multirow{2}{*}{$-\!\!<$} & \varepsilon_u & |U\rangle & u & \multirow{2}{*}{$\left.\begin{array}{c} \\ \\ \end{array}\right\} u, v.$} \\ & \varepsilon_v & |V\rangle & v & \end{array}\right.$$

Just as in the case of octahedral symmetry the orbital angular momentum does not have non vanishing matrix elements between the states $|U\rangle$ and $|V\rangle$.

We can characterize the matrix elements of the tetragonal component by two parameters d and d'.

$$(12)\qquad \left\{\begin{array}{l} \langle u|\mathscr{H}_{\text{tetr.}}|u\rangle = -\langle v|\mathscr{H}_{\text{tetr.}}|v\rangle = {}^1\!/_2\, d' \\ \langle\xi|\,|\mathscr{H}_{\text{tetr.}}|\xi\rangle = \langle\eta|\mathscr{H}_{\text{tetr.}}|\eta\rangle = -{}^1\!/_2\langle\zeta|\mathscr{H}_{\text{tetr.}}|\zeta\rangle = {}^1\!/_3\, d. \end{array}\right.$$

If one writes the tetragonal field in the form

$$(13)\qquad V_{\text{tetr.}} = H'(2z^2-x^2-y^2)+I'(2z^4-x^4-y^4+12x^2y^2-6x^2z^2-6y^2z^2),$$

then one can show

$$(14)\qquad \left\{\begin{array}{l} d = -{}^6\!/_7\, H + {}^8\!/_7\, I \\ d' = -{}^8\!/_7(H+I) \end{array}\right. ,\ \text{where}\ \begin{array}{l} H = eH'\langle r^2\rangle \\ I = eI'\langle r^4\rangle \end{array}$$

assuming, that the one electron states are pure d states, *cf.* [17]. The energy levels in the configurations d^1 and d^6 are given by

$$(15)\qquad \left\{\begin{array}{l} \varepsilon_u = {}^3\!/_5\varDelta + {}^1\!/_2 d' \\ \varepsilon_v = {}^3\!/_5\varDelta - {}^1\!/_2 d' \\ \varepsilon_\xi = \varepsilon^\eta = -{}^2\!/_5\varDelta + {}^1\!/_3 d \\ \varepsilon_\zeta = -{}^2\!/_5\varDelta - {}^2\!/_3 d. \end{array}\right.$$

The energy levels in the configurations d^4 and d^9 can be found from (15) by substituting $\varDelta \to -\varDelta$, $d \to -d$, $d' \to -d'$.

In the case of d^2, d^3, d^7, and d^8 the problem involves the solution of a cubic secular equation and the energy levels and constants α and α'

can be calculated starting from a numerical estimation of the field parameters. This method has been described by ABRAGAM and PRYCE [17] in their detailed analysis of Co^{++} (d^7). More recently analyses have been given for d^2 by PRYCE and RUNCIMAN [18] and CHAKRAVARTY [19].

However, one can get simple closed formulae for the constants α and α' if one starts from the exact solution of the octahedral case treating the tetragonal field as a perturbation. By means of the formulae the effect of the Russell Saunders approximation and the strong field approximation can be investigated. The results will be certainly better than the exact solutions of the tetragonal field, which can be obtained in the Russell Saunders of strong field approximation.

The results of a second order perturbation calculation are for d^2 and d^7

$$(16)\quad \begin{cases} \varepsilon_{T_1xy} = \varepsilon_{T_1} + {}^1/_4 d'b^2 + {}^1/_3(b^2-a^2)d - {}^3/_{16}\dfrac{b^2d'^2}{E_{T_2}-E_{T_1}} - \dfrac{a^2b^2({}^1/_4 d' + {}^2/_3 d)^2}{E_{T_1'}-E_{T_1}} \\ \varepsilon_{T_1z} = E_{T_1} - {}^1/_2 d'b^2 - {}^2/_3(b^2-a^2)d - \dfrac{4a^2b^2({}^1/_4 d' + {}^2/_3 d)^2}{E_{T_1'}-E_{T_1}} \\ \varepsilon_{T_2xy} = E_{T_2} - {}^1/_4 d' + {}^1/_3 d - {}^3/_{16}\dfrac{b^2d'^2}{E_{T_1}-E_{T_2}} - {}^3/_{16}\dfrac{a^2d'^2}{E_{T_1'}-E_{T_2}} \\ \varepsilon_{T_2z} = E_{T_2} + {}^1/_2 d' - {}^2/_3 d, \ \varepsilon_{A_2} = E_{A_2}. \end{cases}$$

$\varepsilon_{T_1'xy}$ and $\varepsilon_{T_1'z}$ follow from ε_{T_1xy} and ε_{T_1z} by substituting

$$a \to b,\ b \to -a,\ E_{T_1} \to E_{T_1'},\ E_{T_1'} \to E_{T_1}.$$

The energies for d^3 and d^8 follow from (16) by substituting

$$d \to -d \text{ and } d' \to -d'.$$

α and α' are given by

(17a) $\alpha = \alpha' = k$ for the T_2 levels of d^1, d^4, d^6, d^9.

$$(17b)\quad \begin{cases} \alpha' = \alpha_0 + C \\ \alpha = \alpha_0 - 2C \end{cases} \text{for the } T_1 \text{ and } T_2 \text{ levels of } d^2, d^3, d^7, d^8,$$

where α_0 is the value in the octahedral case tabulated in (6) and C is given by
for the lowest T_1 level of d^2

$$(17c)\quad C = {}^3/_4\frac{bd'(ak' - {}^1/_2 bk)}{E_{T_2}-E_{T_1}} - \frac{ab({}^1/_4 d' + {}^2/_3 d)}{E_{T_1'}-E_{T_1}}\{(a^2-b^2)k' + {}^3/_2 abk\}$$

and for the T_2 level of d^2 and d^7

$$C = -{}^3/_4 \frac{bd'(ak' - {}^1/_2 bk)}{E_{T_1} - E_{T_2}} + {}^3/_4 \frac{ad'(bk' + {}^1/_2 ak)}{E_{T_1'} - E_{T_2}}. \tag{17d}$$

C for the highest T_1 level of d^2 and d^7 can be found from (17c) by substituting $a \to b$, $b \to -a$, $E_{T_1} \to E_{T_1'}$, $E_{T_1'} \to E_{T_1}$ in (17c).

For d^3 and d^8 the C values can be found from (17) by substituting $d \to -d$, $d' \to -d'$.

The influence of the spin orbit coupling for a T_1 or T_2 level can be written as

$$\mathscr{H}_{so} = \mp \frac{(\boldsymbol{\gamma} \cdot \boldsymbol{l}_p)}{2S} \cdot \mathbf{S}, \tag{18}$$

where

$-$ holds if the d shell is less than half filled

$+$ holds if the d shell is more than half filled

$$\boldsymbol{\gamma} \text{ is diagonal and } \gamma_{xx} = \gamma_{yy} = \gamma', \ \gamma_{zz} = \gamma, \tag{19}$$

where γ and γ' follow from α and α' by substituting ζ and ζ' in stead of k and k'.

§ 6) *Influence of a trigonal field*

We suppose that in addition to the octahedral component the Ligand field has a small trigonal component with C_{3v} or D_3 symmetry around the (1, 1, 1) axis.

It is now convenient to choose another system of coordinates in which the z axis coincides with (1, 1, 1) axis.

$$x' = \frac{1}{\sqrt{6}}(2z - x - y), \ y' = \frac{1}{\sqrt{2}}(x - y), \ z' = \frac{1}{\sqrt{3}}(x + y + z). \tag{20a}$$

Corresponding with this system we introduce the functions

$$\xi' = \frac{1}{\sqrt{6}}(2\zeta - \xi - \eta), \ \eta' = \frac{1}{\sqrt{2}}(\xi - \eta), \ \zeta' = \frac{1}{\sqrt{3}}(\xi + \eta + \zeta) \tag{20b}$$

and the components of the orbital angular momentum

$$L_{x'} = \frac{1}{\sqrt{6}}(2L_z - L_x - L_y), \ L_{y'} = \frac{1}{\sqrt{2}}(L_x - L_y), \ L_{z'} = \frac{1}{\sqrt{3}}(L_x + L_y + L_z). \tag{20c}$$

The action of the trigonal field on a T_1 or T_2 level can be represented by

$$(21)\quad \left\{\begin{array}{lcccc} & \text{energy} & \text{eigenstates} & \begin{array}{c}\text{transformation}\\ \text{relative to } C_{3v}\end{array} & \begin{array}{c}\text{properties}\\ \text{relative to } \mathrm{O_h}\text{, if the}\\ \text{trigonal field} \to 0\end{array} \\ \diagup & \varepsilon_{T_{xy}} & |X'\rangle, |Y'\rangle & L_{x'}, L_{y'}; \xi', \eta' & \left\{\begin{array}{r} L_{x'}, L_{y'}, L_{z'} \text{ in the case}\\ \text{of a } T_1 \text{ level}\\ \xi', \eta', \zeta' \text{ in the case of}\\ \text{a } T_2 \text{ level}\end{array}\right. \\ \diagdown & \varepsilon_{T_z} & |Z'\rangle & L_{z'}; \zeta' & \end{array}\right.$$

If the eigenstates are defined in this way then the effect of the orbital angular momentum on the T level can be represented by [16]

$$(22)\qquad \sum_i \boldsymbol{l}_i' = -\boldsymbol{\alpha}\cdot\boldsymbol{l}_p,$$

where $\boldsymbol{l}_p$ is a fictitious angular momentum operator acting on the states $|X'\rangle, |Y'\rangle, |Z'\rangle$ just as if these were states x, y, z of a p electron.

$\sum_i \boldsymbol{l}_i'$ is defined with respect to the new system of coordinates the components $\sum_i l_{i\,x}'$ etc. can be expressed in the components $\sum_i l_{i_x}$ etc. with the formula (20c).

The tensor $\boldsymbol{\alpha}$ is diagonal with

$$(22b)\qquad \begin{array}{c}\alpha_{xx} = \alpha_{yy} = \alpha'\\ \alpha_{zz} = \alpha\end{array}$$

The trigonal field does not split an E level.

If we introduce states $|U\rangle$ and $|V\rangle$ transforming in the same way as u and v, the orbital angular momentum has a non vanishing matrix-element between $|U\rangle$ and $|V\rangle$.

We can put in a general way:

$$(23)\qquad \langle U|\sum_i \boldsymbol{l}_i'|V\rangle = \beta i.$$

The trigonal field can be represented by two parameters t and t' defined by:

$$\langle\xi'|\mathscr{H}_{\text{trig.}}|\xi'\rangle = \langle\eta'|\mathscr{H}_{\text{trig.}}|\eta'\rangle = -{}^1\!/_2\,\langle\zeta'|\mathscr{H}_{\text{trig.}}|\zeta'\rangle = t$$

and

$$(24)\qquad \langle u|\mathscr{H}_{\text{trig.}}|\xi'\rangle = \langle v|\mathscr{H}_{\text{trig.}}|\eta'\rangle = -t'\sqrt{2}.$$

If one writes the trigonal field in the form [17]

$$V_{\text{trig.}} = H'(yz+zx+xy) + I'\{yz(-6x^2+y^2+z^2)+cycl.\}$$

then it can be shown that for pure d orbitals

$$(25)\qquad \left\{\begin{array}{l} t = {}^1\!/_7\,H - {}^4\!/_{21}\,I\\ t' = -{}^1\!/_7\,[H+I]\end{array}\right.,\quad \text{where}\quad \begin{array}{l} H = eH'\langle r^2\rangle\\ I = eI'\langle r^4\rangle.\end{array}$$

The choice of the parameters t and t' is consistent with the choice of the parameters K and K' by Sugano *et al.* [20]. However the observation that $K = K'$, if the fourth degree part of the trigonal field is neglected, seems to be incorrect, *cf.* also Sugano and Peter [21] and Kamimura [22].

The problem for the configurations d^1, d^4, d^6, d^9 can be solved exactly.

For d^1 and d^6 the energy levels are given by

$$(26)\quad \begin{cases} \varepsilon_{u,v} = {}^1/_{10}\Delta + {}^1/_2 t + \{({}^1/_2\Delta - {}^1/_2 t)^2 + 2t'^2\}^{1/2} \\ \varepsilon_{T_2xy} = {}^1/_{10}\Delta + {}^1/_2 t - \{({}^1/_2\Delta - {}^1/_2 t)^2 + 2t'^2\}^{1/2} \\ \varepsilon_{T_2z} = -\,{}^2/_5\Delta - 2t. \end{cases}$$

For the T_2 level the constants α and α' are given by

$$(27a)\quad \begin{cases} \alpha = \sigma^2 k + 2\varrho\sigma k'\sqrt{2} \\ \alpha' = \sigma k - \varrho k'\sqrt{2}. \end{cases}$$

β for the E level is given by

$$(27b)\quad \beta_x = \beta_y = 0,\ \beta_z = \varrho^2 k - 2\varrho\sigma k'\sqrt{2}$$

with ϱ and σ equal to:

$$(27c)\quad \begin{cases} \varrho = t'\sqrt{2}\,[{}^1/_2(\Delta - t)^2 + 4t'^2 + (\Delta - t)\{({}^1/_2\Delta - {}^1/_2 t)^2 + 2t'^2\}^{1/2}]^{-1/2} \\ \sigma = \dfrac{{}^1/_2(\Delta - t) + \{({}^1/_2\Delta - {}^1/_2 t)^2 + 2t'^2\}^{1/2}}{[{}^1/_2(\Delta - t)^2 + 4t'^2 + (\Delta - t)\{({}^1/_2\Delta - {}^1/_2 t)^2 + 2t'^2\}^{1/2}]^{1/2}}. \end{cases}$$

ε_{uv}, ε_{T_2xy}, ε_{T_2z}, α, α' and β for d^4 and d^9 can be found from (26) and (27) by substituting $\Delta \to -\Delta$, $t \to -t$, $t' \to -t'$.

Contrarely to the case of a tetragonal field the intermixing of E and T_2 states can give rise to a large anisotropy between α and α'. In particular the anisotropy between α and α' is mainly due to the parameter t', whereas the energy splitting (26) is mainly determined by t. Unfortunately Δ, t and t' can not be determined simultaneously from the energy splittings (26). For the case of d^2, d^3, d^7, d^8 the problem involves the solution of a cubic secular equation, *cf.* [17–19], but simple closed formulae for the energy levels and constants α and α' can be obtained by perturbation calculation.

The results are for d^2 and d^7:

$$(28)\quad \begin{cases} \varepsilon_{T_1xy} = E_{T_1} - (a^2 + {}^1/_2 b^2)t + 2abt' - \dfrac{({}^3/_2 bt - at')^2}{E_{T_2} - E_{T_1}} - \dfrac{({}^1/_2 abt + (a^2 - b^2)t')^2}{E_{T_1'} - E_{T_1}} \\ \varepsilon_{T_1z} = E_{T_1} + 2(a^2 + {}^1/_2 b^2)t - 4abt' - \dfrac{(2bt')^2}{E_{A_2} - E_{T_1}} - \dfrac{4({}^1/_2 abt + (a^2 - b^2)t')^2}{E_{T_1'} - E_{T_1}} \\ \varepsilon_{T_2xy} = E_{T_2} - {}^1/_2 t - \dfrac{({}^3/_2 bt - at')^2}{E_{T_1} - E_{T_2}} - \dfrac{({}^3/_2 at + bt')^2}{E_{T_1'} - E_{T_2}} \\ \varepsilon_{T_2z} = E_{T_2} + t \\ \varepsilon_{A_2} = E_{A_2} - \dfrac{(2bt')^2}{E_{T_1} - E_{A_2}} - \dfrac{(2at')^2}{E_{T_1'} - E_{A_2}}. \end{cases}$$

$\varepsilon_{T_1'xy}$ and $\varepsilon_{T_1'z}$ follow from ε_{T_1xy} and ε_{T_1z} by substituting $a \to b$, $b \to -a$, $E_{T_1} \to E_{T_1'}$, $E_{T_1'} \to E_{T_1}$.

The energies for d^3 and d^8 follow from (28) by substituting $t \to -t$, $t' \to -t'$.

For the T_1 and T_2 levels of d^2, d^3, d^7 and d^8 we have

$$(29a)\quad \begin{cases} \alpha' = \alpha_0 + C \\ \alpha = \alpha_0 - 2C \end{cases}$$

where α_0 is given by (6)
and where for the lowest T_1 level of d^2 and d^7

$$(29b)\quad C = \frac{({}^3/_2 bt - at')}{E_{T_2} - E_{T_1}} (ak' - {}^1/_2 bk) - \frac{{}^1/_2 abt + (a^2 - b^2)t'}{E_{T_1'} - E_{T_1}} \{(a^2 - b^2)k' + {}^3/_2 abk\}$$

and for the T_2 level of d^2 and d^7

$$(29c)\quad C = \frac{({}^3/_2 bt - at')}{E_{T_1} - E_{T_2}} (ak' - {}^1/_2 bk) - \frac{({}^3/_2 at + bt')}{E_{T_1'} - E_{T_2}} (bk' + {}^1/_2 ak).$$

C for the highest T_1 level can be found by substituting $a \to b$, $b \to -a$. $E_{T_1} \to E_{T_1'}$, $E_{T_1'} \to E_{T_1}$ in (29b).

The C values for d^3 and d^8 can be found from (29) by substituting $t \to t$, $t' \to -t'$.

The effect of the spin orbit coupling on a T_1 and T_2 level can be written as

$$\mathscr{H}_{so} = \mp \frac{(\boldsymbol{\gamma} \cdot \boldsymbol{l}_p)}{2S} \cdot \boldsymbol{S}$$

where γ is diagonal, $\gamma_{xx} = \gamma_{yy} = \gamma'$, $\gamma_{zz} = \gamma$ and γ and γ' follow from α and α' by substituting ζ and ζ' in stead of k and k'.

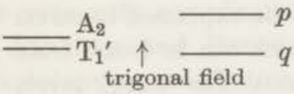
The spin orbit coupling can now have a first order effect on a E level.

The E level of d^1 and d^9 is split into two Kramers doublets with separation $\varrho^2\zeta - 2\varrho\sigma\zeta'\sqrt{2}$, *cf.* (23) and (27b).

The E level of d^4 and d^9 is split into five equidistant levels all double degenerate, with separation $^1/_4(\varrho^2\zeta - 2\varrho\sigma\zeta'\sqrt{2})$.

The second order perturbation due to the T_2 states can greatly disturb this pattern.

Remark: If the E_{A_2} and $E_{T_1'}$ levels nearly coincide, such as can be the case for d^2 and d^7, then the formulae for E_{A_2}, $E_{T_1'}$ and C for the highest T_1 level break down. The other formulae are correct within the order of approximation



If we neglect the off diagonal elements with states of the lowest T_1 level, then we find for the energy levels p and q

$$\text{(30a)} \left\{ \begin{aligned} \varepsilon_{p,q} = {}^1/_2[E_{A_2} + E_{T_1'} + (a^2+2b^2)t + 4abt' \pm \\ \pm \{(E_{T_1'} + (a^2+2b^2)t + 4abt' - E_{A_2})^2 + 16a^2t'^2\}^{1/2}]. \end{aligned} \right.$$

The second order contribution due to the lowest T_1 level can be written in the form:

$$\text{(30b)} \qquad \Delta_{\varepsilon_{p,q}} = \frac{\{4abt' + (E_{A_2} - \varepsilon_{p,q})\,(abt + 2(a^2-b^2)t')\}^2}{\{(2at')^2 + (E_{A_2} - \varepsilon_{p,q})^2\}\{{}^1/_2(E_{A_2} + E_{T_1'}) - E_{T_1}\}}.$$

It does not make much sense to attribute one of the two levels p and q to the A_2 level and the other to the T_1' level. Hence in that case α' for the highest T_1 level is not well defined.

This complication can not occur in the tetragonal case since the tetragonal field does not give an intermixing between the T_1 states and the A_2 state.

§ 7) *The problem for* T_1 *and* T_2 *levels*

If a T_1 or T_2 level is the ground state in an octahedral field, then we have to take into account the states $|X, m_s\rangle$, $|Y, m_s\rangle$, $|Z, m_s\rangle$ where $m_s = -S, \ldots, S$, and S is the maximal spin value.

From now on we shall drop all the primes in the trigonal case, bearing in mind that all the quantities are defined relative to the coordinate system (x', y', z'), in which the z axis coincides with the trigonal axis.

In stead of $|X\rangle$, $|Y\rangle$, $|Z\rangle$ it is convenient to introduce the linear combinations

$$\text{(31)} \qquad |1\rangle = \frac{-|X\rangle - i|Y\rangle}{\sqrt{2}},\ |0\rangle = |Z\rangle,\ |-1\rangle = \frac{|X\rangle - i|Y\rangle}{\sqrt{2}}.$$

By the action of the trigonal or tetragonal field the T level is split in a XY level with energy ε_{xy} and a singlet Z with energy ε_z.

The splitting is denoted by:

$$\varepsilon_{xy} - \varepsilon_z = \delta_0, \ \varepsilon_z - \varepsilon_{xy} = \delta, \ \delta_0 = -\delta. \tag{32}$$

The matrix elements of the trigonal or tetragonal field together with the spin orbit coupling can now be written in the form:

$$\langle i m_s' | \mathscr{H}_{\text{cr.}} + \mathscr{H}_{so} | j\, m_s \rangle = \delta_{m_s' m_s} \delta_{ij}\, \delta_{i0}\, \delta \mp \frac{(\boldsymbol{\gamma} \cdot \langle i | \boldsymbol{l}_p | j \rangle)}{2S} \cdot \langle m_s' | \mathbf{S} | m_s \rangle. \tag{33}$$

The energy levels and eigenstates can be solved in an exact way for $S = {}^1/_2$, $S = 1$, whereas for $S = {}^3/_2$ and $S = 2$, they can be expressed in terms of a parameter x, *cf.* Abragam and Pryce [17], which can be found from a cubic equation starting from numerical estimations. The energy levels can be divided into groups of levels such that the interspacing of the levels belonging to the same group is small (of order of some tens of cm^{-1}). In general we can take as such a group a set of states which are degenerate with respect to the spin orbit coupling within first order.

The states of each group can be associated with states $|m_s'\rangle$, $m_s' = -S', \ldots$ $\ldots, S'$, and a fictitious spin operator $\mathbf{S}'$ can be introduced acting on the states in the same way as a spin angular momentum $\mathbf{S}$ on pure states $|m_s\rangle$.

Then the remaining terms of the Hamiltonian can be replaced by operators in $\mathbf{S}'$, Abragam and Pryce [16].

The second order effect of the spin orbit coupling can cause a small energy splitting between the states belonging to a group. This can be represented in many cases by a term $DS_z'^2$.

(An exception is the case of V^{+++}, d^2, in an octahedral field, where the 5 fold degenerated ground level in second order is split in a triplet and a doublet.)

If the lowest group is a Kramers doublet, then there is no splitting in the absence of a magnetic field and the term $DS_z'^2$ can be omitted. In addition the spin spin coupling [10], [16] can give a contribution to $DS_z'^2$.

The Zeeman term in the Hamiltonian

$$\mathscr{H}_z = \beta \mathbf{H} \cdot (\sum_i \boldsymbol{l}_i + 2\mathbf{S}) \tag{33a}$$

can be replaced by $\beta \mathbf{H} \cdot \mathsf{g} \cdot \mathbf{S}'$. In the case of tetragonal or trigonal symmetry this reduces to

$$\mathscr{H}_z = \beta \{ g_\perp (H_x S_x' + H_y S_y') + g_{\parallel} H_z S_z' \}, \tag{33b}$$

β being the Bohr magneton.

The g values can be calculated using the methods of ABRAGAM and PRYCE [16]. If we are restricted to the lowest T level, using the correct values of γ and γ', then we shall find the g values in a first order approximation of the spin orbit coupling.

This sort of calculations has been treated in many analyses, to some of which we shall refer in the following section.

We shall merely state the results in the notation of the preceding sections.

The intermixing effect between different orbital levels by the spin orbit coupling gives a contribution to the g factors which is small, but certainly not negligible. An exact calculation of this second order contribution in terms of the coefficients of wave functions leads to formulae which can be extremely complicated.

ABRAGAM and PRYCE [17] have obtained numerical values of the second order contributions for d^7. Later on Rei has calculated the second order contributions for d^2 and d^7, taking also into account the effect of covalent bondings [23], [24].

Simple formulae for the second order contributions can be obtained if we neglect the intermixing effect due to the trigonal or tetragonal field, *i.e.* the eigenstates of the orbital levels are approximated by the eigenstates in the limit case of vanishing trigonal or tetragonal field. If the axial field is not very large, the approximation will give good results, since the second order contribution itself is very small.

The hyper fine structure can be written in the form

$$\text{(34a)} \qquad \mathscr{H}_{\text{h.f.s.}} = P\boldsymbol{I}\cdot\left[\sum_i \boldsymbol{l}_i \pm \frac{1}{2S}\left(\sum_i \frac{3\boldsymbol{r}_i\boldsymbol{r}_i - r_i^2\mathsf{U}}{r_i^2}\right)\cdot\boldsymbol{S} - \varkappa\boldsymbol{S}\right]$$

cf. [10], [11], where $P = 2\beta\beta_n g_n\langle r^{-3}\rangle$, U is the unit tensor and $\varkappa$ arises from the contact term.

This term gives a contribution of the spin hamiltonian of the form

$$\text{(34b)} \qquad \mathscr{H}_{\text{h.f.s.}} = AI_zS_z' + B[I_xS_x' + I_yS_y'].$$

Following Abragam and Pryce we can write

$$\text{(34c)} \qquad \begin{cases} A = P[g_{L_{\parallel}} - {}^1/_2\varkappa g_{s_{\parallel}}] + A_{sd} \\ B = P[g_{L_{\perp}} - {}^1/_2\varkappa g_{s_{\perp}}] + B_{sd}, \end{cases}$$

where g_L is the part of g, which arises from the orbital angular momentum and g_S arises from the spin angular momentum.

In the formulae for the g values (see § 8) g_L corresponds with the linear term in α and α'.

Asd and *Bsd* are due to the term

$$\sum_i \frac{3\mathbf{r}_i\mathbf{r}_i - r_i^2\mathsf{U}}{r_i^2}.$$

The exact calculation of *Asd* and *Bsd* is tedious [17], but since *Asd* and *Bsd* only give a small contribution to A and B, a reasonable approximation can be obtained, if the intermixing effect of the trigonal or tetragonal field is neglected.

An exact parametrization of the matrix elements of

$$\sum_i \frac{3\mathbf{r}_i\mathbf{r}_i - r_i^2\mathsf{U}}{r_i^2}$$

taking into account the effect of covalent bonds involves in the octahedral case the introduction of four additional parameters. Since it is impossible to give an unique determination of these parameters from the experiments, we shall assume, that all the matrix elements can be obtained from the matrix elements in the free ion case by multiplication with a factor p with $0<p<1$.

In a simple L.C.A.O. description [10], where the one electron orbitals are written in the form of linear combinations of pure d orbitals and orbitals of the surrounding Ligands with the same transformation properties with respect to the octahedral group, we can assume that the hyper fine structure and the spin orbit coupling, compared with the free ion case, are reduced to the same extent, *i.e.* the probability that the electron in such an orbital is at the nucleus of the d ion. This follows from the fact that the hyper fine structure and the spin orbit coupling mainly are determined by the wave function in the neighbourhood of the nucleus.

The quadrupole coupling can be written in the form

$$\mathscr{H}_Q = \frac{e^2q}{2I(2I-1)} \sum_k \left(\frac{I(I+1)}{r_k^3} - \frac{3(\mathbf{r}_k\cdot\mathbf{I})\,(\mathbf{r}_k\cdot\mathbf{I})}{r_k^5} \right). \tag{35}$$

If the lowest group is a Kramers doublet, then it is possible to represent the quadrupole coupling by a term QI_z^2 in the spin hamiltonian. In other cases the matrices of $\mathscr{H}_Q$ between the states of the lowest level are in general not multiples of the unit matrix and the quadrupole coupling can not be represented by an operator independent of the effective spin. In the case that the lowest level in the crystal field is an orbital singlet, well separated from the other levels, the quadrupole coupling can be represented by QI_z^2 as follows from the theory of the spin hamiltonian for a level without orbital degeneracy, ABRAGAM and PRYCE [16]. The constant Q can be evaluated neglecting the intermixing effect of the axial field. The matrix elements of

$$\sum_i \frac{3\mathbf{r}_i\mathbf{r}_i - r_i^2 \mathsf{U}}{r_i^2}$$

are described with the same reduction factor p.

If the surrounding Ligands have a nuclear spin, then they can give an important contribution to the hyper fine structure and the quadrupole coupling, TINKHAM [25]. We shall however not deal with this effect.

In the following section we shall give the results of the calculations which are straight forward, using the methods of ABRAGAM and PRYCE [16], [17].

§ 8) *The problem* T$_1$ *and* T$_2$ *levels* (*continued*)

i) $S={}^1/_2$, d^1 ground state in octahedral field T$_2$.

Analyses have been given by ABRAGAM and PRYCE [16], BLEANEY [26], BLEANEY *et al.* [27], BOSE *et al.* [28], REÍ [29], [30].

In this case there are three different possibilities,

i) If δ_0 is sufficiently negative, then a spin hamiltonian can be used for the lowest Kramers doublet, the g factors are given by, *cf.* [16]

(36) $$g_{\|} = 2(1-\alpha),\ g_{\perp} = 0.$$

ii) If δ_0 is very small, then a spin hamiltonian can be set up for the lowest quartet Γ_8.

The g value is given by

(37) $$g = {}^2/_3\,(1-\alpha).$$

iii) If δ_0 is sufficiently positive, then a spin hamiltonian can be used for the lowest Kramers doublet, the g factors are given by, *cf.* [26]

$$g_{\|} = -\alpha + \frac{1}{S}\,(\alpha+2)\,(\delta_0 + {}^1/_2\gamma)$$

$$g_{\perp} = \quad 1 + \frac{1}{S}\,(\delta_0 + {}^1/_2\gamma - 2\alpha'\gamma')$$

where

(38) $$S = \{(\delta_0 + {}^1/_2\gamma)^2 + 2\gamma'^2\}^{1/2}.$$

Since in actual situations case iii) occurs, we shall restrict ourselves to that case.

The second corrections to the g factors are given by

i) in the case of tetragonal symmetry

$$\text{(39a)}\qquad \begin{cases} g_{\|}^{(2)} = -\dfrac{8k'\zeta'}{\Delta}\, c_1^2 \\[2ex] g_{\perp}^{(2)} = +\dfrac{2k'\zeta'}{\Delta}\, c_1 c_2 \sqrt{2} \end{cases}$$

ii) in the case of trigonal symmetry

$$\text{(39b)}\qquad \begin{cases} g_{\|}^{(2)} = -\dfrac{4k'\zeta'}{\Delta}\, [c_1 c_2 \sqrt{2} + c_2^2] \\[2ex] g_{\perp}^{(2)} = -\dfrac{2k'\zeta'}{\Delta}\, [2c_1^2 + c_1 c_2 \sqrt{2}], \end{cases}$$

where

$$\text{(39c)}\qquad c_1 = \left\{\frac{1}{2S}\,(S + \delta_0 + {}^1\!/_2\gamma)\right\}^{1/2},\quad c_2 = \left\{\frac{1}{2S}\,(S - \delta_0 - {}^1\!/_2\gamma)\right\}^{1/2}.$$

The hyper fine structure constants and quadrupole coupling are given by

i) in the case of tetragonal symmetry

$$\text{(40a)}\qquad \begin{cases} A = P\left[-(\alpha + {}^3\!/_7 p) + (\alpha - {}^1\!/_7 p - \varkappa)\left(\dfrac{\delta_0 + {}^1\!/_2\gamma}{S}\right) - {}^6\!/_7\dfrac{\gamma'}{S}\right] \\[2ex] B = P\left[(-{}^1\!/_2\varkappa + {}^1\!/_7 p)\left\{1 + \dfrac{\delta_0 + {}^1\!/_2\gamma}{S}\right\} + \dfrac{\gamma'}{S}\,({}^3\!/_7 p - 2\alpha')\right] \\[2ex] Q = {}^3\!/_{28}\,\dfrac{e^2 q p}{I(2I-1)}\,\langle r^{-3}\rangle\left\{1 + \dfrac{3(\delta_0 + {}^1\!/_2\gamma)}{S}\right\}, \end{cases}$$

ii) in the case of trigonal symmetry

$$\text{(40b)}\qquad \begin{cases} A = P\left[(-\alpha + {}^3\!/_7 p) + (\alpha + {}^1\!/_7 p - \varkappa)\left(\dfrac{\delta_0 + {}^1\!/_2\gamma}{S}\right) + {}^2\!/_7\dfrac{\gamma'}{S}\right] \\[2ex] B = P\left[-{}^1\!/_2\varkappa - {}^2\!/_7 p - {}^1\!/_2\varkappa\left(\dfrac{\delta_0 + {}^1\!/_2\gamma}{S}\right) + \dfrac{\gamma'}{S}\,(-{}^1\!/_7 p - 2\alpha')\right] \\[2ex] Q = -{}^3\!/_{28}\,\dfrac{e^2 q p}{I(2I-1)}\,\langle r^{-3}\rangle\left\{1 + \dfrac{3(\delta_0 + {}^1\!/_2\gamma)}{S}\right\}. \end{cases}$$

The formulae (40a) reduce in the absence of covalent bonds, *i.e.*

$\alpha=\alpha'=p=1$, $\gamma=\gamma'=\zeta_0=\lambda$, to the formulae given by ABRAGAM and PRYCE [16]. The formulae for the trigonal case however are different.

The rhombic case for V^{4+} has been dealt with by REÍ [30].

i) $S=1$ d^2, groundstate in octahedral field T_1.

Analyses have been given by ABRAGAM and PRYCE [16], CHAKRAVARTY [19], REÍ [23], [31].

In this case there are three possibilities.

i) If δ_0 is sufficiently negative, then we can set up a spin hamiltonian for the lowest doublet.

The g values are given by

$$\text{(41)} \qquad \begin{cases} g_{\parallel} = 4-2\alpha \\ g_{\perp} = 0. \end{cases}$$

ii) In the octahedral case a spin hamiltonian with $S'=2$ must be used for the five lowest states.

The g factor is given by

$$\text{(42)} \qquad g=(1-{}^1\!/_2\,\alpha).$$

The second order influence of the spin orbit coupling splits the quintet in a doublet and a triplet. This splitting can not be represented by a term of the form $DS_z'^2$.

iii) If δ_0 is sufficiently positive and this is the situation which is met in actual cases, then a spin hamiltonian must be set up for the three lowest states.

The g factors are given by, *cf.* [19].

$$\text{(43a)} \qquad \begin{cases} g_{\parallel} = 2c_4^2-\alpha c_3^2 \\ g_{\perp} = 2(c_1c_3+c_2c_4)-\alpha'(c_2c_3+c_1c_4) \end{cases}$$

where

$$\text{(43b)} \qquad \begin{cases} c_1=\left\{\dfrac{1}{4S_0}\,(S_0-\delta_0-{}^1\!/_2\,\gamma)\right\}^{1/2}, \; c_2=\left\{\dfrac{1}{2S_0}\,(S_0+\delta_0+{}^1\!/_2\,\gamma)\right\}^{1/2} \\ c_3=\left\{\dfrac{1}{2S_1}\,(S_1-\delta_0)\right\}^{1/2}, \; c_4=\left\{\dfrac{1}{2S_1}\,(S_1+\delta_0)\right\}^{1/2} \end{cases}$$

and

$$\text{(43c)} \qquad S_0=\{(\delta_0+{}^1\!/_2\,\gamma)^2+2\gamma'^2\}^{1/2}, \; S_1=\{\delta_0^2+\gamma'^2\}^{1/2}.$$

The second order contribution of the spin orbit coupling splits the triplet in a singlet, energy E_0 and a doublet, energy E_1. This splitting can be represented by $DS_z'^2$, where D is given by, neglecting spin spin interactions.

$$D = E_1 - E_0 = \tfrac{1}{2}[S_0 - S_1 - \tfrac{1}{2}\gamma]. \tag{44}$$

The formulae (43) reduce to the formulae given by ABRAGAM and PRYCE [16] in the absence of covalent bonds, *i.e.*, if $\gamma = 2\alpha\lambda$, $\gamma' = 2\alpha'\lambda$.

The second order corrections to the g factors are given by

i) in the case of tetragonal symmetry

$$\begin{cases} g_{\parallel}^{(2)} = 3(a\zeta' - \tfrac{1}{2}b\zeta)(ak' - \tfrac{1}{2}bk)(E_{T_2} - E_{T_1})^{-1}\, c_3c_4 - \\ \qquad - \{(a^2-b^2)\zeta' + \tfrac{3}{2}ab\zeta\}\{(a^2-b^2)k' + \tfrac{3}{2}abk\}\,(E_{T_1'} - E_{T_1})^{-1}\, c_3c_4 \\ g_{\perp}^{(2)} = -3(a\zeta' - \tfrac{1}{2}b\zeta)(ak' - \tfrac{1}{2}bk)(E_{T_2} - E_{T_1})^{-1} \cdot \\ \qquad\qquad \cdot (c_2c_4 + \tfrac{1}{2}c_1c_3 + \tfrac{1}{2}c_1c_4) - \\ \qquad - \{(a^2-b^2)\zeta' + \tfrac{3}{2}ab\zeta\}\{(a^2-b^2)k' + \tfrac{3}{2}abk\} \cdot \\ \qquad\qquad \cdot (E_{T_1'} - E_{T_1})\,(c_2c_4 + \tfrac{1}{2}c_1c_3 - \tfrac{1}{2}c_1c_4). \end{cases} \tag{45a}$$

ii) in the case of trigonal symmetry

$$\begin{cases} g_{\parallel}^{(2)} = -(a\zeta' - \tfrac{1}{2}b\zeta)(ak' - \tfrac{1}{2}bk)(E_{T_2} - E_{T_1})^{-1}\,(4c_4^2 + c_3c_4) - \\ \qquad - \{(a^2-b^2)\zeta' + \tfrac{3}{2}ab\zeta\}\{(a^2-b^2)k' + \tfrac{3}{2}abk\}\,(E_{T_1'} - E_{T_1})^{-1}\, c_3c_4 \\ g_{\perp}^{(2)} = -(a\zeta' - \tfrac{1}{2}b\zeta)(ak' - \tfrac{1}{2}bk)(E_{T_2} - E_{T_1})^{-1} \cdot \\ \qquad\qquad \cdot (c_2c_4 + \tfrac{3}{2}c_1c_3 - \tfrac{1}{2}c_1c_4) - \\ \qquad - \{(a^2-b^2)\zeta' + \tfrac{3}{2}ab\zeta\}\{(a^2-b^2)k' + \tfrac{3}{2}abk\} \cdot \\ \qquad\qquad \cdot (E_{T_1'} - E_{T_1})^{-1}\,(c_2c_4 + \tfrac{1}{2}c_1c_3 - \tfrac{1}{2}c_1c_4). \end{cases} \tag{45b}$$

The hyper fine structure constants are given by

i) in the case of tetragonal symmetry

$$\begin{cases} A_{sd} = \tfrac{1}{7}Pp[3c_3c_4(a^2 + \tfrac{1}{2}b^2 + 2ab) + 2c_4^2(a^2 - 2b^2)] \\ B_{sd} = \tfrac{1}{7}Pp[c_1c_3(\tfrac{1}{2}a^2 + \tfrac{11}{4}b^2 + 3ab) - \\ \qquad\qquad - c_2c_4(a^2 - 2b^2) - \tfrac{3}{2}c_1c_4(a^2 + \tfrac{1}{2}b^2 + 2ab)]. \end{cases} \tag{46a}$$

ii) in the case of trigonal symmetry

$$\begin{cases} A_{sd} = \tfrac{1}{7}Pp[2c_3c_4(\tfrac{9}{4}b^2 + ab - \tfrac{1}{2}a^2) - 2c_4^2(a^2 + \tfrac{1}{2}b^2 + 2ab)] \\ B_{sd} = \tfrac{1}{7}Pp[c_1c_3(\tfrac{1}{2}a^2 + \tfrac{11}{4}b^2 + 3ab) + \\ \qquad\qquad + c_2c_4(a^2 + \tfrac{1}{2}b^2 + 2ab) - c_1c_4(\tfrac{9}{4}b^2 + ab - \tfrac{1}{2}a^2)]. \end{cases} \tag{46b}$$

If λ/δ_0 is small, then

i) in the case of tetragonal symmetry

$$\text{(47a)}\quad \begin{cases} A = P[-\varkappa + {}^2/_7\, p(a^2-2b^2)] \\ B = P[-\varkappa - {}^1/_7\, p(a^2-2b^2)] \\ Q = {}^3/_7\, \dfrac{e^2qp}{I(2I-1)} \langle r^{-3}\rangle\, (2b^2-a^2). \end{cases}$$

(ii) in the case of tr igonal symmetry

$$\text{(47b)}\quad \begin{cases} A = P[-\varkappa - {}^2/_7\, p(a^2+{}^1/_2\, b^2+2ab)] \\ B = P[-\varkappa + {}^1/_7\, p(a^2+{}^1/_2\, b^2+2ab)] \\ Q = {}^3/_7\, \dfrac{e^2qp}{I(2I-1)} \langle r^{-3}\rangle\, (a^2+{}^1/_2\, b^2+2ab). \end{cases}$$

The formulae given by ABRAGAM and PRYCE [16] apply to the trigonal case in the weak field limit. However in the strong field limit the quadrupole coupling and the hyper fine structure apart from the contact term with $\varkappa$ are 10 times as large. The formulae for the tetragonal case are different, here the quadrupole coupling and the hyper fine structure apart from the contact term are 2,5 times as large in the strong field limit. The hyper fine structure and quadrupole coupling depend strongly on $x=\Delta/E_p$ and the assumption of the weak resp. strong field limit does not lead to correct results.

iii) $S={}^3/_2$, d^7, ground state in octahedral field T_1.

Analyses have been given by ABRAGAM and PRYCE [17] and REÍ [24]. For all values of δ, negative as well as positive, a Kramers doublet is lowest. Since the other levels are some hundreds of cm^{-1} higher, we can set up a spin hamiltonian for the lowest Kramers doublet.

The g factors are given by

$$\text{(48a)}\quad \begin{cases} g_{\|} = 2+4(\alpha+2)\left\{\dfrac{3}{x^2}-\dfrac{4}{(x+2)^2}\right\}\left\{\dfrac{6}{x^2}+\dfrac{\gamma^2}{\gamma'^2}+\dfrac{8}{(x+2)^2}\right\}^{-1} \\ g_{\perp} = 4\left\{\dfrac{\gamma^2}{\gamma'^2}+\dfrac{2\gamma\alpha'}{\gamma'(x+2)}+\dfrac{12}{(x+2)x}\right\}\left\{\dfrac{6}{x^2}+\dfrac{\gamma^2}{\gamma'^2}+\dfrac{8}{(x+2)^2}\right\}^{-1}, \end{cases}$$

where x is the largest root of the equation

$$\text{(48b)}\quad \delta = {}^4/_3\, \frac{\gamma'^2}{\gamma(x+2)} + \frac{\gamma'^2}{\gamma x} - \frac{\gamma}{6}(x+3).$$

These formulae have been given in a slightly different form by Reí and reduce in the absence of covalent bondings, with $\gamma = -{}^3/_2\alpha\lambda$, $\gamma' = -{}^3/_2\alpha'\lambda$ to the formulae given by ABRAGAM and PRYCE [17].

In the octahedral case we have

$$x = 2,\ g = {}^{10}/_3 + {}^2/_3\,\alpha. \tag{49}$$

The second order corrections to the g factors are given by

i) in the case of tetragonal symmetry

$$\left\{\begin{aligned} g_{\parallel}^{(2)} &= (a\zeta' - {}^1/_2\,b\zeta)(ak' - {}^1/_2\,bk)(E_{T_2} - E_{T_1})^{-1}\cdot \\ &\qquad\qquad\cdot(6c_1^2 + 2c_1c_2\sqrt{6} - 4c_2c_3\sqrt{2} + 2c_3^2) + \\ &\quad + \{(a^2-b^2)\zeta' + {}^3/_2\,ab\zeta\}\{(a^2-b^2)k' + {}^3/_2\,abk\}\{E_{T_1'} - E_{T_1}\}^{-1}\cdot \\ &\qquad\qquad\cdot(2c_1^2 - {}^2/_3\,c_1c_2\sqrt{6} + {}^4/_3\,c_2c_3\sqrt{2} - {}^2/_3\,c_3^2) \\ g_{\perp}^{(2)} &= (a\zeta' - {}^1/_2\,b\zeta)(ak' - {}^1/_2\,bk)(E_{T_2} - E_{T_1})^{-1}\cdot \\ &\qquad\qquad\cdot(2c_1c_3\sqrt{3} + 4c_2^2 + c_2c_3\sqrt{2}) + \\ &\quad + \{(a^2-b^2)\zeta' + {}^3/_2\,ab\zeta\}\{(a^2-b^2)k' + {}^3/_2\,abk\}\cdot \\ &\qquad\qquad\cdot\{E_{T_1'} - E_{T_1}\}^{-1}({}^4/_3\,c_2^2 - {}^1/_2\,c_2c_3\sqrt{2} + {}^2/_3\,c_1c_3\sqrt{3} + {}^4/_3\,c_3^2). \end{aligned}\right. \tag{50a}$$

ii) in the case of trigonal symmetry

$$\left\{\begin{aligned} g_{\parallel}^{(2)} &= (a\zeta' - {}^1/_2\,b\zeta)(ak' - {}^1/_2\,bk)(E_{T_2} - E_{T_1})^{-1}\cdot \\ &\qquad\qquad\cdot(2c_1^2 - {}^2/_3\,c_1c_2\sqrt{6} + {}^4/_3\,c_2c_3\sqrt{2} + {}^8/_3\,c_2^2 - {}^2/_3\,c_3^2) + \\ &\quad + \{(a^2-b^2)\zeta' + {}^3/_2\,ab\zeta\}\{(a^2-b^2)k' + {}^3/_2\,abk\}\cdot \\ &\qquad\qquad\cdot\{E_{T_1'} - E_{T_1}\}^{-1}(2c_1^2 - {}^2/_3\,c_1c_2\sqrt{6} + {}^4/_3\,c_2c_3\sqrt{2} - {}^2/_3\,c_3^2) \\ g_{\perp}^{(2)} &= (a\zeta' - {}^1/_2\,b\zeta)(ak' - {}^1/_2\,bk)(E_{T_2} - E_{T_1})^{-1}\cdot \\ &\qquad\qquad\cdot({}^4/_3\,c_2^2 + {}^{10}/_3\,c_1c_3\sqrt{3} - {}^1/_3\,c_2c_3\sqrt{2} - {}^4/_3\,c^2{}_3) + \\ &\quad + \{(a^2-b^2)\zeta' + {}^3/_2\,ab\zeta\}\{(a^2-b^2)k' + {}^3/_2\,abk\}\cdot \\ &\qquad\qquad\cdot\{E_{T_1'} - E_{T_1}\}^{-1}({}^4/_3\,c_2^2 - {}^1/_2\,c_2c_3\sqrt{2} + {}^2/_3\,c_1c_3\sqrt{3} + {}^4/_3\,c_3^2), \end{aligned}\right. \tag{50b}$$

where

$$\left\{\begin{aligned} c_1 &= \frac{\sqrt{6}}{x}\left(\frac{6}{x^2} + \frac{\gamma^2}{\gamma'^2}\quad \frac{8}{(x+2)^2}\right)^{-1/2} \\ c_2 &= \frac{-\gamma}{\gamma'}\left(\frac{6}{x^2} + \frac{\gamma^2}{\gamma'^2} + \frac{8}{(x+2)^2}\right)^{-1/2} \\ c_3 &= \frac{\sqrt{8}}{(x+2)}\left(\frac{6}{x^2} + \frac{\gamma^2}{\gamma'^2} + \frac{8}{(x+2)^2}\right)^{-1/2} \end{aligned}\right. \tag{50c}$$

and x is defined by (48b).

In the octahedral limit these results reduce to

$$\left\{\begin{aligned} g^{(2)} &= \frac{2(a\zeta' - {}^1\!/_2\, b\zeta)(ak' - {}^1\!/_2\, bk)}{E_{T_2} - E_{T_1}} + \\ &\qquad + {}^{10}\!/_9\, \frac{\{(a^2-b^2)\zeta' + {}^3\!/_2\, ab\zeta\}\{(a^2-b^2)k' + {}^3\!/_2\, abk\}}{E_{T_1'} - E_{T_1}} \end{aligned}\right. \tag{51}$$

to a small amount depending on Δ/E_p.

The hyper fine structure constants and quadrupole coupling are given by

i) in the case of tetragonal symmetry

$$\left\{\begin{aligned} A_{sd} &= {}^4\!/_{21}\, Pp\{({}^1\!/_2\, a^2 - b^2)(3c_1^2 - 2c_2^2 - c_3^2) + \\ &\qquad + 3({}^1\!/_2\, a^2 + {}^1\!/_4\, b^2 + ab)(c_1c_2\sqrt{6} - 2c_2c_3\sqrt{2})\} \\ B_{sd} &= {}^4\!/_{21}\, Pp\{(a^2 - 2b^2)(c_2^2 - {}^1\!/_2\, c_1c_3\sqrt{3}) + \\ &\qquad + {}^3\!/_4\, c_2c_3\sqrt{2}\,(a^2 + {}^1\!/_2\, b^2 + 2ab) - 3c_3^2({}^5\!/_4\, b^2 + ab)\} \\ Q &= {}^3\!/_{14}\, \frac{e^2qp}{I(2I-1)}\, \langle r^{-3}\rangle\, (a^2 - 2b^2)(c_1^2 + c_3^2 - 2c_2^2), \end{aligned}\right. \tag{52a}$$

ii) in the case of trigonal symmetry

$$\left\{\begin{aligned} A_{sd} &= {}^4\!/_{21}\, Pp\{-({}^1\!/_4\, b^2 + {}^1\!/_2\, a^2 + ab)(3c_1^2 - 2c_2^2 - c_3^2) + \\ &\qquad + ({}^9\!/_4\, b^2 + ab - {}^1\!/_2\, a^2)(c_1c_2\sqrt{6} - 2c_2c_3\sqrt{2})\} \\ B_{sd} &= {}^4\!/_{21}\, Pp\{-({}^1\!/_2\, b^2 + a^2 + 2ab)(c_2^2 - {}^1\!/_2\, c_1c_3\sqrt{3}) + \\ &\qquad + {}^1\!/_2\, ({}^9\!/_4\, b^2 + ab - {}^1\!/_2\, a^2)\, c_2c_3\sqrt{2} - c_3^2(3b^2 + 4ab + a^2)\} \\ Q &= {}^3\!/_{14}\, \frac{e^2qp}{I(2I-1)}\, \langle r^{-3}\rangle\, ({}^1\!/_2\, b^2 + a^2 + 2ab)(2c_2^2 - c_1^2 - c_3^2). \end{aligned}\right. \tag{52b}$$

In the case of pure octahedral symmetry these results reduce to

$$A_{sd} = B_{sd} = -{}^4\!/_{21}\, Pp({}^1\!/_6\, a^2 + {}^{11}\!/_{12}\, b^2 + ab). \tag{53}$$

The contribution of A_{sd} is small, so that

$$A = P[{}^2\!/_3\alpha - {}^5\!/_3\varkappa] \tag{54}$$

is a good approximation, [32].

iv) $S = 2$, d^6, ground state in octahedral field T_2.

For all values of δ, positive as well as negative, a spin hamiltonian can be used for the three lowest states. If δ is sufficiently large and positive, then a spin hamiltonian may be set up alternatively for the lowest doublet. This has been done by GRIFFITH [33]. We shall however state the results for the triplet hamiltonian which is correct for all values of δ.

The g factors are given by

$$\text{(55a)} \qquad \left\{ \begin{aligned} g_{\parallel} &= 4c_1^2 + 2c_2^2 + \alpha(c_1^2 - c_3^2) \\ g_{\perp} &= 2\sqrt{3}\,[c_2c_5 + c_3c_4] + 2\sqrt{2}\,c_1c_4 - \alpha'(c_2c_4 + c_3c_5), \end{aligned} \right.$$

where

$$\text{(55b)} \qquad \left\{ \begin{aligned} c_1 &= \frac{\sqrt{6}}{x}\left\{\frac{6}{x^2} + {}^4\!/_3\,\frac{\gamma^2}{\gamma'^2} + \frac{9}{(x+3)^2}\right\}^{-1/2} \\ c_2 &= \frac{-2\gamma}{\gamma'\sqrt{3}}\left\{\frac{6}{x^2} + {}^4\!/_3\,\frac{\gamma^2}{\gamma'^2} + \frac{9}{(x+3)^2}\right\}^{-1/2} \\ c_3 &= \frac{3}{x+3}\left\{\frac{6}{x^2} + {}^4\!/_3\,\frac{\gamma^2}{\gamma'^2} + \frac{9}{(x+3)^2}\right\}^{-1/2} \end{aligned} \right.$$

and x is the largest root of the equation

$$\text{(55c)} \qquad \delta = {}^3\!/_8\,\frac{\gamma'}{\gamma}\left\{\frac{2}{x} + \frac{3}{x+3}\right\} + \frac{\gamma}{6}\,(x+3).$$

In addition

$$\text{(55d)} \qquad c_4 = \left\{\frac{(S + \delta + {}^1\!/_4\gamma)}{4S}\right\}^{1/2}, \quad c_5 = -\left\{\frac{(S - \delta - {}^1\!/_4\gamma)}{2S}\right\}^{1/2}$$

where

$$\text{(55e)} \qquad S = \{(\delta + {}^1\!/_4\gamma)^2 + {}^3\!/_2\gamma'^2\}^{1/2}.$$

The zero field splitting is given by DS'^2_z, where

$$\text{(56)} \qquad D = E_1 - E_0 = \frac{-\gamma}{6}\,(x+3) + {}^1\!/_2\,(S + {}^1\!/_4\gamma - \delta).$$

In the octahedral case we have $x = {}^3\!/_2$

$$\text{(57)} \qquad c_1 = \sqrt{{}^3\!/_5},\ c_2 = -\sqrt{{}^3\!/_{10}},\ c_3 = \sqrt{{}^1\!/_{10}},\ c_4 = \sqrt{{}^3\!/_{10}},\ c_5 = -\sqrt{{}^2\!/_5}$$

and $g = 3 + {}^1\!/_2\alpha$.

The second order corrections to the g factors are given by

i) in the case of tetragonal symmetry

$$\text{(58a)} \qquad \left\{ \begin{aligned} g_{\parallel}^{(2)} &= \frac{k'\zeta'}{\Delta}\,[-c_1c_2\sqrt{2} + c_2^2] \\ g_{\perp}^{(2)} &= \frac{k'\zeta'}{\Delta}\,[c_1c_4\sqrt{2} + {}^3\!/_4\,c_3c_4\sqrt{3} - {}^1\!/_4\,c_2c_4] \end{aligned} \right.$$

ii) in the case of trigonal symmetry

(58b) $$\begin{cases} g_{\parallel}^{(2)} = \dfrac{k'\zeta'}{\Delta}\,[2c_1^2 + c_1c_2\sqrt{2} - c_2c_3\sqrt{3}] \\ g_{\perp}^{(2)} = \dfrac{k'\zeta'}{\Delta}\,[{}^1/_2\,c_1c_4\sqrt{2} + {}^1/_2\,c_1c_5\sqrt{3} + {}^1/_2\,c_3c_4\sqrt{3} - {}^1/_2\,c_2c_4]. \end{cases}$$

In the octahedral case all these corrections reduce to

(58c) $$g^{(2)} = {}^9/_{10}\,\frac{k'\zeta'}{\Delta}.$$

The hyper fine structure constants are given by

i) in the case of tetragonal symmetry

(59a) $$\begin{cases} A_{sd} = {}^1/_{14}\,Pp[-2(c_1^2-c_2^2) - 3c_1c_2\sqrt{2} + 3c_2c_3\sqrt{3}] \\ B_{sd} = {}^1/_{14}\,Pp[{}^1/_2\,c_1c_4\sqrt{2} + {}^1/_2\,c_3c_4\sqrt{3} - c_2c_5\sqrt{3} - {}^3/_2\,c_2c_4], \end{cases}$$

ii) in the case of trigonal symmetry

(59b) $$\begin{cases} A_{sd} = {}^1/_{14}\,Pp[2(c_1^2-c_2^2) + c_1c_2\sqrt{2} - c_2c_3\sqrt{3}] \\ B_{sd} = {}^1/_{14}\,Pp[-{}^1/_2\,c_1c_4\sqrt{2} + {}^1/_2\,c_3c_4\sqrt{3} + c_2c_5\sqrt{3} + {}^1/_2\,c_2c_4]. \end{cases}$$

In the octahedral case

(60a) $$A_{sd} = B_{sd} = {}^3/_{140}\,Pp.$$

This contribution is small, so that

(60b) $$A = P[{}^1/_2\,\alpha - {}^3/_2\,\varkappa]$$

is a good approximation in that case.

For the ferrous ion in zinc fluorine another interpretation of the data is necessary, *cf.* GRIFFITH [33], TINKHAM [25]. Here the Ligand field has a component of lower symmetry, *i.e.* orthorhombic symmetry. The lowest level has no orbital degeneracy and the system can be described by a spin hamiltonian $S'=2$, in which $\mathbf{S}'$ is the true spin $\mathbf{S}$. In addition the fluorine ions have a nuclear magnetic moment and give an important contribution to the hyper fine structure [25].

§ 9. *The configurations d^3 and d^8*

The ground state in an octahedral field is an A_2 state with no orbital degeneracy. In that case the theory of the spin hamiltonian for the case of no orbital degeneracy, *cf.* [16], can be applied, the fictitious spin being identical with the true spin.

The zero field splitting due to the high spin states can be represented by DS'^2_z for the case of a tetragonal or a trigonal field.

D is given by

i) in the case of tetragonal symmetry

$$D = -\frac{3\zeta'^2}{S^2}\frac{(^1/_4 d' - {}^1/_3 d)}{(E_{T_2} - E_{A_2})^2} \tag{61a}$$

ii) in the case of trigonal symmetry

$$\left\{\begin{aligned} D = &-{}^3/_2 \frac{\zeta'^2 t}{S^2(E_{T_2} - E_{A_2})^2} - \frac{6bt'\zeta'(a\zeta' - {}^1/_2 b\zeta)}{S^2(E_{T_1} - E_{A_2})(E_{T_2} - E_{A_2})} + \\ &+ \frac{6at'\zeta'(b\zeta' + {}^1/_2 a\zeta)}{S^2(E_{T_1'} - E_{A_2})(E_{T_2} - E_{A_2})}, \end{aligned}\right. \tag{61b}$$

where S is the spin, *i.e.* $S = 1$ in the case of d^8 and $S = {}^3/_2$ in the case of d^3.

The g factors are given by

i) in the case of tetragonal symmetry

$$\left\{\begin{aligned} g_{\parallel} &= 2 \mp \frac{4k'\zeta'}{S(E_{T_2} - E_{A_2})}\left(1 + \frac{{}^1/_2 d' - {}^2/_3 d}{E_{T_2} - E_{A_2}}\right) \\ g_{\perp} &= 2 \mp \frac{4k'\zeta'}{S(E_{T_2} - E_{A_2})}\left(1 - \frac{{}^1/_4 d' - {}^1/_3 d}{E_{T_2} - E_{A_2}}\right) \end{aligned}\right. \tag{62a}$$

ii) in the case of trigonal symmetry

$$g_{\parallel} = 2 \mp \frac{4k'\zeta'}{S(E_{T_2} - E_{A_2})} - 2\mu$$

$$g_{\perp} = 2 \mp \frac{4k'\zeta'}{S(E_{T_2} - E_{A_2})} + \mu,$$

where

$$\left\{\begin{aligned} \mu = &\pm \frac{2k'\zeta' t}{S(E_{T_2} - E_{A_2})^2} \pm \frac{4bt'\{\zeta'(ak' - {}^1/_2 bk) + k'(a\zeta' - {}^1/_2 b\zeta)\}}{S(E_{T_2} - E_{A_2})(E_{T_1} - E_{A_2})} \mp \\ &\mp \frac{4at'\{\zeta'(bk' + {}^1/_2 ak) + k'(b\zeta' + {}^1/_2 a\zeta)\}}{S(E_{T_2} - E_{A_2})(E_{T_1'} - E_{A_2})}. \end{aligned}\right. \tag{62b}$$

In the formula (62) all the upper signs apply to d^3, the lower signs to d^8.

Remarks:

i) In the case of trigonal symmetry the contributions which arise from the admixture of T_1 states in the A_2 ground state can be important and it is not correct to neglect these contributions. However the results (61) and (62) are not very sensitive to a correct choice of $x = \Delta / E_p$. Assuming

$\zeta=\zeta'$ and $k=k'$ the results in the weak field and strong field limit are the same. In intermediate cases slightly different results will be found.

ii) It has to be stressed upon that the low spin states can give an important contribution to the zero field splitting. This contribution can be particularily large in the case of d^8, where a low lying ^1E level (10.000 cm^{-1}) can be expected, *cf.* GRIFFITH [33]. In that case the formulae (61) give a bad approximation. The contribution of the low spin states can not be represented by a simple formula independent of the assumption of the weak or strong field limit. In that case a laborious analysis starting from numerical estimations for the crystal field and Racah parameters is necessary in order to fit correctly the experimental data. On the contrary the lower spin states can not give a contribution to the g factors.

iii) It can be noted that the case of Cr^{+++} in ruby has been the subject of many investigations. From the spectrum a negative value of t (K) was found [20]. At first sight this seems to contradict the negative value of D and positive value of $g_{\perp}-g_{\parallel}$ found by ZVEREV and PROKHOROV [35]. An elaborated analysis taking into account the influence of all t_2^3 and t_2^2e states has been given by PETER and SUGANO [21]. However the agreement with the experiments can be improved, if an additional anisotropy in ζ, ζ', k and k' is introduced. This idea due to SUGANO and TSUJIKAWA [20] was worked out in more detail by KAMIMURA [22]. At the other hand it must be observed that the symmetry in ruby is only C_3, *cf.* [20]. An exact description of the trigonal field involves the introduction of three parameters, whereas in the case of C_{3v} or D_3 symmetry two parameters t and t' are sufficient. In addition, if the fourth degree part of the trigonal field is neglected, which is the case for the analyses mentioned above, then one parameter K will be sufficient.

iv) In the case of d^4 and d^9 the ground state in an octahedral field with 6-co-ordination is an E level. From the JAHN TELLER effect [35], [36], we can expect that the crystal field has a large tetragonal component [37], [38]. We shall not deal with this case, since the correct formulae are simple and well-known, see for instance, [2], [10], [16].

§ 10) *A remark about the Jahn Teller effect*

Another application is the calculation of the constants A and B, for a T_1 and T_2 level such as have been introduced by ÖPIK and PRYCE [38] in their treatment of the static Jahn Teller effect. These constants are related to the constants a and b of VAN VLECK [37], by $A=a\sqrt{2}$, $B=b$.

Van Vleck has calculated these constants assuming an electrostatic model (point charge or dipole model) and Russell Saunders coupling.

For a T_1 or T_2 level however the contributions of the second degree and fourth degree part of the perturbing field largely cancel out. (For the E levels of d^4 and d^9, where this is not the case, the Jahn Teller effect is very large [37], [38].) This is the reason why the constants A and B are extremely dependent on a correct choice of $x = \Delta / E_p$.

Although the electrostatic model may be very insufficient, we shall give here the results without the restriction of the weak or strong field limit.

For the T_2 levels of d^1, d^4, d^6, d^9

$$\text{(63a)} \qquad \begin{cases} A = \pm \sqrt{2}\,\{{}^3/_7\,\varrho_1 - {}^{25}/_{63}\,\varrho_2\} \\ B = \pm \{-{}^6/_7\,\varrho_1 + {}^{10}/_{21}\,\varrho_2\}. \end{cases}$$

For the lowest T_1 levels of d^2, d^3, d^7, d^8.

$$\text{(63b)} \qquad \begin{cases} A = \pm \sqrt{2}\left\{-{}^3/_7\,\varrho_1(a^2 - 2b^2) + \varrho_2\left(\dfrac{100a^2 - 25b^2}{252}\right)\right\} \\ B = \pm \{-{}^6/_7\,\varrho_1(2ab + {}^1/_2\,b^2 + a^2) + {}^5/_{21}\,\varrho_2(3ab - 2a^2 - b^2)\}. \end{cases}$$

The formulae for the highest T_1 level can be found from (63b) by substituting $a \rightarrow b$, $b \rightarrow -a$.

For the T_2 level of d^2, d^3, d^7, d^8

$$\text{(63c)} \qquad \begin{cases} A = \pm\, {}^{25}/_{36}\,\varrho_2 \sqrt{2} \\ B = \pm \{{}^3/_7\,\varrho_1 - {}^5/_{21}\,\varrho_2\}. \end{cases}$$

In (63) all the + signs apply if the d shell is less than half filled, the − signs apply if the d shell is more than half filled.

In the point charge model

$$\text{(63d)} \qquad \begin{cases} \varrho_{2\,\mathrm{p.c.}} = -\,{}^3/_5\,\dfrac{\Delta}{R} \\ \varrho_{1\,\mathrm{p.c.}} = \dfrac{R^2\langle r^2\rangle}{\langle r^4\rangle}\,\varrho_{2\,\mathrm{p.c.}}, \end{cases}$$

R being the distance of the 3d ion to the surrounding ions.

In the dipole model

$$\text{(63e)} \qquad \varrho_{2\,\mathrm{dip.}} = {}^6/_5\,\varrho_{2\,\mathrm{p.c.}}, \quad \varrho_{1\,\mathrm{dip.}} = {}^4/_5\,\varrho_{1\,\mathrm{p.c.}}$$

In the weak field limit these results reduce to the results of VAN VLECK [37]. The criterion of ÖPIK and PRYCE [38] for the stability of the tetragonal or trigonal distortions can be expressed in a convenient way by observing that the stable distortions give rise to the greatest splitting. In addition positive values of A lead to elongated tetragonal structures, positive values of B to a driving away of the ligands from the trigonal axis.

Starting from reasonable numerical estimations one should expect for d^2 that in the weak field limit $A<0$, $B>0$, the trigonal distortions being stable, whereas in the strong field limit and probably also for a reasonable value of $x=\Delta/E_p$, one should expect $A>0$, $B<0$, the tetragonal distortions being stable.

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SAMENVATTING

In dit proefschrift zullen we een behandeling geven van het Hole Equivalence Principle en de van Vleck relatie en hun toepassingen in de theorie van d-ionen in kristal (Ligand) velden. De configuratie met de laagste energie van een gegeven ion bestaat uit een aantal gesloten schillen en een niet geheel gevulde schil. De electronen schillen worden gedefinieerd met behulp van een zelf consistente één electron hamiltoniaan h. Het Hole Equivalence Principle en de van Vleck relatie zijn van toepassing op de niet geheel gevulde schil en we zullen in een inleidend hoofdstuk behandelen in hoeverre de invloed van gesloten schillen kan worden verwaarloosd. De één electron toestanden, die de niet geheel gevulde schil bepalen, kunnen we kiezen van de vorm $u_i(\mathbf{r}) \uparrow$, $u_i(\mathbf{r}) \downarrow$, $i = 1, 2, \ldots, p$, waarbij de u_i orthonormaal zijn en een basis vormen van de lineaire ruimte bestaande uit eigentoestanden van h voor één of meer eigenwaarden. De u_i vormen ook de basis van een aantal irreducibele representaties van de groep G van transformaties, die h invariant laten. $\uparrow$ en $\downarrow$ zijn de spintoestanden $s_z = \frac{1}{2}$ en $s_z = -\frac{1}{2}$.

Het Hole Equivalence Principle kan nu als volgt worden geformuleerd: Uitgaande van een willekeurige basis in de configuratie L met n electronen in de niet geheel gevulde schil kunnen we een basis kiezen in de configuratie R met $2p$-n electronen in de niet geheel gevulde schil zodanig dat
i) beide bases dezelfde transformatie eigenschappen hebben ten opzichte van de groep O_p van orthogonale transformaties in de ruimte van $u_1, u_2, \ldots, u_p$ en in het bijzonder ten opzichte van de groep G,
ii) er eenvoudige relaties zijn tussen de matrix elementen van één- en twee-electron operatoren ten opzichte van beide bases.

De van Vleck relatie kan als volgt worden geformuleerd: Uitgaande van een basis $\varphi^{(n)}$ van de toestanden met maximale S_z in de configuratie met n electronen in de niet geheel gevulde schil kunnen we door deze basis toestanden te koppelen met de toestand met minimale S_z van de half gesloten schil en het verkregen resultaat te antisymmetrizeren een basis $\varphi^{(n+p)}$ verkrijgen van de toestanden met minimale S_z in de configuratie met $n + p$ electronen. Beide bases hebben dezelfde transformatie eigenschappen ten opzichte van de groep SU_p van unitaire transformaties met determinant 1 in de ruimte van $u_1, u_2, \ldots, u_p$ en in het bijzonder transformeert $\varphi^{(n+p)}$ ten opzichte van de groep G op dezelfde wijze als $\varphi^{(n)}o$. o is de maximale spintoestand van de half gesloten schil en vormt de basis van een ééndimensionale representatie van de groep G. Voorts zijn er eenvoudige relaties voor de matrix elementen van één en twee electron operatoren, die niet op de spin inwerken ten opzichte van beide bases. In de hoofdstukken I en II geven we een algemeen bewijs van het Hole Equivalence Principle en de van Vleck relatie, onafhankelijk van de groep G en de keuze van één electron toestanden.

In hoofdstuk III passen we het Hole Equivalence Principle en de van Vleck relatie toe op de theorie van d-ionen in Ligand velden. Het is bekend dat een kristalveld van kubische symmetrie de toestanden van een d^1 ion splitst in een t_2 niveau en een e niveau. e en t_2 zijn bepaalde representaties van de kubische groep. We kunnen nu als maximale S_z toestanden van een d^1 ion kiezen een basis van het t_2 niveau en een basis van het e niveau.

Voor de maximale S_z toestanden van een d^2 ion zijn er verschillende mogelijkheden, in het bijzonder:

i) De zwakveld representatie, waarin de Coulomb wisselwerking diagonaal is.

ii) De sterkveld representatie, waarin de kubische component van het Ligand veld diagonaal is.

iii) De intermediaire representatie, waarin de Hamiltoniaan bestaande uit de Coulomb wisselwerking en de kubische component van het Ligand veld diagonaal is.

In de configuraties d^4, d^6, d^9 en d^3, d^7, d^8 kunnen we bases vinden, die corresponderen met de bases in d^1 en d^2 in overeenstemming met het Hole Equivalence Principle en de van Vleck relatie. De matrix elementen van één en twee electron operatoren ten opzichte van deze bases kunnen gemakkelijk worden berekend uit de matrix elementen voor d^1 en d^2. Hoewel in principe alles op exacte wijze berekend kan worden met behulp van computors, is er behoefte aan gesloten formules, die redelijke benaderingen vormen. Verschillende benaderingen zijn nauw gekoppeld aan de keuze van basis in de configuratie d^2, de zwakveld benadering, de sterkveld benadering en de intermediaire benadering, waarbij de Hamiltoniaan $\mathcal{H}_0$ bestaande uit de Coulomb wisselwerking en de kubische component van het Ligand veld op exacte wijze behandeld wordt en de overige termen van de Hamiltoniaan met behulp van storingsrekening. Hoewel de beide eerstgenoemde benaderingen veelal gebruikt worden, zal toch de intermediaire benadering in veel gevallen beter zijn en we zullen daarom een aantal resultaten geven, die gebaseerd zijn op deze benadering. Uit deze resultaten kan men de invloed van de zwakveld en de sterkveld benadering nagaan. We zijn in het bijzonder geinteresseerd in:

1) het splitsingspatroon ten gevolge van de trigonale of tetragonale component van het Ligand veld en de spinbaankoppeling,

2) enige grootheden, die optreden in de spin hamiltoniaan zoals bijvoorbeeld de g factoren $g_{\parallel}$ en $g_{\perp}$ en de hyperfijnstructuur constanten A en B. Eenvoudige benaderingen voor de zogenaamde tweede orde bijdragen tot de g factoren en de dipool gedeelten van de hyperfijnstructuur constanten kunnen worden verkregen door het mengsel van aangeslagen toestanden in de toestanden van het grondniveau van $\mathcal{H}_0$ ten gevolge van het trigonale of tetragonale veld te verwaarlozen.

In het algemeen zullen de zwak en sterk veld benaderingen geen goede resultaten geven voor de grootheden genoemd onder 1) en 2). Dit is ook het geval voor de constanten die de tetragonale en trigonale distorties in het statische Jahn Teller effect beschrijven.

In hoofdstuk I behandelen we het Hole Equivalence Principle, in hoofdstuk II de van Vleck relatie en in hoofdstuk III de toepassingen op de theorie van d-ionen in Ligand velden. De physische achtergronden worden meer en detail besproken in een inleidend hoofdstuk.

STELLINGEN

I

Een algemene formulering van het "Hole Equivalence Principle" onafhankelijk van de symmetrie-eigenschappen van de één-deeltjes Hamiltoniaan is mogelijk op grond van het feit, dat men corresponderende basistoestanden van aan elkaar toegevoegde configuraties L en R zodanig kan definiëren, dat beide bases dezelfde transformatieeigenschappen hebben ten opzichte van de groep van orthogonale transformaties in de ruimte van één-electron-banen.

Hoofdstuk I van dit proefschrift.

II

De formules, die Abragam en Pryce geven voor de hyperfijnstructuurconstanten van een d^1-ion, zijn alleen juist indien het kristalveld tetragonale symmetrie heeft. De overeenkomstige formules voor een d^2-ion zijn alleen juist in velden van trigonale symmetrie en in de benadering van een zwak veld, die in dit geval niet tot nauwkeurige resultaten zal leiden.

Hoofdstuk III van dit proefschrift.
Abragam A. en M.H.L. Pryce, Proc. Roy. Soc. *A 205* 135 (1951).

III

Tegen de afleiding, die Potts en Ward geven voor de partitiefunctie behorend bij het Ising-model met periodieke randvoorwaarden in 2 dimensies zijn bezwaren aan te voeren. Door twee onnauwkeurigheden, die elkaar opheffen, wordt toch het juiste resultaat gevonden.

Potts R.B. en J.C. Ward, Progr. Theor. Phys. *13* 38 (1955).

IV

Bij het bepalen van de basistoestanden van Γ_8-kwartetten voor ionen van zeldzame aarden door Lea, Leask en Wolf is geen rekening gehouden met een bepaalde representatie volgens welke de basistoestanden getransformeerd moeten worden. De matrix-elementen van de operator van het magnetisch moment ten opzichte van deze bases worden dan ook niet zonder meer voorgesteld door de matrices van Ayant, Bélorizky en Rosset.

Lea K.R., M.J.M. Leask en W.P. Wolf, J. Phys. Chem. Solids *23* 1381 (1962)
Ayant Y., E. Bélorizky en J. Rosset, J. Phys. Rad. *23* 201 (1962).

V

Voor ionen-roosters in zeer sterke magneetvelden kan een analogon van het Jahn-Teller effect optreden. Het is niet uitgesloten, dat de uit dit effect voortkomende deformaties van het rooster aanleiding kunnen geven tot een zwak ferromagnetisme.

Jahn H.A. en E. Teller, Proc. Roy. Soc. *A 161* 220 (1937).
Jahn H.A. Proc. Roy. Soc. *A 164* 117 (1938).

VI

In een Ising-model voor triplet-ionen met nulveld-splitsing kan in een moleculaire-veldbenadering onder bepaalde omstandigheden een magnetische ordening onstaan via een eerste-orde-fase-overgang.

VII

De Bloch-vergelijkingen met één relaxatietijd (in de theorie van paramagnetische relaxatie) kunnen gemotiveerd worden met behulp van een "strong collision model". Tevens kan men gebruik makend hiervan de Bloch-vergelijkingen voor willekeurige tijd gemakkelijk oplossen door directe integratie.

Abragam A., The Principles of Nuclear Magnetism, Ch. III (1961). Oxford University Press.

VIII

Tegen de afleiding, die Ginzburg geeft voor de afhankelijkheid van de frequentie van de dielectriciteitsconstante van een plasma, zijn bezwaren aan te voeren.

Ginzburg V.L., Propagation of Electromagnetic Waves in Plasma, Ch. II (1961), Gordon and Breach, New York.

IX

In het geval van ionen van zeldzame aarden kunnen experimenten in sterke magneetvelden informatie opleveren over de coëfficiënten van de kristalveldontwikkeling. Voor de beschrijving van experimentele resultaten kan het nuttig zijn de matrix-elementen van het magnetisch moment tussen toestanden behorend bij verschillende energie-niveaux voor te stellen door gegeneraliseerde g-factoren.

Capel H.W., On the representation of matrix elements of the magnetic moment operator between states belonging to different energy levels by means of generalized g factors. Proc. Kon. Ned. Akad. van Wetensch., in publikatie.

X

Door gebruik te maken van de symmetrie-eigenschappen van de ruimtegroep van een rooster kunnen moleculaire-veld-behandelingen voor magnetische ordeningsverschijnselen ook in zeer gecompliceerde systemen tot eenvoudige resultaten leiden.

Capel H.W., Rapport Commissariat a l'Energie Atomique R 2705 (1964).
, aangeboden voor publikatie in Physica.

XI

De ontwikkeling van momenten in termen van cumulanten (semi-invarianten) en de ontwikkeling van cumulanten in termen van momenten kunnen op eenvoudige wijze met behulp van diagrammen worden voorgesteld.

Meeron J., J. Chem. Phys. 27 1238 (1957).

XII

Uit de theorie van Öpik en Pryce kan ook gemakkelijk op quantitatieve wijze worden afgeleid aan welke voorwaarden de spin-baankoppeling moet voldoen, opdat er geen Jahn-Teller effect optreedt.

Öpik V. en M.H.L. Pryce, Proc. Roy. Soc. *A 238* 425 (1957).

XIII

Voor een Γ_8-kwartet kan een effectieve (spin)-hamiltoniaan worden opgesteld in termen van Dirac-matrices.

XIV

De ontbinding van de direct-product-representatie $D^{(\frac{1}{2})} \times D^{(\frac{1}{2})} \times \ldots D^{(\frac{1}{2})}$ voor een willekeurig aantal factoren in irreducibele representaties van de rotatiegroep is equivalent met een "random walk-problem."